

The Crystal Structure of μ_4 -Oxo-hexa- μ -bromotetrakis-[pyridine copper(II)], $\text{Cu}_4\text{Br}_6\text{O}(\text{C}_5\text{H}_5\text{N})_4$

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The crystal structure of the tetranuclear copper cluster complex, $\text{Cu}_4\text{Br}_6\text{O}(\text{C}_5\text{H}_5\text{N})_4$ has been determined from single crystal X-ray diffraction data. The cluster consists of trigonal bipyramidally coordinated Cu^{2+} ions, each of which share a common oxygen atom, are bridged to the other three copper ions by bromide ions, and the fifth coordination site is occupied by a pyridine molecule. The compound crystallizes in the space group C2/c, with lattice constants $a = 30.64(1)$, $b = 12.43(2)$, and $c = 20.17(1)$ Å, with $\beta = 129.56(20)^\circ$. A total of 4070 unique reflections were collected on a Picker full-circle diffractometer. The structure was refined to an R value of 0.086.

Introduction

The preparation of the compound $\text{Cu}_4\text{Br}_6\text{O}(\text{C}_5\text{H}_5\text{N})_4$ was first reported by Harris and Sinn¹ in their attempts to prepare $\text{CuBr}_2(\text{C}_5\text{H}_5\text{N})$. In interpreting the physical properties of the compound, they proposed a structure involving an unusual chain type polymeric species. However, the data could equally well be interpreted in terms of structures of the cluster compound first reported by Bertrand and Kelley² for the compound $\text{Cu}_4\text{Cl}_6\text{O}[(\text{C}_6\text{H}_5)_3\text{PO}]_4$. For this reason, we decided to investigate the crystal structure of the compound.

Experimental Section

Preparation. Initial attempts to prepare the desired compound directly from stoichiometric CuBr_2 - CuO , and pyridine solutions in water or alcohol solvents only gave deep purple needles of $\text{CuBr}_2(\text{C}_5\text{H}_5\text{N})$. However, upon continued refluxing for extended periods of time, dark brown prisms of the tetramer crystallized out of solution.

Crystal Data. Examination of precession and Weissenberg photographs established the space group as C2/c or Cc [systematic extinctions: $h+k = 2n+1$ extinct for all reflections, $l = 2n+1$ extinct for h0l reflections]. The lattice constants, determined from least squares refinement of the 2θ values of

twenty high angle reflections obtained on the full-circle diffractometer, are $a = 30.64(1)$, $b = 12.43(2)$, $c = 20.17(1)$ Å, with $\beta = 129.56(20)^\circ$.³ The crystal density was observed to be 2.31 g/cc (floatation in a mixture of ethyl iodide and methylene bromide and the calculated value for 8 molecules per unit cell is 2.39 g/cc. A total of 4070 reflections were measured on a Picker full-circle diffractometer, 3028 of which were considered to be observed (measured intensity greater than 2σ above background).⁴ A 60 second θ - 2θ scan with 20 second background counts before and after was used with Ni filtered $\text{CuK}\alpha$ radiation. Absorption corrections were made ($\mu = 141.3 \text{ cm}^{-1}$).⁵ The crystal size was $0.15 \times 0.46 \times 0.40$ mm and the absorption corrections ranged from .05 to .17.

Structure Analyses. The structure solution was straight forward. Analysis of the distribution of intensities indicated that the structure was centrosymmetric. Phases for the largest 468 reflections were calculated by direct methods⁶ and the positions of the copper, bromine, oxygen, nitrogen, and approximately 1/2 of the carbon atoms were recognizable on the first E-map. Subsequent electron density maps with more complete data sets, using phases calculated from the positions of the known atoms, revealed the remaining carbon atoms. Least squares refinement of the position and thermal (anisotropic for Cu, Br, and O, isotropic for C and N) parameters proceeded in a reasonably straight forward manner. A difference Fourier revealed peaks in the general area expected for hydrogen atoms, but resolution was not good enough to locate them accurately. Their positions were calculated from the location of the atoms in the pyridine ring, and included in the last structure factor calculation. A final value of $R = 0.086$ for observed reflections was obtained ($R = \sum (|F_{\text{obs}}| - |F_{\text{calc}}|) / \sum |F_{\text{obs}}|$). The final parameters are reported in Table I and the observed and calculated structure factors are listed in Table II. Pertinent

(3) These transform to $a = 23.50$, $b = 12.45$, $c = 20.17$, and $\beta = 91^\circ$ in the space group I2/a, in agreement with the lattice constants reported by Bertrand and Kelley.²

(4) Except where specific reference is given, all computations were made utilizing locally written computer programs.

(5) W. Busing and H. A. Levy, *Acta Cryst.*, 10, 180 (1957).

(6) Robert Dewar and Allen Stone, "FORTRAN Program for Automatic Manufacturing of E's," University of Chicago.

(7) W. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A FORTRAN Crystallographic Function and Error Program," Oak National Laboratory, Report ORNL-TM-306 (1964).

(1) C. M. Harris and E. Sinn, *Inorg. Nucl. Chem. Letters*, 5, 125 (1969).

(2) J. A. Bertrand and J. A. Kelley, *JACS*, 88, 4746 (1966).

Table I. Final parameters for $\text{Cu}_2\text{Br}_2\text{O}(\text{C}_5\text{H}_5\text{N})_4$. Standard deviations are in parenthesis. Hydrogen position are calculated, and thermal parameters assumed.

ATOM	X	Y	Z	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
CU1	0.3802(11)	0.2031(13)	0.2140(12)	0.0486(119)	0.0696(124)	0.0407(118)	0.0009(18)	0.0249(16)	-0.0020(18)
CU2	0.4832(11)	0.2580(13)	0.4078(12)	0.0404(118)	0.0787(125)	0.0385(117)	-0.0067(18)	0.0199(15)	0.0008(18)
CU3	0.3585(11)	0.3046(13)	0.3341(12)	0.0550(120)	0.0765(125)	0.0419(118)	0.0036(19)	0.0319(17)	0.0003(18)
CU4	0.4140(11)	0.4422(13)	0.2742(12)	0.0613(122)	0.0771(125)	0.0436(119)	-0.0007(20)	0.0336(18)	0.0031(18)
BR1	0.3313(11)	0.4923(12)	0.2718(12)	0.0650(118)	0.0654(119)	0.0623(117)	0.0158(16)	0.0428(16)	0.0142(16)
BR2	0.4670(11)	0.0875(12)	0.3250(11)	0.0383(115)	0.0696(119)	0.0367(114)	0.0066(14)	0.0142(13)	-0.0039(14)
BR3	0.3019(11)	0.1539(12)	0.2183(11)	0.0346(114)	0.0838(120)	0.0417(114)	-0.0046(14)	0.0216(12)	-0.0108(15)
BR4	0.4363(11)	0.2280(12)	0.4780(11)	0.0438(115)	0.1009(124)	0.0313(113)	0.0111(16)	0.0217(12)	0.0147(15)
BR5	0.3747(11)	0.3592(12)	0.1319(12)	0.1528(132)	0.0720(122)	0.0604(118)	-0.0163(21)	0.0799(22)	-0.0072(17)
BR6	0.4883(11)	0.4457(12)	0.0868(12)	0.0519(118)	0.0753(121)	0.0789(121)	0.0110(17)	0.0177(17)	-0.0072(19)
DX1	0.4084(14)	0.3021(11)	0.3072(17)	0.0072(167)	0.0663(1101)	0.0179(168)	0.0087(71)	0.0058(59)	0.0010(72)
N1	0.3534(7)	0.1106(14)	0.1127(10)	0.0448(50)					
C11	0.2969(11)	0.1021(20)	0.0464(16)	0.0691(79)					
C12	0.2767(10)	0.0462(20)	-0.0290(16)	0.0709(79)					
C13	0.3162(9)	-0.0070(20)	-0.0315(14)	0.0534(66)					
C14	0.3707(10)	0.0058(21)	0.0351(15)	0.0666(75)					
C15	0.3903(9)	0.0627(18)	0.1083(14)	0.0533(68)					
N2	0.0591(6)	0.2973(13)	0.0100(9)	0.0375(44)					
C21	0.1091(13)	0.2501(23)	0.0433(18)	0.0971(99)					
C22	0.1600(11)	0.3005(23)	0.1124(17)	0.0811(87)					
C23	0.1646(11)	0.3833(21)	0.1520(16)	0.0659(78)					
C24	0.1150(10)	0.4300(19)	0.1191(15)	0.0625(73)					
C25	0.0622(9)	0.3852(18)	0.0516(14)	0.0474(64)					
N3	0.3085(7)	0.3202(15)	0.3693(11)	0.0503(53)					
C31	0.2674(10)	0.2505(19)	0.3418(14)	0.0566(68)					
C32	0.2336(12)	0.2728(25)	0.3702(19)	0.1040(107)					
C33	0.2466(11)	0.3521(22)	0.4222(16)	0.0768(86)					
C34	0.2920(10)	0.4185(20)	0.4487(15)	0.0669(78)					
C35	0.3196(9)	0.4005(19)	0.4199(15)	0.0589(72)					
N4	0.0791(7)	0.0890(13)	0.2568(10)	0.0388(46)					
C41	0.0805(11)	0.1069(23)	0.3201(18)	0.0830(93)					
C42	0.0757(12)	0.2066(27)	0.3420(19)	0.1030(104)					
C43	0.0685(11)	0.3001(24)	0.2921(18)	0.0919(95)					
C44	0.0681(10)	0.2744(20)	0.2206(15)	0.0653(76)					
C45	0.0723(10)	0.1674(21)	0.2038(16)	0.0679(78)					
H11	0.2672	0.1356	0.0533	0.0507					
H12	0.2316	0.0474	-0.0854	0.0507					
H13	0.3020	-0.0582	-0.0859	0.0507					
H14	0.4013	-0.0306	0.0315	0.0507					
H15	0.4357	0.0679	0.1621	0.0507					
H21	0.1090	0.1768	0.0153	0.0507					
H22	0.1988	0.2602	0.1341	0.0507					
H23	0.2056	0.4147	0.2072	0.0507					
H24	0.1156	0.5059	0.1467	0.0507					
H25	0.0235	0.4230	0.0342	0.0507					
H31	0.2574	0.1820	0.3006	0.0507					
H32	0.1974	0.2210	0.3471	0.0507					
H33	0.2228	0.3658	0.4446	0.0507					
H34	0.3043	0.4854	0.4928	0.0507					
H35	0.3534	0.4539	0.4404	0.0507					
H41	0.0859	0.0389	0.3578	0.0507					
H42	0.0772	0.2163	0.3968	0.0507					
H43	0.0634	0.3814	0.3064	0.0507					
H44	0.0649	0.3392	0.1812	0.0507					
H45	0.0699	0.1470	0.1492	0.0507					

Table II. Observed and calculated structure factors for Cu₂Bi₂O(C₂H₅N)₄. Unobserved reflections are designated by a negative FO.

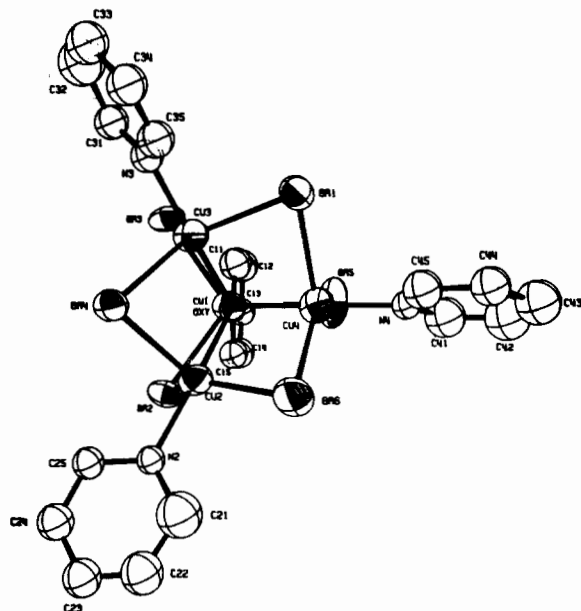
Table with multiple columns for h, k, l, FO, and calculated values. The table lists observed and calculated structure factors for various reflections, with unobserved ones marked as negative. The data is organized in a grid-like format with columns for h, k, l, FO, and calculated values.

Table II. (Continued)

Table with multiple columns (L, F, FC, H, K) and rows of numerical data. The table is organized into several sections, with some rows containing a large number '0' indicating a specific value or state. The data appears to be a continuation of a larger dataset from a previous page.

Table IIIa. Interatomic Distances.

O-Cu1	1.93(1)Å	N1-C11	1.36(3)
O-Cu2	1.93(1)Å	C11-C12	1.41(3)
O-Cu3	1.92(1)Å	C12-C13	1.41(2)
O-Cu4	1.91(1)Å	C13-C14	1.33(3)
Cu1-N1	2.01(2)	C14-C15	1.38(3)
Cu-N2*	2.01(2)	C15-N1	1.33(2)
Cu3-N3	2.07(2)	N2-C21	1.35(3)
Cu4-N4**	1.98(2)	C21-C22	1.41(3)
Cu1-Br2	2.563(3)	C22-C23	1.25(3)
Cu1-Br3	2.531(4)	C23-C24	1.34(3)
Cu1-Br5	2.486(4)	C24-C25	1.40(3)
Cu2-Br2	2.544(4)	C25-N2	1.34(2)
Cu2-Br4	2.609(4)	N3-C31	1.32(2)
Cu2-Br6***	2.470(4)	C31-C32	1.49(3)
Cu3-Br1	2.527(4)	C32-C33	1.30(3)
Cu3-Br3	2.610(4)	C33-C34	1.40(3)
Cu3-Br4	2.490(4)	C34-C35	1.31(3)
Cu4-Br1	2.582(4)	C35-N3	1.31(3)
Cu4-Br5	2.518(4)	N4-C41	1.27(3)
Cu4-Br6***	2.477(4)	C41-C42	1.36(3)
		C42-C43	1.46(4)
		C43-C44	1.47(3)
		C44-C45	1.40(3)
		C45-N4	1.36(3)

* $1/2+x, 1/2-y, 1/2+z$.** $1/2-x, 1/2+y, 1/2-z$.*** $1-x, y, 1/2-z$.**Figure 1.** A stereoscopic illustration of the $\text{Cu}_4\text{Br}_6\text{O}(\text{C}_5\text{H}_5\text{N})_4$ molecule.**Table IIIb.** Interatomic Angles.

Cu1-O-Cu2	109.7(6)	Cu3-Br1-Cu4	76.0(2)
Cu1-O-Cu3	109.9(6)	Cu1-Br2-Cu2	76.5(2)
Cu1-O-Cu4	109.1(6)	Cu1-Br3-Cu3	75.7(2)
Cu2-O-Cu3	109.4(6)	Cu2-Br4-Cu3	76.2(2)
Cu2-O-Cu4	108.4(6)	Cu1-Br5-Cu4	77.4(2)
Cu3-O-Cu4	110.3(6)	Cu2-Br6***-Cu4	78.2(2)
O-Cu1-N1	174.2(6)	O-Cu3-N3	174.7(7)
O-Cu1-Br2	86.2(4)	O-Cu3-Br1	86.9(4)
O-Cu1-Br3	88.1(4)	O-Cu3-Br3	86.1(4)
O-Cu1-Br5	87.4(4)	O-Cu3-Br4	88.9(4)
N1-Cu1-Br2	95.3(5)	N3-Cu3-Br1	90.1(5)
N1-Cu1-Br3	96.6(5)	N3-Cu3-Br3	99.1(5)
N1-Cu1-Br5	87.7(5)	N3-Cu3-Br4	90.2(5)
Br2-Cu1-Br3	108.3(1)	Br1-Cu3-Br3	113.4(1)
Br2-Cu1-Br5	127.7(2)	Br1-Cu3-Br4	134.5(2) ¹
Br3-Cu1-Br5	123.2(2)	Br3-Cu3-Br4	111.4(1)
O-Cu2-N2	176.4(7)	O-Cu4-N4**	178.4(7)
O-Cu2-Br2	86.7(4)	O-Cu4-Br1	85.5(3)
O-Cu2-Br4	85.2(3)	O-Cu4-Br5	86.5(4)
O-Cu2-Br6***	85.8(4)	O-Cu4-Br6***	86.2(3)
N2*-Cu2-Br2	90.2(5)	N4-Cu4-Br1	94.2(5)
N2*-Cu2-Br4	94.2(5)	N4-Cu4-Br5	95.1(5)
N2*-Cu2-Br6***	97.6(5)	N4*-Cu4-Br6***	92.6(5)
Br2-Cu2-Br4	107.0(1)	Br1-Cu4-Br5	109.0(1)
Br2-Cu2-Br6***	137.1(2)	Br1-Cu4-Br6***	118.8(1)
Br4-Cu2-Br6***	114.4(2)	Br5-Cu4-Br6***	130.8(1)

Table IV.

Bond	Ave. Distance	Range
Cu-O	1.92	1.91-1.93(1)
Cu-N	2.02	1.98-2.07(2)
Cu-Br	2.534	2.470-2.610(4)
N-C	1.33	1.27-1.36(3)
C-C	1.38	1.25-1.49(3)
Angle	Ave.	Range
Cu-O-Cu	109.5	108.4-110.3(6)
Br-Cu-Br	120.4	107.0-137.1(2)
N-Cu-Br	93.6	87.7-99.1(5)
O-Cu-Br	175.9	85.2-88.9(4)
O-Cu-N	86.6	174.2-178.4(7)

bond angles and distances are given in Table III. An illustration of the molecule is given in Figure 1 and the packing diagram is shown in Figure 2.⁸

Discussion

The geometry of the molecule is shown in Figure 1. The average distances and bond angles are given in Table IV. It is the same basic structural unit that is found in $\text{Cu}_4\text{Cl}_6\text{O}[\text{C}_5\text{H}_5\text{N}_3\text{PO}]_4$,² $\text{Cu}_4\text{Cl}_6\text{O}(\text{C}_5\text{H}_5\text{N})_4$,⁹

(8) Carrol K. Johnson, "ORTEP, A FORTRAN Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," Oak Ridge National Laboratory, Report ORNL-3794 (1965).

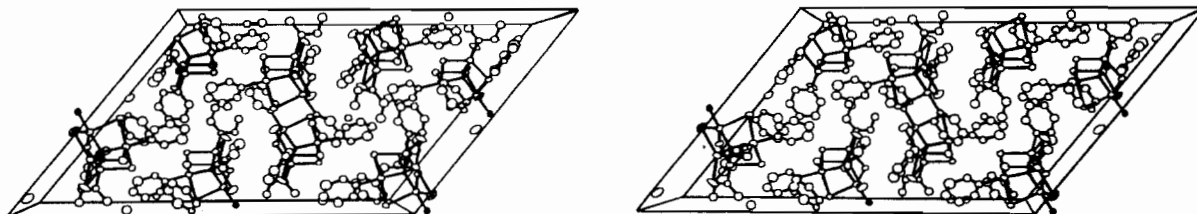


Figure 2. A stereoscopic illustration of the packing of the tetramers in $\text{Cu}_4\text{Br}_6\text{O}(\text{C}_5\text{H}_5\text{N})_4$, as viewed from the (010) direction.

and in $\text{Cu}_4\text{Br}_6\text{O}(\text{NH}_3)_4$.¹⁰ The general comments about these structures apply equally well to the structure reported here and need not be further elaborated upon. This structure adds an additional line of the table given by Bertrand and Kelley¹⁰ which summarizes the results on all of this type of cluster compound. One structural feature which is noticeable is the Cu-N bond length, 1.96 (1)Å in the chloride and 2.02(3)Å in the bromide. This is presumably due to the larger bulk of the bromide ion preventing the pyridine ring from making a closer approach to the copper ion.

The fact that this compound is not isomorphous with the corresponding chloride⁹ is surprising at first. As pointed out by Kilbourn and Dunitz, the only intermolecular contacts between adjacent tetramers in the chloride complex are either pyridine ring-pyridine ring contacts or pyridine ring-chloride ion contacts. In the bromide, this is not the situation. Rather, two tetramers pack around the two-fold axis such that the bromide ions on one tetrahedral face of one cluster

are in contact with the bromide ions on the corresponding face of the other cluster. This is due, presumably, to the increase in the size of the tetramer upon replacement of chloride ion by bromide ion, pushing the pyridine rings further out and allowing the bromide ions in adjacent clusters to interact with each other. In addition, there are close bromide ion-bromide ion contacts between adjacent pairs in the (100) plane. Thus, the structure consists of layers of inorganic material concentrated in planes at $x = 0$ and $1/2$ and layers of organic material concentrated in planes at $x = 1/4$ and $x = 3/4$. These features may be recognized by examination of the stereographic packing diagram reproduced in Figure 2.

Finally, it should be noted that this structure is consistent with the physical properties reported by Harris and Sinn.¹ In particular, the electronic absorption spectrum, with two peaks in the region of $10\text{-}13,000\text{ cm}^{-1}$, is characteristic of trigonal bipyramidal copper(II) complexes.¹⁰

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(9)B. T. Kilbourn and J. D. Dunitz, *Inorg. Chim. Acta*, 1, 209 (1967).

(10)J. A. Bertrand and J. A. Kelley, *Inorg. Chim. Acta*, 4, 526 (1970).

(11)G. C. Allen and N. S. Hush, *Inorg. Chem.*, 6, 4 (1967).