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The crystal structure of dalnegroite, $Tl_{5-x}Pb_{2x}(As,Sb)_{21-x}S_{34}$: a masterpiece of structural complexity

L. Bindi[1,2,*], F. Nestola[3], A. Guastoni[3] and L. Secco[3]

[1] Museo di Storia Naturale, sezione di Mineralogia, Università degli Studi di Firenze, Via La Pira, 4, I-50121, Firenze, Italy
[2] C.N.R. – Istituto di Geoscienze e Georisorse, sezione di Firenze, Via La Pira, 4, I-50121, Firenze, Italy
[3] Dipartimento di Geoscienze, Università degli Studi di Padova, Via Giotto 1, I-35137, Padova, Italy

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ABSTRACT

The crystal structure of the rare mineral dalnegroite, $Tl_{5-x}Pb_{2x}(As,Sb)_{21-x}S_{34}$ with $x \approx 1$, was determined for a crystal from Lengenbach, Binn Valley, Switzerland. The structure is triclinic, space group *P*1, with a = 16.218(3), b = 42.546(7), c = 8.558(1) Å, α = 95.70(4), β = 90.18(3), γ = 96.38(4)º, V = 5838.9(9) Å^3, Z = 4. Refinement of an isotropic model led to an R_1 index of 0.0536 for 22226 observed reflections and 980 parameters, and R_1 = 0.0590 for all 25266 independent reflections. Although dalnegroite cannot be considered a layered compound, its structure can be usefully described as a regular alternation of two kinds of layers stacked along the **b** axis, with four layers in the unit cell: (1) a layer 7.8 Å thick, at $y \approx 0.15$ and 0.65, can be considered as derived from the SnS archetype; (2) a layer 13.6 Å thick, at $y \approx 0.35$ and 0.85, derived from the PbS archetype. Different chemical compositions, such as Tl:Pb and Sb:As ratios, for different samples belonging to the chabournéite-dalnegroite family could play a central role in controlling different degrees of order, leading to different superstructures.

Keywords: dalnegroite, crystal structure, thallium, sulphosalt, Lengenbach, Switzerland.

Introduction

Dalnegroite, $Tl_{5-x}Pb_{2x}(As,Sb)_{21-x}S_{34}$ with $x \approx 1$, is a recently described new mineral from the Lengenbach quarry, Binntal, Canton Valais, Switzerland (Nestola *et al.*, 2010). The mineral has strong chemical and structural affinities with chabournéite, $Tl_4Pb_2(Sb,As)_{20}S_{34}$ (Johan *et al.*, 1981), of which it was considered the As-dominant analogue. However, due to the paucity of dalnegroite crystals and to the extremely broad X-ray diffraction (XRD) peak profiles, Nestola *et al.* (2010) were not able to determine the structure of dalnegroite. Recently, a new sample from Lengenbach quarry was made available to the authors and it contains rare, very small crystals of dalnegroite (up to 90 μm long) of much better quality for diffraction purposes. A structure determination of dalnegroite was, therefore, undertaken, the results of which are presented here.

Experimental

Qualitative chemical analysis using energy-dispersive spectrometry (EDS) on dalnegroite crystals from the new rock sample confirmed the nominal stoichiometry $Tl_{5-x}Pb_{2x}(As,Sb)_{21-x}S_{34}$ with $x \approx 1$ given by Nestola *et al.* (2010), within the experimental error of the method. A tiny black prismatic crystal of dalnegroite (0.018 mm × 0.020 mm × 0.022 mm) was selected from a crushed sample and attached to the tip of a glass capillary by means of solvent-free glue for the single-crystal XRD study. Diffraction quality

* E-mail: luca.bindi@unifi.it
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(peak profiles) was checked initially using a Bruker-P4 single-crystal diffractometer equipped with a conventional point detector. Subsequently, the unit-cell parameters were carefully measured using an Oxford Diffraction Xcalibur 3 single-crystal diffractometer (Enhanced X-ray source) fitted with a Sapphire 2 CCD detector. Information relating to the data collection and structure refinement are listed in Table 1. Data frames were processed using the *CrysAlis* software package running on the Xcalibur 3 control PC. The unit-cell parameters are very similar to those given by Nestola *et al.* (2010) for the type dalnegroite. Integration of reflection intensities and the standard Lorentz-polarization corrections were carried out with the *CrysAlis RED* software package (Oxford Diffraction, 2006). The *ABSPACK* element of the *CrysAlis RED* program was used for the absorption correction.

Solution and refinement of the structure

No systematic absences were observed, implying a choice of the space groups $P1$ and $P\bar{1}$. Although

TABLE 1. Crystallographic data and refinement parameters for dalnegroite.

Crystal data	
Structural formula	$Tl_4Pb_2Sb_8As_{12}S_{34}$
Crystal system	Triclinic
Space group	$P1$
Unit-cell parameters a, b, c, (Å)	16.218(3) , 42.546(7) , 8.558(1)
α, β, γ (º)	95.70(4), 90.18(3), 96.38(4)
Unit cell volume, V (Å^3)	5838.9(9)
Z	4
Calculated density (g/cm^3)	9.515
Absorption coefficient (mm^{-1})	56.76
Crystal size (mm)	$0.018 \times 0.020 \times 0.022$
Data collection	
Diffractometer	Oxford Diffraction Xcalibur 3 (CCD)
Radiation, wavelength (Å)	Mo-$K\alpha$, 0.71073
Temperature (K)	298(3)
θ range for data collection (º)	4.37−28.00
h, k, l ranges	±20, ±51, ±11
Axis, no. frames, width (º), time (s)	ω, 3259, 0.65, 230
Total reflections collected	49766
Unique reflections (R_{int})	25266 (0.077)
Unique reflections $F > 4\sigma(F)$	22226
Data completeness to θ_{max} (%)	93.4
Absorption correction method	Multiscan (ABSPACK Oxford Difffraction, 2006)
Structure refinement	
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	$1/\sigma^2(F)$
Flack parameter	0.041(3)
Data/restraints/parameters	25266/0/980
R_1 [$F > 4\sigma F$], wR_2 [$F > 4\sigma F$]	0.054, 0.050
R_1 all, wR_2 all	0.059, 0.051
Goodness-of-fit on F^2	0.88
Largest diff. peak/hole (e$^-$/A^3)	0.86, −0.39

$R_{int} = (n/n - 1)^{1/2}[F_o^2 - F_o\,(\text{mean})^2]/\Sigma F_o^2$
$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$;
* $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$;
$GoF = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$
where n is the number of reflections and p is the number of refined parameters.

statistical tests on the distribution of |E| values ($|E^2-1| = 0.819$) did not indicate the presence of an inversion centre, thus suggesting the choice of the space group $P1$, the structure was initially solved in the centrosymmetric space group $P\bar{1}$.

The positions of most of the atoms were determined by means of the charge-flipping method (Oszlányi and Süto, 2008) as implemented within the *JANA2006* software package (Petříček *et al.*, 2006). A least-squares refinement on F^2 using heavy-atom positions and isotropic temperature factors gave an R factor of 0.2245. Three-dimensional difference-Fourier synthesis yielded the position of the remaining atoms. *JANA2006* was used for the refinement of the structure. A final model with isotropic temperature factors for all the atoms led to $R = 0.1931$. At this point, a thorough analysis of the structure (essentially based upon the observation of the very large atomic displacement parameters for particular atoms) suggested that refinement in space group $P1$ should be attempted. Atomic coordinates were then recast for an initial $P1$ structure and then refined. Given the very large number of atoms in the $P1$ starting model and the refinement of site occupancies for most of the metal positions, a strong damping factor (<0.1) was used in the full-matrix refinement. After several cycles, an ordered solution with full site occupancies was finally obtained by removing atoms with low site occupancies and/or unrealistic distances to neighbouring atoms, and also by including significant maxima found in the difference-Fourier syntheses. The structure refined smoothly in $P1$ without any imposed damping or restrictions. Some Pb and Sb atoms were found to be partially replaced by Sb and Pb, respectively. For the final stage of refinement with isotropic displacement parameters for all atoms and no constraints, the residual value settled at $R = 0.0536$ for 22226 observed reflections [$2\sigma(I)$ level] and 980 parameters and at $R = 0.0590$ for all 25266 independent reflections.

It is worth noting that the acentric structural model obtained here does not show large values in the correlation matrix between pairs of atoms that are equivalent in the centrosymmetric space group $P\bar{1}$. In spite of the lower values of the R indices obtained for the acentric refinement, the presence of twinning by inversion (twin law: [$\bar{1}00/0\bar{1}0/00\bar{1}$]) in the non-centrosymmetric structure refinement was also tested. It is well known that a centrosymmetric structure refined as a non-centrosymmetric structure will show a twin scale-factor, which is equivalent to the Flack parameter (refined to 50%) in the case of inversion twinning (Flack *et al.*, 2006; Müller *et al.*, 2006). The refined racemic twin-component scale-factor of 0.041(3) is consistent with a highly asymmetrical distribution of the enantiomorphic components and indicates that the acentric model is the correct choice. Moreover, to test the significance of the great improvement of the agreement between observed and calculated structure factors shown by the acentric model, we applied the Hamilton test (Hamilton, 1965). Although Marsh (1981, 1986, 1994, 1995) and Baur and Tillmans (1986) have warned against using the Hamilton test to distinguish between non-centrosymmetric and centrosymmetric models when heavy atoms are present, recent studies by Capelli *et al.* (2000), Du Boulay *et al.* (2004) and Friese *et al.* (2004) show that the test can be used. The results obtained indicate that we may reject (at the 0.005 significance level) the hypothesis that the structure of natural dalnegroite is centrosymmetric. The non-centrosymmetric nature of dalnegroite was also validated by the Add/Symm routine in the Platon software package (Speck, 2003).

Atom coordinates and isotropic displacement parameters are given in Table 2. Structure factors (Table 3) have been deposited with the Principal Editor of *Mineralogical Magazine* and are available at http://www.minersoc.org/pages/e_journals/dep_mat.html.

Description of the structure and discussion

Overall, the crystal structure of dalnegroite is topologically identical to that obtained by Nagl (1979) for the $b/2$ subcell (i.e. $b' \approx 21$ Å) of chabournéite. The structural formula obtained here can be written as $Tl_4Pb_{2.01}Sb_{8.01}As_{12}S_{34}$ ($Z = 4$), with Sb $\rightleftharpoons$ Pb isomorphic substitution in some Pb and Sb sites (i.e. Pb1–Pb5, Pb8, Sb1–Sb10, Sb14, Sb16; Table 4). The huge number of the refined structural positions together with the triclinic, non-centrosymmetric structure, however, does not allow us to rule out further substitutions at other sites of the dalnegroite structure. Nevertheless, the refined formula obtained in this study is very close to that obtained by Nestola *et al.* (2010), i.e. $Tl_{4.15}Pb_{2.03}Sb_{8.20}As_{11.86}S_{34}$ (mean of 11 electron-microprobe analyses) with $Z = 4$.

Although dalnegroite cannot be considered a layered compound, its structure can be usefully described as a regular alternation of two kinds of

TABLE 2. Atoms, site-occupancy factors, fractional atomic coordinates (Å), and equivalent isotropic displacement parameters (Å^2) for the selected dalnegroite crystal.

Atom	Occupancy	*x*	*y*	*z*	U_{iso}
Tl1	1.00	0.2464(8)	0.1580(3)	0.425(2)	0.061(3)
Tl2	1.00	0.2374(8)	0.1577(3)	0.908(1)	0.059(3)
Tl3	1.00	0.7327(9)	0.1609(3)	0.415(2)	0.053(4)
Tl4	1.00	0.7362(8)	0.1590(3)	0.928(2)	0.069(3)
Tl5	1.00	0.277(1)	0.3446(4)	0.071(2)	0.066(4)
Tl6	1.00	0.2749(8)	0.3422(3)	0.554(1)	0.066(3)
Tl7	1.00	0.7705(8)	0.3429(3)	0.060(2)	0.062(3)
Tl8	1.00	0.7748(7)	0.3430(3)	0.584(1)	0.061(3)
Tl9	1.00	0.2462(8)	0.6601(3)	0.425(1)	0.057(3)
Tl10	1.00	0.2375(7)	0.6597(3)	0.909(1)	0.056(3)
Tl11	1.00	0.7345(7)	0.6629(3)	0.415(1)	0.051(2)
Tl12	1.00	0.738(1)	0.6616(4)	0.927(2)	0.066(5)
Tl13	1.00	0.2771(7)	0.8468(3)	0.068(1)	0.054(2)
Tl14	1.00	0.2751(8)	0.8450(3)	0.555(2)	0.054(3)
Tl15	1.00	0.7704(7)	0.8452(3)	0.059(1)	0.059(2)
Tl16	1.00	0.7748(8)	0.8451(3)	0.582(2)	0.060(3)
Pb1	0.69(2)	0.0028(7)	0.1113(5)	0.438(1)	0.061(2)
Pb1(Sb)	0.31	0.0028(7)	0.1113(5)	0.438(1)	0.061(2)
Pb2	0.59(2)	0.5037(6)	0.1121(2)	0.925(1)	0.052(2)
Pb2(Sb)	0.41	0.5037(6)	0.1121(2)	0.925(1)	0.052(2)
Pb3	0.59(2)	0.0090(6)	0.3908(3)	0.060(1)	0.042(2)
Pb3(Sb)	0.41	0.0090(6)	0.3908(3)	0.060(1)	0.042(2)
Pb4	0.63(3)	0.5049(6)	0.3904(2)	0.527(1)	0.038(2)
Pb4(Sb)	0.37	0.5049(6)	0.3904(2)	0.527(1)	0.038(2)
Pb5	0.81(2)	0.0020(8)	0.6140(3)	0.437(2)	0.057(2)
Pb5(Sb)	0.19	0.0020(8)	0.6140(3)	0.437(2)	0.057(2)
Pb6	1.00	0.5041(7)	0.6148(3)	0.923(1)	0.050(2)
Pb7	1.00	0.0117(5)	0.8922(2)	0.064(1)	0.063(1)
Pb8	0.27(3)	0.5083(5)	0.8918(2)	0.530(1)	0.047(1)
Pb8(Sb)	0.73	0.5083(5)	0.8918(2)	0.530(1)	0.047(1)
Sb1	0.83(2)	0.1595(7)	0.0302(2)	0.948(1)	0.061(2)
Sb1(Pb)	0.17	0.1595(7)	0.0302(2)	0.948(1)	0.061(2)
Sb2	0.92(3)	0.331(1)	0.0656(4)	0.224(2)	0.062(5)
Sb2(Pb)	0.08	0.331(1)	0.0656(4)	0.224(2)	0.062(5)
Sb3	0.82(3)	0.6594(7)	0.0329(2)	0.942(1)	0.060(2)
Sb3(Pb)	0.18	0.6594(7)	0.0329(2)	0.942(1)	0.060(2)
Sb4	0.67(2)	0.8342(9)	0.0597(4)	0.230(2)	0.054(4)
Sb4(Pb)	0.33	0.8342(9)	0.0597(4)	0.230(2)	0.054(4)
Sb5	0.71(3)	0.495(1)	0.1186(3)	0.432(2)	0.068(4)
Sb5(Pb)	0.29	0.495(1)	0.1186(3)	0.432(2)	0.068(4)
Sb6	0.95(3)	0.9940(7)	0.1148(2)	0.967(1)	0.050(2)
Sb6(Pb)	0.05	0.9940(7)	0.1148(2)	0.967(1)	0.050(2)
Sb7	0.70(3)	0.0116(7)	0.1963(3)	0.657(1)	0.066(2)
Sb7(Pb)	0.30	0.0116(7)	0.1963(3)	0.657(1)	0.066(2)
Sb8	0.84(2)	0.5083(7)	0.1977(3)	0.162(1)	0.062(2)
Sb8(Pb)	0.16	0.5083(7)	0.1977(3)	0.162(1)	0.062(2)
Sb9	0.65(3)	0.1666(6)	0.2620(2)	0.120(1)	0.062(2)
Sb9(Pb)	0.35	0.1666(6)	0.2620(2)	0.120(1)	0.062(2)
Sb10	0.70(2)	0.3441(8)	0.2429(3)	0.876(2)	0.067(3)
Sb10(Pb)	0.30	0.3441(8)	0.2429(3)	0.876(2)	0.067(3)
Sb11	1.00	0.6685(7)	0.2614(3)	0.621(1)	0.060(2)
Sb12	1.00	0.8467(9)	0.2429(3)	0.378(2)	0.063(3)
Sb13	1.00	0.0073(9)	0.3053(4)	0.836(2)	0.051(3)

Table 2 (*contd.*).

Atom	Occupancy	x	y	z	U_{iso}
Sb14	0.83(3)	0.5034(9)	0.3080(4)	0.337(2)	0.058(4)
Sb14(Pb)	0.17	0.5034(9)	0.3080(4)	0.337(2)	0.058(4)
Sb15	1.00	0.0216(8)	0.3806(3)	0.588(2)	0.084(3)
Sb16	0.94(3)	0.5221(7)	0.3836(3)	0.074(1)	0.071(2)
Sb16(Pb)	0.06	0.5221(7)	0.3836(3)	0.074(1)	0.071(2)
Sb17	1.00	0.1790(8)	0.4404(3)	0.766(1)	0.059(2)
Sb18	1.00	0.6748(9)	0.4373(3)	0.256(2)	0.057(3)
Sb19	1.00	0.6841(9)	0.4420(4)	0.778(2)	0.056(4)
Sb20	1.00	0.8354(7)	0.4664(3)	0.486(1)	0.064(2)
Sb21	1.00	0.4878(7)	0.4904(3)	0.741(1)	0.066(2)
Sb22	1.00	0.1591(8)	0.5324(3)	0.949(2)	0.067(2)
Sb23	1.00	0.329(1)	0.5670(5)	0.230(2)	0.065(6)
Sb24	1.00	0.6596(8)	0.5350(3)	0.943(2)	0.065(2)
Sb25	1.00	0.834(1)	0.5617(4)	0.224(2)	0.065(4)
Sb26	1.00	0.4981(8)	0.6203(3)	0.428(1)	0.057(3)
Sb27	1.00	0.9931(9)	0.6171(3)	0.969(2)	0.058(3)
Sb28	1.00	0.0118(8)	0.6989(3)	0.658(1)	0.061(2)
Sb29	1.00	0.5087(7)	0.6999(3)	0.163(1)	0.061(2)
Sb30	1.00	0.1662(7)	0.7639(3)	0.121(1)	0.060(2)
Sb31	1.00	0.3451(8)	0.7451(3)	0.874(1)	0.056(2)
Sb32	1.00	0.6677(7)	0.7632(3)	0.622(1)	0.059(2)
As1	1.00	0.0223(9)	0.0174(3)	0.261(2)	0.058(3)
As2	1.00	0.1719(9)	0.0352(4)	0.519(2)	0.057(3)
As3	1.00	0.331(1)	0.0667(6)	0.713(3)	0.050(6)
As4	1.00	0.5280(9)	0.0200(3)	0.250(2)	0.058(3)
As5	1.00	0.676(1)	0.0380(4)	0.514(2)	0.058(3)
As6	1.00	0.834(1)	0.0699(5)	0.739(2)	0.062(5)
As7	1.00	0.015(1)	0.1865(4)	0.164(2)	0.064(4)
As8	1.00	0.516(1)	0.1871(4)	0.655(2)	0.064(4)
As9	1.00	0.153(1)	0.2481(4)	0.636(2)	0.060(3)
As10	1.00	0.361(1)	0.2551(4)	0.355(2)	0.059(3)
As11	1.00	0.653(1)	0.2489(4)	0.133(2)	0.061(3)
As12	1.00	0.862(1)	0.2538(4)	0.856(2)	0.057(4)
As13	1.00	-0.001(1)	0.3166(5)	0.333(2)	0.064(5)
As14	1.00	0.493(1)	0.3180(5)	0.833(2)	0.064(5)
As15	1.00	0.188(1)	0.4362(5)	0.268(2)	0.052(4)
As16	1.00	0.3561(9)	0.4716(3)	0.055(2)	0.052(3)
As17	1.00	0.343(1)	0.4673(4)	0.484(2)	0.062(3)
As18	1.00	0.8521(9)	0.4691(3)	0.067(2)	0.055(3)
As19	1.00	0.986(1)	0.4838(3)	0.743(2)	0.064(3)
As20	1.00	0.0229(9)	0.5104(3)	0.262(2)	0.060(3)
As21	1.00	0.1708(8)	0.5283(3)	0.520(2)	0.054(3)
As22	1.00	0.328(2)	0.5611(6)	0.722(2)	0.048(6)
As23	1.00	0.5278(9)	0.5134(3)	0.249(2)	0.058(3)
As24	1.00	0.6770(9)	0.5320(3)	0.514(2)	0.055(3)
As25	1.00	0.833(2)	0.5650(7)	0.731(3)	0.07(1)
As26	1.00	0.0159(9)	0.6788(4)	0.167(2)	0.065(3)
As27	1.00	0.5153(9)	0.6802(4)	0.656(2)	0.063(3)
As28	1.00	0.1542(9)	0.7416(3)	0.637(2)	0.061(3)
As29	1.00	0.359(1)	0.7477(4)	0.354(2)	0.056(4)
As30	1.00	0.6531(9)	0.7430(4)	0.133(2)	0.060(3)
As31	1.00	0.861(1)	0.7465(4)	0.857(2)	0.054(4)
As32	1.00	0.001(2)	0.8095(6)	0.325(3)	0.065(8)
As33	1.00	0.494(1)	0.8102(6)	0.824(3)	0.056(6)

Table 2 (*contd.*).

Atom	Occupancy	x	y	z	U_{iso}
As34	1.00	0.1877(9)	0.9291(4)	0.266(2)	0.055(3)
As35	1.00	0.3562(8)	0.9646(3)	0.057(2)	0.060(3)
As36	1.00	0.3428(9)	0.9607(4)	0.481(2)	0.063(3)
As37	1.00	0.8535(8)	0.9616(3)	0.070(2)	0.061(3)
As38	1.00	0.9880(9)	0.9779(3)	0.745(2)	0.061(3)
As39	1.00	0.848(1)	0.7445(4)	0.373(2)	0.052(4)
As40	1.00	0.008(1)	0.8079(4)	0.829(2)	0.048(4)
As41	1.00	0.505(1)	0.8102(4)	0.330(2)	0.047(4)
As42	1.00	0.0150(9)	0.8886(4)	0.575(2)	0.020(3)
As43	1.00	0.5154(8)	0.8887(3)	0.047(2)	0.021(3)
As44	1.00	0.178(1)	0.9431(5)	0.764(2)	0.058(6)
As45	1.00	0.676(1)	0.9387(5)	0.251(3)	0.059(6)
As46	1.00	0.686(1)	0.9439(5)	0.774(2)	0.060(6)
As47	1.00	0.8341(9)	0.9588(3)	0.482(2)	0.057(3)
As48	1.00	0.4876(9)	0.9828(3)	0.740(2)	0.057(3)
S1	1.00	0.102(2)	0.0587(8)	0.277(4)	0.078(8)
S2	1.00	0.068(2)	0.0555(7)	0.689(3)	0.060(7)
S3	1.00	0.238(2)	0.0837(9)	0.513(5)	0.073(9)
S4	1.00	0.228(2)	0.0826(7)	0.929(3)	0.056(6)
S5	1.00	0.446(2)	0.0433(8)	0.037(4)	0.066(7)
S6	1.00	0.419(2)	0.0368(7)	0.434(3)	0.059(6)
S7	1.00	0.600(2)	0.0643(9)	0.283(4)	0.078(9)
S8	1.00	0.575(2)	0.0564(8)	0.692(4)	0.064(7)
S9	1.00	0.749(2)	0.0888(8)	0.512(4)	0.061(7)
S10	1.00	0.734(2)	0.0821(8)	0.931(4)	0.067(8)
S11	1.00	0.948(2)	0.0409(8)	0.041(4)	0.077(8)
S12	1.00	0.918(2)	0.0293(8)	0.442(4)	0.067(7)
S13	1.00	0.101(2)	0.1362(9)	0.193(4)	0.042(8)
S14	1.00	0.088(3)	0.148(1)	0.686(4)	0.079(9)
S15	1.00	0.277(2)	0.2145(8)	0.108(4)	0.052(8)
S16	1.00	0.279(2)	0.2191(7)	0.663(4)	0.050(8)
S17	1.00	0.384(2)	0.1213(8)	0.204(3)	0.049(7)
S18	1.00	0.380(2)	0.1139(8)	0.698(3)	0.052(7)
S19	1.00	0.434(2)	0.1771(7)	0.461(4)	0.057(7)
S20	1.00	0.439(2)	0.1770(7)	0.863(4)	0.059(7)
S21	1.00	0.580(4)	0.149(2)	0.201(7)	0.08(2)
S22	1.00	0.602(3)	0.140(1)	0.678(4)	0.07(1)
S23	1.00	0.781(2)	0.2192(7)	0.159(4)	0.053(8)
S24	1.00	0.779(2)	0.2147(7)	0.608(4)	0.052(8)
S25	1.00	0.874(2)	0.1165(7)	0.202(3)	0.046(6)
S26	1.00	0.876(2)	0.1198(9)	0.715(4)	0.049(9)
S27	1.00	0.936(2)	0.1748(7)	0.368(4)	0.064(7)
S28	1.00	0.939(2)	0.1746(7)	0.963(4)	0.062(7)
S29	1.00	0.103(2)	0.2218(7)	0.454(4)	0.062(7)
S30	1.00	0.097(2)	0.2221(8)	0.845(4)	0.068(8)
S31	1.00	0.428(2)	0.2798(7)	0.145(4)	0.059(7)
S32	1.00	0.409(2)	0.2823(7)	0.544(4)	0.062(7)
S33	1.00	0.596(2)	0.2241(7)	0.344(4)	0.059(7)
S34	1.00	0.595(2)	0.2225(8)	0.957(4)	0.068(7)
S35	1.00	0.905(2)	0.2829(7)	0.044(4)	0.060(7)
S36	1.00	0.927(2)	0.2797(7)	0.645(3)	0.055(6)
S37	1.00	0.080(2)	0.3266(8)	0.107(4)	0.060(7)
S38	1.00	0.084(3)	0.328(1)	0.534(6)	0.09(1)
S39	1.00	0.138(2)	0.3859(8)	0.282(3)	0.038(7)

Table 2 (*contd.*).

Atom	Occupancy	x	y	z	U_{iso}
S40	1.00	0.127(4)	0.385(1)	0.781(6)	0.07(2)
S41	1.00	0.239(4)	0.285(1)	0.331(7)	0.09(2)
S42	1.00	0.233(3)	0.2868(9)	0.883(5)	0.07(1)
S43	1.00	0.418(2)	0.3591(9)	0.299(3)	0.041(8)
S44	1.00	0.416(3)	0.360(1)	0.799(4)	0.039(9)
S45	1.00	0.580(2)	0.3313(8)	0.023(4)	0.070(8)
S46	1.00	0.580(2)	0.3242(7)	0.618(4)	0.061(7)
S47	1.00	0.632(2)	0.3807(9)	0.264(4)	0.055(7)
S48	1.00	0.629(2)	0.393(1)	0.806(5)	0.067(9)
S49	1.00	0.727(2)	0.2885(9)	0.389(4)	0.073(8)
S50	1.00	0.738(2)	0.2837(9)	0.825(5)	0.073(9)
S51	1.00	0.914(3)	0.361(1)	0.300(4)	0.07(1)
S52	1.00	0.925(2)	0.3609(8)	0.792(3)	0.056(6)
S53	1.00	0.086(2)	0.4677(8)	0.556(4)	0.067(7)
S54	1.00	0.072(2)	0.4628(7)	0.960(3)	0.053(6)
S55	1.00	0.283(2)	0.4262(7)	0.085(3)	0.059(6)
S56	1.00	0.273(2)	0.4240(7)	0.487(3)	0.056(7)
S57	1.00	0.261(2)	0.0036(8)	0.206(4)	0.067(8)
S58	1.00	0.261(2)	0.0018(8)	0.791(4)	0.060(6)
S59	1.00	0.440(2)	0.4568(7)	0.291(3)	0.053(6)
S60	1.00	0.417(2)	0.4412(7)	0.717(3)	0.054(6)
S61	1.00	0.588(2)	0.4705(7)	0.556(3)	0.052(6)
S62	1.00	0.575(2)	0.4674(6)	0.958(3)	0.048(5)
S63	1.00	0.786(2)	0.4234(7)	0.069(3)	0.054(6)
S64	1.00	0.764(2)	0.4205(8)	0.480(4)	0.066(8)
S65	1.00	0.755(2)	0.4955(9)	0.214(5)	0.077(9)
S66	1.00	0.764(2)	0.0060(7)	0.787(3)	0.050(5)
S67	1.00	0.940(2)	0.4530(8)	0.287(3)	0.059(7)
S68	1.00	0.912(2)	0.4390(7)	0.728(4)	0.060(6)
S69	1.00	0.102(2)	0.5518(7)	0.281(3)	0.063(6)
S70	1.00	0.068(2)	0.5450(7)	0.691(3)	0.061(6)
S71	1.00	0.241(2)	0.5759(7)	0.507(4)	0.061(7)
S72	1.00	0.226(2)	0.5731(8)	0.933(4)	0.066(7)
S73	1.00	0.445(2)	0.5354(7)	0.039(3)	0.064(7)
S74	1.00	0.416(2)	0.5292(7)	0.438(3)	0.060(6)
S75	1.00	0.601(2)	0.5581(7)	0.286(4)	0.069(7)
S76	1.00	0.578(2)	0.5470(8)	0.701(4)	0.068(7)
S77	1.00	0.745(2)	0.5780(7)	0.509(4)	0.061(7)
S78	1.00	0.735(2)	0.5736(8)	0.938(4)	0.069(7)
S79	1.00	0.944(2)	0.5317(7)	0.040(3)	0.061(6)
S80	1.00	0.918(2)	0.5228(7)	0.446(3)	0.066(7)
S81	1.00	0.100(2)	0.6320(7)	0.192(3)	0.053(6)
S82	1.00	0.088(4)	0.638(2)	0.684(7)	0.10(2)
S83	1.00	0.278(2)	0.7165(7)	0.106(4)	0.047(7)
S84	1.00	0.280(2)	0.7202(8)	0.661(4)	0.052(7)
S85	1.00	0.384(2)	0.627(1)	0.202(4)	0.07(1)
S86	1.00	0.373(3)	0.612(1)	0.691(5)	0.08(1)
S87	1.00	0.432(2)	0.6783(7)	0.456(4)	0.058(7)
S88	1.00	0.438(2)	0.6783(7)	0.863(4)	0.065(7)
S89	1.00	0.585(2)	0.6476(9)	0.194(4)	0.058(9)
S90	1.00	0.598(2)	0.6433(7)	0.685(3)	0.038(6)
S91	1.00	0.779(2)	0.7197(8)	0.154(5)	0.046(9)
S92	1.00	0.776(2)	0.7164(8)	0.612(5)	0.049(9)
S93	1.00	0.867(3)	0.614(1)	0.187(5)	0.08(2)

S94	1.00	0.877(3)	0.627(1)	0.740(6)	0.10(2)

Table 2 (*contd.*).

Atom	Occupancy	x	y	z	U_{iso}
S95	1.00	0.937(2)	0.6764(7)	0.367(4)	0.062(7)
S96	1.00	0.939(2)	0.6762(7)	0.962(4)	0.058(7)
S97	1.00	0.102(2)	0.7239(7)	0.450(4)	0.064(7)
S98	1.00	0.096(2)	0.7236(7)	0.842(4)	0.059(7)
S99	1.00	0.426(2)	0.7821(7)	0.147(4)	0.059(7)
S100	1.00	0.409(2)	0.7845(7)	0.544(4)	0.062(7)
S101	1.00	0.597(2)	0.7259(7)	0.346(4)	0.064(7)
S102	1.00	0.598(2)	0.7243(7)	0.955(4)	0.061(7)
S103	1.00	0.904(2)	0.7840(7)	0.042(3)	0.059(6)
S104	1.00	0.926(2)	0.7824(7)	0.644(3)	0.057(6)
S105	1.00	0.081(2)	0.8287(8)	0.109(5)	0.071(9)
S106	1.00	0.081(2)	0.8327(8)	0.536(5)	0.075(9)
S107	1.00	0.143(3)	0.888(1)	0.285(5)	0.06(1)
S108	1.00	0.124(4)	0.887(2)	0.784(7)	0.11(2)
S109	1.00	0.233(3)	0.7877(9)	0.332(6)	0.07(1)
S110	1.00	0.231(2)	0.7879(9)	0.871(5)	0.06(1)
S111	1.00	0.428(4)	0.864(2)	0.310(8)	0.09(2)
S112	1.00	0.418(4)	0.866(1)	0.812(6)	0.08(2)
S113	1.00	0.576(2)	0.8345(7)	0.026(4)	0.065(7)
S114	1.00	0.580(2)	0.8249(7)	0.622(4)	0.061(7)
S115	1.00	0.635(2)	0.8831(9)	0.267(4)	0.060(9)
S116	1.00	0.629(2)	0.8929(9)	0.800(4)	0.067(9)
S117	1.00	0.729(2)	0.7772(7)	0.387(4)	0.065(7)
S118	1.00	0.736(2)	0.7728(7)	0.830(3)	0.063(6)
S119	1.00	0.907(2)	0.8474(7)	0.321(3)	0.064(6)
S120	1.00	0.926(3)	0.849(1)	0.795(4)	0.07(1)
S121	1.00	0.084(2)	0.9564(6)	0.566(3)	0.058(6)
S122	1.00	0.075(2)	0.9504(6)	0.951(3)	0.057(5)
S123	1.00	0.283(2)	0.9171(7)	0.081(3)	0.062(7)
S124	1.00	0.271(2)	0.9149(7)	0.483(3)	0.054(6)
S125	1.00	0.263(2)	0.4925(7)	0.198(3)	0.062(6)
S126	1.00	0.258(2)	0.4924(6)	0.791(3)	0.057(6)
S127	1.00	0.441(2)	0.9474(8)	0.286(4)	0.062(7)
S128	1.00	0.419(2)	0.9329(6)	0.716(3)	0.054(5)
S129	1.00	0.589(2)	0.9596(6)	0.558(3)	0.053(5)
S130	1.00	0.575(2)	0.9572(6)	0.950(3)	0.055(6)
S131	1.00	0.788(2)	0.9132(7)	0.066(3)	0.065(7)
S132	1.00	0.765(2)	0.9126(7)	0.478(4)	0.061(7)
S133	1.00	0.755(2)	0.9853(7)	0.211(3)	0.061(6)
S134	1.00	0.765(2)	0.4970(7)	0.790(3)	0.058(6)
S135	1.00	0.943(2)	0.9432(8)	0.285(4)	0.065(7)
S136	1.00	0.915(2)	0.9292(6)	0.735(3)	0.056(5)

layers stacked along the **b** axis, with four layers in the unit cell (Figures 1, 2). According to the modular description for sulphosalts introduced by Makovicky (1993), the first layer, 7.8 Å thick (at $y \approx 0.15$ and 0.65), can be considered as derived from the SnS archetype; the second layer, 13.6 Å thick (at $y \approx 0.35$ and 0.85), is derived from the PbS archetype. In dalnegroite, Tl and Pb atoms exhibit very similar coordination arrangements. Tl polyhedra in both layers form chains parallel to the **c** axis (Figure 2). They are trigonal prisms with variable numbers of additional S atoms (usually three) to complete the coordination sphere (Table 4). Pb polyhedra are very similar to Tl polyhedra, having coordination numbers of six (Pb5), seven (Pb2, Pb3, Pb4 and Pb6), eight (Pb1 and Pb8), and nine (Pb7), depending on the number of additional S atoms outside the prism in

TABLE 4. Main interatomic distances (Å) for the selected dalnegroite crystal.

Tl1–S3	3.31(4)	Tl2–S4	3.20(3)	Tl3–S9	3.30(4)	Tl4–S10	3.27(4)
Tl1–S13	3.07(4)	Tl2–S13	3.42(4)	Tl3–S21	3.04(7)	Tl4–S21	3.46(7)
Tl1–S14	3.42(4)	Tl2–S14	3.03(4)	Tl3–S22	3.22(4)	Tl4–S22	3.03(4)
Tl1–S15	3.80(4)	Tl2–S15	2.83(3)	Tl3–S23	3.49(4)	Tl4–S23	3.09(3)
Tl1–S16	3.14(3)	Tl2–S16	3.52(4)	Tl3–S24	2.72(3)	Tl4–S24	3.81(4)
Tl1–S17	3.34(4)	Tl2–S18	3.52(4)	Tl3–S25	3.53(3)	Tl4–S26	3.40(4)
Tl1–S19	3.06(3)	Tl2–S20	3.31(3)	Tl3–S27	3.32(4)	Tl4–S28	3.28(3)
Tl1–S29	3.76(4)	Tl2–S30	3.83(4)	Tl3–S33	3.76(4)	Tl4–S34	3.72(4)
Tl5–S37	3.22(4)	Tl6–S32	3.53(4)	Tl7–S35	3.53(4)	Tl8–S46	3.20(3)
Tl5–S39	3.42(4)	Tl6–S38	3.09(5)	Tl7–S45	3.08(4)	Tl8–S48	3.74(4)
Tl5–S41	3.54(6)	Tl6–S40	3.61(6)	Tl7–S47	3.30(4)	Tl8–S49	2.75(4)
Tl5–S42	2.82(4)	Tl6–S41	2.94(6)	Tl7–S49	3.83(4)	Tl8–S50	3.42(4)
Tl5–S43	2.97(4)	Tl6–S42	3.86(5)	Tl7–S50	3.06(4)	Tl8–S51	3.40(4)
Tl5–S44	3.31(4)	Tl6–S43	3.26(3)	Tl7–S51	3.08(4)	Tl8–S52	2.99(3)
Tl5–S55	3.45(3)	Tl6–S44	3.08(4)	Tl7–S52	3.47(3)	Tl8–S64	3.52(4)
		Tl6–S56	3.59(3)	Tl7–S63	3.40(3)		
Tl9–S71	3.71(3)	Tl10–S72	3.69(3)	Tl11–S77	3.80(3)	Tl12–S78	3.75(4)
Tl9–S81	3.14(3)	Tl10–S81	3.50(3)	Tl11–S89	3.03(4)	Tl12–S89	3.42(4)
Tl9–S82	3.51(7)	Tl10–S82	3.09(6)	Tl11–S90	3.31(3)	Tl12–S90	3.05(3)
Tl9–S83	3.81(4)	Tl10–S83	2.82(3)	Tl11–S91	3.47(4)	Tl12–S91	3.00(4)
Tl9–S84	3.10(3)	Tl10–S84	3.50(4)	Tl11–S92	2.71(4)	Tl12–S92	3.75(4)
Tl9–S85	3.29(4)	Tl10–S86	3.56(5)	Tl11–S93	3.60(5)	Tl12–S94	3.18(6)
Tl9–S87	3.03(3)	Tl10–S88	3.30(3)	Tl11–S95	3.30(3)	Tl12–S96	3.25(3)
Tl9–S97	3.76(4)	Tl10–S98	3.82(4)	Tl11–S101	3.75(4)	Tl12–S102	3.69(4)
Tl13–S105	3.21(4)	Tl14–S100	3.54(4)	Tl15–S103	3.56(3)	Tl16–S114	3.21(3)
Tl13–S107	3.37(5)	Tl14–S106	3.13(4)	Tl15–S113	3.14(3)	Tl16–S116	3.68(4)
Tl13–S109	3.56(5)	Tl14–S107	3.85(5)	Tl15–S115	3.29(4)	Tl16–S117	3.20(3)
Tl13–S110	2.90(4)	Tl14–S108	3.65(7)	Tl15–S118	3.47(3)	Tl16–S119	3.10(3)
Tl13–S111	3.17(7)	Tl14–S109	2.96(4)	Tl15–S119	3.14(3)	Tl16–S120	3.03(4)
Tl13–S112	3.27(5)	Tl14–S110	3.83(5)	Tl15–S120	3.40(4)	Tl16–S132	3.11(3)
Tl13–S123	2.97(3)	Tl14–S111	3.33(7)	Tl15–S131	2.87(3)		
		Tl14–S112	3.18(5)				
		Tl14–S124	3.10(3)				
*Pb1–S1	3.12(4)	*Pb2–S5	3.21(3)	*Pb3–S37	3.14(4)	*Pb4–S43	2.57(3)
*Pb1–S2	3.60(3)	*Pb2–S8	3.26(3)	*Pb3–S39	2.86(4)	*Pb4–S44	3.06(4)
*Pb1–S12	3.61(3)	*Pb2–S17	3.11(3)	*Pb3–S40	3.08(6)	*Pb4–S46	3.34(3)
*Pb1–S13	2.85(3)	*Pb2–S18	2.79(3)	*Pb3–S51	2.89(4)	*Pb4–S47	3.09(3)
*Pb1–S14	2.77(4)	*Pb2–S20	3.15(3)	*Pb3–S52	2.79(3)	*Pb4–S48	3.11(4)
*Pb1–S25	2.95(3)	*Pb2–S21	2.90(6)	*Pb3–S54	3.32(3)	*Pb4–S60	3.06(3)
*Pb1–S26	3.16(4)	*Pb2–S22	2.92(4)	*Pb3–S67	3.42(3)	*Pb4–S61	3.51(3)
*Pb1–S27	3.13(3)						
*Pb5–S69	3.42(3)	Pb6–S73	3.64(3)	Pb7–S105	3.10(4)	*Pb8–S111	2.43(7)
*Pb5–S81	2.76(3)	Pb6–S76	3.61(4)	Pb7–S107	2.89(5)	*Pb8–S112	3.05(5)
*Pb5–S82	2.58(6)	Pb6–S85	3.13(4)	Pb7–S108	3.02(7)	*Pb8–S114	3.35(3)
*Pb5–S93	3.06(5)	Pb6–S86	2.89(5)	Pb7–S119	3.39(3)	*Pb8–S115	3.07(4)
*Pb5–S94	3.33(5)	Pb6–S88	3.10(4)	Pb7–S120	3.03(4)	*Pb8–S116	3.02(4)
*Pb5–S95	3.08(4)	Pb6–S89	2.83(3)	Pb7–S122	2.84(3)	*Pb8–S127	3.56(4)
		Pb6–S90	2.83(3)	Pb7–S131	3.84(3)	*Pb8–S128	2.77(3)
				Pb7–S135	3.05(3)	*Pb8–S129	3.02(3)
				Pb7–S136	3.78(3)		

Table 4 (*contd.*).

*Sb1–S2	3.01(3)	*Sb2–S3	2.99(4)	*Sb3–S8	2.85(4)	*Sb4–S9	3.01(4)
*Sb1–S4	2.40(3)	*Sb2–S5	2.66(4)	*Sb3–S10	2.31(3)	*Sb4–S11	2.60(4)
*Sb1–S57	3.13(4)	*Sb2–S6	2.75(4)	*Sb3–S66	2.47(3)	*Sb4–S12	2.76(4)
*Sb1–S58	2.46(3)	*Sb2–S17	2.45(4)			*Sb4–S25	2.47(3)
		*Sb2–S57	2.74(4)				
*Sb5–S17	2.68(4)	*Sb6–S13	2.62(3)	*Sb7–S14	2.56(5)	*Sb8–S19	3.01(4)
*Sb5–S18	2.95(3)	*Sb6–S25	2.80(3)	*Sb7–S27	2.78(4)	*Sb8–S20	2.81(3)
*Sb5–S19	2.78(3)	*Sb6–S26	2.91(4)	*Sb7–S28	3.06(4)	*Sb8–S21	2.53(7)
*Sb5–S21	2.76(7)	*Sb6–S28	2.79(3)	*Sb7–S29	2.53(3)	*Sb8–S33	2.24(3)
*Sb5–S22	2.75(4)			*Sb7–S30	2.24(4)	*Sb8–S34	2.50(4)
*Sb9–S15	2.83(4)	*Sb10–S15	2.61(4)	Sb11–S24	2.81(3)	Sb12–S23	2.24(3)
*Sb9–S30	2.91(3)	*Sb10–S16	2.20(4)	Sb11–S33	2.89(3)	Sb12–S24	2.59(4)
*Sb9–S41	2.23(6)	*Sb10–S31	2.90(3)	Sb11–S49	2.53(4)	Sb12–S36	2.86(3)
*Sb9–S42	2.57(5)	*Sb10–S42	2.73(5)	Sb11–S50	2.15(4)	Sb12–S49	2.89(4)
Sb13–S35	2.61(3)	*Sb14–S31	2.22(3)	Sb15–S38	2.57(5)	*Sb16–S43	2.77(3)
Sb13–S36	2.21(3)	*Sb14–S32	2.58(4)	Sb15–S40	2.36(6)	*Sb16–S44	2.93(4)
Sb13–S37	2.63(4)	*Sb14–S43	2.75(4)	Sb15–S51	3.00(4)	*Sb16–S45	2.51(4)
Sb13–S38	3.07(5)	*Sb14–S46	2.69(3)	Sb15–S52	2.50(3)	*Sb16–S47	2.44(3)
Sb13–S52	2.90(4)					*Sb16–S48	2.91(4)
Sb17–S40	2.44(6)	Sb18–S47	2.44(4)	Sb19–S48	2.22(4)	Sb20–S64	2.16(3)
Sb17–S53	2.77(4)	Sb18–S63	2.50(3)	Sb19–S61	2.90(3)	Sb20–S67	2.48(3)
Sb17–S54	2.60(3)	Sb18–S64	2.60(4)	Sb19–S62	2.61(3)	Sb20–S68	2.82(3)
Sb17–S56	2.91(3)	Sb18–S65	2.72(4)	Sb19–S64	2.96(4)	Sb20–S80	2.67(3)
Sb17–S126	2.42(3)			Sb19–S134	2.55(3)	Sb20–S134	3.07(3)
Sb21–S60	2.26(3)	Sb22–S69	3.05(3)	Sb23–S71	2.78(4)	Sb24–S62	3.06(3)
Sb21–S61	2.42(3)	Sb22–S70	2.78(3)	Sb23–S72	3.09(4)	Sb24–S76	2.58(4)
Sb21–S62	2.65(3)	Sb22–S72	1.95(3)	Sb23–S73	2.86(4)	Sb24–S78	1.94(3)
Sb21–S76	2.73(3)	Sb22–S126	2.73(3)	Sb23–S74	2.97(4)	Sb24–S134	2.73(3)
				Sb23–S85	2.63(5)		
Sb25–S65	2.95(4)	Sb26–S85	2.73(4)	Sb27–S81	2.56(3)	Sb28–S82	3.02(7)
Sb25–S77	2.91(3)	Sb26–S86	3.06(5)	Sb27–S82	3.04(7)	Sb28–S95	2.80(3)
Sb25–S78	3.04(4)	Sb26–S87	2.78(3)	Sb27–S93	2.78(5)	Sb28–S96	3.06(4)
Sb25–S79	2.72(3)	Sb26–S89	2.73(4)	Sb27–S94	2.80(6)	Sb28–S97	2.55(4)
Sb25–S93	2.27(5)	Sb26–S90	2.76(3)	Sb27–S96	2.76(3)	Sb28–S98	2.19(3)
Sb29–S87	2.99(4)	Sb30–S83	2.85(3)	Sb31–S83	2.61(4)	Sb32–S92	2.80(4)
Sb29–S88	2.83(3)	Sb30–S98	2.94(3)	Sb31–S84	2.21(3)	Sb32–S101	2.87(3)
Sb29–S89	2.70(4)	Sb30–S109	2.20(4)	Sb31–S99	2.91(3)	Sb32–S117	2.34(3)
Sb29–S101	2.24(3)	Sb30–S110	2.63(5)	Sb31–S110	2.74(4)	Sb32–S118	2.07(3)
Sb29–S102	2.53(3)						
As1–S1	2.06(4)	As2–S1	2.69(4)	As3–S3	2.50(5)	As4–S5	2.59(4)
As1–S11	2.58(4)	As2–S2	2.40(4)	As3–S4	2.59(4)	As4–S6	2.49(3)
As1–S12	2.36(4)	As2–S3	2.22(4)	As3–S18	2.10(4)	As4–S7	2.10(4)
As5–S7	2.73(4)	As6–S9	2.61(4)	As7–S13	2.71(4)	As8–S19	2.10(4)
As5–S8	2.38(4)	As6–S10	2.38(4)	As7–S27	2.23(4)	As8–S20	2.23(4)
As5–S9	2.35(4)	As6–S26	2.19(4)	As7–S28	2.10(4)	As8–S22	2.58(5)
		As6–S66	2.90(4)				
As9–S16	2.52(4)	As10–S15	2.83(4)	As11–S23	2.57(4)	As12–S24	2.80(3)
As9–S29	1.95(3)	As10–S31	2.37(4)	As11–S33	2.32(4)	As12–S35	2.00(3)
As9–S30	2.33(4)	As10–S32	2.00(3)	As11–S34	1.96(3)	As12–S36	2.40(3)
As9–S42	2.77(4)	As10–S41	2.50(7)	As11–S49	2.80(4)	As12–S50	2.52(5)

Table 4 (*contd.*).

As13–S37	2.39(4)	As14–S44	2.34(5)	As15–S39	2.21(4)	As16–S55	2.19(3)
As13–S38	2.17(5)	As14–S45	2.15(4)	As15–S55	2.26(3)	As16–S59	2.59(3)
As13–S51	2.48(5)	As14–S46	2.34(4)	As15–S56	2.45(4)	As16–S73	2.95(3)
				As15–S125	2.69(3)	As16–S125	2.16(3)
As17–S56	2.06(3)	As18–S63	2.11(3)	As19–S53	2.39(4)	As20–S67	2.68(3)
As17–S59	2.34(3)	As18–S65	2.33(4)	As19–S54	2.60(3)	As20–S69	2.05(3)
As17–S60	2.72(3)	As18–S67	2.55(4)	As19–S68	2.13(3)	As20–S79	2.58(3)
As17–S74	2.83(3)	As18–S79	2.93(3)	As19–S70	2.87(3)	As20–S80	2.39(3)
As21–S53	2.83(4)	As22–S71	2.48(4)	As23–S59	2.71(3)	As24–S61	2.90(3)
As21–S69	2.66(3)	As22–S72	2.51(4)	As23–S73	2.55(3)	As24–S75	2.70(4)
As21–S70	2.35(3)	As22–S86	2.24(5)	As23–S74	2.53(3)	As24–S76	2.37(4)
As21–S71	2.22(3)			As23–S75	2.12(3)	As24–S77	2.14(3)
As25–S77	2.51(4)	As26–S81	2.56(4)	As27–S87	2.16(4)	As28–S84	2.35(4)
As25–S78	2.42(4)	As26–S95	2.15(4)	As27–S88	2.17(4)	As28–S97	1.85(3)
As25–S94	2.64(6)	As26–S96	2.14(4)	As27–S90	2.21(4)	As28–S98	2.17(3)
						As28–S110	2.85(4)
As29–S83	2.65(4)	As30–S91	2.38(4)	As31–S92	2.64(4)	As32–S103	2.92(4)
As29–S99	2.58(4)	As30–S101	2.19(4)	As31–S103	2.19(3)	As32–S105	2.43(5)
As29–S100	2.22(3)	As30–S102	1.84(3)	As31–S104	2.65(3)	As32–S106	2.31(4)
As29–S109	2.82(5)	As30–S117	2.71(3)	As31–S118	2.43(4)	As32–S119	2.33(4)
As33–S100	2.82(4)	As34–S107	1.86(5)	As35–S57	2.63(4)	As36–S124	2.16(3)
As33–S112	2.80(6)	As34–S123	2.27(3)	As35–S123	2.26(3)	As36–S127	2.38(4)
As33–S113	2.27(4)	As34–S124	2.46(3)	As35–S127	2.60(4)	As36–S128	2.78(3)
As33–S114	2.32(4)						
As37–S131	2.21(3)	As38–S121	2.38(3)	As39–S91	2.28(4)	As40–S103	2.68(3)
As37–S133	2.27(3)	As38–S122	2.68(3)	As39–S92	2.68(4)	As40–S104	2.18(3)
As37–S135	2.58(4)	As38–S136	2.26(3)	As39–S104	2.89(3)	As40–S105	2.70(4)
				As39–S117	2.50(4)	As40–S120	2.35(5)
As41–S99	2.19(3)	As42–S106	2.71(4)	As43–S111	2.90(7)	As44–S58	2.69(4)
As41–S100	2.65(4)	As42–S108	2.52(7)	As43–S112	2.59(5)	As44–S108	2.47(8)
As41–S111	2.73(8)	As42–S120	2.92(4)	As43–S113	2.60(4)	As44–S121	2.43(3)
As41–S114	2.76(4)	As42–S136	2.77(3)	As43–S115	2.74(4)	As44–S122	2.34(3)
				As43–S116	2.81(4)		
As45–S115	2.41(4)	As46–S66	2.79(3)	As47–S132	2.15(3)	As48–S128	2.27(3)
As45–S131	2.67(4)	As46–S116	2.30(4)	As47–S135	2.53(4)	As48–S129	2.49(3)
As45–S132	2.80(4)	As46–S129	2.60(3)	As47–S136	2.98(3)	As48–S130	2.67(3)
As45–S133	2.30(4)	As46–S130	2.42(3)				

* indicates mixed Sb–Pb sites (the occupancy values for these sites are given in Table 2).

the direction perpendicular to the faces of the prism (Table 4). The ranges of the Tl–S and Pb–S bond distances in dalnegroite (Table 4) are nearly identical to those given by Nagl (1979) for the chabournéite substructure, and they are in the ranges observed for other sulphosalts: for Tl–S: *e.g.* imhofite, (Divjakovic and Nowacki, 1976); vrbaite (Ohmasa and Nowacki, 1971); hatchite (Marumo and Nowacki, 1967); lorandite (Fleet, 1973; Balić-Žunić *et al.*, 1995); for Pb–S: *e.g.* seligmanite (Edenharter *et al.*, 1970); cosalite (Topa and Makovicky, 2010); zinkenite (Portheine and Nowacki, 1975); rathite (Berlepsch *et al.*, 2002); baumhauerite (Engel and Nowacki, 1969); dufrenoysite (Ribar *et al.*, 1969); and owyheeite (Laufek et al. 2007).

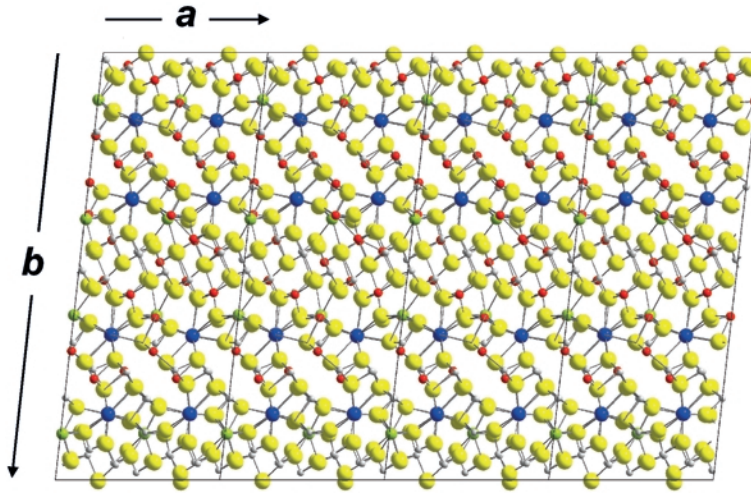

FIG. 1. Projection of the dalnegroite structure along the **c** axis, emphasizing the succession of the two layers (see text for explanation). Blue, dark green, red, grey and yellow circles indicate Tl, Pb, Sb, As and S atoms, respectively. The unit-cell and the orientation of the structure are outlined.

The 32 independent Sb and 48 independent As atoms of dalnegroite are coordinated to three, four or five S neighbours (Table 4), taking 3.1 and 3.0 Å as the limit distance for Sb and As, respectively. If we consider only the nearest neighbours, each Sb and As atom should have a pyramidal coordination of three sulphur atoms, as typically observed in sulphosalts (Moëlo *et al.*, 2008 and references therein). This is not the case for all the Sb and As atoms in dalnegroite. Such a feature is probably due to limitations of the diffraction data and refinement, considering the huge number of refined parameters (980). All Sb and As polyhedra are connected to Tl and Pb polyhedra through one, two or three shared S atoms. Only 18 of the 136 independent S atoms are not connected to Tl or Pb.

Relationships with chabournéite

A recent single-crystal XRD investigation of chabournéite from Monte Arsiccio mine, Apuan Alps, Italy (Bonaccorsi *et al.*, 2010) found that the *a* and *c* parameters are halved [*i.e.* a = 8.150(1), b = 8.716(1), c = 21.579(2) Å, α = 85.12(1), β = 96.94(1), γ = 88.60(1)º, V = 1515(1) Å^3] with respect to those given by both Nagl (1979) and Nestola *et al.* (2010), and that the structure is centrosymmetric ($P\bar{1}$). By means of intensity data collected at the Elettra synchrotron laboratory (Trieste, Italy), Bonaccorsi *et al.* (2010) were able to solve and refine the crystal structure to R = 0.0480. Despite the overall topology being nearly identical to that found here, those authors showed that the structure of the Italian chabournéite has mixed (Tl,Pb), (Pb,Sb), and (Sb,As) sites, together with pure Tl, Pb, and Sb sites.

In the present study it has been shown that the dalnegroite structure, which is related structurally to chabournéite, has a nearly fully ordered structure in which almost all of the cation positions have pure sites, with only a few Pb and Sb sites having mixed occupancies. As such, different degrees of order leading to different superstructures could exist, depending on Tl:Pb and Sb:As ratios observed for this complex group of minerals.

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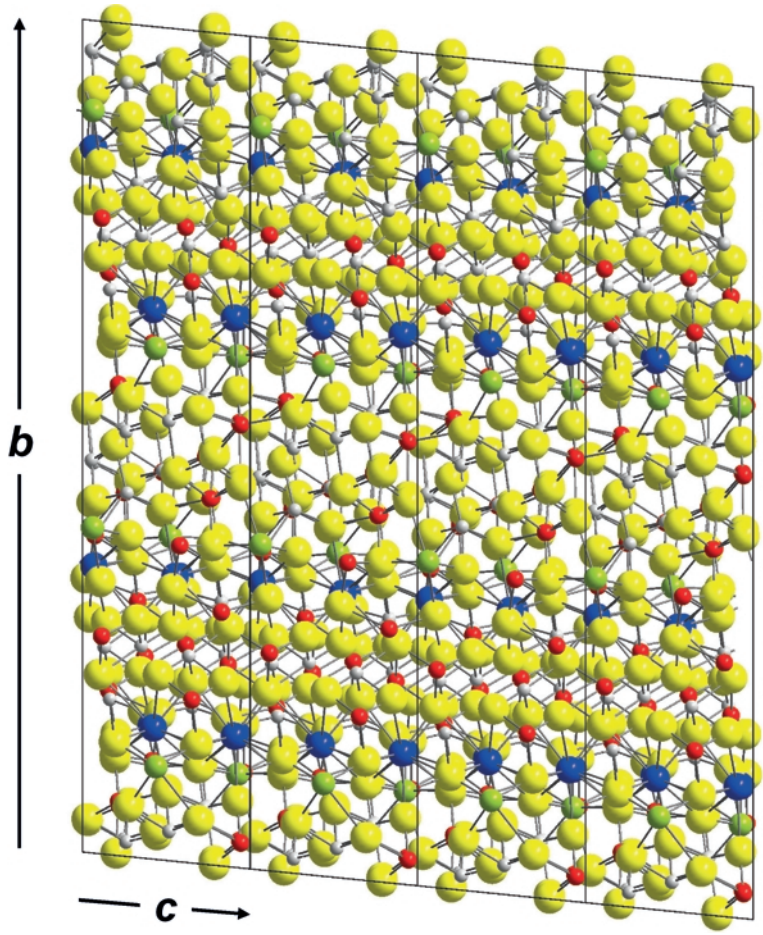

FIG. 2. Projection of the dalnegroite structure along the **a** axis, emphasizing the succession of the two layers (see text for explanation). Blue, dark green, red, grey and yellow circles indicate Tl, Pb, Sb, As and S atoms, respectively. The unit cell and the orientation of the structure are outlined.

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