ligands and O(6)—O(7) as a monodentate ligand. The sixth ligand atom is the terminal O(5) oxide ion. On the other hand, V(2) is connected to two bidentate peroxo ligands O(6)—O(7) and O(8)—O(9), a water O(11) and a terminal O(10) oxide ion. Therefore, the coordination polyhedra of the two V atoms in $[V_2O_2(O_2)_4(H_2O)]^{2-}$ are not equivalent. This is the first crystal structure study of a dimeric peroxovanadate which has non-equivalent V-atom coordination polyhedra within the complex. As mentioned above, each coordination polyhedron can be described as a pentagonal pyramid. The basal planes of the pentagonal pyramids about V(1) and V(2) consist of O(1), O(2), O(3), O(4) and O(6) (the maximum deviation from planarity is 0·026 Å) and O(6), O(7), O(8), O(9) and O(11) (maximum deviation 0·114 Å), respectively. The O(5) apical atom of the V(1) pyramid is located 2·108 Å above the basal plane and the O(10) apical atom of the V(2) pyramid 2·068 Å below the basal plane. Both the V(1) and V(2) atoms are moved (0·509 and 0·479 Å, respectively) from the basal plane towards the apical O atom. The range of the $V—O_{basal}$ distances, 1·863–2·045 Å, indicates that they are normal single bonds, while the $V—O_{apical}$ bonds, 1·601 (4) and 1·591 (4) Å, are double bonds (Stomberg, 1984). The angle V(1)—O(6)—V(2) is 103·8 (2)° and the dihedral angle between the basal planes of connected pyramids is 60·8°. The peroxo—oxygen bond distances are in the range 1·458 (5)–1·468 (5) Å. The shortest nonbonded V—O distances, d[V(1)—O(9)] = 2·707 (4) and d[V(2)—O(4)] = 2·697 (3) Å, may indicate a tendency for both V atoms to attain the pentagonal-bipyramidal coordination. The angle O(5)—V(1)—O(9) is 167·6 (2)° and O(10)—V(2)—O(4) is 169·6 (2)°. The apical atoms O(9) and O(4) are located 2·156 and 2·158 Å from the 'equatorial' planes.

There are two non-equivalent tetramethylammonium groups per unit cell. The N—C bond lengths are in the range 1·461–1·505 Å and the C—N—C angles vary between 107·3 and 112·2°. The average N—C distance and C—N—C angle are 1·489 Å and 109·47°, respectively.

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Euchroite, a Heteropolyhedral Framework Structure

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Abstract. $Cu_2(AsO_4)(OH).3H_2O$, $M_r = 337·1$, orthorhombic, $P2_12_12_1$, $a = 10·056$ (2), $b = 10·506$ (2), $c = 6·103$ (2) Å, $V = 644·8$ (2) Å^3, $Z = 4$, $D_x = 3·47$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 122$ cm^{-1}, $F(000) = 648$, $T = 297$ K, $R = 0·027$ for 1061 observed reflections. The structure is a fairly open heteropolyhedral framework consisting of edge-sharing chains of octahedrally coordinated Cu^{2+} cations that are cross-linked by sharing corners with arsenate tetrahedra. Both unique octahedra show axial Jahn–Teller-type distortions, the direction of which can be predicted from the polyhedral connectivity of the structure. The resulting arrangement is basically close-packed, but has a commensurate modulation along [010].

Introduction. Underestimation of the coordination number of Cu^{2+} has often obscured the relationships between structures, particularly those involving Cu^{2+} and non-Cu^{2+} oxysalts. In particular, common structural elements [structure modules in the hierarchical scheme of Hawthorne (1983, 1985*a*, 1986*a*)]

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relating specific structures become apparent only when the complete coordinations of the Cu^{2+} cations are considered. In such structural arguments, the hydrogen-bonding schemes are often of key importance. In view of these considerations, we have a systematic study of structure solution and/or refinement of Cu^{2+} oxysalt minerals currently underway (Hawthorne & Eby, 1985; Hawthorne & Groat, 1985, 1986; Hawthorne, 1985*b*,*c* 1986*b*; Groat & Hawthorne, 1987). As part of this work, a refinement and reconsideration of the structure of euchroite was initiated.

Experimental. Euchroite from Copper Cliff, Montana, National Museum Collection catalogue number 65222, was obtained from the Geological Survey of Canada. Crystal size: $0{\cdot}24 \times 0{\cdot}28 \times 0{\cdot}32$ mm; unit-cell parameters refined from 25 reflections automatically aligned on a Nicolet *R*3*m* diffractometer at 297 K. Data collection: 1187 reflections, $3 < 2\theta < 60°$, *h*0–13, *k*0–14, *l*0–8, graphite monochromator, Mo $K\alpha$ X-radiation, $\theta/2\theta$ scan, variable scan speed 4·0–29·3° min^{-1}, scan range $(K\alpha_1 - 1) \rightarrow (K\alpha_2 + 1)°$, background/scan = 0·5, two standard reflections every 48 reflections, variation 1·6%, absorption correction by ψ-scan method (minimum transmission 0·017, maximum transmission 0·044), Lorentz and polarization corrections, 1061 observed reflections with $I > 3\sigma(I)$. Structure refinement: atomic scattering factors and anomalous-dispersion coefficients from *International Tables for X-ray Crystallography* (1974), all calculations performed with *SHELXTL* (Sheldrick, 1981) on a Nova 4S computer. Starting parameters from Finney (1966), refinement by full-matrix least squares (on *F*) with anisotropic temperature factors converged to $R = 0{\cdot}037$, $wR = 0{\cdot}036$; refinement of the enantiomorphic structure converged to $R = 0{\cdot}027$, $wR = 0{\cdot}027$, $w = 1/[\sigma^2F + 0{\cdot}00230(F^2)]$, maximum final shift/e.s.d. < 0·05, mean < 0·01, maximum height in final difference Fourier map = 0·70 e Å^{-3}.

Discussion. Fractional coordinates and equivalent isotropic temperature factors of atoms in the asymmetric unit of the correct enantiomorph are listed in Table 1,* and selected interatomic distances and angles are given in Table 2. The As atom is tetrahedrally coordinated by O atoms, and the bond lengths and angles fall within the range typically observed in arsenate structures. There are two unique Cu^{2+} cations, both of which are coordinated

Table 1. *Atomic parameters and equivalent isotropic temperature factors* (Å^2 × 10^3) *for euchroite*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$
Cu(1)	0·75610 (7)	0·99123 (7)	0·0313 (1)	166 (2)
Cu(2)	0·80047 (6)	0·75076 (6)	0·3333 (1)	180 (2)
As	0·60936 (5)	0·76411 (5)	0·7824 (1)	151 (1)
O(1)	0·6732 (4)	0·8303 (4)	0·5455 (7)	180 (10)
O(2)	0·6969 (4)	0·8146 (4)	0·9976 (7)	196 (10)
O(3)	0·4527 (4)	0·8183 (4)	0·8157 (7)	176 (10)
O(4)	0·6118 (4)	0·6063 (3)	0·7508 (7)	190 (10)
OH	0·8473 (4)	0·9326 (3)	0·2930 (7)	163 (9)
O*W*(1)	0·7212 (4)	0·5816 (4)	0·3618 (7)	217 (11)
O*W*(2)	0·5710 (4)	1·0547 (4)	0·2785 (8)	274 (12)
O*W*(3)	0·9321 (5)	0·6894 (5)	0·7223 (9)	314 (13)

Table 2. *Interatomic distances* (Å) *and angles* (°) *in euchroite*

As—O(1)	1·728 (4)	OH—O(4$^{\rm iii}$)	2·705 (5)
As—O(2)	1·668 (4)	O*W*(1)—O(4)	2·630 (6)
As—O(3)	1·687 (4)	O*W*(1)—O(4$^{\rm iv}$)	2·679 (6)
As—O(4)	1·669 (4)	O*W*(2)—O*W*(3$^{\rm i}$)	2·710 (7)
⟨As—O⟩	1·688	O*W*(3)—O(3$^{\rm v}$)	2·829 (7)
Cu(1)—OH	1·942 (4)	Cu(2)—O(1)	2·004 (4)
Cu(1)—O*W*(2)	2·487 (5)	Cu(2)—OH	1·983 (4)
Cu(1)—O(1$^{\rm i}$)	2·007 (4)	Cu(2)—O*W*(1)	1·956 (4)
Cu(1)—O(2$^{\rm ii}$)	1·960 (4)	Cu(2)—O*W*(3)	2·794 (5)
Cu(1)—OH$^{\rm i}$	1·959 (4)	Cu(2)—O(2$^{\rm ii}$)	2·394 (4)
Cu(1)—O*W*(2$^{\rm i}$)	2·374 (5)	Cu(2)—O(3$^{\rm iii}$)	1·922 (4)
⟨Cu(1)—O⟩	2·122	⟨Cu(2)—O⟩	2·176
O(1)—As—O(2)	109·6 (2)	O(1)—O(2)	2·774 (6)
O(1)—As—O(3)	108·2 (2)	O(1)—O(3)	2·766 (6)
O(1)—As—O(4)	107·3 (2)	O(1)—O(4)	2·737 (5)
O(2)—As—O(3)	106·9 (2)	O(2)—O(3)	2·695 (5)
O(2)—As—O(4)	113·5 (2)	O(2)—O(4)	2·791 (6)
O(3)—As—O(4)	111·3 (2)	O(3)—O(4)	2·770 (5)
⟨O—As—O⟩	109·4	⟨O—O⟩As	2·756
OH—Cu(1)—O*W*(2)	86·5 (2)	OH—O*W*(2)	3·061 (6)
OH—Cu(1)—O(1$^{\rm i}$)	95·4 (2)	OH—O(1$^{\rm i}$)	2·921 (6)
OH—Cu(1)—O(2$^{\rm ii}$)	85·9 (2)	OH—O(2$^{\rm ii}$)	2·660 (6)
OH—Cu(1)—O*W*(2$^{\rm i}$)	97·1 (2)	OH—O*W*(2$^{\rm i}$)	3·248 (6)
O*W*(2)—Cu(1)—O(1$^{\rm i}$)	89·3 (2)	O*W*(2)—O(1$^{\rm i}$)	3·177 (6)
O*W*(2)—Cu(1)—O(2$^{\rm ii}$)	95·2 (2)	O*W*(2)—O(2$^{\rm ii}$)	3·303 (6)
O*W*(2)—Cu(1)—OH$^{\rm i}$	86·8 (2)	O*W*(2)—OH$^{\rm i}$	3·079 (6)
O(1$^{\rm i}$)—Cu(1)—OH$^{\rm i}$	80·7 (2)	O(1$^{\rm i}$)—OH$^{\rm i}$	2·568 (6)
O(1$^{\rm i}$)—Cu(1)—O*W*(2$^{\rm i}$)	87·6 (2)	O(1$^{\rm i}$)—O*W*(2$^{\rm i}$)	3·044 (6)
O(2$^{\rm ii}$)—Cu(1)—OH$^{\rm i}$	98·5 (2)	O(2$^{\rm ii}$)—OH$^{\rm i}$	2·969 (6)
O(2$^{\rm ii}$)—Cu(1)—O*W*(2$^{\rm i}$)	87·8 (2)	O(2$^{\rm ii}$)—O*W*(2$^{\rm i}$)	3·020 (6)
OH$^{\rm i}$—Cu(1)—O*W*(2$^{\rm i}$)	89·4 (2)	OH$^{\rm i}$—O*W*(2$^{\rm i}$)	3·062 (6)
⟨O—Cu(1)—O⟩	90·0	⟨O—O⟩Cu(1)	3·009
O(1)—Cu(2)—OH	80·2 (2)	O(1)—OH	2·570 (6)
O(1)—Cu(2)—O*W*(1)	93·5 (2)	O(1)—O*W*(1)	2·885 (6)
O(1)—Cu(2)—O*W*(3)	81·3 (2)	O(1)—O*W*(3)	3·183 (6)
O(1)—Cu(2)—O(2$^{\rm ii}$)	99·1 (2)	O(1)—O(2$^{\rm ii}$)	3·356 (6)
OH—Cu(2)—O*W*(3)	102·4 (2)	OH—O*W*(3)	3·757 (6)
OH—Cu(2)—O(2$^{\rm ii}$)	74·2 (2)	OH—O(2$^{\rm ii}$)	2·660 (6)
OH—Cu(2)—O(3$^{\rm iii}$)	96·6 (2)	OH—O(3$^{\rm iii}$)	2·916 (6)
O*W*(1)—Cu(2)—O*W*(3)	84·7 (2)	O*W*(1)—O*W*(3)	3·259 (6)
O*W*(1)—Cu(2)—O(2$^{\rm ii}$)	98·8 (2)	O*W*(1)—O(2$^{\rm ii}$)	3·315 (6)
O*W*(1)—Cu(2)—O(3$^{\rm iii}$)	91·4 (2)	O*W*(1)—O(3$^{\rm iii}$)	2·775 (6)
O*W*(3)—Cu(2)—O(3$^{\rm iii}$)	86·4 (2)	O*W*(3)—O(3$^{\rm iii}$)	3·292 (6)
O(2$^{\rm ii}$)—Cu(2)—O(3$^{\rm iii}$)	92·7 (2)	O(2$^{\rm ii}$)—O(3$^{\rm iii}$)	3·140 (6)
⟨O—Cu(2)—O⟩	90·1	⟨O—O⟩Cu(2)	3·092

Symmetry code: (i) $\tfrac{3}{2} - x,\ 2 - y,\ -\tfrac{1}{2} + z$; (ii) $x,\ y,\ -1 + z$; (iii) $\tfrac{1}{2} + x,\ \tfrac{3}{2} - y,\ 1 - z$; (iv) $\tfrac{3}{2} - x,\ 1 - y,\ -\tfrac{1}{2} + z$; (v) $\tfrac{1}{2} + x,\ \tfrac{3}{2} - y,\ 2 - z$.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51987 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond-valence table for euchroite*

	Cu(1)	Cu(2)	As	H	H	H	H	H	H	H	
O(1)	0·407	0·397	1·081								1·885
O(2)	0·462	0·135	1·282								1·879
O(3)		0·516	1·212							0·20	1·928
O(4)			1·282	0·35	0·20	0·20					2·032
OH	0·455 0·498	0·415		0·65							2·018
O*W*(1)		0·454			0·80	0·80					2·054
O*W*(2)	0·140 0·101						1·00	0·80			2·041
O*W*(3)		0·053						0·20	1·00	0·80	2·053
	2·068	1·970	4·857	1·0	1·0	1·0	1·0	1·0	1·0		

by six anions in very distorted octahedral arrangements, and the observed geometries (four short meridional bonds and two long axial bonds) are typical for such Jahn–Teller distorted octahedra. There is a significant difference in the ⟨Cu—O⟩ distances for the two octahedra, the more-distorted octahedron having the longer mean bond length as indicated by the distortion theorem of Brown (1981). Note how the local directions of the geometrical Jahn–Teller distortions are controlled by the topological details of the bond connectivity through the need to satisfy local bond-valence requirements of the anions (Table 3).

It should be noted that the assignment of [6]-coordination for each of the Cu^{2+} cations is not made according to bond-valence criteria; it is based on chemical topological grounds, as we have found that the structures of Cu^{2+} oxysalts can be interrelated and compared with non-Cu^{2+} structures much more satisfactorily if the Cu^{2+} cations are considered to have octahedral coordination (where possible). In the present case, the Cu(1) octahedra share *trans* edges to form a rutile-like chain; the Cu(2) octahedra share edges with the Cu(1) octahedra such that they adopt a staggered flanking arrangement, as can be seen in Fig. 1. This type of octahedral chain is found in clinozoisite (Dollase, 1968), as well as some other less-common minerals. The arsenate tetrahedra share corners with both the Cu(1) and Cu(2) octahedra to link the chains into an octahedral–tetrahedral framework that is extremely open (Fig. 2). It is apparent from Fig. 2 that the polyhedral connectivity of euchroite is essentially close-packed. Superimposed upon this close-packed framework are two distinct geometrical distortions. As can be seen in Fig. 2, there is a commensurate modulation along [010]. This does not seem to be related to the Jahn–Teller distortions of the octahedra; it seems the result of tetrahedral tilting that occurs in response to the hydrogen-bonding requirements of the one O^{2-} anion [O(4), see Table 3] that does not bond to Cu^{2+}. The other significant distortion involves elongation of the Cu(2) octahedra such that adjacent chains are alternately shifted slightly along [001]. Here the interplay of the Jahn–Teller effect, polyhedral connectivity and local bond-valence requirements are beautifully illustrated.

Fig. 3 shows the (Pauling) bond-strength sums for the anions of the Cu(2) octahedron in an idealized

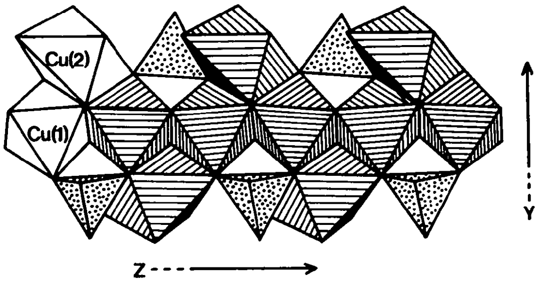

Fig. 1. The structure of euchroite projected down [100]; Cu^{2+} octahedra are line-shaded, As tetrahedra are dot-shaded. Note the edge-sharing chains of octahedra extending along [001], with the flanking octahedra showing strong Jahn–Teller distortion.

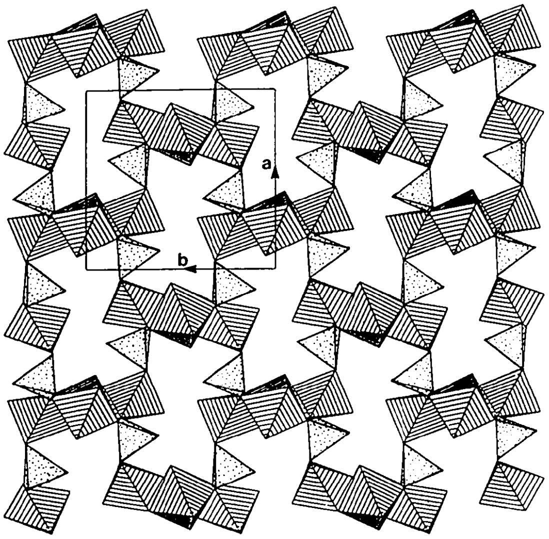

Fig. 2. The structure of euchroite projected down [001]; legend as in Fig. 1. The structure is essentially close-packed with a commensurate modulation along [010].

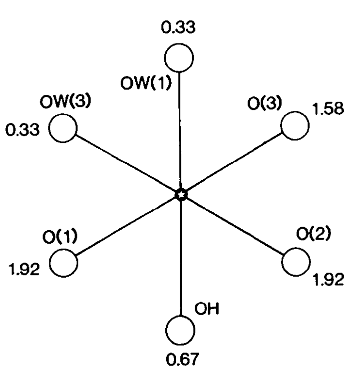

Fig. 3. Pauling bond-strength sums for the anions coordinating Cu(2) in an ideal undistorted structure.

structure with regular polyhedra (and ignoring hydrogen bonds); here the O(1) and O(2) anions have their requirements satisfied, whereas the O(3) and OH anions have low bond-strength sums. According to bond-valence theory (Brown, 1981), the bonds to OH and O(3) will shorten in order to increase their bond-valence sums, and the magnitudes of the Pauling bond-strength sums (0·67 and 1·58, respectively) indicate that this contraction should be considerable. The most common type of distortion of Cu^{2+} octahedra resulting from the Jahn–Teller effect is the shortening of four meridional bonds and the lengthening of two axial bonds. In the present case, the need to shorten Cu(2)—OH and Cu(2)—O(3) defines the two axial bonds as Cu(2)—O(2) and Cu(2)—O*W*(3). As O*W*(3) is an H_2O group, its bond-valence requirements are already (over-) satisfied and this bond can very easily lengthen (to 2·8 Å in this case). Similarly, O(2) is bonded to Cu(2) and Cu(1), and hence a cooperative distortion involving these two octahedra can lengthen Cu(2)—O(2) and shorten Cu(1)—O(2), leaving the bond-valence requirements of O(2) satisfied. Thus the polyhedral distortions within the chain can be seen as resulting from the interaction of polyhedral connectivity and local bond-valence requirements (as is the case for all structures), coupled with the need to incorporate the characteristic local distortions that occur as a result of the Jahn–Teller effect. It is this latter factor that has adversely affected our understanding of topological (graphical) structure relations in Cu^{2+} oxysalts.

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Structure of Bis(tetraphenyldiphosphinomethane)digold(I) Dinitrate

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Abstract. Bis-μ-[bis(diphenylphosphino)methane-*P,P'*]-digold(I) dinitrate, $[Au_2(C_{25}H_{22}P_2)_2](NO_3)_2$, M_r = 1286·7, monoclinic, $P2_1/c$, $a = 20{\cdot}301\ (8)$, $b = 13{\cdot}657\ (4)$, $c = 23{\cdot}515\ (8)$ Å, $\beta = 133{\cdot}92\ (2)°$, $V = 4696\ (3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}82$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 64{\cdot}1$ cm^{-1}, $F(000) = 2496$, $T = 295$ K. Final $R = 0{\cdot}0447$ for 3579 observed reflections $[F_o^2 > 3\sigma(F_o^2)]$. The eight-membered ring, formed by two Au atoms and two bis(diphenylphosphino)methane ligands, has a chair conformation with bond angles P(1)—Au(1)—P(2) = 170·6 (1) and P(3) —Au(2)—P(4) = 176·8 (2)°. The molecule contains a short Au···Au distance, 2·988 (1) Å. One nitrate is weakly interacting with the $Au_2(dppm)_2$ unit with Au(1)···O(3) = 2·987 (8) Å.

Introduction. Numerous binuclear gold(I) compounds with various ligands have short gold—gold

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