Crystal and Molecular Structure Characterization of a Copper Compound of Stoichiometry $Cu_4Br_7L_3\cdot 3H_2O$ (L = Tris(1-pyrazolylethyl)amine)

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Polydentate ligands containing pyrazole groups as donors are increasingly used with the aim to prepare specially designed metal complexes whose spectral and structural properties may be valuable for clarifying the structure of the active site of some metalloenzymes and metallo proteins [1–5].

In this field we have recently reported the synthesis of the ligands I and II (see Scheme) and the characterization of a number of dinuclear complexes with 3d metal ions [6–8]. In an attempt to prepare dinuclear copper complexes, $CuBr_2$ has been reacted with the ligand tris(1-pyrazolylethylamine) (hereafter denoted as TPyEA), and a compound having the formula $Cu_4Br_7(TPyEA)_3\cdot 3H_2O$ has been obtained. The structure of the compound determined by an X-ray diffraction method has revealed that the compound contains three non-equivalent five-coordinate $[CuBr(TPyEA)]^+$ cations, a discrete $[CuBr_3]^{2-}$ anion, and interposed a bromine ion and water molecules.

Experimental

Materials and Preparations

The synthesis of the ligand TPyEA, I, has been described before [6]. The compound $Cu_4Br_7(TPyEA)_3\cdot H_2O$ has been obtained by the reaction of hydrated $CuBr_2$ with the ligand TPyEA in a 1:1 molar ratio, using an acetone–ethanol mixture as solvent. The slow evaporation of the solvent at room temperature led to crystals suitable for X-ray diffraction analysis.

Physical Measurements

Magnetic and spectrophotometric measurements were performed as already described [9].

Collection and Reduction of X-Ray Data

A crystal of the compound $Cu_4Br_7(TPyEA)_3\cdot 3H_2O$ shaped as flat parallelepiped with dimensions 0.025 × 0.2 × 0.48 mm was used for crystal data and intensity data collection. A Philips PW 1100 automated diffractometer was used for all operations. Lattice constants were determined at 20 °C from the setting angles of 21 reflections with $8° < \theta < 14°$. Details of crystal data and data collection are listed in Table I. The variation of intensity of 3 standard reflections measured every 120 min. was less than 3%. The data were collected for Lorentz and polarization effects as well as for absorption. The principal computer programs used in the crystallographic calculations are listed in ref. 10.

TABLE I. Summary of Crystal Data and Intensity Collection.

formula	$C_{45}H_{69}Br_6Cu_4N_{21}O_3$
cryst. system, space group	triclinic, $P\bar{1}$
a, Å	22.430(7)
b, Å	15.488(5)
c, Å	9.738(5)
α, deg	100.0(2)
β, deg	88.33(5)
γ, deg	106.4(3)
V, Å^3	3195.3
Z	2
D_c, g cm^{-3}	1.105
μ(Mo, K$_\alpha$), cm^{-1}	61.91
transmission factors max–min	0.86–0.28
scan type	$\omega - 2\theta$
scan speed	6° min^{-1}
scan width ($\Delta\omega$), deg	1.00 + 0.30 tanθ
background	stationary counter-stationary crystal: symmetric, at each end of scan.
collection range	$\pm h, \pm k, +l$ ($2\theta \leqslant 46°$)
no. of unique dta	6125
no. of data, I > 3σ(I)	4135
no. of variables	437
R^a	0.044
$R_w{}^a$	0.044

$^aR = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$.

Solution and Refinement of the Structure

The position of the copper and bromine atoms were determined using direct methods and those of all the other non-hydrogen atoms were located in subsequent Fourier maps. The structure was refined using a blocked full-matrix least-squares method based on minimization of the function $\Sigma w(|F_o| - |F_o|)^2$ with weights $w = 1/[\sigma^2(F_o) + 0.001\,F_o{}^2]$. Anisotropic thermal parameters were used for copper, bromine and the nitrogen atoms bound to copper atoms. Isotropic thermal parameters were applied to all the other atoms. Hydrogen atoms were introduced in calculated positions (C–H = 1.08 Å)

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TABLE II. Positional Parameters for the Structure of $[CuBr(TPyEA)]_3[CuBr_3]Br\cdot 3H_2O$.[a]

Atom	x	y	z
Cu1	6101(1)	2854(1)	2758(2)
Cu2	3835(1)	2128(1)	1896(2)
Cu3	1379(1)	3807(1)	3201(2)
Cu4	922(1)	7903(1)	2249(1)
Br1	5442(1)	2516(1)	629(1)
Br2	4504(1)	2543(1)	4032(1)
Br3	933(1)	2270(1)	2041(1)
Br4	1851(1)	4892(1)	1740(1)
Br5	1381(1)	4248(1)	5661(2)
Br6	2062(1)	8186(1)	2339(2)
Br7	8504(1)	9407(1)	−6038(2)
N1	7125(4)	3148(6)	2229(9)
N2	6149(5)	4148(6)	2972(9)
N3	6465(4)	4670(6)	2107(10)
N4	6269(4)	3005(6)	4910(10)
N5	6849(4)	3286(6)	5496(9)
N6	6017(5)	1524(7)	2552(11)
N7	6482(5)	1126(7)	2212(10)
N8	2827(4)	1753(6)	2374(10)
N9	3866(5)	3421(7)	2055(11)
N10	3444(5)	3860(6)	2596(10)
N11	3697(4)	1919(6)	−291(9)
N12	3121(5)	1565(6)	−887(10)
N13	3841(4)	848(6)	1752(10)
N14	3549(4)	341(6)	2697(10)
N15	77(4)	8303(6)	2668(8)
N16	554(4)	6650(6)	786(10)
N17	−29(4)	6474(6)	200(9)
N18	1021(4)	8610(7)	709(9)
N19	949(4)	9452(7)	986(10)
N20	829(4)	7301(6)	3886(9)
N21	502(5)	7480(6)	5024(10)
C1	6389(7)	5509(9)	2390(14)
C2	5988(7)	5524(10)	3486(15)
C3	5856(5)	4663(8)	3801(12)
C4	6869(6)	4325(8)	1047(13)
C5	7356(6)	4017(8)	1676(13)
C6	6833(6)	3127(8)	6788(12)
C7	6247(6)	2732(8)	7111(13)
C8	5912(6)	2658(8)	5887(12)
C9	7382(6)	3775(8)	4780(13)
C10	7526(6)	3178(8)	3421(12)
C11	6306(7)	282(10)	2595(15)
C12	5729(7)	149(10)	3155(15)
C13	5561(7)	941(9)	3120(14)
C14	7046(6)	1470(8)	1461(13)
C15	7147(6)	2388(7)	1071(12)
C16	3628(7)	4750(10)	2466(15)
C17	4202(7)	4894(10)	1880(15)
C18	4325(7)	4026(9)	1640(14)
C19	2848(6)	3437(8)	3170(14)
C20	2766(6)	2509(8)	3534(13)
C21	3138(6)	1700(8)	−2211(12)
C22	3728(6)	2153(8)	−2487(13)
C23	4054(6)	2283(8)	−1267(13)
C24	2590(6)	1088(8)	−175(12)
C25	2432(6)	1694(8)	1136(13)
C26	3712(7)	−447(9)	2515(14)
C27	4102(6)	−445(9)	1444(14)
C28	4186(6)	378(8)	988(13)
C29	3137(6)	670(9)	3672(14)
C30	2612(6)	875(8)	2920(13)
C31	451(6)	6846(8)	5843(13)
C32	751(6)	6234(9)	5173(14)
C33	983(6)	6546(8)	3974(13)
C34	188(6)	8197(8)	5179(12)
C35	−264(5)	8029(8)	3948(11)
C36	−88(6)	5875(7)	−1018(12)
C37	439(6)	5648(8)	−1243(13)
C38	830(6)	6150(7)	−109(12)
C39	−510(5)	6818(7)	999(12)
C40	−363(6)	7862(7)	1422(12)
C41	975(6)	9774(9)	−217(13)
C42	1086(6)	9151(9)	−1259(15)
C43	1098(6)	8407(9)	−672(13)
C44	820(6)	9811(8)	2404(12)
C45	195(5)	9326(7)	2872(12)
O1	7800(5)	1061(7)	4101(11)
O2	2478(5)	3438(7)	9590(11)
O3	2037(5)	2856(7)	6815(12)

[a] Multiplied by 10^4. Estimated standard deviations on the last significant digit are in parentheses.

as fixed contributions, each with a temperature factor of 20% larger than that of the respective carbon atom. The scattering factors for the neutral atoms were taken from ref. 11 and the anomalous dispersion correction terms for copper and bromine from ref. 12. The final R values are reported in Table I. The highest peaks in the final difference map were less than 0.6 e $Å^{-3}$. The final positional parameters for the non-hydrogen atoms are given in Table II. Listings of the thermal parameters for the non-hydrogen atoms, of hydrogen atom coordinates, of bond lengths and bond angles (Tables SI–SIII) and of the observed and calculated structure amplitudes are available as supplementary material.

Results and Discussion

By the reaction of hydrated $CuBr_2$ and the ligand TPyEA in a 1:1 molar ratio in ethanol–acetone solution a green crystalline compound having the stoichiometry $Cu_4Br_7(TPyEA)_3\cdot 3H_2O$ has been obtained. The compound has an average magnetic moment value at room temperature of 1.54 μ_B calculated for copper atom. This value does not appreciably change down to the liquid nitrogen temperature. The electronic spectrum of the solid compound exhibits two well resolved bands at 660 and 980 nm. The same absorptions are found at 690

TABLE III. Selected Bond Lengths (Å) and Angles (deg) for the structure of [CuBr(TPyEA)]$_3$[CuBr$_3$]Br·3H$_2$O.

Cu1–Br1	2.474(2)	Cu2–Br2	2.484(2)
Cu1–N1	2.27(1)	Cu2–N8	2.23(1)
Cu1–N2	1.95(1)	Cu2–N9	1.96(1)
Cu1–N4	2.10(1)	Cu2–N11	2.12(1)
Cu1–N6	1.99(1)	Cu2–N13	1.97(1)
Br1–Cu1–N1	111.2(2)	Br2–Cu2–N8	112.3(2)
Br1–Cu1–N2	90.8(3)	Br2–Cu2–N9	88.6(3)
Br1–Cu1–N4	154.9(3)	Br2–Cu2–N11	152.6(3)
Br1–Cu1–N6	88.3(3)	Br2–Cu2–N13	89.7(3)
N1–Cu1–N2	91.1(4)	N8–Cu2–N9	91.5(4)
N1–Cu1–N4	93.8(4)	N8–Cu2–N11	95.1(4)
N1–Cu1–N6	91.1(4)	N8–Cu2–N13	90.7(4)
N2–Cu1–N4	90.0(4)	N9–Cu2–N11	91.1(4)
N2–Cu1–N6	177.8(7)	N9–Cu2–N13	177.6(5)
N4–Cu1–N6	90.0(4)	N11–Cu1–N13	89.6(4)
Cu4–Br6	2.470(2)	Cu3–Br3	2.394(2)
Cu4–N15	2.16(1)	Cu3–Br4	2.388(2)
Cu4–N16	2.16(1)	Cu3–Br5	2.374(2)
Cu4–N18	1.98(1)		
Cu4–N20	1.96(1)		
Br6–Cu4–N15	153.1(2)	Br3–Cu3–Br4	116.1(1)
Br6–Cu4–N16	106.9(3)	Br3–Cu3–Br5	122.9(1)
Br6–Cu4–N18	89.1(3)	Br4–Cu3–Br5	121.0(1)
Br6–Cu4–N20	91.1(3)		
N15–Cu4–N16	99.2(3)		
N15–Cu4–N18	85.1(4)		
N15–Cu4–N20	92.1(4)		
N16–Cu4–N18	90.0(4)		
N16–Cu4–N20	94.7(4)		
N18–Cu4–N20	175.1(4)		

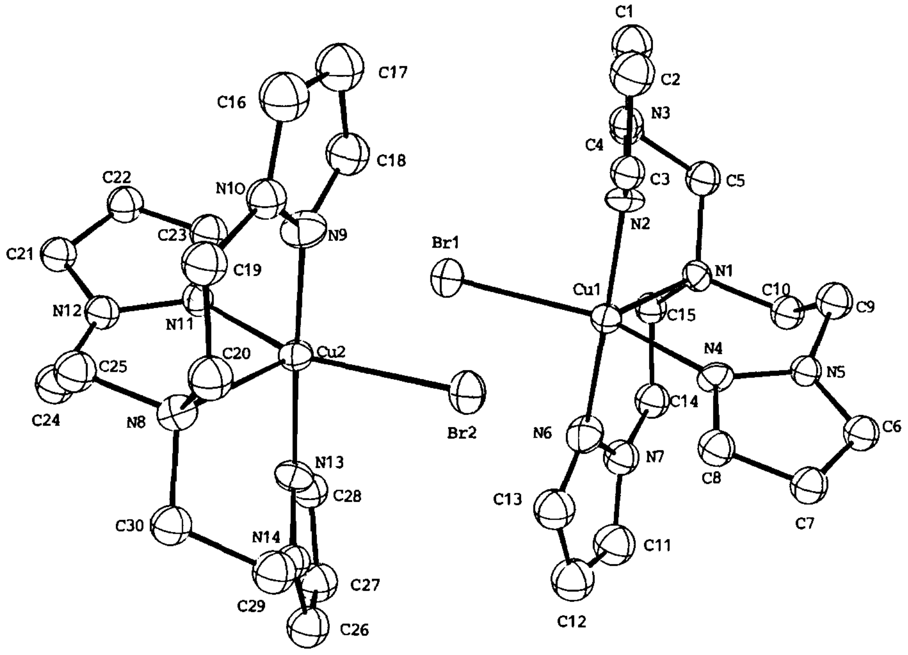

Fig. 1. Perspective view of the two moieties [CuBr(TPyEA)]$^+$ (complexes I and II).

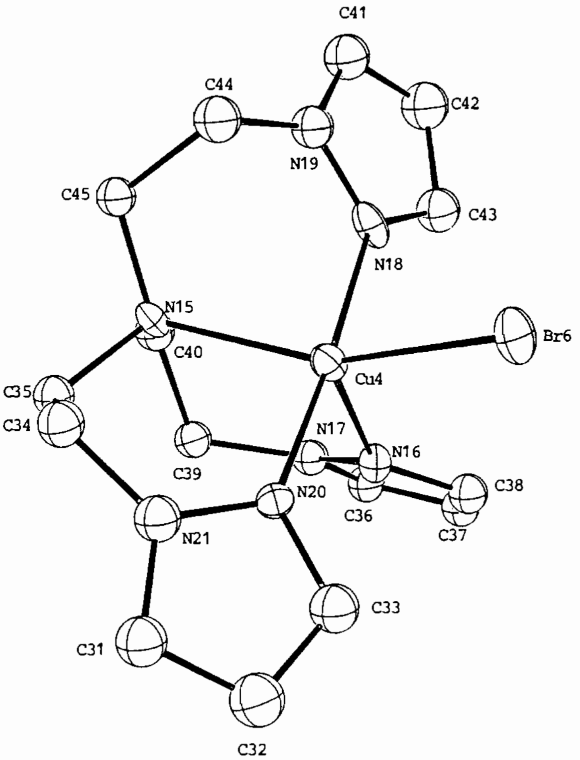

Fig. 2. Perspective view of the isolated $[CuBr(TPyEA)]^+$ cation (complex III).

nm (ϵ = 363 dm^3 mol^{-1} cm^{-1}) and 950 nm (ϵ = 105 dm^3 mol^{-1} cm^{-1}). As the stoichiometry of the $Cu_4Br_7(TPyEA)_3 \cdot 3H_2O$ compound seems to indicate a complicate structure involving both copper(II) and copper(I) an X-ray diffraction study was undertaken on the compound.

The $Cu_4Br_7(TPyEA)_3 \cdot 3H_2O$ derivative is comprised of three non-equivalent five-coordinate cations $[CuBrTPyEA]^+$, a $[CuBr_3]^{2-}$ anion, and interspersed a Br anion and H_2O molecules. Two $[CuBr(TPyEA)]^+$ cations (hereafter indicated as complex I and complex II) approach each other (Fig. 1). However the lengths of the Cu(1)···Br(2) and Cu(2)···Br(1) distances (3.7 Å) allows us to exclude any intermolecular linkage with bromine bridges. Within each complex the copper atom is coordinated by the four nitrogen donors of the TPyEA ligand and by a bromine atom in an overall distorted-square-pyramidal environment. The basal positions of the pyramids are formed by three pyrazole nitrogen donors and by the bromine atom, the apical position being occupied by the tertiary amine nitrogen. In Table III selected bond distances and angles within the coordination sphere of the two adjacent $[CuBr(TPyEA)]^+$ cations are reported. Only marginal differences in terms of bond distances and angles are observed in complexes I and II.

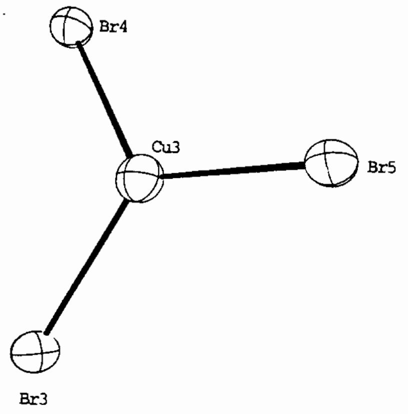

Fig. 3. Perspective view of the $[CuBr_3]^{2-}$ anion.

The isolated $[CuBr(TPyEA)]^+$ cation (complex III) has a geometry intermediate between a square pyramid and a trigonal bipyramid (see Table III for selected bond distances and angles). Referring to the trigonal bipyramidal limiting geometry, the equatorial positions are occupied by a pyrazole nitrogen, by the tertiary amine nitrogen and by the bromine atom, the remaining two pyrazole nitrogens occupying the axial positions (Fig. 2). Distances and angles within the three five-coordinate $[CuBr(TPyEA)]^+$ cations are normal for complexes formed by the ligand TPyEA *e.g.* $[Cu(H_2O)TPyEA]^{2+}$ [13], $[CoI(TPyEA)]^+$, $[CoBr(TPyEA]_2^{2+}$ [6] and $[\{Cr(NCS)(TPyEA)\}_2O]^{2+}$ [14]. In particular, the overall structure of the complexes I and II together can be compared with the structure of the dimeric hexacoordinate $[CoBr(TPyEA)]_2^{2+}$ which exhibits two asymmetric bromine bridges connecting two Co(TPyEA) fragments. The substantial differences amongst the copper and cobalt structures are the two non-bonding Cu···Br distances (3.7 Å) as compared with the corresponding longer Co–Br bond distances (2.7 Å) in the dimeric cobalt complex. However, the dimeric hexacoordinate structure of the cobalt complex is easily destroyed by grinding the compound at room temperature, and two five-coordinate cobalt complexes are obtained which are presumably arranged as the complexes I and II. In the present case the existence of some intermolecular non-bonding contacts Br···C (see for example Br(1)···C(2) and Br(2)···C(8)) in the range 3.5–3.6 Å may disfavor the further reciprocal approaching of complexes I and II and the formation of a dimeric hexacoordinate Cu^{2+} complex. Moreover the well known tendency of this ion to form tetragonally distorted structures [15] does not favor the formation of one more apical Cu–Br linkage.

Finally, in the $[CuBr_3]^{2-}$ anion the copper(I) atom exhibits an almost trigonal planar coordination (Table III and Fig. 3). The structure of $[CuBr_3]^{2-}$ is quite similar to that of the tri-iodocuprate(I) anion which has been very recently found in the [Ph$_3$MeP]$_2$[CuI$_3$] complex [16]. The aforementioned [CuBr$_3$]$^{2-}$ and [CuI$_3$]$^{2-}$ anions are the only examples so far reported of trigonal planar coordination in mononuclear halide complexes. Actually, most of the copper(I) halide complexes which have been structurally characterized so far possess polymeric structures and a tetrahedral coordination [17]. A trigonal coordination achieved through two bridging chlorides has been recently found in the dinuclear [Cu$_2$Cl$_4$]$^{2-}$ anion [18]. Perhaps the discrete [CuBr$_3$]$^{2-}$ species are stabilized by the large [CuBr(TPyEA)]$^+$ cations which maintain the anions well apart from each other, thus preventing them from forming polynuclear species.

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Supplementary Material

Listings of thermal parameters for non-hydrogen atoms (Table SI), hydrogen atom coordinates (Table SII), bond distances (Table SIII), bond angles (Table SIV), and observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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