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Polynuclear Complexes of Copper(II) with the Tetra-aza Ligand 3,6-bis-(2′-pyridyl)pyridazine (L). Crystal Structure of the Bromine Derivative $[Cu_2L(OH)Br_3]_n$

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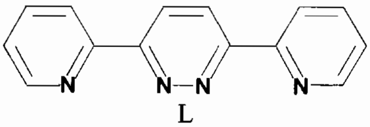
The tetra-aza ligand 3,6-bis(2′-pyridyl)pyridazine (L), when reacting in appropriate conditions with Cu(II) halides, gives rise to polynuclear complexes of general formula $[Cu_2L(OH)X_3]_n$ *(X = Cl or Br). The bromine derivative has been studied by X-ray analysis. The crystals are twins by merohedry of class I, space group* Pn *(*$P2_1/n$ *apparent space group), with the following cell constants:* a *= 13.691(5),* b *= 6.245(3),* c *= 10.298(4) Å, β = 103.92(5)°. The structure was refined by least-squares techniques to a final* R *factor of 0.066. The structure consists of binuclear units joined to each other through bridging bromine atoms to form a polymeric array. The two independent copper atoms of the dinuclear moiety are five-coordinated with a geometry which is intermediate between a square-pyramid and a trigonal-bipyramid.*

Introduction

Much attention has recently been shown in the study of binuclear copper(II) complexes with ligands containing nitrogen as donor atoms [1, 2]. An X-ray analysis performed on one of these complexes, formed with the 1,4-bis[(2-pyridyl)amino]phtalazine, showed a triple bridge constituted by the phtalazine ligand, a hydroxy group and a chlorine atom [3].

In a recent paper [4] the preparation of three binuclear complexes formed by the ligand 3,6-bis(2′-pyridyl)pyridazine (L) with $CuCl_2$, *i.e.* Cu_2LCl_4 (*1*), $Cu_2L(OH)Cl_3$ (*2*), and $Cu_2L(OH)(H_2O)Cl_3$ (*3*) was reported; the latter was characterized by X-ray means.



L

In a subsequent paper the structure of a fourth complex of $CuCl_2$ with the same ligand, $Cu_2L(H_2O)Cl_4$ (*4*), was also reported [5].

We have now extended the study of copper(II) complexes of this tetradentate ligand to bromo-derivatives. The complexes $Cu_2L(OH)Br_3$ (*5*) and Cu_2LBr_4 (*6*) have been synthesized. A preliminary X-ray investigation on crystals of (*5*) and (*2*) showed that these crystals have isomorphous structures. In order to determine this type of structure, a complete X-ray analysis was then undertaken for the bromo-derivative (*5*).

Experimental

Infrared spectra were recorded as nujol mulls with a Perkin-Elmer spectrometer. Reflectance spectra were recorded on a Beckmann DK 2A instrument against MgO reference; solution spectra were obtained with a Cary 118 spectrophotometer. The ligand was prepared as described in the literature [6].

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Synthesis of the Complexes

$Cu_2L(OH)Br_3$ (5)

To a solution of 1 mmol of $CuBr_2 \cdot 2H_2O$ in 50 ml of water, a solution of 0.5 mmol of ligand in 50 ml of acetone was added. On evaporation under continuous stirring, a green microcrystalline precipitate was obtained. The precipitate was then dissolved in 100 ml of warm water. Green crystals were obtained after a few days. These were filtered, washed with ethanol and air-dried. *Anal.* Calcd. for $C_{14}H_{11}N_4Cu_2Br_3O$: C, 27.21; H, 1.80; N, 9.06. Found: C, 27.01; H, 1.98; N, 8.79.

Cu_2LBr_4 (6)

To a warm solution of 0.5 mmol of (*5*) in 50 ml of water, 30 ml of 48% HBr were added. A dark violet microcrystalline precipitate was immediately formed upon stirring; this was filtered, washed with ethanol and air dried. *Anal.* Calcd. for $C_{14}H_{10}N_4Cu_2Br_4$: C, 24.69; H, 1.80; N, 9.06. Found: C, 24.89; H, 1.56; N, 8.49.

$Cu_2L(OH)Cl_3$ (2) and $Cu_2LCl_4 \cdot H_2O$ (1)

The former preparation [1] was modified in order to obtain fine crystals for X-ray investigations. Compound (*2*) was obtained as green crystals from compound (*3*) by keeping the solution of 10^{-4} *M* HCl under refluxing conditions, and then letting the solution evaporate slowly. Compound (*1*) was obtained in the same manner as (*2*), using a solution of 2 *M* HCl. *Anal.* Calcd. for $C_{14}H_{11}N_4Cu_2Cl_3O$: C, 34.69; H, 2.29; N, 11.56. Found: C, 33.85; H, 2.58; N, 11.51. *Anal.* Calcd for $C_{14}H_{12}N_4Cu_2Cl_4O$: C, 32.26; H, 2.32; N, 10.75. Found: C, 32.44; H, 2.81; N, 10.96.

Crystal Data and Data Collection

A parallelepiped green crystal, having dimensions 0.30 X 0.30 X 0.02 mm, was chosen for data collection. The crystals are monoclinic with two $Cu_2L(OH)Br_3$ formulae in the unit cell which has the following dimensions: a = 13.691(5), b = 6.245(3), c = 10.298(4) Å, and β = 103.92(5)°, d_c = 2.40 g cm^{-3}. Cell parameters were determined from the setting angles of 25 reflections, measured on a Philips PW 1100 automatic diffractometer, using Mo-K_α radiation. The intensity data were collected, on the same diffractometer, in the range $6° \leqslant 2\theta \leqslant 50°$ by using graphite-monochromated Mo-K_α radiation and the $\omega-2\theta$ scan technique. Variable scan widths of $(1.00 + 0.30 \text{ tg}\omega)°$ were used with a scan speed of 0.08°/sec. The background counting time was half the peak time for each side. Three standard reflections were measured every 120 min. No systematic loss of intensity was noticed during the data collection. Standard deviations on the intensities were calculated as described elsewhere [7], using a value for the instability factor k of 0.03, The 655 independent reflections having $I \geqslant 3\sigma(I)$ (on a total of 1737 reflections) were considered observed and used in the structure analysis. An absorption correction was applied using a numerical method; intensities were also corrected for Lorentz and polarization effects. Atomic scattering factors were taken from ref. [8] for non-hydrogen atoms and from ref. [9] for hydrogen atoms. Correction for anomalous dispersion were applied as described in ref. [10].

Solution and Refinement of the Structure

The $h0l$ for $h + l$ odd, and the $0k0$ for k odd extinctions are suggestive of a $P2_1/n$ space group that contains four equivalent positions. This space group, however, does not agree with the contents of the unit cell, *i.e.* two molecules whose chemical requirements exclude the presence of an inner centre of symmetry. In fact, the crystal is a twin by merohedry of class I in which the centre of inversion is the twin operation [11]. This produces a $P2_1/n$ apparent space group, whereas that of each single cell is Pn.

The structure has been solved with the heavy atom method which gave the positions of the bromine and copper atoms. Successive F_o Fourier syntheses were then performed in the $P2_1/n$ space group, by assigning a population parameter of 0.5 to the (already-located) atoms. Incidentally, the positions of two of the three bromine atoms are almost related by a screw axis symmetry operation (½ + x + 1, ½ + y, ½ – z) which does not exist in a single cell, but belongs to the $P2_1/n$ apparent space group. For this reason, on account of the impossibility of finding two separate positions, only one position that is inclusive of Br(1) and Br(3) atoms was assigned to these bromine atoms with a total population parameter of 1. The structure was refined in the $P2_1/n$ space group by use of the full-matrix least-squares SHELX program [12]. The minimized function is $\Sigma w(|F_o| - |F_c|)^2$, where w is the weight assigned to the F_o values according to the expression $w = 1/\sigma^2(F_o)$. The hydrogen atoms were introduced in calculated positions with an overall temperature factor U of 0.05 Å^2, and were not refined. Their positions were varied in every cycle on the basis of the shift of carbon atom (the C–H distance was fixed at 1.08 Å). Isotropic temperature factors were used for carbon, nitrogen, and oxygen atoms, and anisotropic temperature factors for bromine and copper atoms. The final conventional R is 0.066. The R_w factor, defined as $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ is 0.064. A final ΔF Fourier synthesis did not show any unusual features. The final values of the parameters are reported in Tables I and II. Tables of structure factors are available from the Editor on request.

TABLE I. Positional Parameters ($\times 10^4$) and Anisotropic Temperature Factors[a] ($\times 10^3$).

Atom	*x/a*	*y/b*	*z/c*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	5301(4)	−1257(9)	3003(5)	39(3)	36(3)	26(3)	−11(3)	−6(2)	−4(3)
Cu(2)	6372(4)	2984(9)	1809(5)	38(3)	31(3)	34(3)	−8(2)	−10(2)	6(3)
Br(1)[b]	6840(2)	−3995(4)	3457(3)	31(1)	37(1)	89(2)	−4(1)	−17(1)	2(2)
Br(2)	4647(4)	−439(10)	4885(6)	70(4)	61(4)	45(3)	−7(3)	15(3)	−5(3)

[a] The temperature factor is defined as $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + \ldots)]$. [b] The Br(1) atom, which has a population parameter equal to 1, also contains the contribution of the Br(3) atom (see the experimental section).

TABLE II. Positional Parameters ($\times 10^4$) and Isotropic Temperature Factors ($\times 10^3$).

Atom	*x/a*	*y/b*	*z/c*	*U* (Å^2)
O(1)	6885(25)	1314(55)	3169(33)	60(8)
N(1)	4289(22)	−3590(52)	2246(31)	27(7)
N(2)	5047(25)	−618(59)	1042(35)	41(8)
N(3)	5470(17)	852(46)	556(24)	22(6)
N(4)	6300(23)	4476(52)	86(31)	35(7)
C(1)	3971(25)	−5138(61)	2957(37)	20(8)
C(2)	3346(34)	−6714(73)	2373(45)	50(10)
C(3)	3084(28)	−6776(64)	1004(38)	32(8)
C(4)	3389(27)	−5361(59)	261(37)	26(8)
C(5)	4013(27)	−3787(60)	788(37)	33(8)
C(6)	4466(25)	−2144(58)	152(33)	18(7)
C(7)	4255(30)	−1705(64)	−1179(39)	34(9)
C(8)	4714(25)	−22(56)	−1726(35)	26(7)
C(9)	5312(26)	1338(59)	−756(35)	31(8)
C(10)	5840(23)	3248(52)	−1111(31)	22(7)
C(11)	5826(25)	3901(63)	−2395(34)	36(7)
C(12)	6316(31)	5906(73)	−2475(45)	60(9)
C(13)	6822(32)	7023(67)	−1411(41)	53(9)
C(14)	6798(29)	6192(63)	−240(39)	42(8)

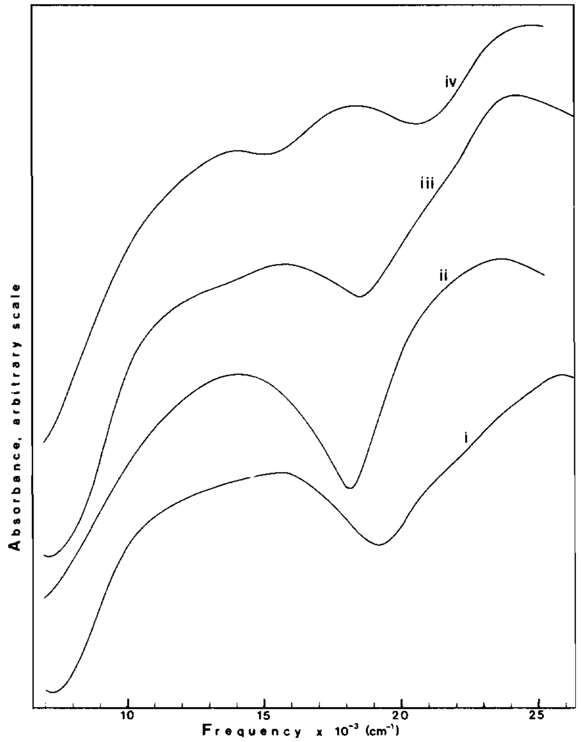
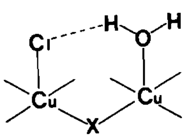


Fig. 1. Reflectance spectra of: (i) complex (*2*), (ii) complex (*1*), (iii) complex (*5*), (iv) complex (*6*).

Discussion

The general strategy for obtaining the complexes (*1*)–(*4*) has been previously described [4, 5]. Complexes (*1*) and (*2*) may also be obtained in aqueous solution at pH ⩽ 1 and pH ≅ 3 respectively upon acidification with HCl. Single crystal X-ray analyses have shown that the most remarkable difference between (*3*) and (*4*) is relative to the nature of the bridging group between the two copper atoms, namely a OH ion in (*3*) and a Cl atom in (*4*). In both cases there is also a hydrogen bonding network, between a water molecule coordinated to one copper atom and a chlorine atom terminally coordinated to the other metal, as shown in (I).



(I)

At variance with the behaviour of $CuCl_2$, $CuBr_2$ does not form the analogous complexes (*3*) and (*4*), either in acidic or neutral aqueous solutions. In any case the species (*5*) and (*6*) that are formed are very similar to the chlorine derivatives (*1*) and (*2*). In fact the IR bands at 924 and 916 cm^{-1} found in the spectra of (*3*) and at 920 and 911 cm^{-1} found in the spectra of (*4*) attributable to a coordinated water molecule are not observable for (*5*) and (*6*). Conversely, the IR spectra of the latter compounds are very similar to those of compounds (*1*) and (*2*).

TABLE III. Bond Distances (Å) and Angles (deg).

Cu(1)–Br(1)	2.666(6)	C(4)–C(5)	1.33(5)
Cu(1)–Br(2)	2.378(9)	C(5)–C(6)	1.44(5)
Cu(1)–O(1)	1.916(35)	N(2)–N(3)	1.25(5)
Cu(1)–N(1)	2.032(31)	N(2)–C(6)	1.42(5)
Cu(1)–N(2)	2.005(36)	C(6)–C(7)	1.36(5)
Cu(2)–Br(3)	2.814(6)	C(7)–C(8)	1.41(6)
Cu(2)–Br(1)′	2.515(6)	C(8)–C(9)	1.41(5)
Cu(2)–O(1)	1.862(36)	C(9)–N(3)	1.35(4)
Cu(2)–N(3)	2.048(25)	C(9)–C(10)	1.49(5)
Cu(2)–N(4)	1.985(33)	C(10)–N(4)	1.46(4)
N(1)–C(1)	1.35(5)	C(10)–C(11)	1.38(5)
N(1)–C(5)	1.46(5)	C(11)–C(12)	1.43(6)
C(1)–C(2)	1.35(6)	C(12)–C(13)	1.34(6)
C(2)–C(3)	1.37(6)	C(13)–C(14)	1.32(6)
C(3)–C(4)	1.30(6)	C(14)–N(4)	1.36(5)
Br(1)–Cu(1)–Br(2)	115.6(2)	Cu(2)–N(3)–N(2)	119.4(22)
Br(1)–Cu(1)–O(1)	96.9(10)	Cu(2)–N(3)–C(9)	114.3(23)
Br(1)–Cu(1)–N(1)	92.6(9)	N(2)–N(3)–C(9)	125.9(28)
Br(1)–Cu(1)–N(2)	104.0(11)	Cu(2)–N(4)–C(10)	115.3(23)
Br(2)–Cu(1)–O(1)	93.4(11)	Cu(2)–N(4)–C(14)	132.3(24)
Br(2)–Cu(1)–N(1)	96.4(10)	C(10)–N(4)–C(14)	110.3(31)
Br(2)–Cu(1)–N(2)	140.4(11)	N(1)–C(1)–C(2)	122.4(36)
O(1)–Cu(1)–N(1)	161.9(13)	C(1)–C(2)–C(3)	117.5(42)
O(1)–Cu(1)–N(2)	83.2(14)	C(2)–C(3)–C(4)	123.0(37)
N(1)–Cu(1)–N(2)	79.6(14)	C(3)–C(4)–C(5)	121.8(36)
Br(3)–Cu(2)–Br(1)′	108.0(2)	N(1)–C(5)–C(4)	117.6(35)
Br(3)–Cu(2)–O(1)	100.0(11)	N(1)–C(5)–C(6)	112.0(29)
Br(3)–Cu(2)–N(3)	93.4(7)	C(4)–C(5)–C(6)	130.4(35)
Br(3)–Cu(2)–N(4)	88.7(10)	N(2)–C(6)–C(5)	114.8(31)
Br(1)′–Cu(2)–O(1)	88.8(10)	N(2)–C(6)–C(7)	117.7(34)
Br(1)′–Cu(2)–N(3)	158.4(8)	C(5)–C(6)–C(7)	126.4(32)
Br(1)′–Cu(2)–N(4)	101.6(9)	C(6)–C(7)–C(8)	123.1(33)
O(1)–Cu(2)–N(3)	84.6(12)	C(7)–C(8)–C(9)	113.8(33)
O(1)–Cu(2)–N(4)	163.9(13)	N(3)–C(9)–C(8)	119.9(33)
N(3)–Cu(2)–N(4)	81.3(12)	C(8)–C(9)–C(10)	122.8(32)
Cu(1)–Br(1)–Cu(2)′	107.5(2)	N(4)–C(10)–C(9)	110.5(28)
Cu(1)–O(1)–Cu(2)	128.1(17)	N(4)–C(10)–C(11)	123.9(31)
Cu(1)–N(1)–C(1)	125.9(24)	C(9)–C(10)–C(11)	125.3(29)
Cu(1)–N(1)–C(5)	116.0(25)	C(10)–C(11)–C(12)	114.5(32)
C(1)–N(1)–C(5)	117.4(30)	C(11)–C(12)–C(13)	124.4(41)
Cu(1)–N(2)–C(6)	116.7(27)	C(12)–C(13)–C(14)	114.8(41)
Cu(1)–N(2)–N(3)	124.3(24)	N(4)–C(14)–C(13)	131.4(36)
N(3)–N(2)–C(6)	118.3(32)	N(3)–C(9)–C(10)	117.2(28)

In particular, both complexes (*1*) and (*6*) do not show the band at 930 cm^{-1}, typical for an OH group bridging two copper atoms.

The electronic spectra of (*5*) and (*2*) are quite similar. The most conspicuous difference is found for the band, shifted from 15.9 kK in (*2*) at 14.1 kK in (*5*), that has the features of charge transfer (see Fig. 1). Also the electronic spectrum of (*6*) has a band almost in the same position as that found in the spectrum of (*1*) (13.7 *vs.* 14.2 kK in (*6*) and (*1*), respectively). However a band at 18.5 kK in the spectrum of (*6*) is missing in the spectrum of (*1*). This band is probably present in (*6*) on account of a charge-transfer mechanism involving the bridging bromine atom between two metals belonging to the same binuclear unit (see Fig. 1). In aqueous solution this band disappears, probably on account of a hydrolysis reaction with a consequent replacement of the bromine atom with an OH group. The electronic spectra in solution for (*5*) and (*6*) are equal and also equal to the spectra of the chlorine derivatives (*1*)–(*4*) (all six complexes show a band at 15.75 kK with $\epsilon \cong 75$), thus substantiating the hypothesis of a prevalent $Cu_2L(OH)(H_2O)_3$ species

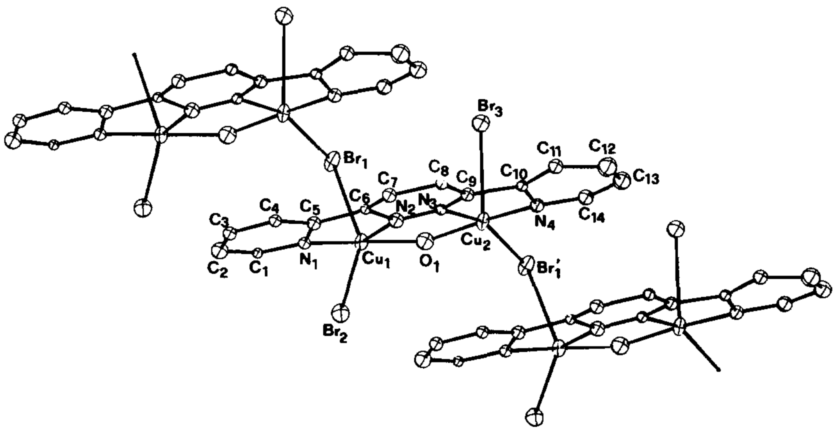


Fig. 2. A perspective view of the polymeric $[Cu_2L(OH)Br_3]_n$ molecule.

in solution [4]; a very similar behavior is also observed in solution between these complexes and those formed by copper(II) halides with the ligand 1,4-di(2′-pyridyl)aminophthalazine [13].

The structure of $Cu_2L(OH)Br_3$ consists of binuclear units joined through bromine atoms to form a polymeric array (see Fig. 2). The two independent copper atoms of each binuclear unit are five-coordinated. The geometry of the two coordination polyhedra is intermediate between square-pyramidal and trigonal-bipyramidal. It is noteworthy that Cu(1) forms a long distance with the bridging Br(1) atom, 2.666(6) Å (Table III), and a shorter one with the terminal Br(2) atom, 2.378(9) Å; *vice-versa*, Cu(2) forms a quite long distance with the terminal Br(3) atom, 2.814(6) Å, and a shorter one with the bridging Br(1) atom, 2.515(6) Å. The trend illustrated above seems meaningful, if we observe that the Br(1) bridging atom is in an apical position for the square-pyramid of Cu(1), whereas it is in the basal plane of that of Cu(2). Care must be taken, however, in comparing the single Cu–Br values which are probably affected by some systematic error due to the overlapping of Br(1) and Br(3) atoms related by a symmetry operation of the $P2_1/n$ space group (see Experimental).

At variance with the other known square-pyramidal structures of the Cu(II) complexes with this tetra-aza ligand [4, 5, 14], in the present complex the coordination about the metal is significantly distorted toward the trigonal-bipyramid. This is clearly shown by the values of angles about the metals (see Table III) and by the following deviations of the atoms N(1), N(2), O(1), Br(2), and N(3), N(4), O(1), Br(1)′ from their least-squares plane: N(1), 0.26; N(2), −0.32; O(1), 0.27; Br(2), −0.21; N(3), −0.14; N(4), 0.11; O(1), 0.13; Br(1)′, −0.09 Å. The deviations of the metals from these planes are 0.47 and 0.29 Å for Cu(1) and Cu(2), respectively.

The Cu(1)···Cu(2) separation of 3.398(8) Å is close to the value of 3.376 Å found for the binuclear complex (*3*), and to the value of 3.387 Å found in another polynuclear complex of copper with the same ligand and an hydroxy group acting as a bridge [14]. As previously mentioned [5], the Cu···Cu separation varies with the nature of the bridging inorganic group (OH, Cl), whereas the tetra-aza ligand may fit different Cu···Cu separations through appropriate distortions of the angles that include the C–C vectors linking the different aromatic rings. In any case the planarity of the ligand is preserved.

In conclusion, all the binuclear copper(II) complexes with this tetra-aza ligand possess two bridges between the copper atoms, *i.e.* the tetra-aza ligand and another group such as hydroxy or halogen. The possibility of observing a third bridge formed by a halogen atom, as found in the analogous binuclear complex of copper(II) with the 1,4-bis[(2-pyridyl)-e amino]phthalazine [3], may be complicated here by steric factors. In fact, even if the triple bridging arrangement may be energetically favoured, the rigidity of the present tetra-aza ligand (which imposes 4 nitrogen atoms almost co-linear) does not allow the sharing of the apex (halogen) for the two square-pyramids.

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