Dukeite, $Bi^{3+}_{24}Cr^{6+}_8O_{57}(OH)_6(H_2O)_3$, a new mineral from Brejaúba, Minas Gerais, Brazil: Description and crystal structure

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ABSTRACT

Dukeite, $Bi^{3+}_{24}Cr^{6+}_8O_{57}(OH)_6(H_2O)_3$, space group $P31c$, $a = 15.067(3)$, $c = 15.293(4)$ Å, $V = 3007(1)$ Å^3, $Z = 2$, is a new mineral found on a museum specimen labeled as originating from the São José Mine, Brejaúba, Minas Gerais, Brazil. The strongest seven lines of the X-ray powder-diffraction pattern [d in Å (I) (hkl)] are: 7.650 (50) (002), 3.812 (40) (004), 3.382 (100) (222), 2.681 (70) (224), 2.175 (40) (600), 2.106 (40) (226), 1.701 (50) (228). It occurs as groupings of tightly bound 1 × 0.3 mm^2 sized sheaves that are associated with pucherite, schumacherite, bismutite, and hechtsbergite. Individual acicular crystals do not exceed 100 μm in length by 1–2 μm in width. Crystals are yellow inclining to a dirty yellow-brown, possess a bright yellow streak, are transparent, brittle, resinous, and do not fluoresce under ultraviolet light. The estimated Mohs hardness is between 3 and 4, the calculated density (for the empirical formula) is 7.171 g/cm^3, and the mineral is slowly soluble in concentrated HCl. Electron-microprobe analyses yielded Bi_2O_3 85.06, CrO_3 11.65, V_2O_5 0.59, H_2O (calc.) [1.67], total [98.97] wt%. The empirical formula, derived from the crystal-structure analysis and electron-microprobe analyses, is $Bi^{3+}_{23.95}(Cr^{6+}_{7.64}V^{5+}_{0.43})_{\Sigma8.07}O_{56.84}(OH)_{6.16} \cdot 3.01\ H_2O$, based on O = 66. In reflected plane-polarized light in air it is gray to purplish gray with strong yellow internal reflections. Bireflectance is very weak. Measured reflectance values, in air and in oil, are tabulated: indices of refraction calculated from these at 590 nm are 2.33 and 2.37. The name honors Duke University, Durham, North Carolina, in whose collection the mineral was found and also recognizes the contribution of the Duke family to the advancement of scientific knowledge.

The crystal structure of dukeite was solved by direct methods and refined on the basis of F^2 using all unique reflections measured with Mo$K\alpha$ X-radiation on a CCD-equipped diffractometer. The final $R1$ index was 8.7%, calculated using 1033 observed reflections. It contains irregular layers of $Bi\phi_n$ polyhedra (ϕ: O, OH$^-$, H_2O) parallel to (001), separated and connected by CrO_4 tetrahedra to form a framework structure. One CrO_4 tetrahedron shares all of its vertices with $Bi\phi_n$ polyhedra, whereas the other three CrO_4 tetrahedra share only three vertices each with the $Bi\phi_n$ polyhedra on either side.

INTRODUCTION

The new mineral, dukeite, was first encountered by one of us (M.N.F.) during a systematic megascopic examination of the mineral collection housed at Duke University, Durham, North Carolina. Minute sheaves of yellow acicular crystals were noted in one area of the surface of a specimen labelled as pucherite from Brazil. This latter mineral is well known, and Brazilian pucherite specimens may be found in many of the world's major collections. However, the color and habit of the associated yellow mineral was unusual enough to warrant further study. Subsequent routine X-ray powder-diffraction char-

acterization, coupled with a scanning electron energy-dispersion study, confirmed that this species is indeed new.

The new mineral is named for Duke University. This name was chosen for two reasons: firstly, the holotype (and only known) specimen was discovered in the mineral collection housed at the university; and secondly, the name recognizes the contribution of the Duke family to the advancement of scientific knowledge. More specifically on the second point, we acknowledge the Mary Duke Biddle Foundation for its support of mineralogical research that directly led to the initial discovery of the mineral. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names (IMA). The holotype specimen has been deposited in the mineral collections at the Smithsonian Institution, Wash-

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ington (catalog number 172012). The polished section used for both the electron microprobe and reflectance studies is preserved at The Natural History Museum, Great Britain, as BM 1999, 26. A small vial of pure dukeite, several single-crystal mounts, and a SEM stub have been deposited in the Systematic Reference Series of the National Mineral Collection of Canada, Geological Survey of Canada, Ottawa, under catalog number NMCC 68082.

DESCRIPTION

Occurrence and paragenesis

The locality label (M219) is São José Mine, Brejaúba, Minas Gerais, Brazil. The correct locality should read as follows: Lavra da Posse, São José de Brejaúba, Conceição do Mato Dentro County, Minas Gerais, Brazil. The geology and mineralogy of the deposit have been studied by Barbosa (1938) and by Rolff (1949). Nothing about the pedigree of the specimen is known other than it is thought to have been collected in the 1920s. Examination of numerous pucherite and bismutite specimens from São José de Brejaúba in three museum collections (U.S. National Museum, Washington, D.C.; Harvard Mineralogical Museum, Cambridge, Massachusetts; The Natural History Museum, London, U.K.) have not revealed any additional specimens of the new phase. It should therefore be considered extremely rare, although, given the small size of the crystals and similar color of other species present, the mineral can easily be overlooked. The specimen measures $4.5 \times 3 \times 2$ cm^3 and the dukeite is segregated in one 3×3 mm^2 region and is somewhat isolated from the other minerals. Associated minerals are dark red-black to red-brown to brown to red crystals and crystal aggregates of pucherite, $BiVO_4$, yellow nodular masses of schumacherite, $Bi_3O(OH)[(V^{5+},As,P)O_4]_2$, yellow transparent platy masses of bismutite, $Bi_2(CO_3)O_2$, as well as late-stage pale yellow powdery crusts of the same mineral. In several areas there has been partial replacement of pucherite crystals by orange crystalline hechtsbergite, $Bi_2O(OH)(VO_4)$, which, in turn, has been replaced by the yellow powdery bismutite.

Dukeite occurs as very tightly bound sheaves of parallel growth acicular crystals. These sheaves do not exceed 1 mm in length by 0.3 mm in width and are randomly dispersed on the specimen as well as being haphazardly scattered on top of each other. The morphology of the crystals certainly does not reflect the near-identical cell parameters; we suspect that dukeite might be pseudomorphous after an unknown mineral.

Mineral data

A SEM photomicrograph of part of a sheave is given in Figure 1. The characteristics of the mineral are given in Table 1 and the fully indexed X-ray powder-diffraction pattern is in Table 2. Precession single-crystal study indicates there is a pronounced subcell with $a_o = 1/2a$. This subcell will index the majority of the strong reflections of the powder-diffraction pattern.

Reflectance studies

Reflectance properties in air are given in Table 1 and the measured reflectance data, in air and in oil, are given in Table
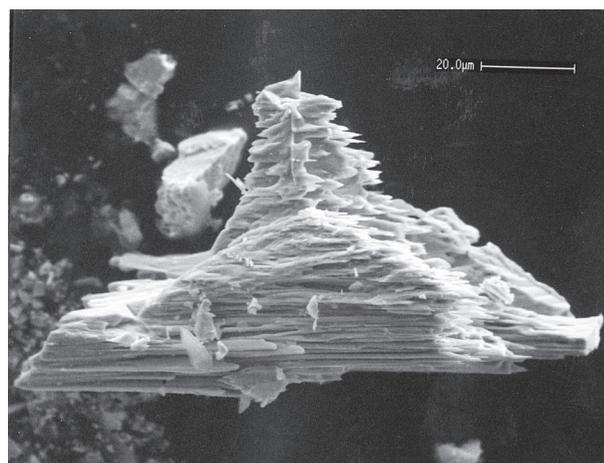
FIGURE 1. SEM photomicrograph showing part of a dukeite sheave. Scale bar = 20 μm.

TABLE 1. Descriptive characteristics of dukeite

Physical Properties	
Color	yellow inclining to dirty yellow-brown
Streak	bright yellow
Luster	resinous
Diaphaneity	translucent (sheaves) to transparent (crystals)
Fluorescence	none observed
Fracture	uneven
Hardness (Mohs)	3–4 (estimated)
Density	7.177$_{calc}$ g/cm^3*; 7.179$_{calc}$ g/cm^3†
Tenacity	brittle
Cleavage	none observed
Solubility	turns colorless immediately in concentrated HCl and grains seem to corrode over a period of several minutes and eventually dissolve; unaffected by concentrated H_2SO_4
Morphology	
Habit	acicular along [001]
General appearance	subhedral to occasionally euhedral
Forms	none observed (even under SEM study)
Crystal size	100 μm in length by 1–2 μm in width (average)
Length-to-width ratio	approximately 50:1
Twinning	none observed megascopically nor during single-crystal study
Optical reflectance properties (in air)	
Color	gray to slightly purplish gray in plane-polarized light
Internal reflections	yellow (along length of crystals but are absent from near-basal sections)
Anisotropy	not observed (if present it is totally masked by internal reflections)
Bireflectance	very weak
Pleochroism	none observed
Calculated indices of refraction	2.33 and 2.37 (at 590 nm)‡
Gladstone-Dale compatibility ($1 - K_p/K_c$)	–0.054 (good)

* Derived from crystal-structure formula and unit-cell parameters.
† Derived from empirical formula and crystal-structure unit-cell parameters.
‡ The average index of refraction (2.35) calculated from the reflectance is probably too high due to interference from the strong yellow internal reflections. Only two small areas (about 15 μm in size) were measurable and even these were not entirely free from internal reflections which add a diffuse component to the measured data.

TABLE 2. X-ray powder-diffraction data for dukeite

I_{obs}	d_{obs}	$d_{(calc.)}$	hkl	I_{obs}	d_{obs}	$d_{(calc.)}$	hkl
5	9.915	9.906	101	1	1.968	1.970	611
50	7.650	7.630	002	20	1.916	1.916	425*
5	6.492	6.512	200	20	1.888	1.887	604*
10	6.010	5.989	201	1	1.848	1.847	701
3	5.392	5.356	112	20	1.826	1.825	442*
10	4.966	4.953	202	3	1.807	1.806	620
3	4.699	4.685	211	1	1.789	1.794	621
3	4.131	4.136	212			1.785	336
30	4.012	4.009	203*	10	1.766	1.769	426*
40	3.812	3.815	004*	10	1.754	1.757	622*
20	3.745	3.760	220*	1	1.724	1.725	710
1	3.519	3.515	311			1.722	525
100	3.382	3.373	222*	50	1.701	1.701	228*
10	3.272	3.292	204	10	1.685	1.686	444*
		3.256	400	20	1.651	1.651	606*
10	3.189	3.184	401*	15	1.633	1.632	427*
10	2.998	2.995	402*	5	1.618	1.619	801
5	2.938	2.932	321	5	1.590	1.589	535
1	2.840	2.842	410	1	1.570	1.572	714
3	2.747	2.742	403	30	1.550	1.550	803*
70	2.681	2.678	224*	5	1.526	1.526	0010
30	2.541	2.543	006*	5	1.509	1.512	446
3	2.467	2.461	420	15	1.487	1.487	641*
30	2.431	2.430	421*	3	1.468	1.469	724
3	2.382	2.381	332			1.468	617
20	2.340	2.342	422*			1.466	642
1	2.277	2.279	414			1.465	730
25	2.216	2.216	423*	5	1.434	1.433	643
40	2.175	2.171	600*	10	1.414	1.414	2210*
40	2.106	2.106	226*	10	1.396	1.396	429*
10	2.064	2.062	432*	1	1.371	1.369	823
3	1.999	2.004	406	20	1.342	1.342	645*

Notes: 114.6 mm Debye-Scherrer camera, Cu$K\alpha$ (Ni-filtered) radiation, observed intensities visually estimated; corrected for shrinkage, no internal standard. Indices marked with an asterisk (*) were used for unit-cell refinement. Unit-cell parameters refined from powder data are a = 15.039(5), c = 15.259(5) Å.

TABLE 3. Reflectance data for dukeite

λ (nm)	R_1 (air)	R_2 (air)	R_1 (oil)	R_2 (oil)
400	19.8	21.4	7.60	9.01
420	19.45	20.85	7.34	8.43
440	18.9	20.05	6.80	7.61
460	18.15	19.0	6.34	6.94
470 (COM)	17.9	18.6	6.11	6.65
480	17.5	18.2	5.85	6.41
500	17.0	17.55	5.48	5.98
520	16.7	17.3	5.47	5.92
540	16.5	17.1	5.46	5.95
546 (COM)	16.45	17.0	5.43	5.94
560	16.3	16.9	5.32	5.88
580	16.2	16.7	5.27	5.82
589 (COM)	16.0	16.5	5.19	5.67
600	15.95	16.45	5.20	5.64
620	15.8	16.25	5.12	5.64
640	15.7	16.2	5.06	5.58
650 (COM)	15.7	16.2	5.00	5.57
660	15.6	16.1	5.01	5.56
680	15.5	15.95	4.95	5.56
700	15.35	15.8	4.90	5.58

Note: Reflectance measurements were made with Zeiss instrumentation (MPM 800), Zeiss reflectance standard (SiC no. 472), and Zeiss immersion oil (N_D = 1.515).

3. Between crossed polars the mineral does not entirely extinguish—basal sections exhibit an unvarying mid orange-brown on rotation. At the same time, bright sulfur-yellow and sulfur-brown internal reflections "flood" the length of the needles and are accompanied at crystal boundaries by light green interference colors. All of these phenomena are enhanced when the mineral is immersed in oil.

Electron microprobe examination

A portion of a sheave of dukeite crystals was analyzed with a Cameca SX-50 electron microprobe, utilizing an operating voltage of 20 kV, a beam current of 10 nA, a beam 3 μm in diameter, and a 10 s count time. Bi metal, Cr metal, and V metal were used as standards. An energy-dispersion and a wavelength-dispersion scan indicated the absence of any other elements with atomic number greater than 9 except those reported here. The valence states for both Bi and Cr, as well as the number of O atoms, were determined by crystal-structure analysis prior to interpretation of the electron-microprobe results. Vanadium was assumed to be in its highest oxidation state because it is partially substituting for Cr. The paucity of pure material prevented the quantitative determination of water. However, its presence as both $(OH)^-$ and H_2O was confirmed by both crystal-structure analysis and powder infrared-absorption study; it was calculated assuming the ideal formula. The average result of eight analyses gave: Bi_2O_3 85.06 (range 83.70–85.94), CrO_3 11.65 (range 11.29–11.92), V_2O_5 0.59 (range 0.40–0.74), H_2O (calc.) (1.67), total (98.97) wt%. With O = 66, the empirical formula for dukeite is $Bi^{3+}_{23.95}(Cr^{6+}_{7.64}V^{5+}_{0.43})\Sigma_{8.07}O_{56.84}(OH)_{6.16}\cdot3.01\ H_2O$. The ideal formula, $Bi^{3+}_{24}Cr^{6+}_8O_{57}(OH)_6(H_2O)_3$, requires Bi_2O_3 86.03, CrO_3 12.31, H_2O 1.67, total 100.00 wt%.

Infrared study

The equipment and procedures for acquiring the infrared spectrum for powdered dukeite are identical to those used to obtain the spectrum for mcalpineite (Roberts et al. 1994). The instrumentation used was a Spectra-Tech IR-Plan infrared microscope accessory interfaced to a Bomen Michelson MB-120 Fourier-transform infrared spectrometer (FTIR), which utilizes a 0.25 mm² liquid nitrogen-cooled Hg Cd Te detector. A large shallow broad band (Fig. 2) with peaks at 3258 and 3597 cm^{-1} is due to O-H stretching in the $(OH)^-$ groups, and the hint of a shoulder, at approximately 1631 cm^{-1}, may be due to H-O-H bending in the H_2O groups. The chromate groups are characterized by a medium band at 826 (v_1), a medium strong band at 842 (v_3) and a strong band at 872 cm^{-1} (v_3), which are all stretching vibrations (Nakamoto 1978).

STRUCTURE DETERMINATION

Single-crystal X-ray data collection

It was impossible to locate a crystal that exhibited uniform optical properties and sharp extinction between crossed polarizers. We concluded that the parallel-intergrown crystals were too small to be separated, and selected a crystal that showed relatively superior optical properties. The crystal was mounted on a Bruker PLATFORM 3-circle goniometer equipped with a 1K SMART CCD (charge-coupled device) detector and a crystal-to-detector distance of 5 cm. A discussion of the application of CCD detectors to the analysis of crystal structures is provided by Burns (1998).
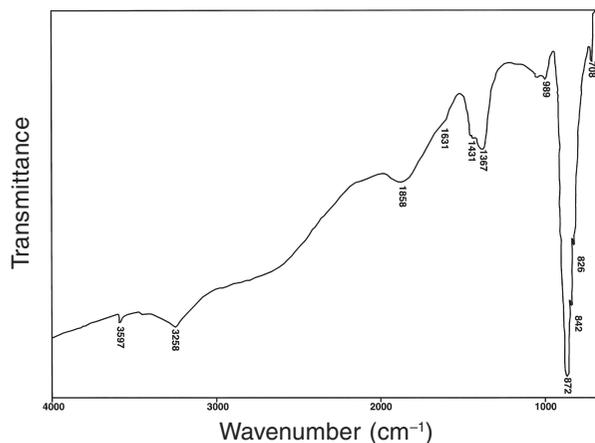
FIGURE 2. Infrared-absorption spectrum for dukeite.

A hemisphere of data was collected using monochromatic MoKα X-radiation and frame widths of 0.3° in ω, with 40 s used to acquire each frame. Several hundred frames of data were analyzed to locate diffraction maxima for the determination of the unit-cell parameters. It was impossible to index all reflections using only one crystal orientation, indicating that the crystal selected was not a single crystal. A subset of reflections accounting for more than half of the total number of reflections was identified that required a single orientation matrix and gave a hexagonal unit-cell with the dimensions a = 15.067(3), c = 15.293(4) Å. The data showed a strong subcell with $a/2$. The three-dimensional data were integrated and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. Data were collected for $3° \leq 2\theta \leq 56.7°$ in approximately 16 hours; comparison of the intensities of equivalent reflections collected at different times during the data collection showed no evidence of significant decay. An empirical absorption-correction based upon the intensities of equivalent reflections was applied using the program SADABS (G. Sheldrick, unpublished). A total of 19 271 reflections was collected; merging of equivalent reflections gave 4122 unique reflections with 1033 classed as observed ($|F_o| \geq 4\sigma_F$). Of the observed reflections, the majority corresponded to the subcell reflections. Of 14 479 intensities collected that would violate the subcell if observed, only 375 were found to be greater than

3σ. Information pertaining to the data collection is summarized in Table 4.

Structure solution and refinement

Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from *International Tables for X-Ray Crystallography* (Ibers and Hamilton 1974). The Bruker SHELXTL Version 5 system of programs was used for the determination and refinement of the crystal structure. Systematic absences and reflection statistics indicated space group $P31c$, with verification provided by the successful solution of the structure. The structure was solved by direct methods, and the initial model included the positions of the Bi atoms. The Cr positions and the anions were located in successive difference-Fourier maps that were calculated after refinement of the model. The structure was refined on the basis of F^2 using all unique reflections. Following refinement of the atomic positional parameters and isotropic-displacement parameters for all atoms the agreement factor ($R1$) was 9.3%, calculated for observed reflections. The displacement parameters for the Bi cations were converted to anisotropic forms, and were refined together with the positional parameters for all atoms and a weighting scheme of the structure factors. A single overall displacement parameter was refined for all anions. The refinement was fairly slow to converge owing to the weakness of the data, the poor data-to-parameter ratio, and the likely interference from other crystal orientations. In particular, refinement of the positional parameters of the anions was difficult, and some of the Cr-O bond-lengths obtained were significantly different from the expected bond-length of ~1.62 Å. In the final cycles of refinement the Cr-O bond-lengths were constrained to be ~1.62 Å; these constraints resulted in a more chemically reasonable structure, and did not increase the final $R1$. The final model resulted in an $R1$ of 8.7%, calculated for the 1033 unique observed reflections ($|F_o| \geq 4\sigma_F$), and a goodness-of-fit (S) of 0.92. In the final cycle of refinement the average parameter shift/esd was 0.000. The final atomic-positional parameters and anisotropic-displacement parameters are given in Tables 5 and 6, and selected interatomic-distances and angles are given in Table 7.

Considerable uncertainty remains as to the exact details of the structure of dukeite. Owing to the problems with the available material and to the dominance of the X-ray scattering efficiency of Bi, the structure refinement did not yield the desired degree of precision. Whereas the precision of the bond-lengths is clearly lacking, the general connectivity of the structure is not in doubt. Furthermore, the structure determination was essential for the realization of the correct chemical formula for dukeite. Improvement of the precision of the structure will only be realized if better quality single crystals are obtained; our search for such crystals has been unsuccessful to date.

Structural formula

The structure contains eight symmetrically distinct Bi cations located on general positions, totaling 48 Bi per unit cell. There are four unique Cr^{6+} cations, two each are on special and general positions, totaling 16 Cr per unit cell. The asymmetric unit contains 24 anions, and analysis of the bond valences in-

TABLE 4. Miscellaneous information pertaining to the structure determination of dukeite

a (Å)	15.067(3)	Crystal size (mm³)	0.10 × 0.04
c (Å)	15.293(4)		× 0.03
V (Å³)	3007(1)	Total ref.	19,271
Space group	$P31c$	Unique ref.	4122
$F(000)$	5448	Unique $|F_o| \geq 4\sigma_F$	1033
m (mm⁻¹)	71.4	Final $R1$* (%)	8.7
D_{calc} (g/cm³)	7.179	S†	0.92

Note: Unit-cell contents: $2[Bi^{3+}_{24}Cr^{6+}_8O_{57}(OH)_6(H_2O)_3]$.
*$R1 = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$.
†$S = [\Sigma w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$, for m observations and n parameters.

TABLE 5. Atomic-position parameters and equivalent isotropic-displacement parameters for the structure of dukeite

	x	y	z	$*U_{eq}$
Bi1	−0.0237(5)	0.8074(4)	0.0630(6)	239(15)
Bi2	0.6928(6)	0.6693(5)	0.0676(2)	179(18)
Bi3	0.8309(4)	0.5245(4)	0.0646(5)	167(14)
Bi4	0.6752(4)	0.4764(4)	0.2600(3)	119(10)
Bi5	0.0251(4)	0.7021(3)	0.2652(3)	132(11)
Bi6	0.2921(4)	0.8245(3)	0.2649(3)	140(12)
Bi7	0.1701(4)	0.9740(4)	0.2603(4)	163(13)
Bi8	0.1261(4)	0.6464(4)	0.0651(4)	304(12)
Cr1	0.166(2)	0.836(1)	−0.089(1)	149(35)
Cr2	⅔	⅓	−0.092(2)	44(75)
Cr3	0	0	−0.088(3)	258(106)
Cr4	−0.002(1)	0.494(2)	−0.0999(9)	133(40)
O1	0.171(5)	0.832(5)	0.328(4)	96(25)
O2	0.290(4)	0.947(4)	0.204(4)	96(25)
OH3	0.830(5)	0.660(5)	−0.004(4)	96(25)
O4	0.553(4)	0.340(5)	0.201(4)	96(25)
O5	0.041(5)	0.841(4)	0.197(5)	96(25)
O6	0.841(5)	0.790(5)	0.122(5)	96(25)
O7	0.709(5)	0.548(5)	0.132(5)	96(25)
O8	0.968(4)	0.655(5)	0.112(4)	96(25)
O9	0.160(5)	0.832(5)	0.019(2)	96(25)
O10	⅔	⅓	0.015(2)	96(25)
O11	0	0	−0.194(3)	96(25)
O12	−0.004(4)	0.497(5)	−0.207(1)	96(25)
O13	−0.020(5)	0.093(3)	−0.062(4)	96(25)
O14	−0.027(4)	0.579(4)	−0.062(4)	96(25)
O15	−0.086(4)	0.380(3)	−0.063(4)	96(25)
O16	0.671(5)	0.234(3)	−0.131(4)	96(25)
O17	0.191(5)	0.751(4)	−0.126(4)	96(25)
O18	0.263(3)	0.942(5)	−0.122(4)	96(25)
O19	0.055(3)	0.813(5)	−0.126(4)	96(25)
O20	0.109(3)	0.516(4)	−0.065(4)	96(25)
O21	⅔	⅓	0.33(1)	96(25)
O22	0.148(5)	0.707(5)	0.193(5)	96(25)
OH23	0.017(4)	0.500(5)	0.105(3)	96(25)
H₂O24	0.339(5)	0.744(4)	0.105(4)	96(25)

* $U_{eq} = U_{eq}$ Å^2 × 10^4.

TABLE 6. Anisotropic-displacement parameters for the Bi cations in the structure of dukeite

	$*U_{11}$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi1	192(35)	379(34)	200(38)	184(30)	38(30)	56(35)
Bi2	160(35)	263(36)	130(39)	117(28)	−23(23)	24(29)
Bi3	149(31)	175(26)	142(31)	54(26)	21(24)	−22(30)
Bi4	176(28)	133(25)	95(26)	112(23)	8(24)	−1(23)
Bi5	155(29)	151(29)	100(27)	83(23)	7(22)	28(21)
Bi6	201(28)	190(29)	78(30)	136(22)	12(20)	2(21)
Bi7	228(34)	163(30)	124(35)	118(24)	−2(23)	−43(23)
Bi8	535(30)	188(22)	50(20)	75(28)	−9(28)	9(20)

* $U_{ij} = U_{ij}$ Å^2 × 10^4.

TABLE 7. Selected interatomic distances (Å) and angles (°) in the structure of dukeite

Bi1-O6a	2.13(6)	Bi5-O22	2.13(6)
Bi1-O5	2.22(7)	Bi5-O5	2.23(6)
Bi1-O8a	2.36(6)	Bi5-O1	2.29(7)
Bi1-OH3a	2.44(7)	Bi5-O19h	2.44(6)
Bi1-O9	2.69(6)	Bi5-O8a	2.48(6)
Bi1-O13b	2.73(6)	<Bi5-ϕ>	2.31
<Bi1-ϕ>	2.43		
		Bi6-O2	2.08(6)
Bi2-O7	2.20(6)	Bi6-O1	2.12(7)
Bi2-O6	2.22(7)	Bi6-O22	2.28(6)
Bi2-O2c	2.31(6)	Bi6-O16i	2.58(6)
Bi2-OH3	2.41(7)	<Bi6-ϕ>	2.26
Bi2-O15d	2.66(6)		
Bi2-OH23d	2.71(6)	Bi7-O5	2.20(6)
<Bi2-ϕ>	2.42	Bi7-O2	2.21(7)
		Bi7-O6d	2.34(7)
Bi3-O8	2.15(6)	Bi7-O1	2.39(7)
Bi3-O7	2.28(6)	Bi7-O18j	2.68(6)
Bi3-OH3	2.30(7)	<Bi7-ϕ>	2.36
Bi3-O4e	2.32(6)		
Bi3-O14f	2.70(6)	Bi8-OH23	2.08(6)
<Bi3-ϕ>	2.35	Bi8-O22	2.11(7)
		Bi8-H₂O24d	2.51(6)
Bi4-O4e	2.14(7)	Bi8-O8a	2.54(6)
Bi4-O4	2.15(6)	Bi8-O9	2.68(7)
Bi4-O7	2.17(7)	Bi8-O20	2.71(6)
Bi4-O21	2.34(7)	<Bi8-ϕ>	2.44
Bi4-O17g	2.47(6)		
<Bi4-ϕ>	2.25		
Cr1-O18	1.61(2)	Cr3-O13,l,m	1.62(2) ×3
Cr1-O17	1.62(2)	Cr3-O11	1.63(2)
Cr1-O19	1.62(2)	<Cr3-O>	1.62
Cr1-O9	1.65(2)		
<Cr1-O>	1.62	Cr4-O20	1.62(2)
		Cr4-O14	1.62(2)
Cr2-O10	1.63(2)	Cr4-O15	1.63(2)
Cr2-O16,e,k	1.64(2) ×3	Cr4-O12	1.64(2)
<Cr2-O>	1.64	<Cr4-O>	1.63

Notes: a = x−1, y, z; b = −y, x−y+1, z; c = y−x, 1−x, z; d = 1−y, x−y+1, z; e = y−x+1, 1−x, z; f = x+1, y, z; g = 1−x, y−x, z+½; h = −x, y−x, z+½; i = y, x, z+½; j = x−y+1, 2−y, z+½; k = 1−y, x−y, z; l = y−x, −x, z; m = −y, x−y, z.

dicates there are 21 O, 2 (OH)⁻, and one (H₂O). Eighteen O are on general positions and three are special, giving 114 O per unit cell. The (OH)⁻ and (H₂O) are all on general positions, giving 12 (OH)⁻ and 6 (H₂O) per unit cell. The formula of the crystal studied is therefore $Bi_{24}^{3+}Cr_8^{6+}O_{57}(OH)_6(H_2O)_3$, $Z = 2$.

DESCRIPTION OF THE STRUCTURE

The eight symmetrically distinct Bi cations are coordinated by from four to six ligands, with <Bi-ϕ> [ϕ: O, (OH)⁻, H₂O] ranging from 2.25 to 2.44 Å. Bond-valence sums incident at the Bi sites, calculated using the parameters of Brown and Altermatt (1985), range from 2.6 to 3.4 valence units (v.u.), presumably reflecting the imprecision of the Bi-ϕ bond lengths. The four symmetrically distinct Cr⁶⁺ cations are tetrahedrally coordinated by O, with average tetrahedral bond angles ranging from 109.1 to 109.5°.

The structure of dukeite projected along [100] (Fig. 3a) contains irregular layers of Biϕ$_n$ polyhedra that are two polyhedra thick and parallel to (001). The layers of Biϕ$_n$ polyhedra are cross-linked by CrO₄ tetrahedra to form a heteropolyhedral framework structure. The bond-valences associated with the Bi-ϕ bonds vary from 0.2 to 1.0 v.u.; anions involved in weaker Bi-ϕ interactions are typically part of CrO₄ tetrahedra. The Cr1O₄ tetrahedron shares all of its vertices with Biϕ$_n$ polyhedra, whereas the other three CrO₄ tetrahedra share only three

vertices with the sheets of Biϕ$_n$ polyhedra on either side.

The structures have been reported for the synthetic compounds BiCrO₄(OH) [orthorhombic and monoclinic modifications, Aurivillius and Loewenhielmÿ (1964)] and HBi₃(CrO₄)₂O₃ (Kodialam et al. 1994). Although none of these compounds is isostructural with dukeite, they are all based upon sheets of Bi polyhedra that are cross-liked through CrO₄ tetrahedra.
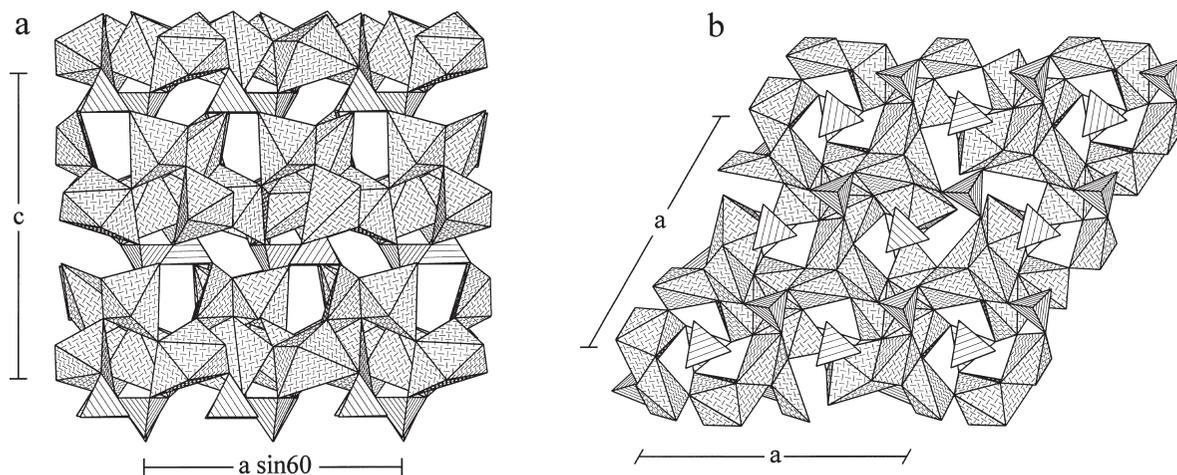
FIGURE 3. Polyhedral representations of thes tructure of dukeite. (**a**) Projected along [100]; (**b**) Projected along [001]. The CrO_4 tetrahedra and $Bi\phi_n$ polyhedra are shaded with parallel lines and herringbone patterns, respectively.

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