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Structure of a Copper(II) Complex of 2-*C*-Carboxypentonic Acid (H_3cpa); $[Cu_9Br_2(cpa)_6]_n^{2-}.xH_2O$

BY RICHARD E. NORMAN* AND RONALD E. STENKAMP†

Department of Chemistry and Department of Biological Structure, University of Washington, Seattle, WA 98195, USA

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Abstract. $[Cu_9Br_2(C_6H_7O_6)_6]_n^{2-}.xH_2O$, where $C_6H_7O_6^{3-}$ is 2-*C*-carboxypentonate (cpa^{3-}), trigonal, $P321$, $a = b = 21{\cdot}273$ (10), $c = 8{\cdot}0168$ (11) Å, $V = 3141{\cdot}9$ (2·1) Å^3, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu = 28{\cdot}9$ cm^{-1}, $F(000) = 877$ (ignoring water molecules), $T = 293$ K, $R = 0{\cdot}081$ for 1182 unique observed reflections. The structure contains copper in two distinct environments, one of which is five-coordinate and the other six-coordinate. cpa^{3-} is a heptadentate ligand to three Cu atoms. Channels of disordered solvent occupy a major fraction of the cell volume.

Introduction. We have recently reported the structure and synthesis of $[Cu_9Cl_2(cpa)_6]_n^{2-}.xH_2O$, where cpa^{3-} is 2-*C*-carboxypentonate, from Cu^{II} and dehydroascorbic acid (Norman, Rose & Stenkamp, 1987). That structure appeared to contain a large amount of disordered solvent, and to determine whether those observations were real or were due to some computational or experimental problem, we also carried out the synthesis and structure of the bromine derivative, $[Cu_9Br_2(cpa)_6]_n^{2-}.xH_2O$, (2).

Experimental. $CuCl_2.2H_2O$ (0·8528 g, 5·0 mmol) was dissolved in 50 ml H_2O. Glycine (0·3760 g, 5·0 mmol) was then added, followed by the addition of ascorbic acid (0·4400 g, 2·5 mmol). The resulting suspension of CuCl was stirred for 30 min and filtered. KBr (2·9749 g, 25 mmol) was added to the filtrate, followed by the addition of copper(II) acetate hydrate (0·498 g, 2·5 mmol). After three days, blue trapezoidal prismatic crystals of (2) were formed.

A crystal (0·10 × 0·27 × 0·30 mm) was mounted in a glass capillary and sealed with mother liquor and silicone oil. Oscillation and Weissenberg photographs indicated that the cell was isomorphous with that of the chlorine derivative. On a Picker FACS-1, cell constants and e.s.d.'s at 293 K were determined from the least-squares refinement of 18 reflections with $60 < 2\theta < 71°$. Data were collected from 2 to 110° in 2θ using $\omega/2\theta$ scans with a scan speed of 2° min^{-1} in 2θ. Of the 1453 reflections measured, 1182 had F_o greater than $4\sigma(F_o)$. h 0–19, k 0–19, l 0–8. Backgrounds were collected for 10 s on either side of the reflection using a stationary-counter–stationary-crystal technique. Five standard reflections were collected every 90 min. The data were corrected for absorption using the empirical method of North, Phillips & Mathews (1968) (minimum value 1·000, maximum value 1·243), deterioration (maximum value of 1·024), and coincidence loss [Sletten, Sletten & Jensen (1969), $\tau = 7{\cdot}273467 \times 10^{-8}$]. The structure was solved by using the Cu-atom positions of the chlorine compound and conventional heavy-atom techniques. Atomic scattering factors were taken from Cromer & Mann (1968). Anomalous-dispersion terms for Cu and Br (f' and f'') were taken from *International Tables for X-ray Crystallography* (1962). All calculations were performed on a VAX 11/780 using the *XRAY* system (Stewart *et al.*, 1976).

Full-matrix least-squares refinement was not well behaved as evidenced by the need to treat many of the atoms with isotropic temperature factors. The maximum shift/e.s.d. on the last cycle was 0·32, but the current model includes a $(\sin\theta)/\lambda$ cutoff of 0·100 Å^{-1} (which excludes 14 low-resolution reflections more seriously affected by the disordered solvent), anisotropic thermal parameters for the Cu and

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* Department of Chemistry.

† Department of Biological Structure.

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Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic thermal parameters* (Å^2 × 10^3)

$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$

	x	y	z	U_{eq}/U_{iso}	Occupancy (if not unity)
Cu(1)	5622 (1)	2802 (2)	− 132 (3)	33	
Cu(2)	4979 (3)	4979	0	33	
Br(1)	6667	3333	− 3096 (4)	62	
C(1)	5083 (17)	3779 (16)	− 434 (35)	19	
C(2)	5809 (18)	4182 (18)	598 (15)	9	
C(3)	5774 (13)	4405 (13)	2486 (18)	13	
C(4)	5381 (11)	3649 (11)	3637 (24)	17	
C(5)	5236 (11)	3751 (11)	5399 (25)	18	
C(6)	6264 (10)	4880 (10)	− 206 (23)	2	
O(1)	4982 (6)	3122 (7)	− 911 (16)	7	
O(2)	4742 (7)	4027 (7)	− 798 (16)	9	
O(3)	6233 (9)	3819 (10)	676 (10)	8	
O(4)	5381 (8)	4787 (8)	2519 (11)	14	
O(5)	4703 (9)	3162 (9)	2880 (18)	27	
O(6)	5857 (15)	4264 (15)	6122 (18)	33	
O(7)	6929 (9)	5115 (8)	− 553 (19)	15	
O(8)	6026 (7)	5336 (7)	− 403 (16)	7	
O(9)	5597 (13)	5597	5000	41	
O(10)	3549 (16)	3485 (16)	2983 (37)	11	0·40
O(11)	3378 (42)	152 (40)	2277 (83)	61	0·40
O(12)	4240 (33)	1729 (28)	3100 (67)	35	0·40
O(13)	1490 (152)	1490	5000	208	0·40
O(14)	0	1930 (74)	5000	102	0·40
O(15)	1997 (46)	3621 (36)	2223 (86)	76	0·40
O(16)	3308 (55)	3308	5000	54	0·30
O(17)	3782 (71)	1668 (70)	2837 (140)	81	0·30

Br atoms, isotropic thermal parameters for the remaining atoms, and only a partial model for the disordered solvent. The presence of the latter will seriously hinder any attempts to continue the refinement. The function minimized by the method of least squares was $\sum w(|F_o| - |F_c|)^2$ using $w = 1/\sigma^2(F)$ where $\sigma(F)$ was derived using $\sigma^2(I)$ = gross counts + (0·02 × net counts)^2 and $\sigma(F) = [F^2 + \sigma(F^2)]^{1/2} - (F^2)^{1/2}$. R is currently 0·081 (wR = 0·093) for 1182 observed reflections [$F_o > 4\sigma(F_o)$]. The goodness of fit $[\sum(F_o - F_c)^2/(N_{\rm ref} - N_{\rm var})]^{1/2}$ is 4·33. The maximum and minimum difference electron densities for the final model are 1·4 and −0·8 e Å^{-3}.

Discussion. The atomic parameters and bond lengths and angles are given in Tables 1 and 2.* Fig. 1 shows the copper environments and the organic ligand, while Fig. 2 shows the unit cell, omitting the disordered solvent. There are two distinct environments for copper, one located near the threefold axis with a square-pyramidal coordination polyhedron of four O atoms and apical Br atom, and the other located on a twofold axis with a tetragonally distorted octahedral coordination polyhedron of six O atoms. The Br atom bridges three Cu atoms which are part of a six-membered alternating Cu—O ring, similar to that found in the copper(II) tartronate complex (Ablov,

Table 2. *Interatomic distances* (Å) *and angles* (°) *involving* Cu *atoms*

Symmetry elements as defined in Fig. 1.

Cu(1)—O(1)	1·91 (2)	O(3)—Cu(1)—O(3^{iii})	98·8 (10)
Cu(1)—O(7^{iii})	1·92 (3)	Br(1)—Cu(1)—O(1)	97·5 (4)
Cu(1)—O(3)	1·99 (2)	Br(1)—Cu(1)—O(7^{iii})	108·2 (5)
Cu(1)—O(3^{iii})	1·87 (4)	Br(1)—Cu(1)—O(3)	83·8 (4)
Cu(1)—Br(1)	3·058 (3)	Br(1)—Cu(1)—O(3^{iii})	85·8 (4)
Cu(2)—O(2)	1·93 (2)	O(2)—Cu(2)—O(8)	90·1 (7)
Cu(2)—O(8)	1·99 (2)	O(2)—Cu(2)—O(4)	91·7 (6)
Cu(2)—O(4)	2·31 (1)	O(2)—Cu(2)—O(2^{i})	98·4 (6)
Cu(1)—Cu(1^{ii})	3·332 (5)	O(2)—Cu(2)—O(8^{i})	168·6 (6)
		O(2)—Cu(2)—O(4^{i})	95·5 (6)
O(1)—Cu(1)—O(7^{iii})	89·7 (10)	O(8)—Cu(2)—O(4)	76·5 (6)
O(1)—Cu(1)—O(3)	85·0 (8)	O(8)—Cu(2)—O(8^{i})	82·7 (6)
O(1)—Cu(1)—O(3^{iii})	175·2 (8)	O(8)—Cu(2)—O(4^{i})	95·1 (6)
O(3)—Cu(1)—O(7^{iii})	167·4 (8)	O(4)—Cu(2)—O(4^{i})	168·9 (5)
O(3^{iii})—Cu(1)—O(7^{iii})	86·0 (12)	Cu(1)—O(3)—Cu(1^{ii})	119·2 (10)

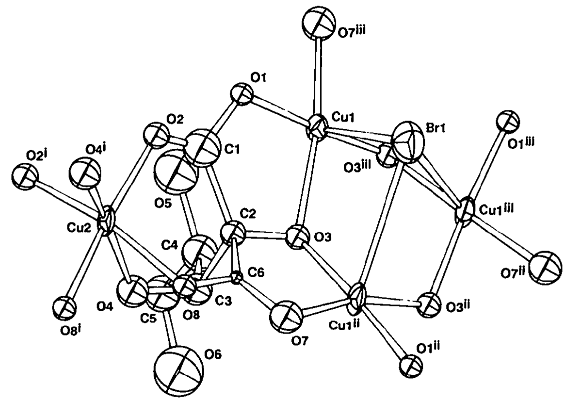

Fig. 1. A view of one portion of $[\mathrm{Cu_9Br_2(cpa)_6}]_n^{2-}.x\mathrm{H_2O}$ containing a single cpa^{3-} ligand showing its bonds to Cu and including ligating atoms of all the Cu atoms. (i) indicates atoms related by the twofold axis passing through Cu(2). (ii) and (iii) denote atoms related by the threefold axis passing through Br. The ligand in this view is shown with the same configuration as that of L-ascorbic acid.

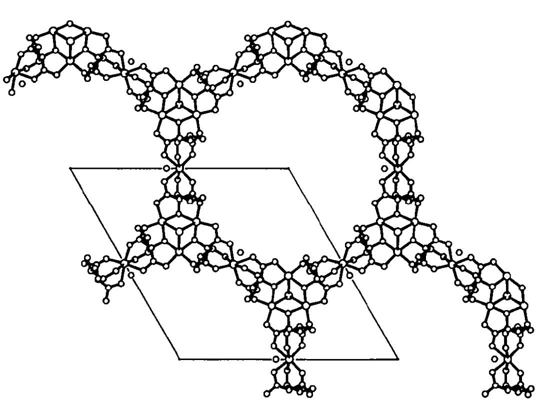

Fig. 2. Unit-cell drawing showing a small portion of one polymeric layer. Disordered water molecules omitted from cylindrical channels. Cu and Br atoms are denoted by larger spheres. *a* axis horizontal, *b* axis vertical.

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* Lists of structure factors, anisotropic thermal parameters and remaining interatomic distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52190 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Popovich, Dimitrova, Kiosse, Burshtein, Malinovskii & Shchedrin, 1976). The ring distances are comparable.

The structure consists of polymeric sheets in the *xy* directions, linked by Cu—O, O—C and C—C bonds. The crystals are made up of stacks of these sheets joined by the bridging Br atoms (which hydrogen bond to the terminal hydroxy groups of the ligand) and water molecules located on the other twofold axis which hydrogen bond to the axial O atoms of the tetragonally distorted octahedral coordination polyhedron of the Cu atom located on a twofold axis. The stacking of these sheets gives rise to cylindrical channels of disordered solvent along the crystallographic *z* axis approximately 15 Å in diameter. The issue of charge neutrality and the nature of the disordered solvent have been discussed previously for the chlorine structure (Norman, Rose & Stenkamp, 1987), and as in that case, we presume that charge neutrality in the present structure is maintained by protons or unidentified cations from the reaction mixture.

The bond distances and angles for this compound are indistinguishable from those reported earlier for the chlorine compound with the exceptions of the interactions holding the layers together. The Cu—Br distance is 0·13 Å longer than the analogous distance in the chlorine derivative, comparable to the differences in ionic radii of chloride and bromide. The situation is similar for the terminal O—Br distance. The hydrogen-bonding distances of the water molecule bridging between the polymeric layers in the crystal are also longer, reflecting the slight increase in the *c* axis.

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Tetraammineplatinum(II) Bis[pertechnetate(VII)]

BY F. D. ROCHON, P. C. KONG AND R. MELANSON

Département de chimie, Université du Québec à Montréal, CP 8888, *Succ. A, Montréal, Canada H*3*C* 3*P*8

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Abstract. $[Pt(NH_3)_4][TcO_4]_2$, $M_r = 589{\cdot}21$, triclinic, $P\bar{1}$, $a = 5{\cdot}178\,(2)$, $b = 7{\cdot}725\,(3)$, $c = 7{\cdot}935\,(3)$ Å, $\alpha = 69{\cdot}33\,(3)$, $\beta = 79{\cdot}74\,(3)$, $\gamma = 77{\cdot}41\,(3)°$, $V = 288{\cdot}0\,(2)$ Å^3, $Z = 1$, $D_x = 3{\cdot}396$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 14·58 mm^{-1}, $F(000) = 268$, room temperature. The structure was refined by full-matrix least-squares calculations to $R = 0{\cdot}026$ and $wR = 0{\cdot}032$ for 1309 unique observed reflections. Pt has square-planar coordination with Pt—N = 2·055 (5) and 2·051 (5) Å. The pertechnetate ions are tetrahedral with Tc—O distances ranging from 1·698 (5) to 1·715 (5) Å. The structure is stabilized by hydrogen bonding between the NH_3 ligands and the O atoms.

Introduction. The chemistry of technetium compounds is of considerable interest in radiopharmacy because of the extensive use of ^{99m}Tc compounds as imaging agents. We have recently started a new program on the synthesis of novel complexes of Tc. We have synthesized $[Pt(NH_3)_4][TcO_4]_2$ and determined its crystal structure. Several pertechnetate salts have been studied by X-ray diffraction. These have been summarized in a recent review by Melnik & Van Lier (1987). The crystal structure of $NH_4[TcO_4]$ has been studied at 295, 208 and 141 K (Faggiani, Lock & Pocé, 1980). The authors found only very minor changes in the structure as a function of temperature. $[Pt(NH_3)_4]^{2+}$ is a large cation which is able to form hydrogen bonds. The results obtained in our study of the structure of $[Pt(NH_3)_4][TcO_4]_2$ are reported below.

Experimental. The title compound was synthesized as follows. $NH_4[TcO_4]$ (0·25 mmol) dissolved in a few ml of water was added to 10 ml of an aqueous

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