Structure of Polymeric Antimony Silver(I) (+)-Tartrate†

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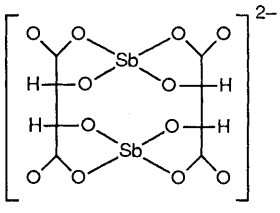
The low-temperature (163 K) structure of the silver(I) complex with antimony(III) (+)-tartrate has been determined by X-ray methods and refined to a residual *R* of 0.027 for 2926 observed reflections. Crystals are orthorhombic, space group $P2_12_12_1$ with cell dimensions $a = 8.942(4)$, $b = 15.272(6)$, $c = 21.552(7)$ Å and $Z = 4$. The repeating unit is described in terms of an unusual complex tetramer with formula $[Ag_4Sb_4(C_4H_2O_6)_4(H_2O)_4]$ in which there are four independent and different silver and antimony centres. Two of the four silvers are four-, one is five-, while the other six-co-ordinate [Ag–O range 2.156–2.666(8) Å]. One silver has three bonded waters with one of these bridging. Although all four antimony ions are involved in two classical four-co-ordinate $[Sb_2(C_4H_8O_6)_2]^{2-}$ dimer associations [Sb–O range 1.967–2.381(7) Å], these are extended into a complex polymer network structure *via* the silver ions and the tartrate oxygens. Only three of the tartrate oxygens are not involved in bonding with the metal ions while another silver is bonded to the fourth water.

The stabilizing effect of tartrate ion in the formation of water-soluble antimony complexes has traditionally been employed in the analytical chemistry of this metal.[1] Aqueous solutions of crystalline water-soluble antimony potassium tartrate (tartar emetic) have also been used for the treatment of blood worms such as schistosomiasis and leishmaniasis.[2] The most studied geometry found for metal complexes involving tartrate ion is a binuclear structure, $[Sb_2(C_4H_2O_6)_2]^{2-}$, with two bridging tartrate(4−) species. The stereochemistry of these bridged tartrate complexes has been reviewed[3] and the effect of steric constraints on co-ordination geometry and isomerism analysed.[4]



The stability of the dimeric bis(tartrato)antimonate(III) ion also has utility as a resolving reagent for optical isomers because of the ready availability of the (+)-tartrate salts such as (+)-tartar emetic. The crystal structures of both (±)-[5] and (+)-potassium bis[(tartrato)antimonate(III)] trihydrate[6] salts have been determined and show the usual bis(tartrate bridged) antimony anions. The same dimer anions are found in other simple cationic complexes of antimony tartrate, *e.g.* NH_4^+, Ca^{2+}, Sr^{2+}, Ba^{2+} [7–9] and $[Fe(phen)_3]^{2+}$ (phen = 1,10-phenanthroline).[10]

The presence of silver(I) ions in aqueous solutions of anionic metal complexes provides counter-ion effects comparable to those of Na^+ and K^+ and may promote their crystallization. An example of this phenomenon is seen in the rapid formation of large crystals of silver(I) aqua(ethylenediaminetetraacetato)-ferrate(III) dihydrate from aqueous solution. This complex has been shown to be isomorphous with the sodium complex.[11] The almost immediate precipitation of a dense crystalline solid from aqueous solutions of tartar emetic on addition of silver nitrate suggested an analogous silver(I) bis{[tartrato(4−)]antimonate(III)} compound. Furthermore, elemental analysis gave an empirical formula of $[AgSb(C_4H_2O_6)(H_2O)]$. However, subsequent crystal-structure analysis showed a more complex tetramer structure in which the tartrate residues and metal ions are involved in a polymer network.

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Experimental

Preparation.—The compound was prepared initially in an attempt to synthesise the silver aluminium complex of (+)-antimony tartrate. This involved the digestion of freshly precipitated aluminium hydroxide (0.5 g) in a 5% aqueous solution of (+)-potassium antimony tartrate (tartar emetic) (100 cm^3), followed by dropwise addition of silver nitrate solution (1.0 mol dm^{-3}). Small dense colourless pseudo-hexagonal crystals formed almost immediately from the pale yellow solution. Similar results were obtained by the slow addition of silver nitrate solution to the aqueous tartar emetic solution. Slower crystal growth gave larger crystals with excellent X-ray diffraction properties, subsequently used in the X-ray analysis (Found: C, 12.3; H, 0.75. Calc. for $C_{16}H_{16}Ag_4O_{28}Sb_4$: C, 12.2; H, 1.00%).

Crystallography.—Crystal data. $C_{16}H_{16}Ag_4O_{28}Sb_4$, $M = 1574.8$, orthorhombic, space group $P2_12_12_1$ (D_2^4, no. 19), $a = 8.942(4)$, $b = 15.272(6)$, $c = 21.552(7)$ Å, $U = 2943(2)$ $Å^{-3}$, $D_m = 3.53$, $Z = 4$, $D_c = 3.55$ g cm^{-3}, Mo-Kα radiation, $\lambda = 0.7107$ Å, μ(Mo-Kα) = 63.0 cm^{-1}, $F(000) = 2912$.

Structure solution and refinement. X-Ray data were collected on a Nicolet R3m four-circle diffractometer equipped with a low-temperature facility, using graphite-crystal monochromatized Mo-Kα X-radiation. Crystal dimensions were 0.24 × 0.20 × 0.16 mm. Of 3261 reflections measured up to $2\theta_{max} = 52°$, 2926 with $I > 2.5\sigma(I)$ were considered observed and were used in structure determination; *h,k,l* limits were 11,18,26 respectively. Data were corrected for Lorentz and polarization effects and for absorption (maximum, minimum transmission factors 0.95, 0.56). The structure was solved by the direct methods of SHELXS 86[12] and refined using SHELX 76[13] to residuals $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.027$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}} = 0.028$. A value of $w = 1/(\sigma^2F_o + 5.5 \times 10^{-4}F_o^2)$ was

Table 1 Atomic coordinates ($\times 10^4$) of $[Ag_4Sb_4(C_4H_2O_6)_4(H_2O)_4]$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sb(1)	4 841(1)	−6 252.1(5)	4 571.0(4)	O(11B)	7 756(9)	−3 604(5)	5 326(3)
Sb(2)	5 545(1)	−4 908.0(6)	6 742.5(4)	O(12B)	6 232(8)	−3 890(4)	6 131(3)
Sb(3)	9 114(1)	−6 525.5(5)	6 849.1(4)	O(2B)	6 930(8)	−5 563(4)	6 207(3)
Sb(4)	2 334(1)	−7 029.0(6)	1 067.7(4)	O(3B)	6 124(8)	−5 270(5)	4 846(3)
Ag(1)	1 988(1)	−4 647.2(7)	3 612.0(5)	O(41B)	9 009(8)	−6 766(6)	5 312(3)
Ag(2)	5 076(1)	−7 783.1(7)	5 798.4(5)	O(42B)	6 631(8)	−6 955(4)	5 007(3)
Ag(3)	−38(1)	−2586.1(8)	2 568.0(5)	C(1C)	−1 105(11)	−3 883(6)	3 633(5)
Ag(4)	2 031(1)	−2 803.3(7)	4 078.6(5)	C(2C)	−2 781(12)	−3 938(6)	3 642(5)
Ow(1)	3 024(9)	−8 743(5)	6 225(3)	C(3C)	−3 316(12)	−4 326(7)	3 024(5)
Ow(2)	4 195(9)	−3 428(5)	4 541(4)	C(4C)	−4 988(11)	−4 333(6)	3 030(4)
Ow(3)	792(10)	−3 058(6)	5 064(4)	O(11C)	−524(8)	−3 107(4)	3 662(3)
Ow(4)	2 525(9)	−2 303(5)	2 986(4)	O(12C)	−416(9)	−4 578(5)	3 584(3)
C(1A)	3 295(11)	−6 360(6)	6 644(5)	O(2C)	−3 486(8)	−3 112(4)	3 751(3)
C(2A)	2 741(12)	−5 628(6)	6 206(5)	O(3C)	−2 686(8)	−3 882(4)	2 502(3)
C(3A)	2 585(11)	−6 046(6)	5 559(4)	O(41C)	−5 671(8)	−3 931(4)	2 587(3)
C(4A)	2 213(11)	−5 323(6)	5 090(4)	O(42C)	−5 604(8)	−4 703(5)	3 457(3)
O(11A)	4 534(8)	−6 190(4)	6 943(3)	C(1D)	7 345(12)	−8 173(6)	6 724(5)
O(12A)	2 591(8)	−7 040(5)	6 691(3)	C(2D)	8 692(11)	−8 404(6)	7 135(5)
O(2A)	3 743(8)	−4 918(4)	6 196(3)	C(3D)	8 062(11)	−8 794(6)	7 740(5)
O(3A)	3 934(8)	−6 481(4)	5 388(3)	C(4D)	9 434(11)	−8 916(6)	8 165(5)
O(41A)	3 114(8)	−5 253(4)	4 628(3)	O(11D)	7 256(9)	−7 339(4)	6 558(3)
O(42A)	1 103(9)	−4 868(5)	5 181(4)	O(12D)	6 473(9)	−8 716(5)	6 541(3)
C(1B)	7 220(12)	−4 115(6)	5 706(5)	O(2D)	9 577(8)	−7 665(4)	7 258(3)
C(2B)	7 721(11)	−5 071(6)	5 744(4)	O(3D)	6 985(8)	−8 271(4)	8 024(3)
C(3B)	7 520(12)	−5 478(7)	5 092(5)	O(41D)	9 338(8)	−8 589(4)	8 712(3)
C(4B)	7 781(12)	−6 484(6)	5 150(5)	O(42D)	10 555(9)	−9 319(5)	7 972(4)

Table 2 Bond distances (Å) and angles (°) about the co-ordination polyhedra

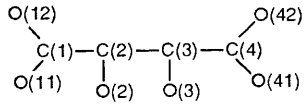
Sb(1)–O(3A)	1.970(7)	Sb(3)–O(11D)	2.169(7)	Ag(1)–O(42C)	2.180(8)	Ag(3)–O(11C)	2.526(8)
Sb(1)–O(41A)	2.175(7)	Sb(3)–O(2D)	1.996(7)	Ag(1)–O(12D)	2.560(8)	Ag(3)–O(3D)	2.389(8)
Sb(1)–O(3B)	1.980(7)	Sb(3)–O(3C)	1.988(7)	Ag(1)–Ag(4)	2.992(1)	Ag(4)–Ow(2)	2.373(8)
Sb(1)–O(42B)	2.144(7)	Sb(3)–O(41C)	2.230(7)	Ag(2)–Ow(1)	2.521(8)	Ag(4)–Ow(3)	2.425(8)
Sb(2)–O(11A)	2.198(7)	Sb(4)–O(11C)	2.381(7)	Ag(2)–O(3A)	2.405(8)	Ag(4)–Ow(4)	2.514(8)
Sb(2)–O(2A)	1.996(7)	Sb(4)–O(2C)	1.987(7)	Ag(2)–O(41B)	2.666(8)	Ag(4)–O(11B)	2.584(7)
Sb(2)–O(12B)	2.130(7)	Sb(4)–O(3D)	2.035(7)	Ag(2)–O(42B)	2.538(8)	Ag(4)–O(11C)	2.499(7)
Sb(2)–O(2B)	1.967(7)	Sb(4)–O(41D)	2.081(7)	Ag(2)–O(11D)	2.634(8)		
Ag(1)–O(41A)	2.581(7)	Ag(3)–Ow(4)	2.501(7)	Ag(2)–O(12D)	2.480(8)		
Ag(1)–O(12C)	2.156(8)	Ag(3)–O(11A)	2.348(7)				
O(3A)–Sb(1)–O(41A)	77.3(3)	O(11D)–Sb(3)–O(2D)	77.7(3)	O(12C)–Ag(1)–O(12D)	82.2(4)	Ow(4)–Ag(3)–O(3D)	115.1(3)
O(3A)–Sb(1)–O(3B)	96.0(3)	O(11D)–Sb(3)–O(3C)	83.8(3)	O(42C)–Ag(1)–O(12D)	96.8(3)	O(11A)–Ag(3)–O(11C)	108.5(3)
O(3A)–Sb(1)–O(42B)	80.0(3)	O(11D)–Sb(3)–O(41C)	125.2(3)	Ow(1)–Ag(2)–O(12D)	78.3(3)	O(11A)–Ag(3)–O(3D)	144.3(3)
O(41A)–Sb(1)–O(3B)	82.1(3)	O(2D)–Sb(3)–O(3C)	95.3(3)	O(3A)–Ag(2)–O(41B)	74.4(3)	O(11C)–Ag(3)–O(3D)	70.3(3)
O(41A)–Sb(1)–O(42B)	148.9(3)	O(2D)–Sb(3)–O(41C)	85.6(3)	O(3A)–Ag(2)–O(42B)	64.8(3)	Ow(2)–Ag(4)–Ow(3)	86.6(3)
O(3B)–Sb(1)–O(42B)	79.4(3)	O(3C)–Sb(3)–O(41C)	78.4(3)	O(3A)–Ag(2)–O(11D)	109.3(3)	Ow(2)–Ag(4)–Ow(4)	111.8(3)
O(11A)–Sb(2)–O(2A)	77.1(3)	O(11C)–Sb(4)–O(2C)	74.4(3)	O(3A)–Ag(2)–O(12D)	157.9(3)	Ow(2)–Ag(4)–O(11B)	85.5(3)
O(11A)–Sb(2)–O(12B)	152.9(3)	O(11C)–Sb(4)–O(3D)	79.4(3)	O(41B)–Ag(2)–O(42B)	73.8(3)	Ow(2)–Ag(4)–O(11C)	145.1(3)
O(11A)–Sb(2)–O(2B)	85.4(3)	O(11C)–Sb(4)–O(41D)	147.5(3)	O(41B)–Ag(2)–O(11D)	83.3(3)	Ow(3)–Ag(4)–Ow(4)	161.5(3)
O(2A)–Sb(2)–O(12B)	82.7(3)	O(2C)–Sb(4)–O(3D)	94.5(3)	Ow(1)–Ag(2)–O(3A)	107.8(3)	Ow(3)–Ag(4)–O(11B)	79.3(3)
O(2A)–Sb(2)–O(2B)	99.1(3)	O(2C)–Sb(4)–O(41D)	83.4(3)	Ow(1)–Ag(2)–O(41B)	85.2(3)	Ow(3)–Ag(4)–O(11C)	82.4(3)
O(12B)–Sb(2)–O(2B)	80.2(3)	O(3D)–Sb(4)–O(41D)	79.1(3)	Ow(1)–Ag(2)–O(42B)	159.0(3)	Ow(4)–Ag(4)–O(11C)	83.1(3)
O(41A)–Ag(1)–O(12C)	115.5(3)	O(42B)–Ag(2)–O(12D)	116.3(3)	Ow(1)–Ag(2)–O(11D)	117.4(3)	Ow(4)–Ag(4)–O(11B)	99.7(3)
O(41A)–Ag(1)–O(42C)	74.5(3)	O(11D)–Ag(2)–O(12D)	51.2(3)	O(41B)–Ag(2)–O(12D)	127.7(3)	O(11B)–Ag(4)–O(11C)	124.2(3)
O(41A)–Ag(1)–O(12D)	80.0(3)	Ow(4)–Ag(3)–O(11A)	99.7(3)	O(42B)–Ag(2)–O(11D)	83.3(3)		
O(12C)–Ag(1)–O(42C)	169.5(3)	Ow(4)–Ag(3)–O(11C)	82.9(3)				

used. Only the antimony, silver and water atoms were refined with anisotropic thermal parameters. Hydrogens were not included in the refinement. Four intense low-angle reflections (4,0,0; 0,2,0; 2,1,1; 0,2,6) were considered to be affected by extinction and were omitted from the last cycle of refinement. Neutral atom scattering factors and values for f',f'' terms for anomalous dispersion were taken from ref. 14.

Final atomic positional parameters are listed in Table 1, interatomic bond distances and angles associated with the metal co-ordination polyhedra in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

The atom numbering scheme used for the tartrate residues is as shown.



Discussion

The structure determined is best described in terms of a repeating tetramer $[Ag_4Sb_4(C_4H_2O_6)_4(H_2O)_4]$ which extends into a complex polymer network. Each tetramer unit (Fig. 1)

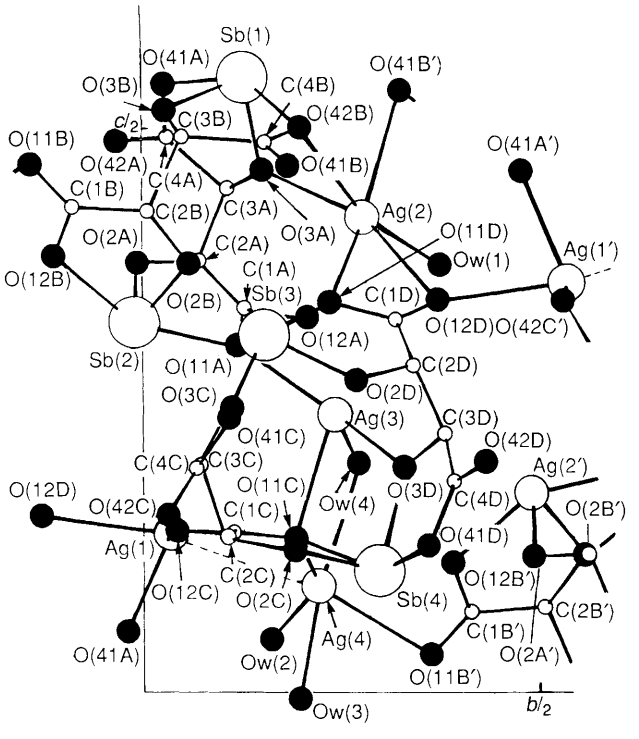


Fig. 1 The $[Ag_4Sb_4(C_4H_2O_6)_4(H_2O)_4]$ molecular unit showing the atom numbering scheme. Primed atoms are generated by a 2_1 screw operation

Table 3 Bonding involving tartrate residues

Residue	O(11)	O(12)	O(2)	O(3)	O(41)	O(42)
A	Ag(3) Sb(2)	*	Sb(2)	Sb(1) Ag(2)	Sb(1) Ag(1)	*
B	Ag(4)	Sb(2)	Sb(2)	Sb(1)	Ag(2)	Ag(2) Sb(1)
C	Ag(3) Ag(4) Sb(4)	Ag(1)	Sb(4)	Sb(3)	Sb(3)	Ag(1)
D	Ag(2) Sb(3)	Ag(2) Ag(1)	Sb(3)	Sb(4) Ag(3)	Sb(4)	*

* Non-bonded.

has four independent and different antimony and silver centres, four conformationally variable tartrate(4−) ligands, and four co-ordinated waters. Three of the waters are bonded to one silver [Ag(4)], one bridging to Ag(3) [Ag(3)–Ow(4)–Ag(4) 97.1(3)°], while the fourth is bonded to Ag(2). All four of the tartrate anions are involved in formation of two classical $[Sb_2(C_4H_2O_6)_2]^{2-}$ dimers, which in turn are linked to the silver complex centres and their associated oxygens. Table 3 lists the associations involving the individual tartrate oxygens, only three of which are not bonded to at least one metal type. To aid general discussion, the individual moieties are discussed separately.

Antimony Co-ordination.—The four antimony ions in the structure are associated with the four tartrate(4−) ligands, giving two dimeric units, Sb(1) and Sb(2) with tartrate residues A and B and Sb(3) and Sb(4) with residues C and D. All centres have the irregular four-co-ordination found typically in dimeric antimony tartrates such as potassium antimony tartrate trihydrate.[6] These have two short (*i*) and two long Sb–O bonds (*ii*) (associated with the hydroxyl and carboxyl oxygens respectively of the tartrate ion) and O–Sb–O bond angles with four contracted (*iii*), two intermediate (*iv*) and two expanded (*v*). The ranges found in the potassium structure are 1.97–2.01(1) (*i*), 2.12–2.21(1) Å (*ii*), 77.2–79.5(5) (*iii*), 101.1–101.4(5) (*iv*), and 147.7–148.8(5)° (*v*). In the present structure, the values (*i*)–(*iv*) are generally comparable but are less regular [1.970–2.035(7) (*i*), 2.081–2.381(7) Å (*ii*), 74.4–85.6(3) (*iii*), 94.5–99.1(3) (*iv*), 125.2–152.9(3)° (*v*)]. The value of 125.2(3)° for the expanded angle in Sb(3) and 2.381(7) Å for Sb(4)–O(11C) are atypical and may be the result of the conformational constraints imposed by additional bridging groups (and their silver centres) which extend the structure into a polymer net. Associated with Sb(4) there is a complex bridge network with O(11C) linking three metal centres including Ag(3) and Ag(4). Ligand D is also involved in a bidentate carboxylate-*O,O'* link to Ag(2) while O(12D) also bridges to Ag(1) (*via* a 2_1 screw translation along *b*). Additional links to ligands A and B are O(3A) and O(42B) to Ag(2), O(41B) to Ag(2'), O(41B) to Ag(1), O(3A) to Ag(2) and O(11A) to Ag(3).

Silver Co-ordination.—The presence of silver in this system results in an enhancement of stability *via* a number of strong silver–oxygen interactions. These are typical of the associative bonding found among silver carboxylates[15] and result in the polymer network structure observed here. In this respect the structure differs from the usual anion–cation associations in the alkali- and alkaline-earth-metal antimony tartrates. Atoms Ag(1) and Ag(4) form a monocarboxylate-bridged dimer *via* the carboxyl group of tartrate residue C [Ag(1)–O(12C) 2.156(8), Ag(4)–O(11C) 2.499(7) and Ag(1)–Ag(4) 2.992(1) Å]. However, in contrast to the typical bis(*O,O'*-bridged) silver(I) carboxylate dimers,[16] this structure is open ended, with co-ordination completed about each silver by other oxygen donor groups. Atom Ag(1) is four-co-ordinate and is bonded to carboxylate oxygens from three different tartrate residues [O(41A), O(12C), O(42C), O(12D): Ag–O 2.156(8)–2.581(7) Å], with O(12D) also bridging to Ag(2). In contrast, the co-ordination about Ag(4) is completed by three waters Ow(2)–Ow(4) [Ag–O 2.373–2.514(8) Å] and a carboxylate oxygen [O(11B)] forming part of an *O,O'* bridge to Ag(2'). One of these waters [Ow(4)] also bridges to Ag(3), with a bridge angle of 97.3°. The carboxylate oxygen [O(11C)] also bridges to Ag(3) [Ag–O–Ag 97.0(3)°]. The only other variation of the carboxyl-bridged dimer known for silver carboxylates is the zigzag linear polymer found for silver(I) 2,4-dichlorophenoxyacetate,[16] in which the carboxyl groups adopt the *anti-syn* conformation. The stereochemistry about Ag(3) is very distorted tetrahedral having, in addition to those bonds already described, bridging bonds to tartrate residues D [O(3D)] and A [O(11A)]. The Ag–O bond distances about Ag(3) range from 2.348 to 2.526(8) Å. The final silver centre [Ag(2)] is distorted octahedral six-co-ordinate involving the fourth water [Ag–Ow(1) 2.521(8) Å] and five oxygens from four different tartrate residues. Two are from asymmetric bidentate carboxylate groups of ligand D [Ag(2)–O(12D) and Ag(2)–O(11D) 2.480(8) and 2.634(8) Å], two from bridging hydroxyl and carboxylate groups [O(3A), O(42B)] and one from a symmetry-related B ligand [O(41B')].

Tartrate Residues.—Intraligand bond distances and angles within the four independent tartrate residues are considered normal when compared with both tartaric acid and metal tartrates.[17,18] Conformationally, all residues are variable, as might be expected in such a structure, considering the number of associative interactions involved with each metal. Of all the tartrate oxygens, only three [O(12A), O(42A), O(42D)] are not involved in bonding to at least one metal centre. These three are carboxylate oxygens which in turn stabilize the packing of the polymer net *via* hydrogen-bonding interactions.

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References

1 R. B. Hahn, in *Treatise on Analytical Chemistry*, eds. I. M. Koltoff, P. J. Elving and F. B. Sandell, Wiley-Interscience, New York,1978, part 2, vol. 10, p. 279.
2 *The Merck Index*, ed. P. G. Stecher, Merck & Co., Rahway, NJ, 8th edn., 1960, p. 91.
3 R. E. Tapscott, R. L. Belford and I. C. Paul, *Coord. Chem. Rev.*, 1969, **4**, 323.
4 R. E. Tapscott, *Inorg. Chim. Acta*, 1974, **10**, 183.
5 B. Kamenar, D. Grdenic and C. K. Prout, *Acta Crystallogr., Sect. B*, 1970, **26**, 181.
6 M. Xiangqi, *K'o Hsueh T'ung Pao*, 1966, **17**, 502; M. E. Gress and R. A. Jacobson, *Inorg. Chim. Acta.*, 1974, **8**, 209.
7 G. A. Kiosse, N. I. Golovastikov and N. V. Belov, *Dokl. Akad. Nauk SSSR*, 1964, **155**, 545; G. A. Kiosse, N. I. Golovastikov, A. V. Ablov and N. V. Belov, *Dokl. Akad. Nauk SSSR*, 1967, **177**, 329.
8 L. Bohaty, R. Frohlich and K.-F. Tebbe, *Z. Kristallogr.*, 1982, **159**, 21; *Acta Crystallogr., Sect. C*, 1983, **39**, 59.
9 L. Bohaty and R. Frohlich, *Z. Kristallogr.*, 1983, **163**, 261.
10 A. Zalkin, D. H. Templeton and T. Ueki, *Inorg. Chem.*, 1973, **12**, 1641.
11 X. Solans, M. Font-Altaba and J. Garcia-Oricain, *Acta Crystallogr., Sect. C*, 1984, **40**, 635; J. M. Lopez-Alcala, M. C. Puerta-Vizcaino, F. Gonzalez-Vilchez, E. N. Duesler and R. E. Tapscott, *Acta Crystallogr., Sect. C*, 1984, **40**, 939; V. Novozhilova, T. N. Polynova and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, 1975, **16**, 865.
12 G. M. Sheldrick, SHELXS 86, Program for Solution of Crystal Structures, University of Göttingen, 1986.
13 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.
14 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
15 F. Charbonnier, R. Faure and H. Loiseleur, *Rev. Chim. Miner.*, 1981, **18**, 245; T. C. W. Mak, W.-H. Yip, C. H. L. Kennard, G. Smith and E. J. O'Reilly, *Aust. J. Chem.*, 1986, **39**, 541.
16 T. C. W. Mak, W.-H. Yip, C. H. L. Kennard, G. Smith and E. J. O'Reilly, *J. Chem. Soc., Dalton Trans.*, 1988, 2353.
17 R. E. Tapscott, *Prog. Inorg. Chem.*, 1982, **8**, 253.
18 M. D. Newton and G. A. Jeffrey, *J. Am. Chem. Soc.*, 1977, **99**, 2413.

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