Crystal and Molecular Structure of Di[iodobis-(2,2′-bipyridylamine)-copper(II)] Iodide Perchlorate

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The crystal and molecular structure of the title compound has been determined by single-crystal *X*-ray techniques. Crystals are monoclinic, space group $P2_1/c$ with a = 19·21, b = 13·47, c = 19·50 Å, β = 111·88°, and Z = 4. The structure was solved by conventional Patterson and Fourier methods, and block-diagonal least-squares refinement of 3921 observed reflections measured on a diffractometer gave R 0·086. The two symmetry-independent copper(II) moieties in the unit cell adopt essentially identical trigonal bipyramidal geometries with two bidentate ligands and an iodide co-ordinated to each metal ion. The iodide occupies an equatorial position, hence minimizing steric repulsions.

In any complex containing the ligand 2,2′-bipyridylamine ligand–ligand repulsions are important and, in fact essentially eliminate the possibility of a *trans*-planar configuration without severe ligand distortion. In this way the ligand is similar to 2,2′-bipyridyl,[1] but the amine ligand is more flexible and can adapt to a greater variety of geometries.

Although many copper(II) complexes have been formed containing this ligand,[2-4] few have been characterized structurally and in some cases even the stoicheiometry is in doubt. There is also considerable current interest in the electronic properties of copper(II) and their correlation with structure.[5] In previous studies of compounds of this type we have shown that, depending on the anion used, a distorted tetrahedral, a distorted square pyramidal, or a distorted octahedral geometry can result. The first configuration occurs in $CuL_2(ClO_4)_2$ [6] (L = 2,2′-bipyridylamine) while the second and third are both found in $(CuL_2NCS)[CuL_2(NCS)_2](ClO_4)$.[7]

In the present study we have determined the structure of $(CuL_2I)_2I(ClO_4)$ which was prepared by the method reported [3] for $CuL_2I(ClO_4)$. A recent study of the visible, i.r., and e.s.r. spectra of the latter compound indicated a five-co-ordinate copper(II) species, as found for the related 2,2′-bipyridyl complex,[8] and a square pyramidal geometry was postulated.[4]

EXPERIMENTAL

The preparation given in ref. 3 for $CuL_2I(ClO_4)$ was followed; although the reaction appeared to proceed as had been reported and similar small dark green crystals were obtained, analysis, later confirmed by the single-crystal *X*-ray investigation, indicated a greater percentage of iodine (28·5% compared to 20%) than expected for the simple stoicheiometry $CuL_2I(ClO_4)$. The crystals, however, displayed a reflectance spectra similar to that reported in ref. 3.

Crystal Data.—$C_{40}H_{36}ClCu_2I_3N_{12}O_4$, M = 1292, Monoclinic, $a = 19{\cdot}21 \pm 0{\cdot}01$, $b = 13{\cdot}47 \pm 0{\cdot}01$, $c = 19{\cdot}50 \pm 0{\cdot}05$ Å, $\beta = 111{\cdot}88 \pm 0{\cdot}15°$, U = 4687 Å^3, D_m = 1·85, Z = 4, D_c = 1·83, $F(000)$ = 2504. Space group $P2_1/c$ (C^5_{2h}) from systematic absences: $h0l$ for $l = 2n + 1$, and $0k0$ for $k = 2n + 1$. Mo-K_α *X*-radiation, λ = 0·7107 Å; μ(Mo-K_α) = 29·47 cm^{-1}.

Unit-cell parameters and their standard deviations were determined by a least-squares fit to twelve independent reflection angles whose centres were determined by left–right top–bottom beam splitting on a previously aligned Hilger and Watts four-circle diffractometer. Any error in the instrumental zero was eliminated by centring the reflection at both +2θ and −2θ. For data collection a crystal having dimensions *ca.* 0·25 × 0·25 × 0·15 mm was mounted with the *b* axis aligned along the spindle axis of the goniometer.

Data were collected at room temperature on a Hilger and Watts four-circle diffractometer equipped with scintillation counter and by use of zirconium-filtered Mo-K_α radiation. Within a 2θ sphere of 40°, all data in the hkl and $\bar{h}kl$ octants were collected by the stationary-counter–stationary-crystal technique. Intensities were measured by counting at the peak centre $\theta(hkl)$ for 10 s and subtracting two 5 s background counts at $\theta(hkl) \pm [0{\cdot}25 + 0{\cdot}01 \times \theta(hkl)]$. A total of 8477 reflections were measured in this manner. Also 100 reflections covering a range of sin θ/λ values were remeasured *via* the step-scan method (moving-crystal–moving-counter) for later use in a peak-height to step-scan conversion.[9] The plot of the ratio of I_i/I_p *vs.* sin θ/λ (i = integrated, p = peak height) of these reflections increased smoothly from 0·95 at low values of sin θ to 1·60 at large values and no χ or φ dependencies were indicated.

As a general check on electronic and crystal stability the intensity of three large reflections (5,5,1, 6,0,0, 0,0,4) were checked periodically during the data collection. No significant decrease in the intensity of these reflections was observed. The intensities were corrected for Lorentz-polarization effects, but no absorption correction was deemed necessary.

Equivalent reflections were averaged to yield 8259 independent intensities. The estimated error in each intensity was calculated from: $[\sigma(I)]^2 = C_t + C_b + (K_tC_t)^2 + (K_bC_b)^2$, where C_t and C_b are the total and background counts, K_t and K_b are estimates for non-statistical errors in C_t and C_b and both were assigned values

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[1] E. D. McKenzie, *Co-ordination Chem. Rev.*, 1971, **6**, 187.

[2] For a review covering many of these complexes see W. R. McWhinnie, *Co-ordination Chem. Rev.*, 1970, **5**, 293.

[3] W. R. McWhinnie, *J. Chem. Soc.*, 1964, 5165.

[4] J. C. Lancaster, W. R. McWhinnie, and P. L. Welham, *J. Chem. Soc.* (*A*), 1971, 1742.

[5] B. J. Hathaway and D. E. Billing, *Co-ordination Chem. Rev.*, 1970, **5**, 143.

[6] J. E. Johnson, T. A. Beineke, and R. A. Jacobson, *J. Chem. Soc.* (*A*), 1971, 1371.

[7] J. E. Johnson and R. A. Jacobson, unpublished work.

[8] G. A. Barclay, B. F. Hoskins, and C. H. L. Kennard, *J. Chem. Soc.*, 1963, 5691.

[9] L. E. Alexander and G. S. Smith, *Acta Cryst.*, 1962, **15**, 983.

of 0·05. The estimated deviations in the structure factors were calculated from the finite-difference method.[10] Of all the measured independent reflections, 3921 having $I \geqslant 3\sigma(I)$ were considered observed and used for the structure determination.

TABLE 1

Final atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses *

Atom	x	y	z
I(1)	3214(1)	794(1)	4382(1)
I(2)	331(1)	4096(1)	1820(1)
I(3)	−1767(1)	3858(1)	4414(1)
Cu(1)	3855(1)	1652(2)	3526(1)
Cu(2)	540(1)	6094(2)	1897(1)
Cl(1)	5274(2)	373(3)	1663(2)
N(1)	3493(9)	2958(11)	3739(9)
N(2)	4554(9)	3206(12)	4794(9)
N(3)	4936(9)	2246(13)	4005(10)
N(4)	3595(9)	1923(11)	2420(9)
N(5)	3180(10)	285(11)	2089(9)
N(6)	4144(9)	300(12)	3312(9)
N(7)	1226(9)	5897(11)	1362(10)
N(8)	250(10)	6185(15)	183(10)
N(9)	−83(9)	7087(13)	1102(10)
N(10)	1244(11)	7053(14)	2642(10)
N(11)	870(10)	6324(14)	3599(10)
N(12)	−143(8)	6162(12)	2473(8)
C(1)	2777(12)	3233(17)	3333(14)
C(2)	2403(13)	3964(17)	3488(13)
C(3)	2763(14)	4471(18)	4151(13)
C(4)	3485(14)	4181(18)	4589(12)
C(5)	3847(11)	3427(15)	4358(11)
C(6)	5116(11)	2867(15)	4594(12)
C(7)	5854(12)	3165(17)	4948(13)
C(8)	6406(13)	2873(18)	4691(16)
C(9)	6233(13)	2246(19)	4093(16)
C(10)	5463(12)	1939(18)	3769(14)
C(11)	3696(12)	2852(17)	2197(13)
C(12)	3477(13)	3113(16)	1426(13)
C(13)	3131(15)	2424(18)	938(12)
C(14)	2990(13)	1514(16)	1144(10)
C(15)	3237(10)	1269(14)	1889(11)
C(16)	3763(12)	−169(13)	2705(12)
C(17)	3882(14)	−1188(16)	2630(14)
C(18)	4421(14)	−1669(17)	3206(15)
C(19)	4870(15)	−1172(16)	3828(14)
C(20)	4720(14)	−212(18)	3869(15)
C(21)	1931(12)	5670(14)	1738(16)
C(22)	2368(13)	5352(19)	1430(14)
C(23)	2131(14)	5227(19)	661(16)
C(24)	1398(15)	5512(18)	273(13)
C(25)	942(12)	5845(15)	582(11)
C(26)	−173(13)	6941(15)	360(12)
C(27)	−655(15)	7493(21)	−207(14)
C(28)	−1010(19)	8293(19)	2(19)
C(29)	−937(14)	8450(19)	700(17)
C(30)	−449(15)	7856(23)	1229(14)
C(31)	1623(14)	7739(22)	2466(18)
C(32)	2113(14)	8369(21)	2944(16)
C(33)	2248(18)	8261(17)	3659(15)
C(34)	1819(14)	7639(20)	3897(14)
C(35)	1320(11)	6990(19)	3334(15)
C(36)	146(11)	6085(17)	3211(12)
C(37)	−287(14)	5788(21)	3576(15)
C(38)	−1023(14)	5665(23)	3240(15)
C(39)	−1326(12)	5790(19)	2431(15)
C(40)	−852(12)	6008(16)	2118(12)

Solution of the Structure.—A sharpened Patterson map was computed and initial positions of the two copper atoms and three iodine atoms were determined. A structure-factor calculation with these atoms and the chlorine atom gave R 27·8%. The remaining atoms were located from successive structure-factor and electron-density map calculations, except for the perchlorate oxygen atoms which could not be located or refined because of severe disorder. With all the atoms allocated isotropic thermal parameters, the structure refined to R 12·5%. At this point a difference electron-density map indicated anisotropic motion, especially about the copper and iodine atoms. Refinement with these heavy atoms given anisotropic thermal parameters produced R 9·16%. The perchlorate oxygen atoms were taken into account by allowing both the occupation parameter and the isotropic temperature factor of the chlorine to increase. All atoms, except the chlorine, were now refined with anisotropic temperature factors;

TABLE 2

Anisotropic thermal parameters *

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{23}$	$10^4\beta_{13}$	$10^4\beta_{12}$
I(1)	59(1)	64(1)	40(1)	−23(1)	61(12)	−40(2)
I(2)	69(1)	55(1)	30(1)	−2(1)	38(1)	−21(2)
I(3)	64(1)	95(1)	37(1)	11(2)	38(1)	−10(2)
Cu(1)	34(1)	51(2)	25(1)	0(2)	22(2)	2(2)
Cu(2)	37(1)	61(2)	24(1)	−2(2)	28(2)	−9(2)
Cl	6·57(13) †	0	0	0	0	0
N(1)	35(8)	54(11)	28(7)	−28(14)	9(12)	−18(14)
N(2)	32(7)	53(12)	31(7)	3(14)	24(12)	13(14)
N(3)	35(8)	70(14)	38(8)	19(16)	30(13)	0(16)
N(4)	35(7)	37(10)	36(7)	−7(13)	50(12)	−37(13)
N(5)	48(8)	33(11)	30(7)	20(13)	22(12)	6(15)
N(6)	40(8)	64(13)	26(7)	23(15)	22(12)	17(16)
N(8)	49(7)	105(11)	41(16)	−17(31)	57(13)	−12(15)
N(9)	26(7)	85(15)	40(8)	−24(18)	16(13)	3(16)
N(10)	55(9)	90(16)	29(8)	25(17)	44(14)	−26(19)
N(11)	45(9)	93(17)	40(9)	4(14)	42(14)	−25(18)
N(12)	25(7)	81(14)	24(14)	−27(15)	27(10)	−18(15)
C(1)	42(11)	76(19)	50(10)	12(22)	51(17)	30(23)
C(2)	46(11)	82(21)	36(9)	19(22)	21(18)	23(24)
C(3)	53(11)	101(21)	32(9)	4(22)	51(22)	45(24)
C(4)	69(13)	99(21)	34(9)	−5(22)	92(19)	1(25
C(5)	28(8)	60(15)	28(8)	−11(17)	35(14)	−20(18)
C(6)	34(9)	48(15)	33(9)	59(19)	−12(15)	−14(18)
C(7)	27(9)	77(18)	46(17)	53(22)	−18(16)	−25(20)
C(8)	35(11)	75(20)	86(17)	36(29)	40(22)	2(21)
C(9)	41(11)	104(24)	75(15)	−3(30)	70(22)	−6(25)
C(10)	38(10)	93(21)	51(12)	37(34)	50(19)	16(22)
C(11)	34(9)	83(20)	41(11)	−22(22)	24(17)	23(21)
C(12)	61(12)	62(17)	43(11)	54(21)	58(19)	28(22)
C(13)	89(15)	77(18)	22(9)	−2(20)	43(20)	−24(27)
C(14)	60(12)	85(18)	9(7)	−26(18)	28(15)	11(23)
C(15)	25(7)	49(14)	34(9)	4(18)	22(14)	−3(16)
C(16)	46(10)	32(13)	37(9)	4(17)	45(16)	−18(17)
C(17)	64(13)	53(17)	54(12)	−20(22)	60(21)	−19(23)
C(18)	66(13)	52(17)	64(14)	33(24)	60(22)	−3(24)
C(19)	80(14)	49(17)	48(11)	30(21)	69(21)	55(24)
C(20)	62(13)	79(20)	57(13)	62(25)	70(22)	27(25)
C(21)	35(10)	29(14)	94(16)	23(22)	64(21)	47(18)
C(22)	43(11)	91(20)	50(12)	−9(26)	−4(19)	78(25)
C(23)	40(11)	107(23)	80(16)	4(29)	87(22)	−5(25)
C(24)	82(15)	73(18)	41(11)	−14(22)	92(21)	3(26)
C(25)	41(9)	51(14)	24(8)	30(17)	18(14)	24(19)
C(26)	49(11)	48(15)	33(9)	−5(19)	3(17)	17(20)
C(27)	69(14)	126(25)	32(11)	49(25)	29(20)	84(31)
C(28)	115(20)	64(20)	109(21)	61(32)	168(35)	52(32)
C(29)	56(13)	87(21)	85(16)	6(29)	94(24)	52(26)
C(30)	63(14)	171(32)	31(11)	−26(29)	12(20)	121(33)
C(31)	40(11)	135(28)	93(18)	33(35)	85(24)	−29(28)
C(32)	49(12)	116(25)	71(16)	80(32)	36(23)	−9(28)
C(33)	116(19)	41(17)	55(14)	10(14)	52(27)	−58(29)
C(34)	63(13)	111(24)	37(26)	−5(20)	22(20)	22(29)
C(35)	20(9)	105(22)	59(13)	−60(28)	−13(17)	−1(21)
C(36)	31(9)	81(19)	31(9)	−5(20)	23(15)	−28(20)
C(37)	49(12)	127(27)	49(13)	−22(28)	28(20)	−42(28)
C(38)	48(12)	165(31)	59(14)	28(32)	72(22)	−54(30)
C(39)	30(9)	92(21)	61(13)	29(28)	3(18)	−20(22)
C(40)	53(11)	69(17)	35(9)	−29(20)	62(17)	−37(22)

* In the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{23}kl + \beta_{13}hl + \beta_{12}hk)]$. † Isotropic temperature factor.

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[10] S. L. Lawton and R. A. Jacobson, *Inorg. Chem.*, 1968, **7**, 2124.

R was then 8·80%. A difference electron-density map at this stage showed no significant peaks other than some diffuse electron density in the area of the perchlorate.

Hydrogen positions for the aromatic rings were calculated assuming a benzoid structure with C–H 1·08 Å. The hydrogen atoms were assigned the isotropic temperature factor of the attached carbon. A final structure-factor calculation with these atoms present gave R 8·63% and a weighted discrepancy factor R' $\{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}\}$ 9·8%. The scattering factors were taken from ref. 11, with those for copper, iodine, and chlorine modified for the real and imaginary parts of anomalous dispersion. Owing to the large number of variables, block-diagonal least-squares were used throughout; local programs were used and those described in ref. 12. The final positional parameters and anisotropic thermal parameters for non-hydrogen atoms are given in Tables 1 and 2, and calculated hydrogen positions in Table 3. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20611 (3 pp. 1 microfiche).*

TABLE 3

Fractional co-ordinates ($\times 10^4$) and isotropic thermal parameters for calculated hydrogen atoms. The atom number and temperature factor are those of the carbon atom to which it is attached

Atom	x	y	z	B/Å^2
H(1)	2490	2819	2840	4·51
H(2)	1848	4158	3124	5·29
H(3)	2491	5065	4316	4·32
H(4)	3767	4538	5109	4·24
H(7)	6001	3628	5427	5·32
H(8)	6968	3136	4959	5·99
H(9)	6645	2003	3883	5·53
H(10)	5306	1435	3313	5·11
H(11)	3946	3408	2607	4·14
H(12)	3592	3832	1259	4·47
H(13)	2956	2593	362	5·20
H(14)	2689	981	733	4·62
H(17)	3559	−1578	2135	5·06
H(18)	4493	−2452	3168	5·68
H(19)	5318	−1536	4258	5·11
H(20)	5055	913	4351	4·91
H(21)	2146	5756	2326	5·58
H(22)	2935	5172	1770	7·15
H(23)	2488	4937	399	5·90
H(24)	1189	5458	−317	5·40
H(27)	−757	7328	−773	6·77
H(28)	−1349	8791	−417	7·81
H(29)	−1249	9019	841	6·07
H(30)	−353	8024	1793	7·92
H(31)	1540	7811	1894	6·25
H(32)	2384	8934	2753	7·41
H(33)	2699	8665	4056	7·19
H(34)	1850	7633	4456	5·98
H(37)	−32	5645	4157	6·82
H(38)	−1373	5487	3539	6·00
H(39)	−1912	5704	2113	6·68
H(40)	−1064	6064	1528	4·38

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The crystal and molecular structure consists of two crystallographically independent five-co-ordinate copper(II) moieties in the asymmetric unit along with non-bonded iodide and perchlorate anions. The two five-co-ordinate species are both slightly distorted trigonal bipyramids with no structurally significant differences.

The geometry and chemical constitution of chromophore (I) is shown in Figure 1 while Figure 2 is a view of the asymmetric unit displaying the two cations, the iodide, and the chlorine of the perchlorate group. Table 4 lists all distances and angles about the two copper atoms and the mean distances for chemically equivalent bonds within the ligands. In the following discussion all structural data quoted will be for chromophore (I) [containing Cu(1) and I(1)], with the equivalent data for chromophore (II) in parentheses where significant.

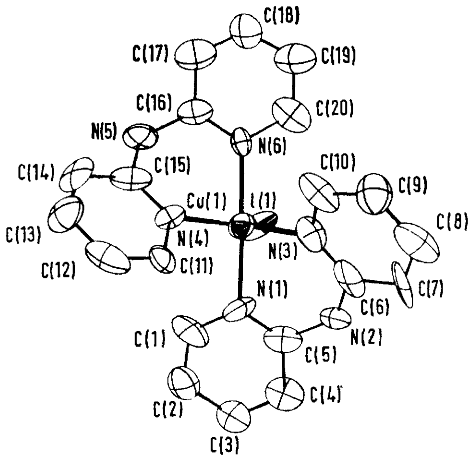

FIGURE 1 Chromophore (I) of $(CuL_2I)_2I(ClO_4)$ displaying the trigonal bipyramidal co-ordination geometry

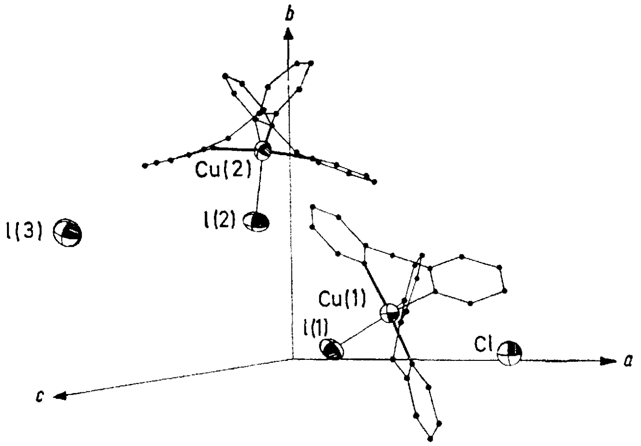

FIGURE 2 A formula unit of $(CuL_2I)_2I(ClO_4)$

The equatorial atoms of each trigonal bipyramid consist of two nitrogen atoms from different bidentate ligands and an iodine atom, all of which lie within 0·01 Å of the equatorial plane containing the copper(II) ion. The axial positions are occupied by the remaining two nitrogen atoms. By adopting this geometry,

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[11] H. P. Hansen, F. Herman, J. D. Lee, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

[12] Programs: N.R.C. Structure Factor and Least Squares, F. R. Ahmed and M. E. Pippy; ORTEP, C. K. Johnston, for the preparation of Figures 1 and 2.

ligand–ligand non-bonded repulsions are minimized. The copper–nitrogen equatorial bonds appear to be slightly but significantly elongated compared with the axial ones, the mean equatorial distance being 2·06 *vs*. 2·00 Å for the mean axial distance. This type of equatorial elongation has been observed to various extents in other complexes of this type.[13,14] The copper–iodide distances agree well with that reported by Barclay.[8] The bound iodide atoms display pronounced anisotropic thermal motions (Figure 1); the smallest component, approximately in the direction of the copper–iodide bond, is 0·193 Å (0·201 Å) and the largest, 0·324 Å (0·350 Å), is at an angle of 41° (50°) with the equatorial plane. This pattern of motion is quite consistent with the steric restrictions imposed by the axial nitrogens and the other ligand repulsions.

TABLE 4

Bond lengths (Å) and bond angles (°) with standard deviations in parentheses

Cu(1)–N(1)	1·992(15)	Cu(2)–N(7)	1·981(13)
Cu(1)–N(6)	1·992(15)	Cu(2)–N(12)	2·024(12)
Cu(1)–N(4)	2·056(16)	Cu(2)–N(10)	2·036(17)
Cu(1)–N(3)	2·094(13)	Cu(2)–N(9)	1·060(18)
Cu(1)–I(1)	2·679(3)	Cu(2)–I(2)	2·717(3)
N(1)–Cu(1)–N(6)	175·6(10)	N(7)–Cu(2)–N(12)	174·7(10)
N(1)–Cu(1)–N(4)	95·4(10)	N(7)–Cu(2)–N(10)	93·7(11)
N(1)–Cu(1)–N(3)	86·3(10)	N(7)–Cu(2)–N(9)	90·3(11)
N(1)–Cu(1)–I(1)	88·4(7)	N(7)–Cu(2)–I(2)	87·3(8)
N(6)–Cu(1)–N(4)	85·5(10)	N(12)–Cu(2)–N(10)	88·4(11)
N(6)–Cu(1)–N(3)	97·8(11)	N(12)–Cu(2)–N(9)	94·2(10)
N(6)–Cu(1)–I(1)	88·0(8)	N(12)–Cu(2)–I(2)	87·8(7)
N(4)–Cu(1)–N(3)	102·3(10)	N(10)–Cu(2)–N(9)	99·8(11)
N(4)–Cu(1)–I(1)	137·9(7)	N(10)–Cu(2)–I(2)	135·5(8)
N(3)–Cu(1)–I(1)	119·8(8)	N(9)–Cu(2)–I(2)	124·7(8)

Mean distances in:

(i) Ligand (1) [C(1)—(10), N(1) —(3)]

C–C	1·39(2)	C–N (bridge)	1·35(2)
C–N (pyridyl)	1·34(2)		

(ii) Ligand (2) [C(11)—(20), N(4)—(6)]

C–C	1·37(2)	C–N (bridge)	1·42(2)
C–N (pyridyl)	1·35(2)		

(iii) Ligand (3) [C(21)—(30), N(7)—(9)]

C–C	1·36(2)	C–N (bridge)	1·39(2)
C–N (pyridyl)	1·36(2)		

(iv) Ligand (4) [C(31)—(40), N(10)—(12)]

C–C	1·37(2)	C–N (bridge)	1·41(2)
C–N (pyridyl)	1·31(2)		

The deviation from trigonal-bipyramidal geometry manifests itself primarily in angular distortions about the equator. Although the I(1)–Cu(1)–N(3) angle is normal at 119·8° (124·7°), I(1)–Cu(1)–N(4) is 137·9° (135·5°) reducing the N(3)–Cu(1)–N(4) angle to 102·3° (99·8°).

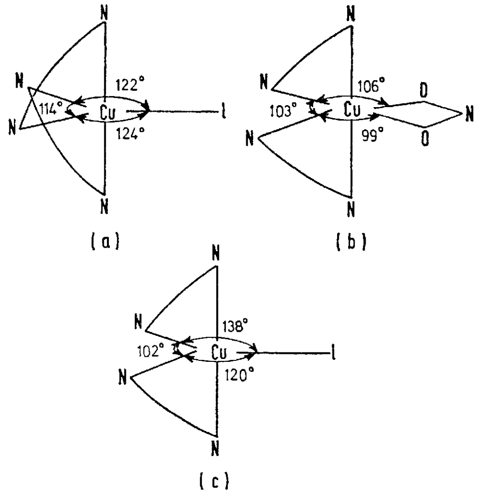
In the amine ligand itself, some mean distances are: C–N (pyridine ring) 1·34, C–N (bridge) 1·39, and C–C 1·37 Å. The individual pyridine rings are planar, within standard deviations. The ligands themselves are bent considerably about the bridging nitrogen atoms with dihedral angles between the pyridine rings of 33 (33) and 37 (40). In $CuL_2(ClO_4)_2$ the dihedral angle was found to be 9·6°; the variation in this angle illustrates the flexibility of the ligand. The six-membered chelate rings formed by the copper and the bidentate ligands are all in a boat configuration, with the copper atom 0·78 Å below the plane of the other four atoms of the ring, and the bridging nitrogen 0·29 Å below this plane. The shorter non-bonded distances between atoms in the same co-ordination species are listed in Table 5, the minimum distance being 2·80 Å between H(10) and H(20).

TABLE 5

Non-bonded intramolecular distances (Å)

N(1) ··· N(3)	2·80	N(7) ··· N(9)	2·87
H(10) ··· H(20)	2·80	H(30) ··· H(40)	2·93
N(1) ··· N(4)	2·99	N(7) ··· N(10)	2·93
N(3) ··· N(6)	3·08	N(9) ··· N(12)	2·99
H(1) ··· H(11)	3·10	H(21) ··· H(31)	3·00
Cu(1) ··· N(2)	3·13	Cu(2) ··· N(8)	3·15
Cu(1) ··· N(5)	3·19	Cu(2) ··· N(11)	3·18
I(1) ··· N(6)	3·28	I(2) ··· N(12)	3·33
I(1) ··· N(1)	3·29	I(2) ··· N(7)	3·33
N(3) ··· N(4)	3·33	N(9) ··· N(10)	3·13
I(1) ··· N(3)	4·15	I(2) ··· N(9)	4·23
I(1) ··· N(4)	4·42	I(2) ··· N(10)	4·41

The non-bonded iodide is 6·78 from Cu(1) and 5·52 Å from Cu(2) while the chlorine of the perchlorate group is 5·56 from Cu(1) and 7·35 Å from Cu(2). There are no unusually short contacts between the two chromophores, the shortest being 2·34 Å between H(14) and H(28).



(a) (b) (c)

FIGURE 3 Comparison of co-ordination geometries of similar 2,2′-bipyridyl (bipy) complexes with that of the 2,2′-bipyridylamine (bipyam) complex; a, $[Cu(bipy)_2I]I$; b, $[Cu(bipy)_2(NO_2)]NO_3$; and c, $[Cu(bipyam)I]_2IClO_4$

There are no apparent steric effects which would lead to the nearly identical distortions from the trigonal-bipyramidal geometry displayed by both chromophores; electronic effects must therefore be considered. Hathaway and his co-workers have suggested that in the similar compound iodobis-(2,2′bipyridyl)copper(II)

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iodide,[15] the bound iodide may be occupying two co-ordination sites of a *cis*-distorted octahedron, thereby explaining the reduction of the equatorial N–Cu–N bond angle from 120 to 114°.[16] This *cis*-distorted geometry has been observed in nitritobis-(2,2'bipyridyl)-copper(II) nitrate where the angle is 102°.[17]

Figure 3 shows schematic drawings of the co-ordination geometries of the aforementioned 2,2′-bipyridyl complexes together with that of the 2,2′-bipyridylamine complex. The equatorial N–Cu–N bond angles of the nitrito-complex and the 2,2′-bipyridylamine iodide complex are similarly reduced.

An alternative explanation for the equatorial angular asymmetry, as well as the reduction of the equatorial N–Cu–N bond angle, would be that the trigonal bipyramid is distorting toward a square pyramid with N(3) at the apex. This view is supported by the large N(4)–Cu(1)–I(1) angle, while all but the N(3)–Cu(1)–I(1) angles involving N(3) are within 12° of the 90° angle expected for the square pyramid. McWhinnie had predicted, on the basis of electronic spectra, a square pyramid with the iodide at the apex for iodobis-(2,2′-bipyridylamine)copper(II) iodide perchlorate.[4]

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[17] I. M. Proctor and F. S. Stephens, *J. Chem. Soc.* (*A*), 1969, 1248.