BULLETIN DE L'ASSOCIATION MINÉRALOGIQUE DU CANADA

THE CANADIAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL ASSOCIATION OF CANADA

Volume 37 August 1999 Part 4

The Canadian Mineralogist
Vol. 37, pp. 865-891 (1999)

THE CRYSTAL CHEMISTRY OF THE EUDIALYTE GROUP

OLE JOHNSEN[§]

Geological Museum, University of Copenhagen, Øster Voldgade 5-7, DK-1350 Copenhagen, Denmark

JOEL D. GRICE

Research Division, Canadian Museum of Nature, P.O. Box 3443, Station D, Ottawa, Ontario K1P 6P4, Canada

ABSTRACT

Seventeen crystals of eudialyte (*sensu lato*) differing in provenance and showing a wide range of chemical compositions were chosen for crystal-structure analysis and electron-microprobe analysis, supplemented with thermogravimetric analysis, infrared analysis, Mössbauer and optical absorption spectroscopy on selected samples. The structure consists of layers of six-membered rings of [$M(1)O_6$] octahedra linked together by [$M(2)O_n$] polyhedra sandwiched between two pseudocentrosymmetrically related layers of three-membered and nine-membered silicate rings forming a 2:1 composite layer. The 2:1 composite layers are cross-linked by Zr in octahedral coordination and are related to one another in accordance with the rhombohedral symmetry. This open structure is filled with [$Na\phi_n$] polyhedra in which Na may have various coordinations. The silicate network is relatively uniform in composition. The *Zr* site usually has a small amount of Ti. *M*(1) is normally occupied mostly by Ca; the main substitutions are Mn, *REE* and Y. In one crystal, more than 50% Ca is replaced by Mn and *REE*, resulting in an ordering in two distinct sites, *M*(1a) (Mn) and *M*(1b) (Ca + *REE*), and the symmetry reduced to *R*3. *M*(2) is either a four-fold Fe- dominated site, or a five-fold site, usually Mn-dominated. *M*(3) and *Si*(7) are two central sites of the two crystallographically distinct nine-membered silicate rings, and related by the substitution $^{[6]}M(3) + ^{[4]}Si(7) \Leftrightarrow 2^{[4]}Si(7)$. *M*(3) is dominated by Nb (or W), and *Si*(7), by (Si,Al). Na is present in five distinct sites (acentric eudialyte) of which the *Na*(4) site is particularly prone to incorporation of heavy elements such as *REE* and Sr. The *O*(19) site plays a key role in the structure, being the ligand shared by the *M*(3), *M*(2,5) and *Na*(4) sites. The degree of acentricity is strongly correlated with the chemical elements in specific atomic sites. Eudialyte *sensu stricto* represents the most centrosymmetric structure, $R\bar{3}m$. As substitutions such as Si ⇒ (Nb,W), Fe ⇒ Mn, (Ca,Na) ⇒ (*REE*,Sr) take place, the structures become more and more noncentrosymmetric, *R*3*m*. The *R*3 eudialyte has an incongruously low $|E^2 - 1|$ value as a result of merohedral twinning. A complete formula for eudialyte requires structural data. An acceptable empirical formula, $Na_{15}[M(1)]_6[M(2)]_3Zr_3\,[M(3)](Si_{25}O_{73})\,(O,OH,H_2O)_3\,X_2$, can be calculated on the basis of 29 (Si,Al,Zr,Ti,Hf,Nb,W,Ta) *apfu* (*Z* = 3).

Keywords: eudialyte, kentbrooksite, crystal chemistry, single-crystal X-ray diffraction, electron-microprobe data.

SOMMAIRE

Nous avons sélectionné dix-sept cristaux d'eudialyte (*sensu lato*) de provenances différentes et définissant un grand intervalle de compositions chimiques pour une étude de leur structure cristalline, leur composition étant établie par analyse avec une microsonde électronique, et avec apport de résultats d'analyses thermogravimétrique, dans l'infra-rouge, et spectroscopiques

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[§] *E-mail address*: oj@savik.geomus.ku.dk

(Mössbauer et absorption optique) sur certains de ces échantillons. La structure est faite de couches d'anneaux à six octaèdres $[M(1)O_6]$ liés l'un à l'autre par des polyèdres $[M(2)O_n]$; ces couches sont intercalées entre deux autres couches possédant une relation par pseudocentrosymétrie, faites d'anneaux à trois et à neuf tétraèdres de silicate, le tout formant une couche composée 2:1. Ces couches 2:1 sont liées transversalement par des octaèdres contenant le Zr et sont en relation l'une avec l'autre selon une symétrie rhomboédrique. Les interstices de cette structure ouverte sont occupés par des polyèdres $[Na\phi_n]$ dans lesquels le Na fait preuve d'une variété de coordinences. La trame silicatée est relativement uniforme en composition. Le site *Zr* contient une faible proportion de Ti, en général. Le site $M(1)$ contient normalement le Ca; les substitutions principales impliquent le Mn, les terres rares et l'yttrium. Dans un cristal, plus de 50% du Ca est remplacé par Mn et les terres rares, avec comme résultat une mise en ordre de ces cations sur deux sites distincts, $M(1a)$ (Mn) et $M(1b)$ (Ca + terres rares), et une réduction de la symétrie à celle du groupe spatial $R3$. Le site $M(2)$ possède soit une coordinence quatre où le Fe est dominant, soit une coordinence cinq, en général où le Mn est dominant. Les sites $M(3)$ et $Si(7)$ sont situés au centre des deux anneaux à neuf tétraèdres, qui sont cristallographiquement distincts; l'occupation de ces sites est régie selon la substitution $^{[6]}M(3) + {}^{[4]}Si(7) \Leftrightarrow 2{}^{[4]}Si(7)$. Le site $M(3)$ contient surtout le Nb (ou le W), et $Si(7)$ contient (Si,Al). Le Na occupe cinq sites distincts (eudialyte acentrique), parmi lesquels le site $Na(4)$ est particulièrement sujet à l'incorporation d'éléments lourds, tels les terres rares et le strontium. Le site $O(19)$ joue un rôle-clé dans la structure, étant partagé par les sites $M(3)$, $M(2,5)$ et $Na(4)$. Le degré d'acentricité dépend fortement des occupants des divers sites. L'eudialyte *sensu stricto* représente la structure centrosymétrique, $R\bar{3}m$. A mesure que les substitutions telles Si ⇒ (Nb,W), Fe ⇒ Mn, (Ca,Na) ⇒ (terres rares, Sr) prennent de l'ampleur, la structure devient de plus en plus non centrosymétrique, $R3m$. L'eudialyte $R3$ fait preuve d'une valeur anormalement faible de $|E^2 - 1|$ à cause d'un maclage méroédrique. Pour écrire une formule complète d'un échantillon, il est nécessaire d'avoir des données sur la structure. En revanche, on peut calculer une formule acceptable, $Na_{15}[M(1)]_6[M(2)]_3Zr_3\,[M(3)](Si_{25}O_{73})\,(O,OH,H_2O)_3\,X_2$, en supposant 29 atomes de (Si,Al,Zr,Ti,Hf,Nb,W,Ta) par unité formulaire ($Z = 3$).

(Traduit par la Rédaction)

Mots-clés: eudialyte, kentbrooksite, chimie cristalline, diffraction X, cristal unique, données de microsonde électronique.

INTRODUCTION

Minerals of the eudialyte group are Na-rich zirconosilicates with varying amounts of Ca, Fe, Mn, rare-earth elements (*REE*), Sr, Nb, K, Y and Ti. They occur characteristically in agpaitic nepheline syenites and their associated pegmatites; rarely, eudialyte is encountered in peralkaline granites.

Eudialyte was first described from Kangerdluarssuk, in the Ilímaussaq alkaline complex, South Greenland (Stromeyer 1819). Since then, a very large number of eudialyte samples have been analyzed from other localities. These display a wide variation that results from real compositional variations as well as from significant analytical errors inherent in some of the methods used.

Golyshev *et al.* (1971) and Giuseppetti *et al.* (1971) independently solved the basic structure of eudialyte and showed it to be a cyclosilicate with both nine- and three-membered rings of $[SiO_4]$ tetrahedra. The former authors solved the structure in space group $R3m$, the latter in $R\bar{3}m$. Subsequent refinements of the structure, *e.g.*, those by Rastsvetaeva & Andrianov (1987), Rastsvetaeva & Borutskii (1988), Rastsvetaeva *et al.* (1988, 1990), provided additional structural information on eudialyte-group phases of different compositions, all in $R3m$. Still, until recently, some aspects of the crystal chemistry of the group remained obscure. For example, the nature of the principal substitutions, the number of anions and the number of Si atoms per formula unit (*apfu*) were still associated with considerable uncertainty.

Johnsen & Gault (1997) studied the chemical variation in the eudialyte group using results of electron-microprobe analyses performed under uniform conditions. They concluded that a solid-solution series exists between the classic type of eudialyte rich in Si, Ca, Fe and Cl, and compositions rich in Nb, *REE*, Mn and F, such as kentbrooksite (Johnsen *et al.* 1998). On the basis of electron- microprobe information alone, that study could only address certain problems concerning this complex group of minerals.

In the present work, we examine the crystal-chemical properties of eudialyte (*sensu lato*) samples specifically selected from the material of Johnsen & Gault (1997). The study is based on single-crystal structure-refinement data (SREF) and subsequent electron-microprobe analysis of the crystals used for SREF to ensure maximum compatibility within datasets. For selected samples, we had sufficient material for thermogravimetric analysis (TGA), infrared spectroscopy (IR), optical absorption spectroscopy (OAS) and Mössbauer spectroscopy.

EXPERIMENTAL METHODS AND PROCEDURES

Table 1 lists the provenance of the seventeen samples used in this study. All samples come from different specimens except for sample 11 and 12, which come from rim and core, respectively, of the same crystal. We attempted to cover the entire observed range of compositions of eudialyte-group minerals from samples analyzed by Johnsen & Gault (1997). In particular, we were interested in variations in Ca, Mn, *REE*, Si, Nb and Na contents. We kept the experimental method uniform for all samples in order to minimize systematic errors; we

TABLE 1. THE PROVENANCE OF THE EUDIALYTE SAMPLES USED IN THIS STUDY

#	ps	specimen number	locality
1	M	CMNMC 36596	Mont Saint-Hilaire, Rouville County, Quebec, Canada
2	S	CMNMC 81563	Mont Saint-Hilaire, Rouville County, Quebec, Canada
3	s	CMNMC 81561	Mont Saint-Hilaire, Rouville County, Quebec, Canada
4	H	CMNMC 81562	Mont Saint-Hilaire, Rouville County, Quebec, Canada
5	h	CMNMC 81565	Mont Saint-Hilaire, Rouville County, Quebec, Canada
6	m	CMNMC 81557	Mont Saint-Hilaire, Rouville County, Quebec, Canada
7	w	CMNMC 81564	Kipawa alkaline complex, Villedieu Township, Temiscaminque County, Quebec, Canada
8	W	CMNMC 31174	
9	V	CMNMC 81560	Saint-Amable sill, Varennes, Vercheres County, Quebec, Canada
10	G	GM-1983.639	Gardiner complex, East Greenland
11	r	GM-1983.643r	Gardiner complex, East Greenland
12	c	GM-1983.643c	Gardiner complex, East Greenland
13	A	GM-1971.461	Amdrup Fjord, Kangerdlugssuaq intrusion, East Greenland
14	N	GM-1907.170b	Narssârssuk pegmatite, South Greenland
15	I	GM-1998.100	Ilímaussaq complex, South Greenland
16	K	GM-1988.98	Khibina, Kola Peninsula, Russia
17	B	GM-1998.99	Burpala massif, Siberia, Russia

#: sample number; ps: plot symbol. CMNMC: Canadian Museum of Nature, Mineral Collection; GM: Geological Museum, University of Copenhagen. Sample 13 is kentbrooksite type material.

thus are able to make meaningful comparisons of the crystal chemistry of various members of this complex group of minerals.

Electron-microprobe analysis

Chemical analyses were done in wavelength-dispersion (WD) mode on a JEOL 733 electron microprobe using Tracor Northern 5500 and 5600 automation. Data were reduced with a conventional ZAF routine in the Tracor Northern TASK series of programs. Johnsen & Gault (1997) gave the experimental details. For each sample but one, the actual crystal used in the structure refinement was analyzed chemically. Only sample 7 was lost during transfer to a probe mount. Fortunately, this material from the Kipawa complex, is quite homogeneous, such that the composition of the remaining crystal fragment was used.

Standards used in the analyses were vlasovite (Na$K\alpha$, Si$K\alpha$, Zr$L\alpha$, Hf$L\alpha$), rutile (Ti$K\alpha$), manganocolumbite (Nb$L\alpha$), $NiTa_2O_6$ (Ta$M\alpha$), $CoWO_4$ (W$M\alpha$), almandine (Fe$K\alpha$, Al$K\alpha$), yttrium iron garnet (YIG) (Y$L\alpha$), a set of synthetic *REE* phosphates (La$L\alpha$, Ce$L\alpha$, Nd$L\alpha$, Gd$L\alpha$, Dy$L\beta$, Er$L\alpha$, Yb$L\alpha$, Pr$L\beta$, Sm$L\alpha$), tephroite (Mn$K\alpha$), diopside (Ca$K\alpha$, Mg$K\alpha$), celestine (Sr$L\alpha$), sanbornite (Ba$L\alpha$), sanidine (K$K\alpha$), marialite (Cl$K\alpha$) and phlogopite (F$K\alpha$). Sought but not detected in any of the samples were Eu, Tb, Tm and Lu. A beam 20 μm in diameter was used with all samples. Eudialyte itself seems quite stable in the electron beam with respect to all elements, but the vlasovite standard exhibited problems with Na migration. From a series of decomposition curves, correction factors of 0.859 and 1.006 were derived to apply to the wt.% Na_2O and SiO_2, respectively. The relative error associated with this correction factor is 1.4%. With the vlasovite standard, it was found that the correction could be applied equally well to the wt.%, or as is more normal, to the counts before ZAF calculations. Still, a consistent disparity between Na content derived from the electron-microprobe analyses and structure refinements persists, as discussed later. The chemical compositions are given in Table 2.

Normalization of the formula unit

Formula calculation for eudialyte has always been problematic because of the wide variety of chemical substitutions, disorder within the crystal structure and site vacancies. On the basis of a large dataset of over 60 chemical analyses in Johnsen & Gault (1997) and the initial crystal-structure refinement of Johnsen *et al.* (1998), it became evident that unless specific structural information was available, normalization of the analytical data was best done on the basis of 78 anions (O, Cl, F), with $Z = 3$ for the unit cell. In the present study, we have calculated the number of atoms per formula unit (*apfu*) on an individual basis using the number of anions inferred from SREF data. The *apfu* and the number of anions are given in Table 2.

Collection of X-ray-diffraction data

Crystals were selected for crystallographic data on the basis of optical clarity. In all cases, crystals were ground to spheres ranging in diameter from 0.12 to 0.20 mm. Each crystal was mounted on a Siemens fully automated four-circle diffractometer operated at 50 kV and

TABLE 2. COMPOSITIONS AND ATOMS PER FORMULA UNIT (*apfu*) OF EUDIALYTE SAMPLES [§]

Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
SiO_2	48.53	46.32	45.12	46.91	43.46	43.70	48.95	48.43	50.30	49.67	47.23	49.00	45.34	50.23	48.33	43.87	43.90
TiO_2	0.12	0.13	0.00	0.32	0.00	0.11	0.10	0.46	1.93	0.52	0.82	0.48	0.56	0.20	0.00	0.07	0.83
ZrO_2	11.48	11.22	10.70	10.35	11.44	10.62	11.17	11.55	10.80	10.90	9.85	10.92	11.08	11.23	11.27	10.62	11.22
HfO_2	0.15	0.12	0.19	0.00	0.16	0.18	0.39	0.13	0.00	0.10	0.00	0.10	0.36	0.16	0.13	0.21	0.18
Nb_2O_5	1.47	2.49	2.97	3.02	3.48	1.33	0.47	0.58	0.45	0.60	2.64	1.07	2.26	0.58	0.85	3.53	1.78
Ta_2O_5	0.07	0.31	0.26	0.10	0.14	0.02	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.13	0.04	0.25	0.00
WO_3	0.00	0.00	0.00	0.00	0.00	3.80	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al_2O_3	0.13	0.09	0.08	0.05	0.18	0.09	0.21	0.13	0.18	0.12	0.00	0.08	0.21	0.03	0.34	0.00	1.22
REE_2O_3	1.62	4.69	6.49	4.34	10.15	0.39	0.87	2.88	1.74	0.15	0.52	0.17	5.36	1.66	2.12	5.37	5.60
La_2O_3	0.54	1.53	2.32	1.45	2.88	0.21	0.32	0.37	0.80	0.00	0.25	0.00	2.23	0.29	0.58	1.75	1.75
Ce_2O_3	0.92	2.49	3.47	2.35	5.14	0.18	0.55	0.76	0.94	0.15	0.27	0.17	2.44	0.84	0.95	2.83	2.73
Pr_2O_3	0.00	0.00	0.00	0.00	0.48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Nd_2O_3	0.00	0.62	0.70	0.54	1.45	0.00	0.00	0.35	0.00	0.00	0.00	0.00	0.69	0.53	0.59	0.64	0.69
Sm_2O_3	0.00	0.18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Gd_2O_3	0.16	0.15	0.00	0.00	0.20	0.00	0.00	0.15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.15	0.11
Dy_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Er_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.37	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Yb_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.32
Y_2O_3	0.19	0.59	0.59	0.42	0.78	0.00	2.09	2.82	0.56	0.24	0.25	0.22	1.46	0.75	0.49	0.81	1.66
FeO	3.98	5.04	3.12	2.32	3.00	4.33	1.53	1.94	3.42	4.05	2.32	3.74	1.58	5.97	7.26	2.20	3.18
MnO	3.01	3.98	4.89	7.46	7.70	1.63	1.54	1.16	5.14	1.01	3.00	1.45	8.01	1.33	0.54	5.19	4.52
CaO	9.77	7.95	7.89	6.24	2.90	10.42	13.44	11.56	6.77	11.88	11.91	11.88	5.62	9.36	9.65	8.44	5.60
SrO	0.39	0.43	0.19	0.42	0.09	8.45	0.00	0.18	0.34	2.30	4.13	2.73	0.49	0.20	0.13	2.02	1.71
BaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.14	0.00	0.24	0.32	0.20	0.00	0.00	0.00	0.14	0.17
MgO	0.04	0.00	0.04	0.00	0.00	0.04	0.00	0.11	0.00	0.00	0.00	0.00	0.06	0.03	0.00	0.00	0.06
Na_2O	14.89	13.92	13.79	14.53	13.60	11.35	13.04	14.45	15.22	15.61	14.18	15.43	14.51	15.32	14.49	13.12	11.69
K_2O	0.43	0.43	0.33	0.33	0.28	0.52	0.31	0.61	0.52	0.56	0.44	0.41	0.43	0.45	0.42	0.42	0.38
Cl	0.77	0.83	1.14	0.42	0.76	0.67	1.07	1.07	0.50	1.15	0.95	1.11	0.29	1.83	1.29	0.47	0.88
F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.32	0.00	0.00	0.00	0.00	0.88	0.00	0.00	0.00	0.71
H_2O*	0.69	0.70	0.45	0.31	0.63	0.87	0.67	0.57	0.10	0.39	0.38	0.69	0.33	0.08	0.26	0.70	0.00
$O\equiv Cl$	-0.17	-0.19	-0.26	-0.09	-0.17	-0.15	-0.24	-0.24	-0.11	-0.26	-0.21	-0.25	-0.07	-0.41	-0.29	-0.11	-0.20
$O\equiv F$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.13	0.00	0.00	0.00	0.00	-0.37	0.00	0.00	0.00	-0.30
SUM	97.56	99.05	97.98	97.45	98.58	98.37	95.61	98.71	97.86	99.23	98.75	99.43	98.39	99.13	97.32	97.18	94.79
Si	25.79	25.12	25.12	25.39	24.77	24.78	26.11	25.55	25.84	25.79	25.14	25.77	25.09	26.04	25.74	24.92	24.93
Al	0.08	0.06	0.05	0.03	0.12	0.06	0.13	0.08	0.11	0.07	0.00	0.05	0.14	0.02	0.21	0.00	0.82
Zr	2.98	2.97	2.91	2.73	3.18	2.94	2.91	2.97	2.71	2.76	2.56	2.80	2.99	2.84	2.93	2.94	3.11
Hf	0.02	0.02	0.03	0.00	0.03	0.03	0.06	0.02	0.00	0.01	0.00	0.02	0.06	0.02	0.02	0.03	0.03
Ti	0.05	0.05	0.00	0.13	0.00	0.05	0.04	0.18	0.75	0.20	0.33	0.19	0.23	0.08	0.00	0.03	0.35
Nb	0.35	0.61	0.75	0.74	0.90	0.34	0.11	0.14	0.10	0.14	0.64	0.25	0.57	0.14	0.20	0.91	0.46
Ta	0.01	0.05	0.04	0.01	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.01	0.04	0.00
W	0.00	0.00	0.00	0.00	0.00	0.56	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	1.77	2.29	1.45	1.05	1.43	2.05	0.68	0.86	1.47	1.76	1.03	1.64	0.73	2.59	3.23	1.05	1.51
Mn	1.35	1.83	2.31	3.42	3.72	0.78	0.70	0.52	2.24	0.44	1.35	0.65	3.75	0.58	0.24	2.50	2.17
Mg	0.03	0.00	0.03	0.00	0.00	0.03	0.00	0.09	0.00	0.00	0.00	0.00	0.05	0.02	0.00	0.00	0.05
REE	0.32	0.93	1.32	0.86	2.12	0.08	0.17	0.56	0.33	0.03	0.10	0.03	1.09	0.32	0.41	1.12	1.16
Y	0.05	0.17	0.17	0.12	0.24	0.00	0.59	0.79	0.15	0.07	0.07	0.06	0.43	0.21	0.14	0.24	0.50
Ca	5.56	4.62	4.71	3.62	1.77	6.33	7.68	6.53	3.73	6.61	6.79	6.69	3.33	5.20	5.51	5.14	3.41
Sr	0.12	0.14	0.06	0.13	0.03	2.78	0.00	0.06	0.10	0.69	1.27	0.83	0.16	0.06	0.04	0.67	0.56
Ba	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.05	0.07	0.04	0.00	0.00	0.00	0.03	0.04
K	0.29	0.30	0.23	0.23	0.20	0.38	0.21	0.41	0.34	0.37	0.30	0.28	0.30	0.30	0.29	0.30	0.28
Na	15.34	14.64	14.89	15.25	15.03	12.48	13.49	14.78	15.16	15.71	14.64	15.73	15.57	15.40	14.96	14.45	12.87
Cl	0.69	0.76	1.08	0.39	0.73	0.64	0.97	0.96	0.44	1.01	0.86	0.99	0.27	1.61	1.16	0.45	0.85
F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.53	0.00	0.00	0.00	0.00	1.54	0.00	0.00	0.00	1.28
H	2.45	2.53	1.67	1.12	2.40	3.29	2.38	2.01	0.34	1.35	1.35	2.42	1.22	0.28	0.92	2.65	0.00
Anions*	77.48	77.67	77.90	76.63	78.09	78.70	77.45	77.35	75.39	76.91	77.00	77.96	78.10	76.40	76.75	78.53	77.10

[§] All analyses except of sample 7 are performed on the very same crystal used for SREF. * H_2O and total number of anions calculated from SREF data; for details see text. The calculation of *apfu*'s is based on number of anions.

TABLE 3. UNIT-CELL DIMENSIONS (Å) AND STRUCTURE-REFINEMENT DATA FOR EUDIALYTE SAMPLES

	a	*c*	Space Group*	$\lvert E^2\text{-}1\rvert$	N_{coll}**	data/restraints/params	*R*1 / *wR*2 / Goof ***
1	14.2646(9)	30.186(1)	166	1.041	8216	1934 / 0 / 182	0.031 / 0.073 / 1.090
2	14.2277(6)	29.987(2)	160	0.871	3824	3824 / 0 / 292	0.042 / 0.083 / 1.017
3	14.2602(9)	29.980(3)	160	0.814	3838	3838 / 0 / 282	0.034 / 0.071 / 1.042
4	14.1854(9)	30.101(3)	160	0.916	4990	3503 / 0 / 279	0.044 / 0.086 / 1.052
5	14.2084(8)	29.959(3)	146	0.702	3815	3803 / 0 / 426	0.032 / 0.072 / 1.043
6	14.2959(8)	30.084(3)	160	0.790	3863	3863 / 0 / 282	0.050 / 0.082 / 1.020
7	14.256(1)	30.351(2)	166	0.972	3879	1945 / 0 / 177	0.035 / 0.076 / 1.041
8	14.225(2)	30.302(5)	166	0.967	3858	1934 / 0 / 164	0.033 / 0.070 / 1.006
9	14.1697(9)	30.142(3)	166	0.960	3807	1909 / 0 / 171	0.048 / 0.092 / 1.028
10	14.273(1)	30.131(3)	166	0.972	3860	1935 / 0 / 177	0.039 / 0.073 / 1.017
11	14.271(1)	30.160(3)	160	0.957	4977	3536 / 0 / 284	0.043 / 0.084 / 1.026
12	14.2691(8)	30.163(3)	166	0.965	3858	1935 / 0 / 181	0.033 / 0.071 / 1.023
13	14.199(2)	30.139(4)	160	0.847	2649	2024 / 0 / 283	0.041 / 0.084 / 1.171
14	14.2257(6)	30.006(2)	166	0.999	3835	1923 / 0 / 169	0.039 / 0.071 / 1.022
15	14.242(1)	30.004(6)	166	0.991	2983	1921 / 0 / 173	0.037 / 0.081 / 1.029
16	14.2784(8)	30.089(3)	160	0.802	3855	3855 / 0 / 276	0.043 / 0.078 / 1.040
17	14.220(2)	30.150(7)	160	0.878	2984	2119 / 0 / 281	0.052 / 0.095 / 1.099

*166 = $R\bar{3}m$; 160 = $R3m$; 146 = $R3$. ** Number of reflections collected. *** Goof = Goodness-of-fit on F^2

40 mA with graphite-monochromated Mo*K*α radiation. A set of 25 to 30 reflections were used to center the crystal and refine the cell parameters. Assuming a noncentrosymmetric rhombohedral cell, one asymmetric unit of intensity data was collected (*i.e.*, $+h+k\pm l$) up to $2\theta = 60°$ using a θ:2θ scan-mode, with scan speeds inversely proportional to intensity, varying from 4 to 29.3°/minute. The data collection for each crystal consisted of approximately 3800 reflections with more than 85% observed (*i.e.*, $F_o > 4\sigma\ F_o$). Information relevant to the data collection and structure determination is given in Table 3. For the ellipsoidal absorption correction, 10 to 14 intense diffraction-maxima in the range 12 to 60° 2θ were chosen for Ψ diffraction-vector scans after the method of North *et al.* (1968). The merging *R* for the Ψ-scan dataset decreased from approximately 1.5% before the absorption correction to approximately 1.0% after the absorption correction. The excellent merging *R*-values attest to the near-spherical shape of the crystals. Reduction of the intensity data, and determination and initial refinement of the structure were done with the SHELXTL (Sheldrick 1990) package of computer programs. Structure-refinement data for all crystals are given in Table 3. A set of normalized structure-factors, *E*, were calculated, and the $\lvert E^2 - 1\rvert$ statistic is listed in Table 3. It should be noted that there is a distinct trimodal grouping; centrosymmetric eudialyte ($R\bar{3}m$) has $\lvert E^2 - 1\rvert$ values in the range 0.96 to 1.04, the noncentrosymmetric eudialyte ($R3m$) has $\lvert E^2 - 1\rvert$ values in the range 0.75 to 0.96, and the noncentrosymmetric ($R3$) eudialyte has an $\lvert E^2 - 1\rvert$ of 0.70 (See below). The latter, an incongruously low value for $\lvert E^2 - 1\rvert$, is a result of merohedral twinning (Herbst-Irmer & Sheldrick 1998). A discussion on these statistics is given later in the *Degree of acentricity* section.

Final strategy in the refinements

The final refinements were done with the SHELXL–93 program (Sheldrick 1993). The strategy applied to all crystals during the final stages of the refinement was to keep all atomic coordinates except *Zr*(*z*) variable, and thus refinable, as well as all anisotropic-displacement factors for all sites (except a few disordered sites). For disordered sites with low occupancy, such as the *X* sites and the extra *M*(3) or *Si*(7a) sites, an isotropic displacement parameter was kept fixed. SHELXL–93 recommendations for the splitting of sites were followed in those cases where the refinements remained stable.

The site-occupancy factors (*sof*) were fixed to unity for *Si*(1)–*Si*(6) and *O*(1)–*O*(18), and generally refined for the other sites. Wherever initial refinements indicated a site accommodating essentially only one atomic species, this species was assigned to the site, and the *sof* refined without constraints. In cases where initial refinements showed that the site accommodates, to a significant degree, more than one atomic species, and that the site is fully occupied, the two dominant elements assigned to the site are refined by coupling the positional and anisotropic-displacement parameters allowing the proportion of each *sof* to vary. Where substantial amounts of two elements are present in one site and the site is not fully occupied [*e.g.*, *M*(3) in sample 6], the two elements were assigned to the site in a ratio established by the electron-microprobe data, and the *sof* of one element was allowed to refine in the final stage.

TABLE 4. ATOMIC COORDINATES (x 10^4) AND ISOTROPIC DISPLACEMENT PARAMETERS (Å^2 x 10^3) FOR THREE EUDIALYTE SAMPLES IN SPACE GROUPS $R\bar{3}m$ (166), $R3m$ (160) AND $R3$ (146)

Site	*N*	*x*	*y*	*z*	*U*(eq)
#8: 166					
M(1)	6	0	7384(1)	5000	10(1)
M(2,4)	3	0	5000	5000	64(5)
M(2,5)	6	-607(17)	4697(9)	4979(11)	20
M(3)	2	0	0	1201(1)	39(1)
Si(7)	2	0	0	782(2)	13(2)
Si(7a)	2	0	0	8309(9)	30
Na(1a)	6	2260(3)	-2260(3)	110(2)	44(2)
Na(1b)	6	2531(6)	-2531(6)	-45(4)	23(4)
Na(4)	6	5646(1)	-5646(1)	1177(1)	53(1)
Na(5)	6	-732(4)	732(4)	117(3)	107(4)
Zr	3	5000	5000	0	11(1)
Si(1)	6	4035(1)	-4035(1)	847(1)	11(1)
Si(3)	6	1252(1)	-1252(1)	909(1)	14(1)
Si(3s)	6	1046(19)	-1046(19)	1055(14)	20
Si(5)	12	3410(1)	2778(1)	698(1)	12(1)
O(1)	6	2717(1)	-2717(1)	884(1)	22(1)
O(2)	6	4459(1)	-4459(1)	1239(1)	24(1)
O(3)	6	4290(1)	-4290(1)	363(1)	27(1)
O(7)	12	2319(2)	2857(2)	602(1)	27(1)
O(8)	6	1531(1)	-1531(1)	1380(1)	21(1)
O(9)	6	602(2)	-602(2)	935(2)	55(1)
O(13)	12	4364(2)	3631(2)	393(1)	28(1)
O(14)	12	3708(2)	2965(2)	1210(1)	23(1)
O(15)	6	8435(1)	-8435(1)	542(1)	21(1)
O(19)	6	583(7)	-583(7)	8376(5)	61(6)
O(20)	2	0	0	265(6)	24(6)
X(1a)	2	0	0	7396(3)	69(3)
X(1b)	6	488(11)	-488(11)	7452(8)	30
X(1c)	6	500(15)	-500(15)	7937(11)	30
X(1d)	2	0	0	8003(16)	30
X(1e)	2	0	0	6908(22)	30
#13: 160					
M(1)	6	5940(1)	9257(1)	1674(1)	17(1)
M(2,5)	3	8179(2)	1821(2)	1693(1)	14(1)
M(2,4)	3	8430(21)	1570(21)	1643(11)	30
M(3)	1	0	0	-1281(1)	14(1)
Si(7)	1	0	0	780(2)	11(2)
Si(7a)	1	0	0	1169(11)	30
Na(1a)	3	2221(7)	7779(7)	156(6)	33(4)
Na(1b)	3	2492(38)	7508(38)	-3(20)	77(26)
Na(2)	3	4442(3)	5558(3)	-6787(3)	23(2)
Na(3a)	3	889(20)	9111(20)	2049(11)	73(8)
Na(3b)	3	1151(22)	8849(22)	2155(11)	33(10)
Na(4)	3	5670(1)	4330(1)	1204(1)	15(1)
Na(5)	3	7386(4)	2614(4)	3139(3)	65(3)
Zr	3	4980(1)	5020(1)	0	9(1)
Si(1)	3	2628(1)	7372(1)	2489(1)	14(1)
Si(2)	3	4036(2)	5964(2)	875(1)	17(1)
Si(3)	3	5394(2)	4606(2)	2446(1)	11(1)
Si(4)	3	1248(2)	8752(2)	920(1)	10(1)
Si(5)	6	9460(2)	6764(2)	2632(1)	9(1)
Si(6)	6	7229(2)	626(2)	697(1)	10(1)
O(1)	3	3951(4)	6049(4)	2450(4)	24(2)
O(2)	3	2218(5)	7782(5)	2078(4)	33(3)
O(3)	3	2349(5)	7651(5)	2966(4)	34(3)
O(4)	3	2712(4)	7288(4)	923(4)	29(2)
O(5)	3	4473(5)	5527(5)	1252(4)	36(3)
O(6)	3	941(5)	9059(5)	3713(4)	30(3)
O(7)	6	6098(5)	380(6)	2742(2)	15(1)
O(8)	3	5159(4)	4841(4)	1959(3)	15(2)
O(9)	3	6044(4)	3956(4)	2484(3)	23(2)
O(10)	6	7159(7)	9452(6)	599(2)	25(2)
O(11)	3	1551(4)	8449(4)	1385(3)	17(2)
O(12)	3	596(4)	9404(4)	1004(4)	36(3)
O(13)	6	3022(6)	8981(6)	-6267(2)	22(2)
O(14)	6	7036(6)	742(5)	1211(2)	16(1)
O(15)	3	8435(4)	1565(4)	530(3)	16(2)
O(16)	6	7497(6)	7755(6)	2945(3)	21(2)
O(17)	6	9607(6)	7038(6)	2108(2)	17(1)
O(18)	3	8202(4)	1798(4)	2781(3)	14(2)
O(19)	3	7299(4)	2701(4)	1707(3)	21(3)
O(20)	1	0	0	248(6)	22(5)
X(1a)	1	0	0	-2661(27)	30
X(1b)	3	501(23)	1002(47)	-2609(18)	30
X(1c)	3	258(51)	517(102)	-2454(37)	30
X(2a)	1	0	0	2385(24)	30
X(2b)	1	0	0	2091(15)	30
X(2c)	3	197(17)	394(34)	2920(14)	30
X(2d)	1	0	0	2615(23)	30
X(2e)	1	0	0	1728(20)	30
#5: 146					
M(1a)	3	3937(1)	640(1)	8328(1)	12(1)
M(1b)	3	4214(1)	3328(2)	8325(1)	17(1)
M(2,5)	3	1741(2)	8108(2)	8302(1)	13(1)
M(2,4)	3	1435(23)	8355(21)	8347(6)	23(6)
M(3)	1	0	0	1293(1)	12(1)
M(3b)	1	0	0	777(25)	30
Si(7)	1	0	0	9205(2)	10(1)
Si(7a)	1	0	0	8728(8)	26
Na(1a)	3	7400(17)	2490(24)	10035(10)	46(11)
Na(1b)	3	7708(15)	2196(11)	9863(3)	30(3)
Na(2)	3	5544(8)	4323(7)	6760(2)	44(2)
Na(3)	3	8984(7)	1038(7)	7880(2)	64(2)
Na(4)	3	4405(1)	5696(1)	8800(1)	14(1)
Na(5)	3	2738(7)	7515(8)	6852(2)	55(2)
Zr	3	5119(1)	5052(1)	0	9(1)
Si(1)	3	7487(3)	2748(3)	7514(1)	11(1)
Si(2)	3	6092(3)	4158(3)	9120(1)	13(1)
Si(3)	3	4619(4)	5412(4)	7554(1)	12(1)
Si(4)	3	8751(4)	1212(3)	9073(1)	13(1)
Si(5a)	3	611(3)	3258(3)	7370(2)	10(1)
Si(5b)	3	486(3)	7250(3)	7370(2)	11(1)
Si(6a)	3	2667(3)	-673(3)	9299(2)	11(1)
Si(6b)	3	561(3)	7134(3)	9305(2)	10(1)
O(1)	3	5984(9)	3880(9)	7540(2)	21(1)
O(2)	3	7970(7)	2410(6)	7917(2)	21(2)
O(3)	3	7794(9)	2483(9)	7028(2)	24(2)
O(4)	3	7150(7)	2593(7)	9052(3)	20(2)
O(5)	3	5681(7)	4690(8)	8755(3)	29(2)
O(6)	3	9232(9)	1050(9)	6293(2)	22(2)
O(7a)	3	3844(7)	-438(8)	7248(3)	17(2)
O(7b)	3	3970(7)	4274(7)	7269(4)	19(2)
O(8)	3	4924(9)	5239(10)	8047(2)	21(2)
O(9)	3	3927(9)	6008(10)	7507(2)	26(2)
O(10a)	3	2592(7)	418(8)	9404(4)	26(2)
O(10b)	3	-605(6)	7055(7)	9393(3)	14(2)
O(11)	3	8526(10)	1628(9)	8614(2)	19(2)
O(12)	3	9178(6)	359(6)	8986(3)	23(2)
O(13a)	3	7111(9)	1081(9)	6252(4)	23(2)
O(13b)	3	3592(8)	-671(10)	9599(5)	25(2)
O(14a)	3	2862(8)	9227(8)	8774(4)	14(2)
O(14b)	3	689(9)	6935(8)	8785(4)	17(2)
O(15)	3	1526(9)	8341(9)	9475(2)	19(1)
O(16a)	3	2559(8)	2251(8)	7046(4)	20(2)
O(16b)	3	-211(8)	2236(8)	7074(4)	18(2)
O(17a)	3	448(9)	2980(9)	7891(4)	18(2)
O(17b)	3	350(9)	7369(9)	7892(4)	19(2)
O(18)	3	1734(8)	8133(8)	7218(2)	16(1)
O(19)	3	2652(9)	7276(10)	8308(2)	25(2)
O(20)	1	0	0	9733(4)	14(3)
X(1a)	1	0	0	2660(4)	30
X(1b)	3	-508(22)	506(22)	2597(4)	30
X(1c)	1	0	0	2153(35)	30
X(2a)	1	0	0	7543(4)	30
X(2b)	1	0	0	7897(20)	30
X(2c)	1	0	0	7117(11)	30
X(2d)	1	0	0	8219(22)	30

TABLE 5. ATOMIC COORDINATES (x 10^4) OF EUDIALYTE SAMPLES IN SPACE GROUP $R\bar{3}m$

	#1			#7			#9			#10			#12			#14			#15		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
M(1)	0	7398	5000	0	7389	5000	0	7397	5000	5937	9270	1667	5937	9270	1667	0	7399	5000	5935	9268	1667
M(2,4)	0	5000	5000	0	5000	5000	0	5000	5000	8333	1667	1667	8333	1667	1667	0	5000	5000	8333	1667	1667
M(2,5)	-501	4749	4973	-503	4749	4977	-369	4816	4980	-647	4676	4957	-618	4691	4967	-555	4723	4966	8090	-8090	1713
M(3)	0	0	1272	0	0	1230	0	0	1195	0	0	1282	0	0	1292	0	0	-1270	0	0	-1302
M(3a)	222	111	1115	362	181	1153	354	177	1179	209	105	1114	208	104	1114	0	0	7763	125	63	1147
M(3b)							0	0	7835							132	-132	-1133			
Si(7)	0	0	789	0	0	779	0	0	784	0	0	795	0	0	789	0	0	808	0	0	802
Si(7a)				0	0	8345				0	0	-1668									
Na(1a)	2211	-2211	142	2260	-2260	109	2206	-2206	141	2223	-2223	132	2226	-2226	134	2250	-2250	116	2228	-2228	133
Na(1b)	2468	-2468	-2	2522	-2522	-35	2483	-2483	-20	2465	-2465	-1	2462	-2462	-8	2493	-2493	-27	2487	-2487	-21
Na(4)	5607	-5607	1181	5641	-5641	1180	5619	-5619	1200	5633	-5633	1168	5634	-5634	1171	5623	-5623	1167	5640	-5640	1184
Na(5)	-766	766	108	-729	729	124	-760	760	93	-796	796	77	-780	780	100	-661	946	52	7438	-7438	3247
Zr	5000	5000	0	5000	5000	0	5000	5000	0	5000	5000	0	5000	5000	0	5000	5000	0	5000	5000	0
Si(1)	4036	-4036	845	4036	-4036	845	4038	-4038	848	2630	-2630	2493	2630	-2630	2491	4035	-4035	840	2632	-2632	2490
Si(3)	1249	-1249	912	1250	-1250	910	1252	-1252	912	5425	-5425	2420	5421	-5421	2421	1241	-1241	919	5423	-5423	2413
Si(3s)	1009	-1009	1040	1046	-1046	1058	1008	-1008	1074	1059	-1059	1053	1022	-1022	1022	2014	-1007	1048	989	-989	1067
Si(5)	3397	2761	698	3407	2776	700	3413	2780	699	9426	6727	2637	9427	6728	2637	3391	2756	700	9424	6728	2632
O(1)	2715	-2715	887	2714	-2714	886	2715	-2715	881	2714	-2714	885	2715	-2715	885	2717	-2717	890	2715	-2715	890
O(2)	4474	-4474	1228	4467	-4467	1232	4459	-4459	1241	4474	-4474	1224	4474	-4474	1223	4475	-4475	1222	4479	-4479	1225
O(3)	4278	-4278	352	4284	-4284	357	4294	-4294	362	4274	-4274	345	4279	-4279	346	4267	-4267	340	4270	-4270	346
O(7)	2330	2877	596	2336	2886	603	2339	2891	597	2312	2843	594	2319	2859	595	2305	2827	597	2315	2846	603
O(7s)	2084	2385	650	2072	2378	669	2017	2330	659	2080	2440	663	2087	2385	644	2002	2257	667	2020	2242	669
O(8)	1530	-1530	1381	1519	-1519	1384	1536	-1536	1380	1527	-1527	1381	1525	-1525	1382	1537	-1537	1382	1534	-1534	1388
O(9)	601	-601	934	603	-603	924	603	-603	942	594	-594	951	598	-598	939	595	-595	967	6065	-6065	2384
O(13)	4369	3645	405	4362	3636	395	4372	3647	395	4360	3654	406	4361	3653	403	4351	3669	413	4366	3654	411
O(14)	3667	2886	1218	3712	2964	1211	3694	2929	1216	3667	2891	1215	3670	2895	1215	3663	2880	1223	3669	2881	1223
O(15)	8434	-8434	518	8433	-8433	537	8427	-8427	530	8425	-8425	517	8429	-8429	517	8413	-8413	511	8429	-8429	519
O(19)	618	-618	8391	599	-599	8387	489	-489	8362	7211	-7211	1700	7286	-7286	1700	469	-469	8381	7218	-7218	1691
O(19a)	-1183	4409	4965							1347	4326	4957	7745	-7745	1732						
O(20)	0	0	269	0	0	257	0	0	260	0	0	277	0	0	265	0	0	278	0	0	278
X(1a)	0	0	7410	0	0	7396	0	0	7545	0	0	7380	0	0	7354	0	0	7428	0	0	7442
X(1b)	206	-206	7003	483	-483	7458	0	0	7312	0	0	7611	0	0	7574				403	-403	7733
X(1c)	509	-509	8068	518	-518	7936	0	0	7011	503	-503	7883	465	-465	7769						
X(1d)	0	0	7890	0	0	8093				0	0	7873	517	-517	8001						
X(1e)	0	0	6877	0	0	6911				0	0	6979	0	0	7879						
X(1f)	398	-398	7780	0	0	7751							0	0	6926						

TABLE 6. ATOMIC COORDINATES (x 10^4) OF EUDIALYTE SAMPLES IN SPACE GROUP *R*3*m*

	#2			#3			#4			#6			#11			#16			#17		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
M(1)	5943	9259	1672	4056	745	8325	4071	743	8328	5946	9258	1675	4057	731	8331	5951	9260	1676	5949	9263	1672
M(2,5)	8201	1799	1693	1829	8171	8295	1831	8169	8309	8180	1820	1702	1793	8207	8314	8169	1831	1696	8172	1828	1697
M(2,4)	8411	1589	1647	1707	8293	8354	1459	8541	8345	8313	1687	1654	1502	8498	8366	8371	1629	1671	8368	1632	1661
M(3)	0	0	-1301	0	0	1297	0	0	1275	0	0	-1318	0	0	1302	0	0	-1295	0	0	-1290
M(3a)	0	0	-1175	0	0	1117	0	0	1676	0	0	-1318	0	0	1684				0	0	-1670
M(3b)	0	0	-799	0	0	1652	0	0	776				0	0	768						
Si(7)	0	0	789	0	0	9208	0	0	9220	0	0	773	0	0	9214	0	0	782	0	0	780
Si(7a)	0	0	1198	0	0	8798	0	0	8775	0	0	1233	0	0	8774	0	0	1169	0	0	1192
Na(1a)	2251	7749	128	7482	2518	34	7758	2242	9870	2187	7813	153	7833	2167	9834	2255	7745	135	2213	7787	128
Na(1b)	2577	7423	-63	7761	2239	9861	7378	2622	74	2385	7615	55	7584	2416	-25	2568	7432	-43	2543	7457	-26
Na(2)	4397	5603	-6763	5618	4382	16754	5551	4449	6796	4378	5622	-6757	5597	4403	6780	4391	5609	-6755	4368	5632	-6750
Na(3a)	883	9117	2075	8962	1038	7861	8965	1035	7891	973	9027	2149	8961	1039	7839	859	9141	2063	982	9018	2150
Na(3b)	1064	8936	2149							973	9027	2149				1116	8884	2167			
Na(4)	5662	4338	1196	4344	5656	8809	4343	5657	8797	5670	4330	1173	4332	5668	8815	5664	4336	1188	5655	4345	1180
Na(5)	7399	2601	3168	2610	7390	6849	2614	7386	6839	7361	2639	3142	2586	7414	6821	7382	2618	3136	7311	2689	3221
Zr	4979	5021	0	5034	4966	10000	5013	4987	10000	4968	5032	0	5006	4994	10000	4967	5033	0	4975	5025	0
Si(1)	2630	7370	2493	7371	2629	7498	7372	2628	7516	2630	7370	2502	7371	2629	7507	2629	7371	2501	2629	7371	2493
Si(2)	4036	5964	865	5968	4032	9132	5964	4036	9137	4033	5967	861	5966	4034	9154	4033	5967	868	4032	5968	868
Si(3)	5403	4597	2434	4599	5401	7557	4601	5399	7561	5408	4592	2435	4580	5420	7568	5398	4602	2446	5393	4607	2433
Si(4)	1238	8762	926	8770	1230	9071	8755	1245	9089	1233	8767	923	8749	1251	9090	1232	8768	924	1239	8761	920
Si(5)	9441	6746	2630	559	3255	7368	551	3249	7366	9429	6736	2636	563	3264	7359	9443	6746	2634	9439	6736	2634
Si(6)	7238	10626	698	2759	-624	9304	2779	-624	9302	7247	10620	694	2762	-631	9304	7241	10622	693	7235	10630	698
O(1)	3946	6054	2458	6053	3947	7528	6050	3950	7556	3945	6055	2482	6049	3951	7539	3946	6054	2479	3946	6054	2463
O(2)	2210	7790	2097	7785	2215	7896	7776	2224	7921	2221	7779	2105	7802	2198	7895	2220	7780	2095	2232	7768	2077
O(3)	2367	7633	2986	7647	2353	7017	7644	2356	7043	2350	7650	2990	7639	2361	7019	2348	7652	2984	2321	7679	2964
O(4)	2711	7289	927	7284	2716	9062	7286	2714	9102	2715	7285	923	7285	2715	9105	2723	7277	937	2711	7289	916
O(5)	4488	5512	1237	5497	4503	8767	5523	4477	8752	4496	5504	1224	5523	4477	8771	4493	5507	1232	4481	5519	1240
O(6)	922	9078	3698	9098	902	6311	9052	948	6301	913	9087	3688	9069	931	6314	910	9090	3698	911	9089	3701
O(7)	6116	10418	2736	3902	-377	7263	3882	-406	7257	6097	10388	2734	3840	-530	7266	6101	10367	2738	6109	10423	2743
O(8)	5153	4847	1949	4836	5164	8050	4855	5145	8036	5160	4840	1952	4843	5157	8049	5164	4836	1956	5134	4866	1960
O(9)	6047	3953	2465	3955	6045	7511	3950	6050	7552	6055	3945	2469	3948	6052	7553	6043	3957	2495	6043	3957	2423
O(10)	7185	9471	605	2767	507	9397	2847	548	9402	7219	9486	599	2903	562	9413	7227	9485	598	7176	9465	608
O(11)	1546	8454	1390	8452	1548	8612	8454	1546	8615	1542	8458	1387	8467	1533	8622	1546	8454	1385	1557	8443	1386
O(12)	594	9406	1007	9406	594	8982	9401	599	9045	591	9409	996	9414	586	9022	593	9407	1006	594	9406	977
O(13)	3001	8988	-6263	7025	993	16257	6948	1003	16271	2982	9005	-6257	6971	1022	16269	2981	9008	-6259	3015	9013	-6263
O(14)	7076	774	1219	2935	9236	8783	2939	9243	8782	7084	765	1216	2910	9215	8795	7053	752	1212	7063	748	1215
O(15)	8414	1586	522	1598	8402	9485	1571	8429	9467	8408	1592	503	1561	8439	9480	8407	1593	520	8435	1565	531
O(16)	7461	7736	2929	2516	2255	7068	2545	2242	7065	7465	7731	2936	2593	2275	7070	7493	7752	2939	7463	7739	2938
O(17)	9566	7010	2106	436	2995	7891	387	2991	7884	9546	7006	2115	412	2997	7888	9571	7011	2111	9593	7007	2113
O(18)	8203	1797	2800	1802	8198	7206	1784	8216	7203	8189	1811	2805	1762	8238	7183	8195	1805	2797	8216	1784	2787
O(19)	7297	2703	1694	2693	7307	8309	2700	7300	8295	7306	2694	1695	2684	7316	8307	7305	2695	1694	7290	2710	1669
O(20)	0	0	260	0	0	9738	0	0	9751	0	0	254	0	0	9748	0	0	254	0	0	224
O(20a)													0	0	264				0	0	-303
X(1a)	0	0	-2628	0	0	2649	0	0	2688	0	0	-2677	0	0	2682	0	0	-2654	0	0	-2706
X(1b)	485	971	-2594	9486	8973	2613	0	0	2382	-990	-495	-2642	0	0	2368	501	1003	-2622	474	-474	-2615
X(1c)	502	1005	-2283				9575	9149	2536	0	0	-3194				0	0	-3082			
X(1d)	241	482	-2033																		
X(2a)	0	0	2437	0	0	7511	0	0	8005	0	0	2811	0	0	7355	0	0	2804	0	0	2516
X(2b)	0	0	1732	0	0	7104	0	0	7397	0	0	2477	0	0	7001	0	0	2458	0	0	2721
X(2c)	175	350	2931				0	0	7052	0	0	1738	484	968	7851				191	382	2921
X(2d)	0	0	2627							-370	-739	1931	0	0	7877				0	0	

Corrections refined for secondary isotropic extinction were found to be insignificant and hence were omitted. For the noncentrosymmetric samples, incorporation of a twin fraction according to merohedral twinning in the refinements resulted in slight improvements of the agreement indices for some crystals and were kept. In the case of sample 5, belonging to space group *R*3, introduction of a twin operation corresponding to the lost mirror plane in *R*3*m* resulted in a significant improvement in the refinement, as the *R*-index dropped from 0.107 to 0.032.

Table 4 contains complete sets of the final positional and equivalent isotropic-displacement parameters for a representative example of each of the three space groups concerned. Tables 5 and 6 list the positional parameters of the remaining samples in $R\bar{3}m$ and *R*3*m*, respectively. Selected interatomic distances for one crystal in each space group are given in Table 7. Anisotropic-displacement factors and observed and calculated structure-factors for all samples have been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

Site-assignment procedure

Table 8 presents the site-scattering values of the refined cation sites expressed in terms of electrons per formula unit (*epfu*) and atoms per formula unit (*apfu*), along with bond-valence and valence sums. Table 9

TABLE 7. SELECTED INTERATOMIC DISTANCES (Å) FOR THREE EUDIALYTE SAMPLES IN SPACE GROUPS $R\bar{3}m$, $R3m$ AND $R3$.

#8 ($R\bar{3}m$)	
Si(1)-*O*(1)	1.638(1) x 2
Si(1)-*O*(2)	1.582(3)
Si(1)-*O*(3)	1.595(3)
Si(3)-*O*(7)	1.630(2) x 2
Si(3)-*O*(8)	1.585(3)
Si(3)-*O*(9)	1.602(4)
Si(3)-*Si*(3s)	0.67(5)
Si(5)-*O*(7)	1.637(2)
Si(5)-*O*(13)	1.589(2)
Si(5)-*O*(14)	1.594(2)
Si(5)-*O*(15)	1.636(1)
Zr-*O*(3)	2.067(3) x 2
Zr-*O*(13)	2.065(2) x 4
M(1)-*O*(2)	2.311(2) x 2
M(1)-*O*(14)	2.326(2) x 2
M(1)-*O*(8)	2.387(2) x 2
M(2,4)-*O*(14)	2.151(2) x 4
M(2,4)-*M*(2,5)	0.75(2)
M(2,5)-*O*(14)	2.16(2) x 2
M(2,5)-*O*(14)	2.39(2) x 2
M(2,5)-*O*(19)	1.92(3)
M(3)-*O*(9)	1.689(5) x 3
M(3)-*O*(19)	1.92(2) x 3
Si(7)-*O*(9)	1.555(4) x 3
Si(7)-*O*(20)	1.57(2)
Si(7a)-*X*(1c)	1.67(4) x 3
⟨*Na*(1a)-ϕ⟩	2.68
⟨*Na*(1b)-ϕ⟩	2.61
Na(1a)-*Na*(1b)	0.82(2)
⟨*Na*(4)-ϕ⟩	2.60
⟨*Na*(5)-ϕ⟩	2.83
#13 ($R3m$)	
Si(1)-*O*(1)	1.638(5) x 2
Si(1)-*O*(2)	1.59(1)
Si(1)-*O*(3)	1.59(1)
Si(2)-*O*(4)	1.639(5) x 2
Si(2)-*O*(5)	1.56(1)
Si(2)-*O*(6)	1.60(1)
Si(3)-*O*(7)	1.643(7) x 2
Si(3)-*O*(8)	1.573(9)
Si(3)-*O*(9)	1.60(1)
Si(4)-*O*(10)	1.626(8) x 2
Si(4)-*O*(11)	1.584(9)
Si(4)-*O*(12)	1.62(1)
Si(5)-*O*(7)	1.641(7)
Si(5)-*O*(16)	1.597(7)
Si(5)-*O*(17)	1.612(7)
Si(5)-*O*(18)	1.652(4)
Si(6)-*O*(10)	1.643(7)
Si(6)-*O*(13)	1.579(8)
Si(6)-*O*(14)	1.592(7)
Si(6)-*O*(15)	1.634(4)
Zr-*O*(3)	2.05(1)
Zr-*O*(6)	2.07(1)
Zr-*O*(13)	2.073(7) x 2
Zr-*O*(16)	2.071(8) x 2
M(1)-*O*(2)	2.239(6)
M(1)-*O*(5)	2.283(7)
M(1)-*O*(8)	2.426(6)
M(1)-*O*(11)	2.338(6)
M(1)-*O*(14)	2.348(7)
M(1)-*O*(17)	2.314(7)
M(2,4)-*O*(14)	2.16(2) x 2
M(2,4)-*O*(17)	2.09(2) x 2
M(2,4)-*M*(2,5)	0.64(5)
M(2,5)-*O*(14)	2.142(7) x 2
M(2,5)-*O*(17)	2.151(7) x 2
M(2,5)-*O*(19)	2.16(1)
M(3)-*O*(9)	2.01(1) x 3
M(3)-*O*(19)	1.87(1) x 3
Si(7)-*O*(12)	1.61(1) x 3
Si(7)-*O*(20)	1.60(2)
Si(7a)-*O*(12)	1.54(1) x 3
Si(7a)-*X*(2e)	1.68(7)
⟨*Na*(1a)-ϕ⟩	2.71
⟨*Na*(1b)-ϕ⟩	2.59
Na(1a)-*Na*(1b)	0.82(9)
⟨*Na*(2)-ϕ⟩	2.66
⟨*Na*(3a)-ϕ⟩	2.69
⟨*Na*(3b)-ϕ⟩	2.75
Na(3a)-*Na*(3b)	0.72(2)
⟨*Na*(4)-ϕ⟩	2.65
⟨*Na*(5)-ϕ⟩	2.75
#5 ($R3$)	
Si(1)-*O*(1)	1.59(1)
Si(1)-*O*(1)	1.68(1)
Si(1)-*O*(2)	1.579(7)
Si(1)-*O*(3)	1.618(7)
Si(2)-*O*(4)	1.622(9)
Si(2)-*O*(4)	1.672(9)
Si(2)-*O*(5)	1.596(8)
Si(2)-*O*(6)	1.602(7)
Si(3)-*O*(7a)	1.657(9)
Si(3)-*O*(7b)	1.64(1)
Si(3)-*O*(8)	1.592(6)
Si(3)-*O*(9)	1.591(7)
Si(4)-*O*(10a)	1.62(1)
Si(4)-*O*(10b)	1.652(9)
Si(4)-*O*(11)	1.592(7)
Si(4)-*O*(12)	1.626(8)
Si(5a)-*O*(7a)	1.633(9)
Si(5a)-*O*(16b)	1.60(1)
Si(5a)-*O*(17a)	1.60(1)
Si(5a)-*O*(18)	1.66(1)
Si(5b)-*O*(7b)	1.65(1)
Si(5b)-*O*(16a)	1.61(1)
Si(5b)-*O*(17b)	1.60(1)
Si(5b)-*O*(18)	1.64(1)
Si(6a)-*O*(10a)	1.64(1)
Si(6a)-*O*(13b)	1.59(1)
Si(6a)-*O*(14a)	1.62(1)
Si(6a)-*O*(15)	1.61(1)
Si(6b)-*O*(10b)	1.625(9)
Si(6b)-*O*(13a)	1.59(1)
Si(6b)-*O*(14b)	1.61(1)
Si(6b)-*O*(15)	1.65(1)
Zr-*O*(3)	2.059(8)
Zr-*O*(6)	2.105(7)
Zr-*O*(13a)	2.07(1)
Zr-*O*(13b)	2.06(1)
Zr-*O*(16a)	2.07(1)
Zr-*O*(16b)	2.06(1)
M(1a)-*O*(2)	2.124(8)
M(1a)-*O*(5)	2.174(9)
M(1a)-*O*(8)	2.35(1)
M(1a)-*O*(11)	2.23(1)
M(1a)-*O*(14a)	2.25(1)
M(1a)-*O*(17a)	2.24(1)
M(1b)-*O*(2)	2.364(8)
M(1b)-*O*(5)	2.391(9)
M(1b)-*O*(8)	2.52(1)
M(1b)-*O*(11)	2.45(1)
M(1b)-*O*(14b)	2.43(1)
M(1b)-*O*(17b)	2.42(1)
M(2,4)-*O*(14a)	2.18(2)
M(2,4)-*O*(14b)	2.19(2)
M(2,4)-*O*(17a)	2.13(3)
M(2,4)-*O*(17b)	2.01(3)
M(2,4)-*M*(2,5)	0.69(3)
M(2,5)-*O*(14a)	2.13(1)
M(2,5)-*O*(14b)	2.15(1)
M(2,5)-*O*(17a)	2.16(1)
M(2,5)-*O*(17b)	2.11(1)
M(2,5)-*O*(19)	2.145(7)
M(3)-*O*(9)	2.054(7)
M(3)-*O*(19)	1.901(7)
M(3b)-*O*(9)	1.55(1) x 3
Si(7)-*O*(12)	1.629(7) x 3
Si(7)-*O*(20)	1.58(1)
Si(7a)-*O*(12)	1.68(1) x 3
Si(7a)-*X*(2d)	1.52(7)
⟨*Na*(1a)-ϕ⟩	2.55
⟨*Na*(1b)-ϕ⟩	2.66
Na(1a)-*Na*(1b)	0.90(3)
⟨*Na*(2)-ϕ⟩	2.36
⟨*Na*(3a)-ϕ⟩	2.69
⟨*Na*(4)-ϕ⟩	2.67
⟨*Na*(5)-ϕ⟩	2.57

ϕ: unspecified anion.

gives the *epfu* numbers for the refined anion sites. The site-assignment procedure applied includes the following steps:

(i) Calculation of the number of anions: Site-scattering values (*epfu*) of the refined anion-sites are converted to *apfu*. *O*(19) and *O*(20) are considered to contain oxygen only, whereas the *X* sites accommodate (Cl,F) derived from electron-microprobe data, and (OH) is added to total 2 *apfu*. The remaining *epfu* in *X* sites are considered to be (H_2O). The *apfu* from these sites are added to the 72 atoms of oxygen belonging to the silicate ring system, giving the total amount of anions that, together with the derived number of (H), form the basis of a recalculation of electron-microprobe data to give the *apfu* shown in Table 2.

(ii) Knowing the *epfu* of the cation-sites and the numbers of these sites in the structural formula (*N* in Table 4), and assuming full occupancy, an *apfu* population of each site can be assessed on the basis of electron-microprobe data and guided by calculations of bond-valence and valence sums (Table 8). This procedure is valid for fully ordered structures covering most of the acentric crystals, whereas it becomes problematic in cases with extensive disorder. In crystals where the pseudocentrosymmetrically related sites *M*(3) and *Si*(7) are disordered to such an extent that they are best refined in $R\bar{3}m$, the scattering overlap precludes the determination of which cation is bonded to which ligand. In such cases, bond-valence sums cannot be calculated, and an *apfu* population for *M*(3) and *Si*(7) together is

TABLE 8. SITE-SCATTERING VALUES (*epfu*), SITE POPULATIONS (*apfu*), BOND-VALENCE SUM AND VALENCE SUM FOR CATION SITES WITH REFINED OCCUPANCY IN EUDIALYTE SAMPLES

site	*epfu***	*apfu* assignment	BVS*	VS
#1:				
M(1)	131.4(5)	$Ca_{5.32}Mn_{0.40}REE_{0.23}Y_{0.05}$	2.06	2.05
M(2,5)	20(5)	$Mn_{0.82}$	0.53	0.55
M(2,4)	49(4)	$Fe_{1.77}Mn_{0.13}$	1.05	1.27
M(3)	17(1)	$Si_{1.67}Nb_{0.33}$	§	
M(3a)	8(1)			
Si(7)	11.6(3)			
Zr	119.8(4)	$Zr_{2.97}Ti_{0.03}$	4.12	4.00
Na(1)	65.2(7)	$Na_{5.92}$	0.88	0.99
Na(4)	78.0(6)	$Na_{5.26}K_{0.29}Ca_{0.24}Sr_{0.12}REE_{0.09}$	1.14	1.09
Na(5)	32.8(7)	$Na_{2.98}$	0.75	1.00
#2:				
M(1)	134.7(5)	$Ca_{4.46}Mn_{1.23}Y_{0.17}REE_{0.14}$	2.06	2.05
M(2,5)	61(2)	$Fe_{1.78}Mn_{0.60}$	1.43	1.59
M(2,4)	13(2)	$Fe_{0.52}$	0.27	0.35
M(3)	25(1)	$Nb_{0.62}Ti_{0.06}Ta_{0.04}$	3.58	3.54
M(3a)	4(1)			
M(3b)	1.7(3)	$Si_{0.12}$	0.45	0.48
Si(7)	9.4(3)	$Si_{0.67}$	2.67	2.68
Si(7a)	4.6(4)	$Si_{0.33}$	1.25	1.32
Zr	119.8(4)	$Zr_{3.00}$	4.15	4.00
Na(1)	30.5(4)	$Na_{2.77}$	0.83	0.92
Na(2)	32.2(6)	$Na_{2.93}$	0.86	0.98
Na(3)	38.9(5)	$Na_{2.87}REE_{0.13}$	0.85	1.09
Na(4)	71.9(5)	$Na_{1.66}REE_{0.67}K_{0.30}Ca_{0.24}Sr_{0.13}$	1.72	1.57
Na(5)	30.4(5)	$Na_{2.76}$	0.84	0.92
#3:				
M(1)	132.3(5)	$Ca_{4.84}Mn_{0.88}Y_{0.18}REE_{0.10}$	2.06	2.05
M(2,5)	56(4)	$Mn_{1.45}Fe_{0.77}$	1.41	1.48
M(2,4)	18(4)	$Fe_{0.68}$	0.36	0.45
M(3)	36.0(4)	$Nb_{0.78}Ta_{0.07}$	4.18	4.25
M(3a)	1.4(5)			
Si(7)	11.8(2)	$Si_{0.84}$	3.35	3.36
Si(7a)	1.3(2)	$Si_{0.09}$	0.31	0.36
Zr	119.5(3)	$Zr_{2.99}$	4.12	3.99
Na(1)	30.3(4)	$Na_{2.76}$	0.85	0.92
Na(2)	32.9(5)	$Na_{2.99}$	0.88	1.00
Na(3)	36.5(5)	$Na_{2.92}REE_{0.08}$	0.85	1.05
Na(4)	91.9(4)	$Na_{1.50}REE_{1.20}K_{0.24}Sr_{0.06}$	1.65	1.82
Na(5)	32.1(5)	$Na_{2.91}$	0.84	0.97
#4:				
M(1)	142.2(4)	$Ca_{3.70}Mn_{1.88}REE_{0.29}Y_{0.12}$	2.09	2.06
M(2,5)	53.3(6)	$Mn_{1.56}Fe_{0.55}$	1.26	1.41
M(2,4)	13.1(7)	$Fe_{0.50}$	0.21	0.33
M(3)	24.1(3)	$Si_{1.33}Nb_{0.67}$	§	
M(3a)	1.9(2)			
M(3b)	2.1(3)			
Si(7)	6.9(3)			
Si(7a)	11.2(6)			
Zr	117.9(4)	$Zr_{2.76}Ti_{0.13}Nb_{0.11}$	4.16	4.05
Na(1)	32.4(4)	$Na_{2.95}$	0.84	0.98
Na(2)	30.7(5)	$Na_{2.79}$	0.86	0.93
Na(3)	37.3(5)	$Na_{2.91}REE_{0.09}$	0.95	1.13
Na(4)	53.6(4)	$Na_{2.31}REE_{0.34}K_{0.23}Sr_{0.12}$	1.19	1.27
Na(5)	26.4(6)	$Na_{2.40}$	0.77	0.80
#5:				
M(1a)	79.6(6)	$Mn_{2.75}Y_{0.25}$	2.01	2.08
M(1b)	75.1(4)	$Ca_{1.77}REE_{0.57}Na_{0.66}$	1.80	1.97
M(2,5)	62.6(8)	$Fe_{1.13}Mn_{0.95}Zr_{0.24}$	1.45	1.71
M(2,4)	7.3(8)	$Fe_{0.28}$	0.13	0.19
M(3)	35.7(3)	$Nb_{0.87}$	4.21	4.34
Si(7)	11.2(3)	$Si_{0.80}$	3.09	3.20
Si(7a)	2.9(2)	$Si_{0.20}$	0.65	0.80
Zr	119.0(4)	$Zr_{2.93}Nb_{0.05}$	4.16	3.99
Na(1)	30.8(6)	$Na_{2.80}$	0.81	0.93
Na(2)	33.2(6)	$Na_{3.02}$	0.86	1.01
Na(3)	41.5(6)	$Na_{2.82}REE_{0.18}$	0.94	1.12
Na(4)	96.6(5)	$Na_{1.44}REE_{1.35}K_{0.19}$	1.88	1.90
Na(5)	31.6(6)	$Na_{2.87}$	0.79	0.96
#6:				
M(1)	121.7(6)	$Ca_{6.08}$	2.07	2.03
M(2,5)	60(6)	$Fe_{1.55}Mn_{0.80}$	1.45	1.57
M(2,4)	13(6)	$Fe_{0.53}$	0.28	0.35
M(3)	51.3(4)	$W_{0.52}Nb_{0.31}$	4.75	4.67
Si(7)	8.7(3)	$Si_{0.62}$	2.46	2.48
Si(7a)	5.9(4)	$Si_{0.42}$	1.58	1.68
Zr	118.3(5)	$Zr_{2.96}$	4.11	3.95
Na(1)	31.7(6)	$Na_{2.88}$	0.80	0.96
Na(2)	36.1(6)	$Na_{3.28}$	0.89	1.09
Na(3)	45.1(8)	$Na_{2.03}Ca_{0.40}K_{0.37}Sr_{0.13}REE_{0.07}$	1.09	1.22
Na(4)	103.0(6)	$Sr_{2.60}Na_{0.40}$	2.05	1.87
Na(5)	32.2(7)	$Na_{2.93}$	0.87	0.98
#7:				
M(1)	141.7(6)	$Ca_{5.08}Y_{0.69}REE_{0.23}$	2.21	2.15
M(2,5)	10(1)	$Mn_{0.40}$	0.21	0.27
M(2,4)	48(1)	$Fe_{1.52}Mn_{0.30}$	0.81	1.21
M(3)	21(1)	$Si_{1.71}Nb_{0.29}$	§	
M(3a)	6(1)			
Si(7)	8.5(3)			
Zr	119.7(4)	$Zr_{2.90}Ti_{0.05}Hf_{0.04}$	4.15	3.99
Na(1)	64.8(7)	$Na_{5.89}$	0.81	0.98
Na(4)	94.0(6)	$Ca_{2.92}Na_{2.87}K_{0.21}$	1.49	1.49
Na(5)	33.4(8)	$Na_{3.04}$	0.65	1.02
#8:				
M(1)	152.3(4)	$Ca_{4.74}Y_{0.79}REE_{0.47}$	2.34	2.21
M(2,5)	7(2)	$Fe_{0.25}Mg_{0.09}$	0.15	0.26
M(2,4)	48(2)	$Fe_{1.32}Mn_{0.55}$	0.85	1.25
M(3)	24.6(3)	$Si_{1.63}Ti_{0.21}Nb_{0.16}$	§	
Si(7)	8.1(3)			
Si(7a)	2.9(2)			
Zr	120.00	Zr_3 (fixed)	4.24	4.00
Na(1)	64.3(6)	$Na_{5.84}$	0.81	0.97
Na(4)	89.6(5)	$Na_{3.77}Ca_{1.70}K_{0.39}Sr_{0.06}REE_{0.07}$	1.39	1.32
Na(5)	29.8(6)	$Na_{2.71}$	0.64	0.90
#9:				
M(1)	139.7(4)	$Ca_{3.79}Mn_{1.48}REE_{0.38}Zr_{0.18}Y_{0.17}$	2.11	2.15
M(2,5)	40(4)	$Fe_{0.57}Mn_{0.79}Ti_{0.25}$	0.86	1.24
M(2,4)	24(4)	$Fe_{0.92}$	0.46	0.61
M(3)	15(4)	$Si_{1.89}Nb_{0.11}$	§	
M(3a)	7(4)			
Si(7)	8.0(4)			
Zr	111.0(6)	$Zr_{2.50}Ti_{0.50}$	4.26	4.00
Na(1)	60.0(6)	$Na_{5.45}$	0.80	0.91
Na(4)	71.4(9)	$Na_{5.56}K_{0.34}Sr_{0.10}$	0.92	1.02
Na(5)	27.5(9)	$Na_{2.50}$	0.61	0.84
#10:				
M(1)	122.8(5)	$Ca_{5.89}Y_{0.08}REE_{0.03}$	2.05	2.02
M(2,5)	12(1)	$Mn_{0.47}$	0.32	0.32
M(2,4)	54.7(9)	$Fe_{1.90}Mn_{0.20}$	1.13	1.40
M(3)	9(1)	$Si_{1.84}Nb_{0.16}$	§	
M(3a)	10(1)			
Si(7)	13.6(3)			
Zr	115.7(4)	$Zr_{2.78}Ti_{0.22}$	4.14	4.00
Na(1)	63.5(6)	$Na_{5.77}$	0.82	0.96
Na(4)	92.6(6)	$Na_{4.29}Ca_{0.71}Sr_{0.65}K_{0.35}$	1.23	1.23
Na(5)	33.2(6)	$Na_{3.05}$	0.73	1.02

TABLE 8 CONTINUED

site	*epfu***	*apfu* assignment	BVS*	VS
#11				
M(1)	121.5(5)	$Ca_{5.93}Y_{0.07}$	2.07	2.01
M(2,5)	49(3)	$Mn_{1.43}Fe_{0.49}$	1.13	1.28
M(2,4)	15(3)	$Fe_{0.58}$	0.26	0.39
M(3)	14.4(4)	$Si_{1.37}Nb_{0.63}$	§	
M(3a)	1.9(2)			
M(3b)	5.6(3)			
Si(7)	7.3(4)			
Si(7a)	16.1(6)			
Zr	114.5(4)	$Zr_{2.59}Ti_{0.34}Nb_{0.07}$	4.10	4.02
Na(1)	40.5(6)	$Na_{2.17}Ca_{0.83}$	1.04	1.23
Na(2)	25.0(8)	$Na_{2.27}$	0.80	0.76
Na(3)	62(1)	$Na_{1.85}Sr_{0.68}K_{0.30}\mathit{REE}_{0.13}Ba_{0.07}$	1.30	1.32
Na(4)	59.9(6)	$Na_{2.38}Sr_{0.62}$	0.95	1.21
Na(5)	33.7(8)	$Na_{3.06}$	0.87	1.02
#12				
M(1)	122.2(5)	$Ca_{5.91}Y_{0.06}\mathit{REE}_{0.03}$	2.05	2.02
M(2,5)	10(1)	$Mn_{0.39}$	0.42	0.26
M(2,4)	55(1)	$Fe_{1.77}Mn_{0.35}$	1.15	1.41
M(3)	12.7(8)	$Si_{1.73}Nb_{0.27}$	§	
M(3a)	10.3(6)			
Si(7)	12.4(3)			
Zr	116.4(4)	$Zr_{2.80}Ti_{0.20}$	4.19	4.00
Na(1)	63.3(6)	$Na_{5.75}$	0.81	0.96
Na(4)	94.7(6)	$Na_{4.26}Sr_{0.76}Ca_{0.72}K_{0.26}$	1.25	1.25
Na(5)	35.4(6)	$Na_{3.22}$	0.71	1.08
#13				
M(1)	152.5(5)	$Ca_{3.37}Mn_{1.79}Y_{0.43}\mathit{REE}_{0.41}$	2.17	2.14
M(2,5)	63(1)	$Mn_{1.99}Fe_{0.45}Al_{0.14}$	1.51	1.75
M(2,4)	7(1)	$Fe_{0.29}$	0.14	0.19
M(3)	29.6(4)	$Nb_{0.55}Zr_{0.13}Ti_{0.08}$	3.83	3.59
Si(7)	11.8(4)	$Si_{0.85}$	3.50	3.40
Si(7a)	3.7(4)	$Si_{0.26}$	1.04	1.04
Zr	119.3(6)	$Zr_{2.82}Ti_{0.13}Hf_{0.05}$	4.15	4.00
Na(1)	37.8(6)	$Na_{2.90}\mathit{REE}_{0.10}$	1.02	1.07
Na(2)	26.1(9)	$Na_{2.37}$	0.69	0.79
Na(3)	41.5(6)	$Na_{2.82}\mathit{REE}_{0.18}$	1.08	1.12
Na(4)	70.8(4)	$Na_{1.86}\mathit{REE}_{0.68}K_{0.30}Sr_{0.16}$	1.40	1.51
Na(5)	33.2(9)	$Na_{3.02}$	0.96	1.01
#14				
M(1)	136.9(5)	$Ca_{5.20}Mn_{0.31}\mathit{REE}_{0.26}Y_{0.23}$	2.12	2.08
M(2,5)	13(1)	$Mn_{0.29}Fe_{0.21}$	0.26	0.33
M(2,4)	62(1)	$Fe_{2.40}$	1.39	1.60
M(3)	5.6(7)	$Si_{1.88}Nb_{0.12}$	§	
M(3b)	13(3)			
Si(7)	12.5(3)			
Zr	119.0(4)	$Zr_{2.86}Ti_{0.09}Nb_{0.03}Hf_{0.02}$	4.20	4.01
Na(1)	63.6(7)	$Na_{5.78}$	0.80	0.96
Na(4)	76.5(6)	$Na_{5.48}K_{0.31}Ce_{0.13}Sr_{0.08}$	0.87	1.06
Na(5)	32.7(7)	$Na_{2.97}$	0.76	0.98
#15				
M(1)	133.6(6)	$Ca_{5.15}Fe_{0.25}Mn_{0.24}\mathit{REE}_{0.22}Y_{0.14}$	2.11	2.06
M(2,5)	12(2)	$Fe_{0.46}$	0.24	0.31
M(2,4)	65(2)	$Fe_{2.52}$	1.47	1.68
M(3)	10(1)	$Si_{1.85}Nb_{0.15}$	§	
M(3a)	14(1)			
Si(7)	11.4(3)			
Zr	119.6(4)	$Zr_{2.93}Nb_{0.05}Hf_{0.02}$	4.17	4.02
Na(1)	65.1(6)	$Na_{5.92}$	0.84	0.99
Na(4)	86.6(6)	$Na_{4.91}Ca_{0.44}K_{0.31}Ce_{0.27}Sr_{0.06}$	1.08	1.17
Na(5)	35.3(7)	$Na_{3.20}$	0.76	1.06
#16				
M(1)	138.0(5)	$Ca_{4.95}Mn_{0.67}\mathit{REE}_{0.38}$	2.12	2.06
M(2,5)	66(2)	$Mn_{1.83}Fe_{0.79}$	1.63	1.75
M(2,4)	7(1)	$Fe_{0.26}$	0.13	0.17
M(3)	38.9(3)	$Nb_{0.95}$	4.92	4.75
Si(7)	11.5(3)	$Si_{0.82}$	3.38	3.28
Si(7a)	1.6(2)	$Si_{0.11}$	0.41	0.44
Zr	118.4(4)	$Zr_{2.96}$	4.09	3.95
Na(1)	32.3(5)	$Na_{2.94}$	0.81	0.98
Na(2)	30.7(5)	$Na_{2.79}$	0.82	0.93
Na(3)	34.6(5)	$Na_{3.15}$	0.90	1.05
Na(4)	96.9(3)	$Na_{0.96}\mathit{REE}_{0.74}Sr_{0.72}K_{0.33}Y_{0.25}$	1.64	1.71
Na(5)	32.9(5)	$Na_{2.99}$	0.91	1.00
#17				
M(1)	155.2(6)	$Ca_{3.50}Mn_{1.51}Y_{0.50}\mathit{REE}_{0.49}$	2.20	2.17
M(2,5)	37(8)	$Mn_{0.66}Al_{0.42}Fe_{0.37}Ti_{0.24}$	0.94	1.43
M(2,4)	30(8)	$Fe_{1.14}$	0.56	0.76
M(3)	25.1(6)	$Si_{0.93}Nb_{0.45}Al_{0.42}Zr_{0.20}$	§	
M(3a)	1.4(4)			
Si(7)	4.2(5)			
Si(7a)	14.3(7)			
Zr	118.0(7)	$Zr_{2.89}Ti_{0.11}$	4.17	4.00
Na(1)	35(1)	$Na_{2.90}\mathit{REE}_{0.05}$	1.08	1.07
Na(2)	28(1)	$Na_{2.51}$	0.66	0.84
Na(3)	40(1)	$Na_{2.84}\mathit{REE}_{0.16}$	0.98	1.11
Na(4)	71.8(9)	$Na_{1.69}Sr_{0.56}\mathit{REE}_{0.43}K_{0.28}Ba_{0.04}$	1.42	1.49
Na(5)	33.00	Na_3 (fixed)	0.65	1.00

* Parameters from Brese & O'Keeffe (1991). ** Standard deviations in parentheses estimated from s.d. of the site occupancy factors.
§ For disordered structures, bond-valence sum for these sites cannot be calculated; for detailed discussion, see text.

VS for *Na*(5) in $R\bar{3}m$ eudialytes are calculated with multiplicity as in $R3m$.

proposed based on the sum of *epfu* from both *M*(3) and *Si*(7) and their satellite sites and assuming $N = 2$. The overall excellent agreement between the *apfu* derived from electron-microprobe data (Table 2) and those derived from structure refinements (Table 8) clearly indicates that this procedure is valid.

(iii) Assessment of the site population for the partly vacant *M*(2) sites is generally done by first allocating Fe to *M*(2,4), and secondly to *M*(2,5), then the same procedure with Mn. All remaining Mn is allocated to *M*(1).

Thermogravimetric analysis

The thermogravimetric analysis (TGA) of two eudialyte samples, 8 (10 mg) and 10 (16 mg), was done using a Stanton Redcroft TGA–DTA system; dry argon was used as purge gas. In both samples, weight loss was below the detection limits of the instrument.

TABLE 9. SITE-SCATTERING VALUES (*epfu*) OF REFINED ANION SITES IN EUDIALYTE SAMPLES

	O(19)	*O*(20)	*X*(1)	*X*(2)
#1	11.9	6.8	29.3	
#2	18.2	5.8	18.0	11.6
#3	21.6	6.7	20.3	10.6
#4	20.1	4.8	11.4	7.2
#5	21.7	6.4	17.5	12.1
#6	24*	5.8	19.2	13.7
#7	16.0	6.0	32.7	
#8	16.3	4.6	32.2	
#9	17.0	3.8	10.6	
#10	8.4	7.9	27.9	
#11	15.2	3.0	25.9	
#12	11.2	7.4	33.0	
#13	20.9	7.6	9.1	16.3
#14	12.3	7.9	29.8	
#15	14.2	7.2	28.2	
#16	24*	7.6	20.4	7.0
#17	20.5	1.0	10.7	15.4

* not refined. *O*(19a) *epfu* for samples 1, 10 and 12 are 4.5, 5.6 and 7.5, respectively. *O*(20a) *epfu* for samples 11 and 17 are 4.9 and 2.1, respectively.
e.s.d. for *epfu*'s are: *O*(19) 2-5%; *O*(19a) ~10%; *O*(20) 4-6%; *O*(20a) ~15%; *X*(1) and *X*(2) 3-8%.

Infrared analysis

Infrared spectra of selected samples of eudialyte (5, 8, 10 and 13) were obtained using a Bomem Michelson MB-120 Fourier-transform infrared spectrometer with a diamond-anvil cell microsampling-device (sample 13) or a Perkin Elmer 1000 Fourier-transform instrument (samples 5, 8 and 10). The dominant absorption bands (cm^{-1}) are: that of the [OH] stretching modes (broad 3440 and 3150); the [H_2O] bending mode (weak peak at 1655); the [SiO_4] symmetric stretching mode (major band with peaks at 1040, 980 and 940); the [SiO_4] bending modes (sharp peaks at 760, 710 and 660). A complete description of an IR spectrum for kentbrooksite (sample 13) is given in Johnsen *et al.* (1998). The primary purpose in obtaining several selected IR spectra was to evaluate the role of OH and H_2O in eudialyte. From these data, it is evident that both the OH and H_2O species exist in eudialyte, but the latter seems of minor importance, whereas the proportion of OH is significant in the samples tested.

Mössbauer and optical absorption spectroscopy

Mössbauer and optical absorption spectroscopy were performed on five samples of eudialyte (*s.l.*) given in Johnsen & Gault (1997), one of which is included in the present study as sample 10 (U. Hålenius, pers. commun.). The general results of the Mössbauer spectroscopy, performed at room temperature, are very similar to those of Pol'shin *et al.* (1991) with the exception that no evidence is found for ferric iron (Fe^{3+}). Neither is there any evidence for Mn^{3+} or Fe^{3+} in the data obtained from the optical absorption spectra. These observations are in accordance with the findings of Mn^{2+} only in kentbrooksite (Johnsen *et al.* 1998).

TOPOLOGY OF THE STRUCTURE

The site nomenclature for the *R*3*m* type of eudialyte adopted here is based on that of kentbrooksite (Johnsen *et al.* 1998), with minor modifications. The *F* sites in kentbrooksite are relabeled as *X* sites, which is more appropriate for sites accommodating Cl, OH, H_2O and F, whereas *M*4 is relabeled *Si*(7) since Si has proven to be the predominant element at the site. *M*2 is changed to *M*(2,5), and *M*2a, to *M*(2,4), in order to incorporate the coordination number in the notation.

The center of symmetry in the $R\bar{3}m$ type of eudialyte reduces the number of distinct sites, and *Si*(2) becomes symmetry-equivalent to *Si*(1), *Si*(4) to *Si*(3), whereas *O*(4), *O*(5) and *O*(6) become equivalent to *O*(1), *O*(2) and *O*(3), and *Na*(2) and *Na*(3) become equivalent to *Na*(1) and *Na*(4). The reduction of symmetry from *R*3*m* to *R*3 results in a doubling of every general site in *R*3*m*, *i.e.*, *M*(1) degenerates into *M*(1a) and *M*(1b), *etc.* The full notation for members of all three space groups is given in Table 4.

Overview of the structure

The most characteristic property of the eudialyte structure is the unique combination of three- and nine-membered rings of [SiO_4] tetrahedra (Golyshev *et al.* 1971, Giuseppetti *et al.* 1971). These [Si_3O_9]$^{6-}$ and [Si_9O_{27}]$^{18-}$ rings are arranged in layers perpendicular to [001], with the configuration shown in Figure 1. Two such layers, related by a center or a pseudocenter of symmetry, embrace a layer of discrete rings of six [$M(1)O_6$] octahedra linked together by [$M(2)O_n$] polyhedra forming a 2:1 composite layer. The 2:1 composite layers are cross-linked by Zr in octahedral coordination and related to one another in accordance with rhombohedral symmetry. This open structure is filled with {$Na\phi_n$} polyhedra in which Na may have various coordinations.

In the stacking sequence of the 2:1 layers and the layers with [ZrO_6] octahedra, twelve levels can be recognized within the repeat distance of the *c* cell dimension. Figures 2 and 3 give a simplified representation of these levels from one six-fold ring of [$M(1)O_6$] octahedra to the next ring, for an acentric and a centric eudialyte, respectively. Oblong cages exist along the triad axes, reaching from one constriction made by a [Si_3O_9]$^{6-}$ ring up through the layer sequence to the next constriction by a [Si_3O_9]$^{6-}$ ring, including nine of the

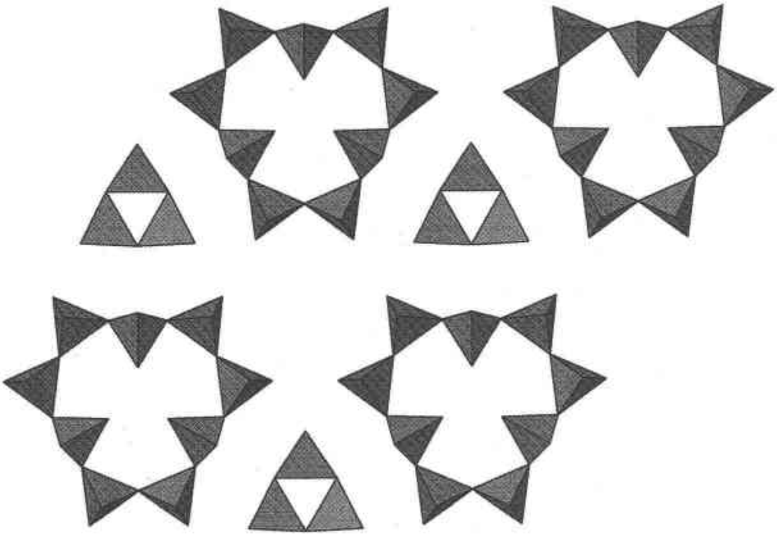

FIG. 1. The nets of three-fold and nine-fold silicate rings in eudialyte-group minerals seen along [001].

twelve levels. In these cages, the central level comprises a region surrounded by six [ZrO_6] octahedra (only four of them are shown in the figures), and on either side followed by (i) an intra [Si_9O_{27}]$^{18-}$ ring level, (ii) a level with a region surrounded by [$M(1)O_6$] and [$M(2)O_n$] polyhedra, (iii) an inter [Si_9O_{27}]$^{18-}$ ring level, and (iv) a level with a region surrounded by three [ZrO_6] octahedra. Na is the dominant cation in the cavities at the levels of [ZrO_6] octahedra and in other cavities in or at the border of other levels. Cl, F, OH and H_2O are accommodated in the inter [Si_9O_{27}]$^{18-}$ ring levels, whereas the central parts of the [Si_9O_{27}]$^{18-}$ rings offer space for a cation in tetrahedral or octahedral coordination. Which is present depends on the incorporation or not of *O*(19) which, where present, is shared with the [$M(2)O_5$] polyhedra. This important phenomenon will be discussed in detail below.

DESCRIPTION AND DISCUSSION OF THE ATOMIC SITES

The Si in three-membered rings

The [Si_3O_9]$^{6-}$ rings are uniform building blocks in all eudialyte crystals. In *R*3*m*, they are composed of *Si*(1) and *Si*(2) with their respective ligands, all atoms having point symmetry *m*. As seen in Figure 4, the [Si_3O_9]$^{6-}$ rings are linked to the six-membered rings of [$M(1)O_6$] octahedra by sharing the three innermost atoms of oxygen on each side. Figure 5 illustrates the corresponding configuration in *R*3, where all positions are reduced to general positions and where the mutual angle of rotation between the two three-membered silicate rings is other than 180°. In $R\bar{3}m$, the *Si*(1) and *Si*(2) tetrahedra are related by a center of symmetry. The tilt of the *Si*(1) and *Si*(2) tetrahedra toward the *Z*-axis differs from each other in acentric examples of eudialyte, and the degree of tilt varies from sample to sample: the largest difference is seen in sample 5, the *R*3 eudialyte.

For all crystals, the Si–$O_{\text{non-bridging}}$ bond-lengths are 1.58–1.60 Å, whereas the Si–O_{bridging} bond-lengths are ~1.64 Å. These are the expected values for essentially Al-free tetrahedra. The bond-valence sum of *Si*(1) for all samples is 4.09(5). For the noncentrosymmetric samples, the bond-valence sum of *Si*(2) is 4.07(6).

The Si in nine-membered rings

When referring only to *R*3*m* and *R*3 types of eudialyte, the Si atoms involved in the [Si_9O_{27}]$^{18-}$ rings are labeled so that all Si atoms in one silicate layer are either odd-numbered or even-numbered. Thus in the layer including the three-membered *Si*(1) ring, the nine-membered ring is composed of a set of three *Si*(3) tetrahedra [*Si*(3) having point symmetry *m* in *R*3*m*] and a set of six *Si*(5) tetrahedra, with *Si*(5) in a general position. In the next silicate layer, the tetrahedra are correspondingly labeled *Si*(2), *Si*(4) and *Si*(6) except in $R\bar{3}m$, where these are generated by the center of symmetry.

The shape of the [Si_9O_{27}]$^{18-}$ rings varies by tilting and rotation of the individual tetrahedra. The most pronounced shifts are exemplified by rotation of the *Si*(5) and *Si*(6) tetrahedra about [001] (or a direction close to

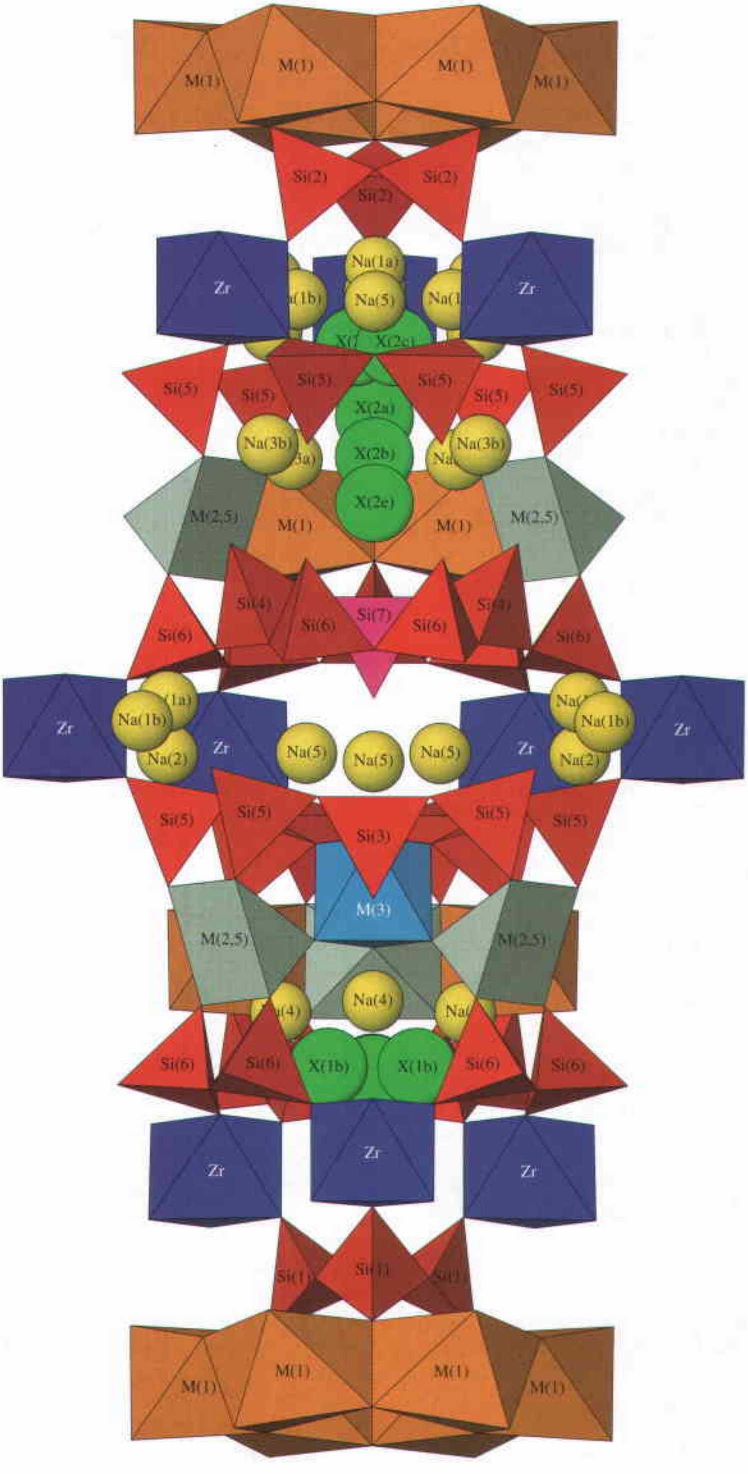

FIG. 2. A simplified polyhedral model of noncentrosymmetric, *R*3*m* eudialyte (*s.l.*), viewed approximately along [210].

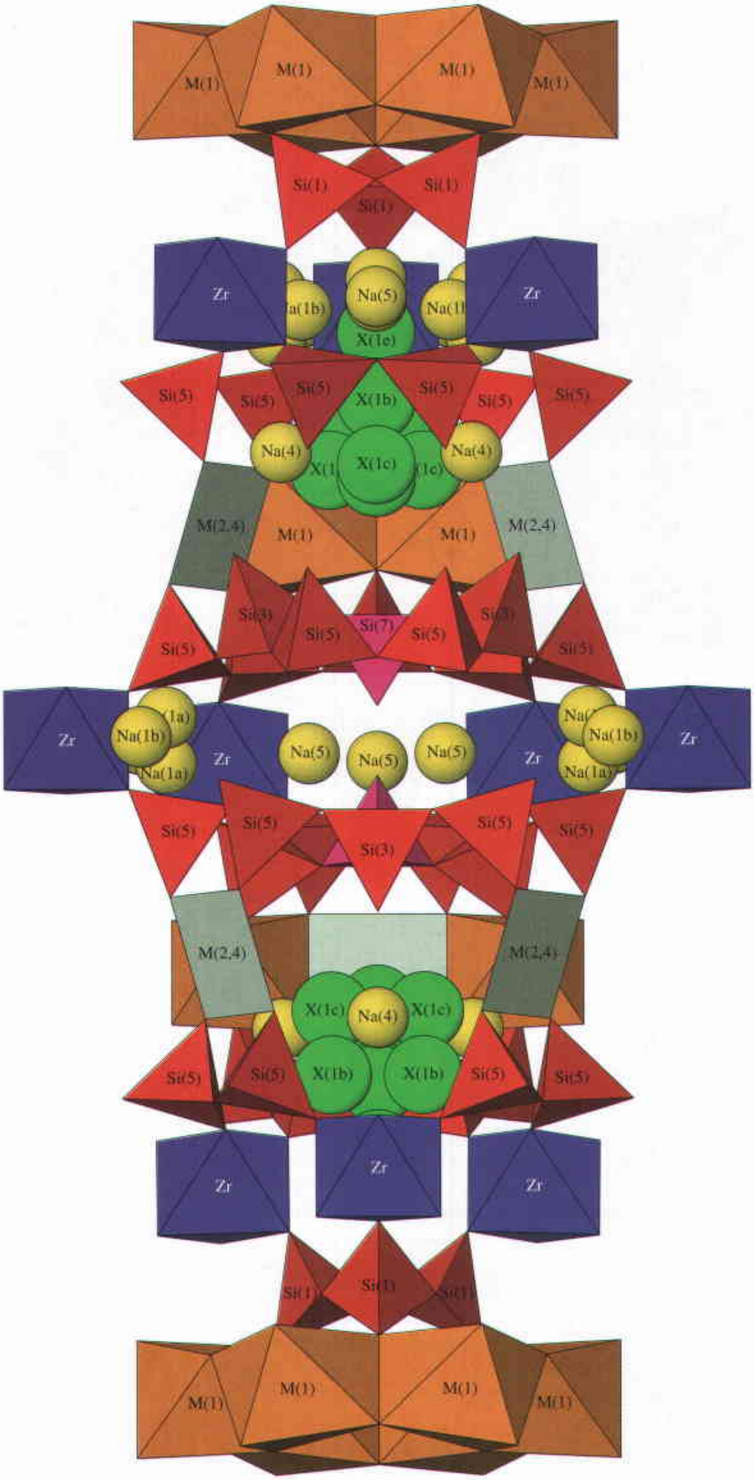

FIG. 3. A simplified polyhedral model of centrosymmetric, $R\bar{3}m$ eudialyte (*s.s.*), viewed approximately along [210].

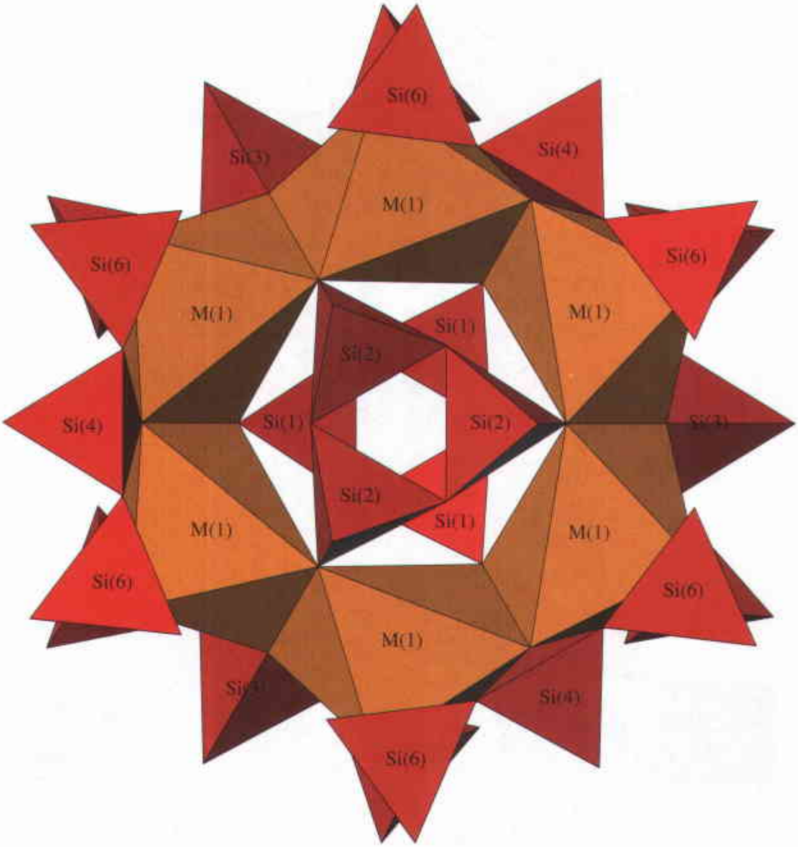

FIG. 4. A six-fold ring of [$M(1)O_6$] octahedra with attached [SiO_4] tetrahedra in a $R3m$ type of eudialyte viewed along [001].

[001]) and tilting of the *Si*(3) and *Si*(4) tetrahedra equivalent to a rotation about [100]. Thus, owing to such adjustments, the distances between the three innermost atoms of oxygen of the rings can be made to fit the face of a tetrahedron or a face of an octahedron. For example, the distance between the *O*(9) atoms of oxygen belonging to the *Si*(3) tetrahedra is typically 2.65 Å, matching the edge of a [NbO_6] octahedron, whereas the similar distance *O*(12)–*O*(12) is on the order of 2.52 Å, matching the edge of a [SiO_4] tetrahedron.

The [Si_9O_{27}]$^{18-}$ ring with a tenth Si tetrahedron in the center can also be described as a [$Si_{10}O_{28}$]$^{16-}$ platform. We prefer to keep the ring terminology, which we consider more applicable in the discussion of the crystal-chemical characteristics of this group of minerals.

In $R\bar{3}m$ structures, small maxima labeled *Si*(3s) are observed in some cases. They are produced because *Si*(3) and *Si*(4), which ideally are related by the center of symmetry, are not completely superimposed in all parts of the crystal, indicating that the centricity is imperfect. This misalignment results in domains within the structure. Although of very minor significance in general, these maxima have been included in the refinement.

As in the case of the three-membered silicate rings, all crystals have Si–$O_{\text{non-bridging}}$ bond-lengths in the range 1.58–1.60 Å, whereas Si–O_{bridging} bond-lengths are ~1.64 Å for the nine-membered silicate rings. Again, these are the expected values for essentially Al-free tetrahedra. The only sample in the present selection with appreciable amounts of Al is sample 17 from the Burpala massif, with 0.82 Al, all of which has been allocated to *M*(2,5) and *M*(3)/*Si*(7). The bond-valence sums of *Si*(3) and *Si*(5) for all samples are 4.07(5) and 4.05(5), respectively.

The Zr site

Zr is accommodated in a nearly regular octahedron interconnecting one three-membered and two nine-membered silicate rings in one layer with a correspond-

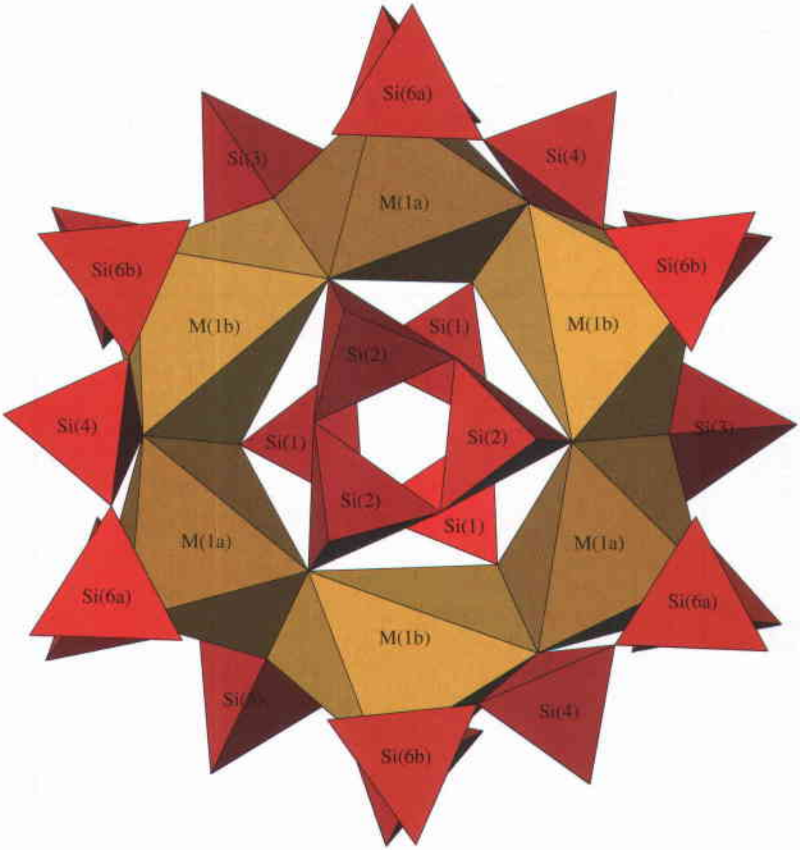

FIG. 5. A six-fold ring of alternating [$M(1a)O_6$] and [$M(1b)O_6$] octahedra with attached [SiO_4] tetrahedra in a $R3$ type of eudialyte viewed along [001].

ing set of rings in the next layer. Consequently, all ligands in this octahedron are shared with Si atoms. The mean Zr–O bond-length for all samples is 2.068(7) Å, but an anomaly is noted. Within the dataset, sixteen samples have a mean Zr–O distance of 2.070(4) Å, and one sample (sample 9 from Varennes) is characterized by a significantly shorter Zr–O distance, 2.046 Å. This exception is in accordance with a substantial substitution of Ti for Zr in this sample, in which the site is occupied with 2.50 Zr + 0.50 Ti *apfu* (Table 8). Among the other samples, only those from the Gardiner complex (samples 10, 11 and 12) contain appreciable amounts of Ti (0.20–0.34 *apfu*) in this site. Niobium plays a subordinate role in the *Zr* site; the highest amount of Nb assigned is 0.11 *apfu* in sample 4. Hafnium never exceeds 0.05 *apfu*. As seen in Table 8, the bond-valence sum of the *Zr* site is consistently about 4% higher than the corresponding sum of valences, an indication that the bond-valence parameter for Zr (Brese & O'Keeffe 1991) is slightly too high for this type of structure.

Khomyakov *et al.* (1990) described alluaivite from the Lovozero complex as having a eudialyte structure in which Ti replaces Zr entirely in this site. Recently, another eudialyte-group mineral has been found in Lovozero in which Ti substitutes for approximately one-half the Zr (A.P. Khomyakov, pers. commun.). In that case, the two ions order to occupy positions in every second layer, causing the *c* cell dimension to double. The only sample in the present dataset with appreciable amounts of Ti, sample 9 from Varennes, does not show any sign of ordering of the Zr and Ti at the *Zr* site.

The M(1) site

The *M*(1) site is octahedrally coordinated and shares all O ligands with Si atoms. It occupies a special position with point symmetry 2 in space group $R\bar{3}m$, but a general position in space group $R3m$ (Fig. 4) and two general positions *M*(1a) and *M*(1b) in space group $R3$ (Fig. 5). Edge-sharing [$M(1)O_6$] octahedra form six-membered rings that on both sides are connected to a central three-membered silicate ring and three nine-membered silicate rings.

Plotted in Figure 6a, for all samples, are the mean bond-lengths of the [$M(1)O_6$] octahedra *versus* the ratio Ca/(Ca + Mn + *REE* + Y) in *M*(1), an expression that incorporates the most important elements of the site. In all samples, the [$M(1)O_6$] octahedra are somewhat distorted. The degree of distortion is related to nature of occupant, as shown in Figure 6b, in which a distortion index, $\Delta = 1/6\ \Sigma^6_{i=1}[(R_i - \bar{R})/\bar{R}]^2$ (Brown & Shannon 1973), is plotted against the components described above. In this context, it should be noted that the correlation shown is relatively poor, owing to the fact that all elements involved, like most elements in eudialyte, occupy more than one site in the structure. In addition, the degree of distortion of the [$M(1)O_6$] octahedra is not only dependent on the nature of the occupant, but also

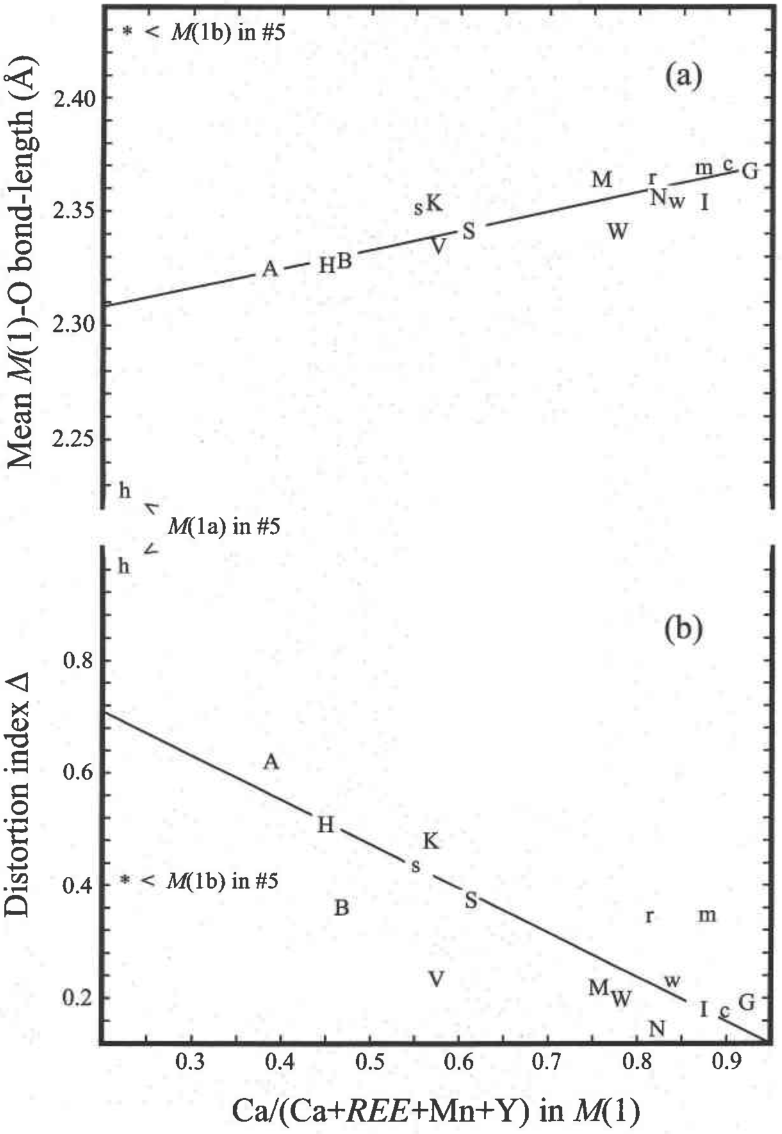

FIG. 6. The ratio Ca / (Ca + *REE* + Mn + Y) in *M*(1) plotted against the mean bond-length of the [$M(1)O_6$] octahedron (a) and the distortion index of the [$M(1)O_6$] octahedron (b). The distortion index Δ is equal to $1/6\ \Sigma^6_{i=1}[(R_i - \bar{R})/\bar{R}]^2$ (Brown & Shannon 1973). The symbols chosen are as in Table 1.

is influenced by the geometry of the surrounding structural blocks as well as by the different constraints on symmetry imposed in the three space groups concerned.

In most samples, Ca is the dominant element in *M*(1), and in centrosymmetric eudialyte, it is the only significant element. The average Ca content in *M*(1) is 4.69 *apfu*. Mn is next in importance with an average of 0.79 *apfu*, followed by *REE* and Y with ~0.24 *apfu* each. In sample 13 (labeled A in Fig. 6), almost half the Ca is substituted by Mn, Y and *REE* in *M*(1). This appears to be close to the limit where Ca and Mn order in two crystallographically distinct sites, as seen in sample 5. Ordering results in a distorted, Mn-dominant [$M(1a)O_6$] octahedron, with a relatively small mean bond-length of 2.227 Å, and a less distorted, Ca- and *REE*-dominant [$M(1b)O_6$] octahedron, with a relatively large mean bond-length of 2.431 Å. As illustrated in Figure 5, the result is a loss of the mirror planes in *R*3*m*, and the symmetry thus is reduced to *R*3.

The highest content of Y is found in samples 7 and 8 from the Kipawa complex, and all the Y is accommodated in *M*(1). A small part of Fe (0.25 *apfu*) in sample 15 from the Ilímaussaq complex is allocated to *M*(1), and 0.66 *apfu* Na is assigned to the large [$M(1b)O_6$] octahedron in sample 5. The iterative process of assigning several elements to several sites resulted, in the case of sample 9 from Varennes, in a small amount of Zr (0.18 *apfu*) being assigned to *M*(1). In this particular case, the assignment appears insubstantial. It is maintained, however, because another crystal from the same locality, although excluded from the selection presented here owing to poor refinement results, shows an extremely high site-scattering value at the *M*(1) site, which could only be attributed to a population including some Zr.

The M(2) sites

The *M*(2) notation includes two sites, the four-fold-coordinated *M*(2,4) site and the five-fold-coordinated *M*(2,5) site. The distance between these sites is on the order of 0.7 Å. They are positioned on the mirror plane, except in *R*3, and bridge the six-membered rings of [$M(1)O_6$] octahedra. The *M*(2,4) site is located on a center line between the six-membered rings on a position that in $R\bar{3}m$ has point symmetry 2/*m*, whereas the *M*(2,5) site is shifted toward the *M*(3) site (Figs. 2, 3).

The four-fold coordination of *M*(2,4) is an almost planar arrangement with mean bond-lengths of 2.11(6) and 2.09(4) for *M*(2,4)–*O*(14) and *M*(2,4)–*O*(17), respectively. Golyshev *et al.* (1971) and Giuseppetti *et al.* (1971) both assigned Fe to this site and made reference to gillespite (Pabst 1943), in which this unusual type of coordination was first observed. The Fe–O distances in gillespite are ~2.00 Å, *i.e.*, slightly smaller than in eudialyte. In the present samples, Fe is assigned to *M*(2,4) as well, and Mn subsequently, both elements as divalent ions in accordance with the results of the selected tests for valence mentioned in the Methods section.

As seen in Table 8, the bond-valence sums (BVS) for *M*(2,4) are consistently lower than the corresponding valence-sums (VS), on average ~25% (this discrepancy would be even larger if trivalent ions were assigned). This overall BVS–VS discrepancy indicates that Fe is relatively poorly bonded in *M*(2,4), which is also supported by very strong anisotropic displacement factors perpendicular to the plane of the oxygen atoms.

The five-fold coordination of *M*(2,5) constitutes a distorted square pyramid involving the two pairs of *O*(14) and *O*(17) plus the extra *O*(19); the mean bond-lengths are as follows: *M*(2,5)–*O*(14) 2.12(3), *M*(2,5)–*O*(17) 2.20(9), and *M*(2,5)–*O*(19) 2.1(2) Å. The *O*(19) site has the same point symmetry as *M*(2,5), and it constitutes the shared ligand between the [$M(2,5)O_5$] and [$M(3)O_6$] polyhedra. Not considering the *X* sites, *O*(19) is thus the only atom of oxygen in the eudialyte structure not bonded to Si. The anisotropic displacement parameters for *M*(2,5) are relatively small compared with those of *M*(2,4).

Whereas Fe distinctly predominates in *M*(2,4), Mn is in general more abundant than Fe in *M*(2,5). On average, *M*(2,5) accommodates 0.85 Mn *apfu* and 0.55 Fe *apfu*. The highest content of Mn is 1.97 *apfu*, in sample 13. Note that in the assignment procedure, it is commonly impossible to distinguish between Fe and Mn where both are present in ample amounts unless specific spectroscopic information is available. Such information was sought on selected samples, but owing to serious overlap conditions, no conclusive results have been obtained so far (U. Hålenius, pers. commun.).

As seen in Table 8, the bond-valence sums (BVS) for *M*(2,5) are in general lower than the corresponding valence-sums (VS) by an average of ~15%, which is less than for *M*(2,4).

The site-occupancy factors (*sof*) for *M*(2,4) and *M*(2,5) are strongly correlated, such that during the refinement, great care was exercised in order to give realistic *sof* values. Figure 7 shows the distribution of the *epfu* in the two sites. It is obvious that the population is divided in two: some samples, in which the scattering power is concentrated in *M*(2,4), refine as the centric type, whereas samples of a second group, with most electrons concentrated in *M*(2,5), refine as the acentric type (an exception is sample 9). The role of the *M*(2) site in the question of the acentricity in eudialyte, as well as the relations to neighboring sites, is discussed in greater detail below.

The total number of atoms per formula unit occupying the two *M*(2) sites is 3; as shown in Figure 7, only two samples (14 and 15) reach about 77 *epfu*, corresponding to full occupancy with (Fe,Mn). We also note that among the present samples, none have less than 55.7 *epfu*, equivalent to ~2 *apfu* (Fe,Mn). The observation that other elements enter the Fe site, partly or entirely, as an integral part of the structure indicates that Fe itself

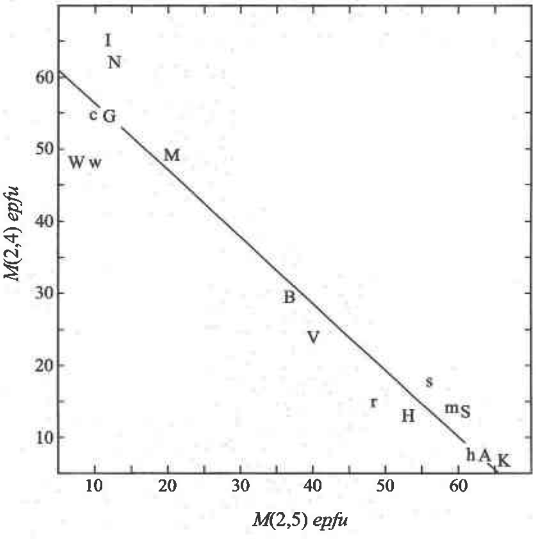

FIG. 7. The site-scattering power at site *M*(2,4) plotted against the site-scattering power at site *M*(2,5). The symbols chosen are as in Table 1.

is not essential for the stability of the eudialyte structure, as had been claimed by Christophe-Michel-Lévy (1961) on the basis of hydrothermal syntheses of eudialyte.

The *M*(2) site (or an equivalent site) in six-fold coordination as described by Rastsvetaeva *et al.* (1990) has not been observed in this selection of eudialyte samples. The samples that refined centrosymmetrically did indicate six-fold coordination because of doubling the multiplicity of the *O*(19) site, but subsequent refinement in the acentric space-group showed that all the scattering power originated from the "acentric" *O*(19) site with half the multiplicity.

The M(3) site in acentric crystals

In the nine ordered structures of eudialyte belonging to space groups *R*3*m* and *R*3, *M*(3) is a well-defined octahedral site with point symmetry 3*m*, and bonded to three *O*(19) atoms and the three innermost atoms of oxygen of the nine-membered silicate ring having odd-numbered Si atoms (Fig. 8). The mean bond-lengths are 2.00(6) and 1.88(2) Å for *M*(3)–*O*(9) and *M*(3)–*O*(19), respectively.

Nb is clearly the dominant element in *M*(3), except in sample 6, where W dominates. The highest Nb content, 0.95 *apfu*, occurs in sample 16, whereas the remaining samples show some degree of site vacancy. The average of the bond-valence sums and valence sums for the *M*(3) population in acentric crystals seen in Table 8 are 4.0(6) and 3.9(6) respectively, which gives an excellent overall agreement.

The Si(7) site in acentric crystals

Si(7) and *M*(3) are pseudocentrosymmetrically related. *Si*(7) is a tetrahedral site with point symmetry 3*m* bonded to *O*(20), which also has point symmetry 3*m*, and the three innermost atoms of oxygen of the nine-membered silicate ring with even-numbered Si atoms (Fig. 8). The mean bond-lengths are 1.60(2) and 1.60(3) for *Si*(7)–*O*(12) and *Si*(7)–*O*(20), respectively. In some crystals, there is an alternative position about 1.2 Å removed from *Si*(7), still on the three-fold axis and more distant from *O*(20) (Fig. 8). This site, labeled *Si*(7a), also is tetrahedrally coordinated, where one of the disordered *X* sites is incorporated as an apical ligand. It simply represents a reversed tetrahedron with the same mean bond-lengths. In the most ordered crystals, these two sites together have a site-scattering value that roughly corresponds to one Si *apfu*. In other crystals, incipient disorder of the *M*(3) and *Si*(7) sites impede the interpretation of the stereochemistry along the triad axes, although these crystals still refine best in the acentric space-groups. Accordingly, for these crystals, assignment of a certain scattering power to a certain site becomes dubious.

The M(3) and Si(7) sites in centric crystals

As the disorder on the triad axes becomes more extensive and the stereochemical substitution $^{[6]}M(3) + {}^{[4]}Si(7) \leftrightarrow 2^{[4]}Si(7)$ proceeds to the right, the data will give a superior refinement as a centrosymmetric structure. In such crystals, the scattering overlap precludes a reliable interpretation of the local stereochemistry except, of course, in the ideal situation of a full $2^{[4]}Si(7)$ substitution. Sample 9 is the closest we get to this situation among the present samples. It should be stressed, however, that other features elsewhere in the structure also exert an influence on the degree of acentricity.

The scattering overlap results in small additional maxima along or very close to the three-fold axes. These "sites" have been labeled *M*(3a) and *M*(3b), and their position is indicated in Figure 8. Their limited significance in relation to the important *Si*(7) and *M*(3) sites in the various crystals can be read from Table 8. In Table 8, the site-scattering value of all *Si*(7) and *M*(3) sites including the small additional maxima has been added up and converted to 2 *apfu*.

Johnsen & Gault (1997) showed that a strong negative correlation exists between the presence of Nb and Si. The present study documents that this correlation is the chemical expression of the stereochemical substitution: $^{[6]}M(3) + {}^{[4]}Si(7) \leftrightarrow 2^{[4]}Si(7)$. On the basis of the site assignment in Table 8, this correlation can be further refined as shown in Figure 9. In this plot, the abscissa

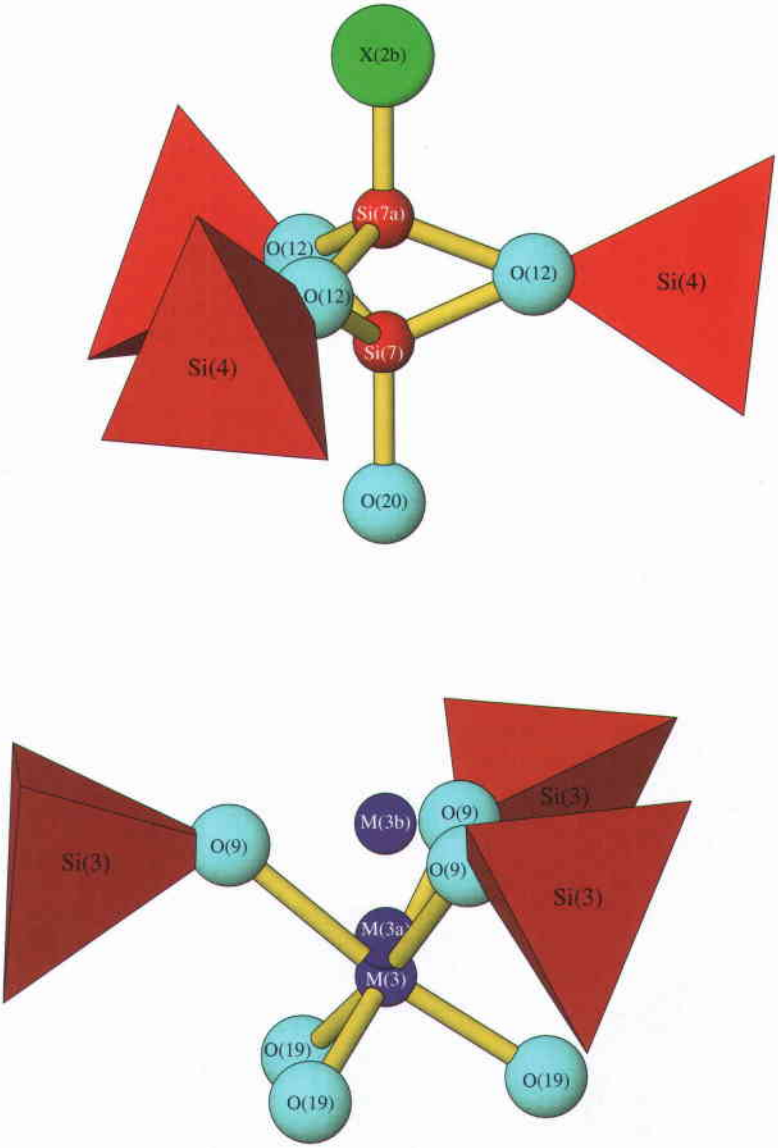

FIG. 8. A ball-and-stick model of *Si*(7) and *M*(3) sites surrounded by the three innermost [SiO_4] tetrahedra in the nine-membered rings.

represents the chemical content of $2^{[4]}$*Si*(7), which is the total amount of Si and Al minus the Si in the silicate ring system (24 *apfu*) and a correction for Al in *M*(2,5). The component represented along the ordinate axis is somewhat more elaborate. Although Nb is primarily accommodated in *M*(3), small amounts of this element are found in the *Zr* site. In addition, Ti may be present in both *Zr* and *M*(3), as well as in *M*(2,5) in some cases. In order to compensate for these complications, the chemical content of *M*(3) is expressed as the sum of all elements assigned to *M*(3) and *Zr* minus 3 *apfu* contained in *Zr* site and a correction for (Ti,Zr) assigned in *M*(2,5) and *M*(1). The corrections made are indicated on the plot with dashed lines. The coefficient of correlation after the corrections is $r = -0.96$.

The plot in Figure 9 and the incorporated corrections confirm that the result of the site-assignment procedure seen in Table 8 is reasonable. It also shows that there is

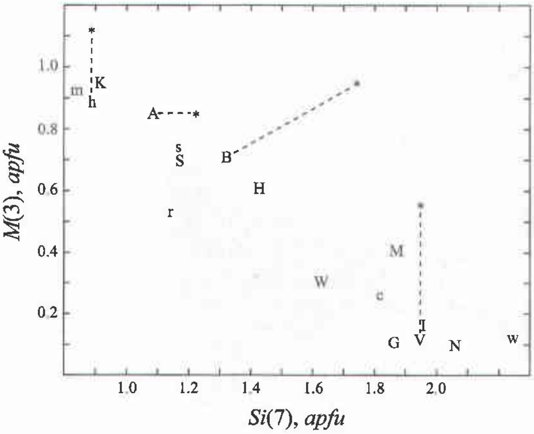

FIG. 9. The correlation between the occupancy of $M(3)$ and $Si(7)$, both defined in text. The symbols chosen are as in Table 1. The dashed lines signify the following corrections made: sample h: –0.24 Zr in $M(2,5)$; sample A: –0.14 Al in $M(2,5)$; sample B: –(0.42 Al + 0.24 Ti) in $M(2,5)$; sample V: –0.18 Zr in $M(1)$ and –0.25 Ti in $M(2,5)$.

an excellent agreement overall between the *apfu* derived from structural calculations and those from the electron-microprobe data. Most important, however, is the conclusion drawn from Figure 9 that the $^{[6]}M(3)$ + $^{[4]}Si(7)$ ↔ $2^{[4]}Si(7)$ relation is substantiated, *i.e.*, Nb, and substitutions, in $M(3)$ do not exceed 1 *apfu*. In other words, there is no indication in the present dataset that $M(3)$ can be found in both crystallographically distinct nine-membered silicate rings, yet the structural explanation for this finding is not clear. Two $^{[6]}M(3)$ sites would require doubling of the multiplicity of $O(19)$ and a change of the coordination of $M(2)$ from five to six. The extra $O(19)$ atoms of oxygen can be accommodated in the cages, and the six-fold coordination of $M(2)$ has been observed (Rastsvetaeva *et al.* 1990). In addition, the rest of the eudialyte structure is already essentially centrosymmetric in nature. At present, we do not exclude the possible existence of two $M(3)$ sites.

The Na sites

The structural framework hitherto described is saturated with Na; its locations are indicated in Figures 2 and 3. In $R3m$ and $R3$, five distinct Na sites are recognized. In $R\bar{3}m$, these five are reduced to three as $Na(2)$ is included in $Na(1)$, and $Na(3)$ in $Na(4)$, whereas $Na(5)$ is unchanged except for the site-occupancy factor, which drops to one-half. Doubling the multiplicity of the $Na(5)$ site results in Na atoms being positioned closer than 2 Å apart. Valence sums for $R\bar{3}m$ eudialyte samples in Table 8 are therefore calculated on the basis of the same multiplicity for the site as in $R3m$.

All five Na sites have point symmetry m (except in $R3$) and thus add up to 15 *apfu*. Some Na sites, mainly $Na(1)$ and $Na(3)$, have such large anisotropic displacement-parameters within the mirror planes that they are best described as split positions.

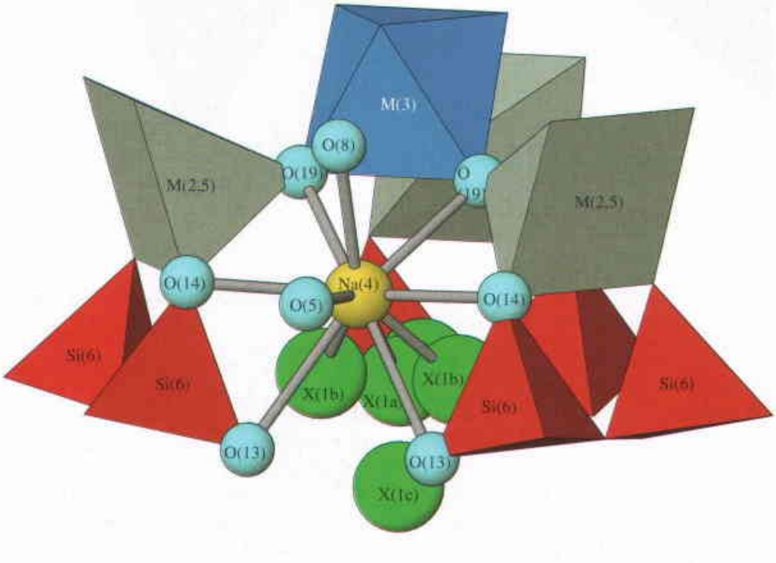

FIG. 10. A ball-and-stick model of the $Na(4)$ site surrounded by selected polyhedra. Notice the strong disorder of the large X anions and the sharing of $O(19)$ with the $[M(2,5)O_5]$ and $[M(3)O_6]$ polyhedra.

Selected mean bond-lengths for the [Naϕ_n] polyhedra (ϕ: unspecified anion) are presented in Table 7. The coordination number of Na out to a distance of 3.10 Å ranges from 6 to 10, counting the disordered *X* sites as one ordered site only. The [Naϕ_n] polyhedra are very irregular, and it is evident that Na simply must accept the space determined by the framework. In particular, Na is concentrated in the [110] channels running between silicate rings as well as between [ZrO_6] octahedra. It is probable that these channels constitute the paths through which Na may be leached out and exchanged for H_2O or H_3O^+, as described by Rastsvetaeva *et al.* (1990). We also attempted to include a Na-poor eudialyte in this study, but we were unable to achieve an acceptable refinement of this particular crystal. Regardless of this, as mentioned in the section on microprobe analyses, Na volatilization or migration does not appear to be a major problem in eudialyte-group phases, indicating that Na generally bonds well within the structure. A different perspective on this matter might be extracted from the bond-valence sums and valence sums cited for the *Na* sites in Table 8. For *Na*(1), *Na*(2), *Na*(5) and in part *Na*(3), the VS values are 10–20% higher than the corresponding BVS values, indicating fairly weak bonding, whereas atoms in *Na*(4) and in part *Na*(3) seem more tightly bonded, judging from the better agreement between BVS and VS results.

With very few exceptions, Na is the only element in *Na*(1), *Na*(2) and *Na*(5). A small proportion of vacancies in *Na*(5) is encountered in some crystals. Sites *Na*(3) and *Na*(4), on the other hand, do carry substantial amounts of other elements; in *Na*(4) in particular, the site-scattering values may be high enough in some crystals that Na can no longer be the dominant element. For example, in sample 5, almost half of the site population in *Na*(4) consists of *REE*, and in sample 16, Na constitutes only a third of the site population, whereas the rest is a mixture of heavier elements. In sample 6, the crystal in which W exceeds Nb in *M*(3), Na is almost fully replaced by Sr. The reason for the capability of the *Na*(4) site to incorporate such elements as *REE* and Sr is found in the local stereochemistry around the *Na*(4) site (Fig. 10). Two of the nine ligands to *Na*(4) are *O*(19) ions that are shared with *M*(3) and *M*(2), the latter of which becomes five-fold-coordinated because of *O*(19). In the present selection of crystals, the site-occupancy factor for *O*(19) varies from about one third to unity (Table 9). It follows from the configuration around *O*(19) that its presence not only facilitates the accommodation of di- and trivalent elements in *Na*(4), but also ensures the six-fold coordination of *M*(3) and favors the five-fold coordination of *M*(2) at the expense of four-fold coordination. As would be expected, there is a strong correlation between the site-occupancy factors of *O*(19) and the site-scattering values of *Na*(4), *M*(3) and *M*(2,5), respectively.

The X sites

The two *X* sites in the *R*3*m* type of eudialyte ideally have point symmetry 3*m*. However, both sites are strongly disordered along the triad axes and along the mirror planes; a typical situation is seen in Figure 10. The same situation occurs in the *R*3 and $R\bar{3}m$ type of eudialyte.

The *X* sites are bonded only to Na. Their site-scattering values are shown in Table 9. When converted to 2(Cl, F,OH) *apfu*, any of which may be dominant, there is usually a surplus of electron density that is calculated as H_2O.

DEGREE OF ACENTRICITY

In Figures 11a, b and c, the $|E^2 - 1|$ values listed in Table 3 are plotted against various chemical quantities that prove to be determining factors in the degree of acentricity of structures of eudialyte (*s.l.*). *E*-statistics are often not very useful in determining acentricity in mineral structures, as many of these statistics are strongly affected by heavy, centrosymmetrically related cations. In the eudialyte structure, a large number of atoms has an approximately uniform atomic number (228 atoms of oxygen, 9 transition metals, 75 atoms of Si, 63 atoms of alkaline-earth elements per unit cell). This uniform mass of scatterers effectively overcomes the problem of non-uniform statistics. The one anomalous value of $|E^2 - 1|$ noted earlier for sample 5 (labeled h in Fig. 11) is a consequence of merohedral twinning. The result of twin overlap of two diffracting lattices is an increase in all $|E|$ values, thus lowering $|E^2 - 1|$ beyond the theoretical value of 0.736 for acentric structures.

The framework consisting of the silicate rings and [ZrO_6] octahedra is essentially centrosymmetric. The violation of centricity is due to minor adjustments in the rest of the structure. Likewise, the [*M*(1)O_6] octahedron is not found to play a major role in this context; the substitutions taking place in *M*(1) are not well correlated with $|E^2 - 1|$. Only a few parameters related to *M*(1), such as the bond-length *M*(1)–O(8), show a good correlation, possibly because of the interaction with other polyhedra like *Na*(4) and the tilted *Si*(3) tetrahedron. The [*M*(2)O_n] polyhedra, on the other hand, do show a correlation with acentricity, not by considering individual elements, but by considering the ratio of the site-scattering values of *M*(2,4) and *M*(2,5), *i.e.*, the quantity *M*(2,5) *epfu* / [*M*(2,5) *epfu* + *M*(2,4) *epfu*], which clearly is negatively correlated with $|E^2 - 1|$.

The elemental contents in the *M*(3) and *Si*(7) sites have the primary influence on acentricity. The correlation between these parameters is best illustrated as a *M*(3) / [*M*(3) + *Si*(7)] *versus* $|E^2 - 1|$ diagram. The *M*(3) and *Si*(7) elemental quantities are defined in Figure 9.

In simplified terms, the Nb-rich samples of eudialyte are the most strongly acentric, whereas the Si-rich samples of eudialyte are the most strongly centric. As would be expected from this relationship, there is also a strong positive correlation between the site-occupancy factor for $O(19)$ and the degree of acentricity.

It has been shown that *REE* and Sr are the main elements substituting for Na, and that the substitution primarily involves $Na(4)$, to a much lesser extent in the pseudocentrosymmetrically related $Na(3)$, and only infrequently in other *Na* sites. Figure 11b shows how this heterogeneous distribution of *REE* in *Na* sites results in a significant impact on the acentricity. The pronounced outlier in the plot trend is the Sr-rich sample 6 (labeled m), which would have been compliant if Sr had been included in the ordinate component.

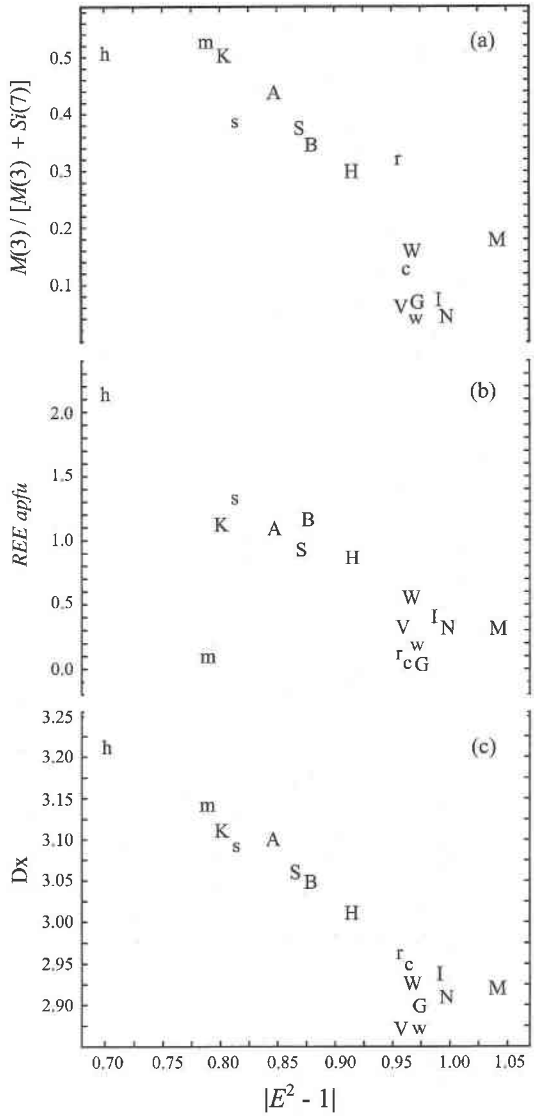

FIG. 11. The correlation between the $|E^2 - 1|$ values from Table 3 and a) the ratio $M(3)$ / [$M(3)$ + $Si(7)$] (defined in text), b) the proportion of *REE* in *apfu*, and c) the calculated density. The symbols chosen are as in Table 1.

With a classic eudialyte rich in Na, Ca, Fe and Si as a starting point, we conclude that all major substitutions, except the Fe ⇔ Mn substitution, proceed from relatively light elements toward relatively heavier elements. Consequently, the correlations hitherto described in Figures 11a and 11b can be combined as shown in Figure 11c, where the calculated density is plotted against $|E^2 - 1|$. The correlation shown is almost perfect ($r = -0.96$), with only two samples slightly off the trend. Sample 9 (labeled V) is actually on a different slope because one sixth of the Zr is substituted by Ti, *i.e.*, it is on a trend toward alluaivite. The deviation of the other sample 7 (labeled w) may be because the microprobe data do not pertain to the crystal used in the structure analysis but is actually from another fragment of the same specimen.

SOLID-SOLUTION SERIES

The solid-solution series between the classic eudialyte (rich in Si, Ca, Fe and Cl) and kentbrooksite (rich in Nb, *REE*, Mn and F) suggested by Johnsen & Gault (1997) was based on a number of simple correlations between individual elements or small groups of elements. The present crystal-chemical study confirms this series, with minor modifications. A first modification is that the anion parts of the end members may not be significant in the definition of the solid-solution series. Another modification of limited impact is the replacement of Si with (Si,Al) in the expression for the eudialyte end-member. The most significant modification is the replacement of Nb in the expression for the kentbrooksite end-member with the component defined as the $M(3)$ elements in accordance with Figure 9 and the discussion connected to it. These modifications result in the correlation diagram shown in Figure 12, where it is particularly notable that the series extends beyond kentbrooksite (sample 13, labeled A) and right up to crystal 5 (labeled h), the *R*3 eudialyte. Also, note that the degree of acentricity is an integral part of the description of the series, with the most centric samples of eudialyte being confined to the right part of the trend and an increasing degree of acentricity to the left. The coefficient of correlation in Figure 12 is $r = -0.97$.

THE DERIVATION OF A STRUCTURAL FORMULA

One of the primary objectives of this study was the derivation of a method for the calculation of a structural formula. Until now, there has been no clear means of determining an empirical formula for eudialyte from the results of a chemical analysis. Ambiguities in number, and types, of atomic sites have led to great confusion and significant errors in the formulae assigned to this mineral. Indeed, this study confirms the complexity of the structure, with almost all sites being able to accommodate more than one cation, and with a notable variation in the total number of anions. Therefore, an accurate formula can only be constructed from data based on structural information. An empirical formula acceptable in most cases may, however, be derived from results of a chemical analysis by use of two different points of reference: 1) total number of anions, or 2) the sum of cations in *Si*(1) to *Si*(7), *M*(3) and *Zr* sites.

The total number of anions ($Z = 3$) seen in Table 2 ranges from 75.39 to 78.70 *apfu*, with a mean of 77.38(83) *apfu* for all samples. This gives a standard deviation of 1.07% of the mean value, which is somewhat higher than desirable. More important, however, is the fact that unless a determination of the proportion of H_2O is available (usually it is not), the *apfu* values based on numbers of anions become systematically too high. As an example, in a typical sample of eudialyte, the proportion of Si (*apfu*) will decrease from 25.90 to 25.30 with the incorporation of 1 wt.% H_2O. The lack of determinations of other cations will, of course, give a similar effect. Therefore, additional corrections may be required if this method of formula calculation is adopted.

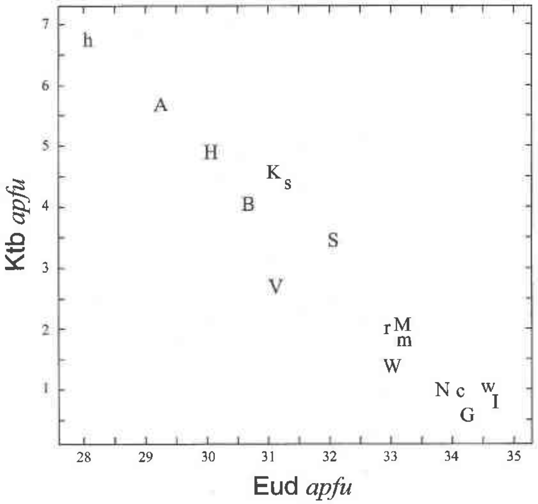

FIG. 12. The solid-solution series between eudialyte (Eud) and kentbrooksite (Ktb), with an extension to the *R*3 type of eudialyte. The proportions of the Eud and Ktb components are expressed in terms of the amounts of [(Si,Al) + Ca + Fe] and [(Nb, other *M*(3) elements) + *REE* + Mn], respectively, expressed in *apfu*. The symbols chosen are as in Table 1.

The second method is based on the number of cations accommodated in the framework composed of the silicate rings and the *Zr* octahedra, supplemented with the two sites [*M*(3) and *Si*(7)] in the centers of the nine-membered rings, *i.e.*, Si + Al + Zr + Ti + Hf + Nb + W + Ta, ideally adding to 29 *apfu* ($Z = 3$). In all the present samples, these elements add to 29.08(26) *apfu* with the standard deviation being 0.89%, *i.e.*, slightly better than in the anion-based method of calculation. The real advantage of this second method is the fact that it is fully applicable without determinations of hydrogen or other cations, making the method very practical, as most chemical information is obtained by electron-microprobe analysis. One disadvantage is that some of the elements involved (Al, Ti and Zr) occasionally also occur in other parts of the structure. For instance in samples 9 and 17, quantities of Al, Ti and Zr are found in *M*(1) and *M*(2), although only in small amounts. If these two crystals were omitted from the average, the mean would be 29.01(18) *apfu*, *i.e.*, a standard deviation of 0.62% only, demonstrating that this method of calculation works well for the majority of eudialyte-group samples. Another minor disadvantage of the method is that it does not account for any site vacancy in *M*(3), as has been observed in some crystals. Everything considered, though, we conclude that the second method is definitely superior to the first. Thus we recommend the following procedure to arrive at the empirical formula of a eudialyte-group mineral on the basis of chemical data only:

i) For the majority of the eudialyte (*s.l.*) samples, the empirical formula will be of the type: $Na_{15}[M(1)]_6 [M(2)]_3Zr_3 [M(3)] (Si_{25}O_{73}) (O,OH,H_2O)_3 X_2$

ii) Calculate the *apfu* based on 29 (sum of Si, Al, Zr, Ti, Hf, Nb, W and Ta), and constrain all Fe and Mn to be divalent.

iii) Assign all Si + Al to sum to 25 Si *apfu*. Any excess Si should be added to *M*(3).

iv) Assign all Zr to the *Zr* site, and if deficient make up a total to 3 atoms with Ti.

v) Assign all Nb and W to *M*(3).

vi) Assign all Fe and Mn to *M*(2). Any excess Mn should be assigned to *M*(1).

vii) Assign all Ca to *M*(1) and any remaining Mn then Y and *REE* to bring the total to 6 atoms. Any excess Ca should be assigned to the *Na* sites.

viii) Assign all Na, K, Sr and remaining Ca and *REE* to the *Na* sites.

ix) Assign 73 of the O atoms to the silicate rings, with the remaining anions partitioned into an O fraction and a halogen fraction.

x) The number of H atoms is based on charge balance.

Within the eudialyte group, the species eudialyte [*i.e.*, the type material of the original description of Stromeyer (1819)] would have the formula $Na_{15}Ca_6 Fe_3Zr_3 Si (Si_{25}O_{73}) (O,OH,H_2O)_3 (Cl,OH)_2$, and kentbrooksite (Johnsen *et al.* 1998), the formula

$Na_{15}Ca_6Mn_3Zr_3\,Nb(Si_{25}O_{73})\,(O,OH,H_2O)_3\,(F,Cl)_2$.

In order to encompass all samples studied, the empirical formula must be expanded to: $Na_{12}[Na(4)]_3[M(1a)]_3[M(1b)]_3[M(2)]_3Zr_3\,[M(3)]\,(Si_{25}O_{73})\,(O,OH,H_2O)_3X_2$. Rare cases where Ca *apfu* is below 50% of the $M(1)$ site or Na is below 50% in the $Na(4)$ site will become evident during the course of formula calculation. However, in such cases, we believe that a crystal-structure refinement is required in order to calculate a reliable formula.

CONCLUSIONS

Minerals of the eudialyte group have a complex structure with a wide variation in chemical substitutions. A complete formula requires crystal-structure data. An acceptable empirical formula, based on chemical analysis only, can be calculated from the relationships derived in this study, however. Relationships determined in this study that are of particular importance are summarized here:

1) A fundamental property of the eudialyte structure is a stable network of three-membered and nine-membered rings of $[SiO_4]$ tetrahedra. No chemical substitution is noted in these tetrahedra. Only small adjustments involving tilting or rotation of the $[SiO_4]$ tetrahedra are required to accommodate other modules.

2) The $[M(1)O_6]$ octahedron is more or less distorted. It is usually dominated by Ca, but variable amounts of Mn, *REE* and Y can be present. Both bond lengths and the degree of distortion of the octahedron are well correlated with chemistry. In one crystal, more than half the Ca is replaced by Mn and *REE*, resulting in an ordering of these cations in a Mn-dominated $M(1a)$ site and a Ca- and *REE*-dominated $M(1b)$ site.

3) The $M(2)$ site has either four-fold coordination with an almost planar arrangement or five-fold coordination with a distorted square pyramid, $O(19)$ being the fifth ligand. Iron definitely prefers the $M(2,4)$ site, whereas Mn generally dominates in $M(2,5)$. The occupancy of the two sites combined seldom reaches the maximum 3 *apfu*, but is invariably higher than ~2 *apfu*, indicating that the $M(2)$ site is an integral part of the structure.

4) The $M(3)$ and $Si(7)$ sites, the two central sites of the two crystallographically distinct nine-membered silicate rings, are related by the substitution $^{[6]}M(3) + {}^{[4]}Si(7) \leftrightarrow 2^{[4]}Si(7)$. The $[M(3)O_6]$ octahedron incorporating $O(19)$ is predominantly occupied by Nb (seldom W), whereas the $[Si(7)O_4]$ tetrahedron pointing upward or downward accommodates (Si,Al).

5) Na occupies sites varying in coordination number from 6 to 10. The $Na(4)$ site, with nine-fold coordination, is particularly suitable for incorporation of elements such as *REE*, Sr, Ca and K.

6) $O(19)$ plays a key role in the eudialyte structure, being the ligand shared by the $M(3)$, $M(2,5)$ and $Na(4)$ sites. The site-occupancy factor of $O(19)$ and the *epfu* values of these cations sites are strongly correlated.

7) Eudialyte *sensu lato* crystallizes in space groups $R\bar{3}m$, $R3m$ or $R3$, depending on the degree of disorder and the chemical content of certain sites. Eudialyte *sensu stricto* is ideally centrosymmetric, and as substitutions of the type Si → (Nb,W), Fe → Mn, (Ca,Na) → (*REE*,Sr) take place, the structure becomes progressively more noncentrosymmetric.

8) $|E^2 - 1|$ values prove useful in displaying the degree of acentricity in the eudialyte structure, as this parameter shows strong negative correlations with the chemical quantities such as $M(3)\,/\,[(M(3) + Si(7)]$ and the proportion of *REE* in *apfu*. Since the substituting elements are in general heavier than those replaced, an almost perfect negative correlation exists between $|E^2 - 1|$ and the calculated density.

9) The solid-solution series between the classic eudialyte and kentbrooksite is confirmed with minor modifications. The series extends beyond kentbrooksite to the $R3$ eudialyte. The degree of acentricity is an integral property of the series.

10) From results of a chemical analysis, the number of atoms in the formula may be calculated on the basis of the cation sum (Si + Al + Zr + Ti + Hf + Nb + W + Ta) = 29. As the number of anions varies, an approach based on anions is not a suitable basis for the calculation of a formula.

11) The generalized empirical formula is $Na_{15}[M(1)]_6[M(2)]_3Zr_3\,[M(3)]\,(Si_{25}O_{73})\,(O,OH,H_2O)_3\,X_2$. Elements may be reliably assigned to each site with a series of prescribed steps.

12) To date, only two species have been formally described within the eudialyte group, but several more are imminent. The described species are eudialyte, $Na_{15}Ca_6Fe_3Zr_3\,Si(Si_{25}O_{73})\,(O,OH,H_2O)_3\,(Cl,OH)_2$, and kentbrooksite, $Na_{15}Ca_6Mn_3Zr_3\,Nb\,(Si_{25}O_{73})\,(O,OH,H_2O)_3\,F_2$.

Even after this extensive study, eudialyte remains an enigmatic mineral, as a number of problems still exist. Several eudialyte crystals originally included in this study did not refine well, although the crystals look good physically, and the intensity data give sharp reflections, with good cell refinements. In spite of the experience we have gained with the eudialyte structure (*i.e.*, trying various models with differing space-groups, twin laws and order–disorder arrangements), we have no explanation for the poor refinements, which generally do not attain *R* indices below 0.07. Of particular interest for future investigation will be eudialyte crystals with extraordinary compositions, for example with exceptional enrichments in Zr, *REE* or Nb, or depletions in Na. These further studies are primarily of crystal-chemical interest, whereas the present paper establishes the chemical formula and major chemical substitutions within this group of minerals for those species of economic and petrological importance.

ACKNOWLEDGEMENTS

We are indebted to R.A. Gault, Canadian Museum of Nature, for his continued and stimulating interest in minerals of the eudialyte group and for his very careful electron-microprobe analyses of the crystals used in this study. We thank F.C. Hawthorne, University of Manitoba, for the use of the single-crystal diffractometer, and M.A. Cooper, also at that institution, for some of the data collections. R.W. Berg, the Technical University of Denmark, and E.A. Moffat, Canadian Conservation Institute, are thanked for providing the infrared spectra, and J.-E. Jørgensen, the University of Århus, for supplying the thermogravimetric analyses. U. Hålenius, the Swedish Museum of Natural History, is thanked for sharing his Mössbauer and optical absorption spectroscopy data with us. The manuscript was improved by the comments and suggestions of the referees A.R. Chakhmouradian and J. Swope, and of Associate Editor R.H. Mitchell and Editor R.F. Martin. The work at the University of Copenhagen was supported by the Danish Natural Science Research Council.

NOTE ADDED IN PROOF

Sample numbers 6 and 5 in the present study have subsequently gained status as new mineral species. They are named khomyakovite (Johnsen *et al.* 1999a) and oneillite (Johnsen *et al.* 1999b), respectively. The new mineral species and their names have been approved by the Commission on New Minerals and Mineral Names, IMA.

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Received December 26, 1998, revised manuscript accepted June 5, 1999.