The Preparation and Properties of [Cu(chelate)X_2] Complexes. Crystal Structure and Electronic Properties of [Bis(2-pyridyl)amine]dibromocopper(II)

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The preparation and properties of a series of [Cu(chelate)X_2] complexes are reported, where ' chelate ' = 1,10-phenanthroline (phen) and bis(2-pyridyl)amine (bipyam) and X = Cl^- and Br^-. The crystal structure of [Cu(bipyam)Br_2] has been determined; the crystals are monoclinic, space group $C2$, with a = 14.44(5), b = 7.92(3), c = 5.26(3) Å, β = 94.7(5)°, and Z = 2. The structure has been solved using microdensitometer estimated photographic data using 509 reflections and refined to R 0.1022. The structure involves a distorted CuN_2Br_2 chromophore, with two-fold symmetry, and Cu–N = 1.96, Cu–Br = 2.40 Å, which from a consideration of the e.s.r. spectrum is best described as compressed, rather than elongated, tetrahedral. The electronic spectra of the [Cu(phen)X_2] complexes are considered to involve an elongated rhombic octahedral $CuN_2X_2X'_2$ chromophore stereochemistry.

A REGULAR tetrahedral stereochemistry [1] is unknown in complexes of the copper(II) ion, but a number of complexes are known which involve a compressed tetrahedral structure.[2,3] To date there is no crystallographic evidence for the alternative elongated tetrahedral structure for the copper(II) ion, although the crystal structures [4,5] of [Cu(dppoe)Cl_2] (1) and [Cu(tppo)Cl_2] (2) [dppoe = 1,2-bis(diphenylphosphoryl)ethane, tppo = triphenylphosphine oxide] do suggest a twisted elongated tetrahedral stereochemistry. Nevertheless, the single-crystal e.s.r. spectra of [Cu(dppoe)Cl_2] indicate [6] that the crystallographic C_2 axis of the CuO_2Cl_2 chromophore is not the principal electronic axis as required by the elongated tetrahedral description and the stereochemistry is best considered to be compressed tetrahedral. As the electronic properties of [Cu(bipyam)Br_2] (3) [bipyam = bis(2-pyridyl)amine] suggest that the CuN_2Br_2 chromophore could have a tetrahedral structure and as the bipyam ligand could impose a C_2 axis of symmetry, the X-ray crystal structure of (3) has been determined as a potential elongated tetrahedral structure.

EXPERIMENTAL

Preparation of Complexes.—All complexes were prepared by adding 0.8 mmol of phen (1,10-phenanthroline) or bipyam in hot ethanol (15 cm^3) to 0.8 mmol of $CuCl_2 \cdot 2H_2O$ (or $CuBr_2$) in hot water (10 cm^3, 70 °C), the mixture boiled, filtered, and allowed to stand. Table 1 lists the colour, analysis, and electronic properties of the polycrystalline samples. The solution of (3) gave fine dark brown crystals on standing.

Crystal Data for (3).—$C_{10}H_9Br_2CuN_3$, M = 394.38. Monoclinic, space group $C2$, with a = 14.44(5), b = 7.92(3), c = 5.26(3) Å, β = 94.7(5)°, U = 599.42 Å^3, D_m = 2.24(2), Z = 2, D_c = 2.19(2) g cm^{-3}, $F(000)$ = 373.94, Cu-K_α radiation, λ = 1.5418 Å, μ(Cu-K_α) = 9.56 mm^{-1}.

Crystal and refinement data for (3) are summarised in Table 2. The unit-cell parameters were measured from precession photographs about each axis, and the space group determined as $C2$, Cm, or $C2/m$ from systematic absences [7] hkl for h and k odd. Intensities were collected photographically using multi-film equi-inclination Weissenberg techniques and were measured by the S.R.C. Microdensitometer Service (Rutherford Laboratory). The main collection yielded 850 reflections for the levels $h0l$—$h6l$ and the cross-reference, 605 reflections for $hk0$—$hk2$. All reflections were retained in data reduction in which Lorentz and polarisation corrections were applied, but none for absorption.

The structure was solved using three-dimensional Patterson and Fourier techniques. Structure determination was initially attempted in $C2$, as no evidence for Cm could be found in the Patterson map, and $C2/m$ appeared unlikely in view of the unacceptable conformational constraints imposed on the bipyam system for Z = 2. Subsequent attempts to develop a structure in $C2/m$ were not successful. In $C2$ the highest intensity non-trivial Patterson peak was interpreted as a Br–Br vector, and yielded x/a = 0.1227 and z/c = 0.4249. With y/b arbitrarily fixed at 0.2450 to specify the origin, a difference Fourier based in this position indicated a metal ion on a two-fold site of the form $(c,y,\frac{1}{2})$ and subsequent Fourier calculations yielded the positions of all the non-hydrogen atoms. Complex neutral-atom scattering factors [8,9] were used and anisotropic thermal parameters were introduced for the heavy atoms. The structure was refined by full-matrix least-squares (minimising $\Sigma|F_o - F_c|^2$) until the shift in any parameter was $<0.02\sigma$. Hydrogen atoms were geometrically calculated (C–H, N–H = 1.08 Å), and floated on the associated parent atom [H(5) disordered about the

TABLE 1

Analysis, electronic reflectance spectra, and polycrystalline e.s.r. spectra for the complexes [Cu(chelate)X_2] (X = Cl or Br)

	Analysis * (%)						Electronic spectrum (cm^{-1})		E.s.r. spectrum	
	C	H	N	X	Cu	Colour			$g_\perp$	$g_\parallel$
[Cu(phen)Cl_2]	46.1 (45.8)	2.60 (2.55)	9.1 (8.9)	22.6 (22.6)	20.0 (20.2)	Green	14 000	—	2.042	2.257
[Cu(phen)Br_2]	37.0 (35.7)	2.10 (2.00)	7.4 (6.9)	39.9 (39.7)	13.9 (15.75)	Brown	14 900	—	2.10	(Exchanged)
[Cu(bipyam)Cl_2]	39.9 (39.3)	3.05 (2.95)	13.8 (14.0)	23.8 (23.2)	20.1 (20.8)	Dark green	14 080	9 230	2.054	2.310
[Cu(bipyam)Br_2]	30.8 (30.4)	2.30 (2.30)	10.8 (10.7)	40.0 (40.6)	16.0 (16.1)	Dark brown	13 000	9 000	2.075	2.298

* Calculated values in parentheses.

two-fold axis, with site occupation factor 0.5]. Two reflections, for which $|F_o - F_c| > 5\sigma$, were omitted from the final refinement cycles. The final difference map featured some positive and negative peaks in the vicinity of the heavy atoms (maximum 4 e Å^{-3}) which were considered to arise from series termination effects, and attempts to refine the weighting scheme from unity were not successful. The final R value was 0.1022. All calculations were carried out using SHELX-76 [10] and XANADU (G. M. Sheldrick), PLUTO (S. Motherwell), and XPUB (R. Taylor) on an IBM 4341 computer. The final atomic co-ordinates are given in Table 3, selected bond lengths and bond angles are given in Table 4, and Table 5 summarises the mean-plane data. The final structure factors, isotropic and anisotropic temperature factors, calculated hydrogen atom positions, and full bond-length, angle, and mean-plane data are given in Supplementary Publication No. SUP 23185 (14 pp.).*

TABLE 2

Refinement data for [Cu(bipyam)Br$_2$] (3)

Data used	$h0l$—$h6l$; $hk0$—$hk2$
Unique reflections	509
Varied parameters	50
$R(=\Sigma\Delta/\Sigma\|F_o\|)$	0.1022
Weighting scheme	unit weighting
Maximum final shift/e.s.d.	0.02
Residual electron density (e Å^{-3})	*ca.* 4.0 (special position) 0.9
Anisotropic atoms	2

Figure 1 shows the molecular structure of (3) and the atom numbering used; Figure 2 shows the projection down the *b* axis and crystal packing in the *ac* plane.

Electronic Properties.—These were determined as previously described [11] and are reported in Table 1.

RESULTS AND DISCUSSION

Crystal Structure.—The structure of (3) consists of discrete molecules of [Cu(bipyam)Br$_2$] involving a distorted tetrahedral CuN_2Br_2 chromophore. The value of Cu–N of 1.96 Å and Cu–Br of 2.40 Å are typical copper–ligand bond distances [12] for these ligands. The N(1)–Cu–N(1^i) angle of 94.8° is a normal bipyam bite angle [13] and is clearly reduced from a regular tetrahedral angle of 109.5°. Equally, the Br–Cu–Br^i angle is also reduced to 98.3° for no obvious reason, as there are no constraints imposed by a chelate ligand; there is one reasonable non-bonded interaction, Br • • • C(1^{ii}) 3.50 Å (superscript ii indicates atom at position x, y, $-1.0 + z$), but this seems hardly sufficient to justify a bond angle decrease of >10°. The planes of the N(1)–Cu–N(1^i) and Br–Cu–Br^i units are inclined at 116.6° (Figure 2), representing a considerable twist away from the 90° of an elongated tetrahedral structure. The bond lengths and bond angles of the bipyam ligand show no unusual values [13] (see SUP 23185) and the planes of the atoms of the N(1), C(1)—C(5) and N(1^i) C(1^i)—C(5^i) planes are inclined to each other at an angle of 7.0°.

TABLE 3

Fractional co-ordinates (× 10^4) for non-hydrogen atoms

	x	y	z
Cu	0	4 435(8)	5 000
Br	1 206(2)	2 450(0)	4 236(6)
N(1)	696(17)	6 110(32)	7 128(47)
C(1)	1 269(25)	5 509(54)	9 056(68)
C(2)	1 682(26)	6 564(55)	10 849(76)
C(3)	1 623(27)	8 291(55)	10 801(77)
C(4)	1 046(22)	8 953(42)	8 813(59)
C(5)	601(19)	7 841(36)	6 943(51)
N(2)	0	8 537(44)	5 000

TABLE 4

Selected bond lengths (Å) and bond angles (°)

(i) Bond lengths		(ii) Bond angles	
Cu–N(1)	1.96(3)	N(1)–Cu–Br	101.2(10)
Cu–Br	2.40(1)	N(1)–Cu–Br^i	133.8(12)
		N(1)–Cu–N(1^i)	94.8(15)
		Br–Cu–Br^i	98.3(15)

Superscript i refers to atoms in the position $-x, y, 1.0 - z$

TABLE 5

Summary of mean-plane data

	Root-mean-square deviation (Å)
Plane 1: N(1),Cu,N(1^i)	0.0
Plane 2: Br,Cu,Br^i	0.0
Plane 3: N(1),C(1)—C(5)	0.01(1)
Plane 4: N(1^i), C(1^i)—C(5^i)	0.01(1)
Angle (°) between planes:	
1—2, 116.6(10)	
3—4, 7.0 (10)	

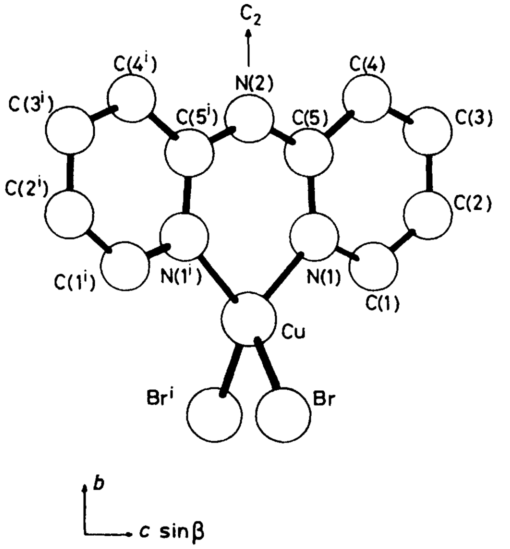

FIGURE 1 The local molecular structure of [Cu(bipyam)Br$_2$] and the atom numbering scheme used

The twisted tetrahedral structure has been observed previously [4,5] in the CuO_2Cl_2 chromophores of [Cu(dppoe)-Cl$_2$] (1), and [Cu(tppo)$_2$Cl$_2$] (2) (Table 6) and described in the former as compressed *cis*-distorted tetrahedral. Although the *cis* distortion of (3) could be imposed by the chelated bipyam ligand, no such constraint is imposed in (1), where a bridging bidentate ligand is involved or in (2) where tppo is monodentate.[5] The compressed tetrahedral structure of (3) has not been observed previously

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

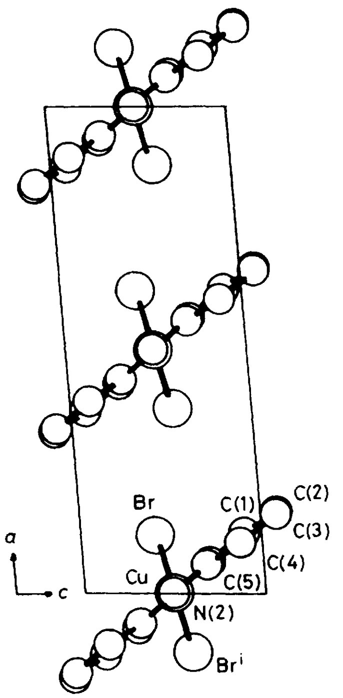

FIGURE 2 A projection of the structure of [Cu(bipyam)Br$_2$] down the two-fold axis (b axis), and the packing in the ac plane

TABLE 6

A comparison of the bond angles (°) in some copper(II)–chelate complexes

	CuL_2X_2 chromophore	L–Cu–L(°)	X–Cu–X(°)	Twist (90°)
[Cu(bipyam)Br$_2$]	CuN_2Br_2	94.8	98.3	112.0
[Cu(dppoe)Cl$_2$]	CuO_2Cl_2	90.6	100.3	124.0
[Cu(tppo)$_2$Cl$_2$]	CuO_2Cl_2	93.0	102.0	109.0

in a [Cu(chelate)X$_2$] complex, but may occur in [Cu(bipyam)Cl$_2$] (Table 1, see later) and contrasts with the more usual elongated rhombic octahedral structure[14] of [Cu(en)Cl$_2$] (en = 1,2-diaminoethane). The crystal structure of only one other mono(bipyam)copper(II) complex is known,[15] namely, [Cu(bipyam)(O$_2$CCH$_3$)]-[ClO$_4$]·H$_2$O, in which the $CuN_2O_2O'_2$ chromophore has an elongated rhombic octahedral stereochemistry.

Electronic Properties.—The polycrystalline e.s.r. spectra of [Cu(phen)Cl$_2$], [Cu(bipyam)Cl$_2$], and [Cu(bipyam)Br$_2$] are all axial with $g_{\parallel} > g_{\perp} > 2.0$, while that of [Cu(phen)Br$_2$] is near isotropic, but exchange-type.[16] The axial e.s.r. spectra could be consistent with an elongated rhombic octahedral $CuN_2X_2X'_2$ chromophore stereochemistry as in [Cu(en)Cl$_2$][14] or with the compressed tetrahedral CuO_2Cl_2 structures[4,5] of (1) and (2). The polycrystalline e.s.r. spectrum of (3) showed no significant variation with temperature and rules out the presence of a fluxional stereochemistry.[17] Attempts to obtain single-crystal e.s.r. spectra of (3) were unsuccessful due to the very fine needle form of the crystals, but a crystal with $g = 2.074$ was recorded along the needle axis, the b axis of the monoclinic crystal, and suggests that one of the components of $g_{\perp}$ lies along the crystallographic two-fold axis, and not $g_{\parallel}$. This implies that the direction of the crystal g values of (3) correlate with the directions of the g values previously observed in the compressed rhombic tetrahedral stereochemistry of (1) and suggests that the local molecular structure of (3) is best considered as a compressed tetrahedral stereochemistry.

The electronic reflectance spectra of Table 1 divide into two groups, the [Cu(phen)X$_2$] complexes have a single peak at *ca.* 14 000 cm^{-1}, while the [Cu(bipyam)X$_2$] complexes have two equally intense peaks at *ca.* 9 000 and 13 000—14 000 cm^{-1}. The former spectra are consistent with the single peak of 14 200 cm^{-1} previously reported[16] for [Cu(en)Cl$_2$] which increases to 14 900 cm^{-1} in [Cu(en)Br$_2$], and is consistent with the known elongated rhombic octahedral structure[14] of [Cu(en)Cl$_2$], and suggests that both of the phen complexes have a $CuN_2X_2X'_2$ chromophore with this elongated rhombic octahedral structure. The two peaks in the electronic spectra of the two bipyam complexes are consistent with the twin peaks observed in the electronic spectra of (1) and (2), and suggest that both complexes have a compressed tetrahedral stereochemistry as determined above for (3). This also suggests that the spectrum of (3) may be tentatively assigned[6] by analogy with the polarised single-crystal electronic spectra of (1) (Table 7), assuming a d_{xy} ground state.

TABLE 7

The tentative one-electron orbital energies (cm^{-1}) for (*a*) [Cu(dppoe)Cl$_2$] and (*b*) [Cu(bipyam)Br$_2$] in D_2 symmetry

Transition	(*a*)	(*b*)
$d_{xz} \longrightarrow d_{xy}$	8 800	9 000
$d_{yz} \longrightarrow d_{xy}$	9 100	
$d_{x^2-y^2} \longrightarrow d_{xy}$	*ca.* 11 500	13 000
$d_{z^2} \longrightarrow d_{xy}$	*ca.* 11 500	

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