Crystal and Molecular Structure of Tris-(2,2′-bipyridyl)copper(II) Perchlorate

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The crystal and molecular structure of the title compound has been determined from three-dimensional single crystal X-ray diffraction data, collected by counter techniques. Crystals are triclinic, space group $P\bar{1}$, with $Z = 2$ in a unit cell of dimensions: $a = 12{\cdot}673(17)$, $b = 18{\cdot}440(21)$, $c = 7{\cdot}937(7)$ Å, $\alpha = 90{\cdot}37(14)°$, $\beta = 120{\cdot}56(13)°$, and $\gamma = 98{\cdot}80(11)°$. The structure was refined by full-matrix least-squares methods on alternate sets of atoms to R 0·091 for 3972 observed reflections. The monomeric complex ions exhibit a distorted octahedral configuration, with unequal distortions of the axial Cu–N bonds. Mean distances: Cu–N(eq) is 2·031(6), Cu–N(ax) 2·226(7), and 2·450(7) Å.

SOME recent X-ray structural investigations of copper(II) complexes have shown that it is possible for the copper(II) ion to occupy a site which requires higher symmetry than is allowed by the Jahn–Teller theorem. For example, the complex ion $[Cu(en)_3]^{2+}$ (en = ethylenediamine) is situated at sites requiring 32 (D_3) symmetry in the sulphate salt.[1] The same result for the site-symmetry at the copper(II) ion has been found for tris(octamethylpyrophosphoramide)copper(II) perchlorate.[2] In the first case, analysis of the anisotropic thermal parameters of the ligand atoms was said to support either a dynamic distortion of the co-ordination octahedron or random trapping of statically distorted complex ions, while in the second case, no such effect was found. Several studies on potassium lead hexanitrocuprate(II) have also found six identical Cu–N bonds in the CuN_6 co-ordination polyhedron.[3] A similar result is found for the complex $Mn(acac)_3$ (acac = acetylacetonate), where all six Mn–O bonds are of equal length (though bond angle distortions are present).[4] It has even been suggested that this type of apparent Jahn–Teller violation is general for tris-(bidentate) chelate systems of copper(II).[5] However, a recent structural report on the tris(hexafluoroacetylacetonato)cuprate(II) anion has shown the presence of a static distortion in the metal–ligand bond distances.[6] In view of this situation, further structural information on complexes of this type was thought to be desirable.

The most thoroughly investigated complexes of the type $[Cu(AA)_3]^{2+}$ (where AA = a bidentate ligand) are the complex ions $[Cu(bipy)_3]^{2+}$ and $[Cu(phen)_3]^{2+}$ (bipy = 2,2′-bipyridyl and phen = 1,10-phenanthroline). Single-crystal polarized electronic spectra of the bromide and sulphate salts have indicated that the complex ion $[Cu(bipy)_3]^{2+}$ possesses trigonal symmetry, and that the strong Jahn–Teller distortion forces may be overcome by the rigidity of the ligand.[7] An e.s.r. study of $[Cu(phen)_3]^{2+}$ in a single crystal of $[Zn(phen)_3](NO_3)_2,2H_2O$ showed significant anisotropy of the g tensor at liquid nitrogen temperatures, and nearly isotropic behaviour at 350 K, interpretable in terms of a dynamic Jahn–Teller effect.[8] Further e.s.r. and ^{17}O n.m.r. studies on aqueous and alcoholic solutions of the copper(II) ion and 2,2′-bipyridyl gave evidence for the existence of a dynamic Jahn–Teller effect for the complex ion $[Cu(bipy)_3]^{2+}$.[9]

Thus, these studies agree that the tris-(2,2′-bipyridyl)- and tris-(1,10-phenanthroline)-copper(II) complexes should appear essentially non-distorted at room temperature, with strong dynamic Jahn–Teller effects operative. The results of an X-ray structural investigation of these compounds should be similar to the results quoted earlier for other complex ions of the type $[Cu(AA)_3]^{2+}$. Furthermore, it was hoped that the structural evidence from the X-ray experiments would indicate the presence of the dynamic Jahn–Teller distortion inferred from the e.s.r. results as a heightened thermal motion of the nitrogen atoms, especially along the Cu–N bond. Consequently, the study of the structure of $[Cu(bipy)_3](ClO_4)_2$ was undertaken.

EXPERIMENTAL

Crystal Data.—$C_{30}H_{24}Cl_2CuN_6O_8$, $M = 731{\cdot}0$, Triclinic, $a = 12{\cdot}673(17)$, $b = 18{\cdot}440(21)$, $c = 7{\cdot}937(7)$ Å, $\alpha = 90{\cdot}37(14)°$, $\beta = 120{\cdot}56(13)°$, $\gamma = 98{\cdot}80(11)°$, $U = 1572{\cdot}9$ Å^3,‡ $Z = 2$, $D_c = 1{\cdot}55$, $F(000) = 750$. Space group $P\bar{1}$ (No. 2). Mo-$K_{\alpha 1}$ radiation, $\lambda = 0{\cdot}70926$ Å; μ(Mo-K_α) = 9·41 cm^{-1}.

Crystals were grown from aqueous solutions of copper(II) perchlorate with a 3·5-fold excess of 2,2′-bipyridyl, as long, dark blue columns, which were easily cleaved across the long dimension to give crystals of suitable length.

Preliminary oscillation and Weissenberg photographs about three independent axes indicated the space group and axes were chosen in accord with the conventions in ref. 11. The crystal chosen for data collection was mounted along

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‡ *Cf. U* 1720 Å^3 for two formula units of the slightly bulkier tris-(1,10-phenanthroline)copper(II) perchlorate.[10]

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the *c* axis, and placed on a Siemens automatic four-circle diffractometer, with the *c* axis nearly coincident with the ϕ axis of the instrument. Values of 2θ for 21 high-order reflections ($2\theta > 28°$) were measured, and the unit-cell constants calculated from them by a least-squares procedure.

Data were collected by the θ—2θ technique with a five-value scan. The scan range was 0·30° for the bottom half of the scan, and $(0{\cdot}30 + 0{\cdot}15 \tan \theta_{\text{max.}})°$ for the upper half of the scan, where $\theta_{\text{max.}}$ is the peak maximum position calculated by least-squares techniques from the measured positions of eight high-order reflections. The minimum scan rate was 2·5 deg. min^{-1}, and automatically coupled attenuators made coincidence losses negligible. The scintillation counter aperture was 3·0 mm in diameter. The intensities of two reference reflections did not vary during the data collection.

The data set comprised all reflections in a unique half of the sphere of reflection, with values of θ from 1—25°. 5566 Reflections were obtained of which 3972 (71·4%) had $I > 2\sigma(I)$ and were considered observed. The standard deviation in the intensity is defined as the square root of the total number of counts during the five-value measurement. For those reflections which were unobserved by this definition, the measured intensity was replaced by twice the standard deviation, with a label to indicate that these reflections were unobserved.

Lorentz and polarization corrections were applied. The dimensions of the crystal used for data collection, given as the distance (mm) from the face concerned to the point taken as the crystal centre, were: 0·155 [(001) and $(00\bar{1})$], 0·059 [(100) and $(\bar{1}00)$], 0·072 [(120), $(1\bar{2}0)$, $(\bar{1}\bar{2}0)$, and $(\bar{1}20)$], and 0·074 [(010) and $(0\bar{1}0)$]. An absorption correction, based on the Gaussian grid technique,[12] was applied to the data. With a $4 \times 4 \times 6$ grid, values of the reciprocal transmission coefficient ranged from 1·10 to 1·14.

Calculations. Several of the computer programs used in this study were made available to the Chemical Institute, University of Bergen, by the Weizmann Institute of Science, Rehovoth, Israel, and modified for use on the University of Bergen's IBM 360 50H computer. Programs from this library used in the present work included CELL (least-squares calculation of cell parameters), BDLS (structure-factor calculation and full-matrix refinement), DIAN and INTA (calculation of intra- and inter-molecular atomic distances and angles), and ORTHO (vibration tensors for anisotropically vibrating atoms). Local programs written at the University of Bergen by K. Åse, were DAT 1 (Lorentz polarization correction and data reduction for diffractometer data), ABCD (absorption correction), and ASEN (calculation of Fourier maps). Figures were drawn using the Oak Ridge thermal ellipsoid plotting program ORTEP at the University of Leicester.

Solution and Refinement.—The position of the copper(II) ion was assigned from the highest non-origin peak in the initial Patterson map. The positions of all atoms were obtained from a series of Fourier syntheses phased by the atoms in known positions. Scattering factors for copper(II) were taken from ref. 13, and for chloride ion, atomic nitrogen, carbon, and oxygen, from ref. 14; for copper corrections for anomalous dispersion, $\Delta f'$ and $\Delta f''$, were taken from ref. 15. The positions of the four oxygen atoms O(5)—(8) surrounding Cl(2) gave satisfactory bond lengths and angles, whereas the Cl(1) perchlorate ion appeared seriously distorted, and O(2)—(4) would not refine satisfactorily. Despite this, *R* was 0·14. As O(1) was refining, the most likely form of disorder was felt to be rotation about the Cl(1)–O(1) bond axis. A Fourier map constructed by use of all atoms except the unsatisfactory oxygen atoms O(2)—(4) indicated a solution might be obtained by putting in two sets of atoms, each with only one-half occupancy. After this had been done, all atoms were refining satisfactorily. The equality of the final isotropic thermal parameters obtained for O(2)—(4) and O(2′)—(4′) (see Table 1) indicates that these occupancy factors are very close to being correct.

TABLE 1

Atomic co-ordinates (fractional) and thermal parameters with standard deviations in parentheses

Atom	x	y	z	U *
Cu$^{\text{II}}$	0·23592(8)	0·23971(5)	0·22795(14)	
N(1)	0·3553(5)	0·3116(3)	0·4703(8)	
N(2)	0·1052(5)	0·1916(3)	−0·0453(8)	
N(3)	0·3733(5)	0·2036(3)	0·2090(9)	
N(4)	0·1110(5)	0·2788(3)	0·2764(9)	
N(5)	0·1990(6)	0·3379(3)	0·0085(9)	
N(6)	0·2654(5)	0·1435(3)	0·4045(9)	
C(1)	0·4819(8)	0·3195(5)	0·5705(12)	0·058(2)
C(2)	0·5563(9)	0·3666(5)	0·7460(14)	0·071(3)
C(3)	0·4965(9)	0·4048(5)	0·8122(14)	0·079(3)
C(4)	0·3668(9)	0·3978(5)	0·7092(13)	0·069(3)
C(5)	0·2995(7)	0·3491(4)	0·5361(11)	0·048(2)
C(6)	0·1631(7)	0·3367(4)	0·4157(11)	0·049(2)
C(7)	0·0902(9)	0·3827(5)	0·4403(13)	0·069(3)
C(8)	−0·0395(9)	0·3628(5)	0·3177(14)	0·075(3)
C(9)	−0·0938(8)	0·3018(5)	0·1826(13)	0·068(3)
C(10)	−0·0150(8)	0·2597(5)	0·1635(12)	0·057(2)
C(11)	0·0789(7)	0·1170(5)	−0·0824(12)	0·053(2)
C(12)	−0·0126(8)	0·0832(5)	−0·2744(13)	0·066(3)
C(13)	−0·0746(8)	0·1277(5)	−0·4209(13)	0·071(3)
C(14)	−0·0480(8)	0·2039(5)	−0·3808(13)	0·065(2)
C(15)	0·0443(7)	0·2335(4)	−0·1881(12)	0·050(2)
C(16)	0·0812(7)	0·3152(4)	−0·1332(12)	0·049(2)
C(17)	−0·0054(8)	0·3613(5)	−0·2221(12)	0·061(2)
C(18)	0·0350(9)	0·4375(5)	−0·1585(14)	0·074(3)
C(19)	0·1607(8)	0·4626(5)	−0·0113(13)	0·067(3)
C(20)	0·2391(8)	0·4104(5)	0·0691(12)	0·060(2)
C(21)	0·4108(8)	0·2319(5)	0·0889(13)	0·064(2)
C(22)	0·5114(9)	0·2069(5)	0·0842(14)	0·078(3)
C(23)	0·5663(9)	0·1550(5)	0·2118(15)	0·080(3)
C(24)	0·5292(9)	0·1263(5)	0·3337(14)	0·077(3)
C(25)	0·4266(8)	0·1524(5)	0·3271(12)	0·053(2)
C(26)	0·3755(7)	0·1239(4)	0·4500(12)	0·051(2)
C(27)	0·4328(8)	0·0788(5)	0·6035(13)	0·067(3)
C(28)	0·3759(9)	0·0538(5)	0·7046(14)	0·074(3)
C(29)	0·2607(9)	0·0727(5)	0·6565(14)	0·074(3)
C(30)	0·2099(8)	0·1188(5)	0·5045(13)	0·063(2)
Cl(1)	0·2256(2)	0·9285(1)	0·0278(3)	
Cl(2)	0·3214(2)	0·5883(1)	0·6161(4)	
O(1)	0·0972(7)	0·9278(4)	−0·1148(11)	0·111(3)
O(2) †	0·3113(14)	0·9596(9)	−0·0376(23)	0·109(5)
O(3) †	0·2553(14)	0·8560(9)	0·0826(23)	0·101(5)
O(4) †	0·2572(15)	0·9727(9)	0·2014(24)	0·114(5)
O(2′) †	0·2991(16)	1·0013(10)	0·0891(26)	0·124(6)
O(3′) †	0·2623(15)	0·8888(10)	−0·0741(25)	0·119(5)
O(4′) †	0·2304(13)	0·8890(9)	0·1855(23)	0·100(5)
O(5)	0·2617(6)	0·5534(4)	0·7176(10)	0·094(2)
O(6)	0·2700(8)	0·5448(5)	0·4337(13)	0·122(3)
O(7)	0·2995(7)	0·6615(5)	0·5820(12)	0·116(3)
O(8)	0·4513(6)	0·5888(4)	0·7299(10)	0·086(2)

* Isotropic thermal parameters (Å^2) in the form $\exp[-8\pi^2 U(\sin^2\theta/\lambda^2)]$. † These atoms were allocated an 0·5 occupancy factor.

The final refinement steps were carried out in alternate full-matrix cycles, because of program limitations. In one

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[14] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

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cycle the overall scale factor, together with the positions and thermal parameters of the copper(II) ion, six nitrogen atoms, thirty carbon atoms, and two chlorine atoms, were refined. Thermal parameters for copper(II), nitrogen, and chlorine were anisotropic, with all others isotropic. The next cycle substituted the eleven oxygen atoms for the thirty carbon atoms in the refinement. After only two repetitions of this process, R had reached its final value of 0·091 (observed reflections only, 0·093 for all reflections). The program BDLS minimizes the function $R' = \Sigma(|F_o| - KW|F_c|)^2$, where K is the scale factor and W is the weight. The weight, W, in this refinement was set equal to $1/\sigma^2(F_o)$, where $\sigma(F_o)$, the standard deviation in the observed structure factor, is evaluated from considerations of counting statistics. On the last pair of cycles, all positional shifts for Cu^{II}, Cl, and N were less than $0{\cdot}1\sigma$ for the parameters involved, as were those for most of the carbon and oxygen atoms. A few carbon and oxygen atoms had shifts of up to $0{\cdot}3\sigma$ of their positional parameters. Examination of the observed and calculated structure factors of the strongest reflections indicated that extinction was not serious for this crystal, and the refinement was terminated at this point without any attempt to locate hydrogen atoms. A final difference Fourier map showed no peak higher than 0·8 eÅ^{-3}, and no depression lower than −0·7 eÅ^{-3}. Observed and calculated structure factors are listed in Supplementary Publication No. 20469 (4 pp., 1 microfiche).* Atomic positions and isotropic thermal parameters are listed in Table 1, and anisotropic thermal parameters in Table 2.

TABLE 2

Anisotropic thermal parameters (Å^2) * with estimated standard deviations in parentheses

	10^4U_{11}	10^4U_{22}	10^4U_{33}	10^4U_{12}	10^4U_{23}	10^4U_{13}
Cu^{II}	332(5)	473(6)	412(6)	92(4)	−39(4)	128(4)
N(1)	489(39)	415(39)	452(40)	112(31)	53(31)	219(33)
N(2)	400(37)	443(39)	456(39)	105(30)	35(31)	193(32)
N(3)	430(39)	557(43)	435(40)	59(33)	−138(33)	136(32)
N(4)	418(38)	459(40)	497(40)	66(31)	83(32)	214(32)
N(5)	432(39)	571(45)	504(42)	48(34)	31(34)	159(33)
N(6)	403(38)	565(44)	575(44)	163(33)	34(35)	196(34)
Cl(1)	541(14)	598(15)	546(14)	125(12)	70(12)	260(12)
Cl(2)	445(14)	723(17)	667(16)	81(12)	55(13)	134(12)

* In the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots)]$.

RESULTS AND DISCUSSION

Bond lengths and angles for all bonds involving the copper(II) ion are in Table 3; those within the ligands and the perchlorate ions are in Table 4 (standard deviations in these Tables are calculated from those of Table 1 without regard to co-ordinate covariance or to standard deviations in the unit-cell dimensions). Figure 1 shows the co-ordination geometry about the copper(II) ion, with the six co-ordinating nitrogen atoms and the carbon atoms which link together the two nitrogen atoms of each bipyridyl ligand. Figure 2 shows the labelling of the individual ligand ring systems.

The co-ordination geometry about the copper(II) ion is not that expected from the earlier spectroscopic studies. Table 3 shows that there are four Cu–N bonds

TABLE 3

Bond lengths (Å) and angles (°) involving Cu^{II} with standard deviations in parentheses

(*a*) Bond lengths

Cu–N(1)	2·035(5)	Cu–N(4)	2·034(8)
Cu–N(2)	2·026(5)	Cu–N(5)	2·450(7)
Cu–N(3)	2·030(8)	Cu–N(6)	2·226(7)

(*b*) Bond angles

N(1)–Cu–N(4)	80·4(3)	N(5)–Cu–N(6)	174·8(2)
N(2)–Cu–N(5)	73·9(2)	Cu–N(1)–C(1)	125·3(6)
N(3)–Cu–N(6)	78·2(3)	Cu–N(1)–C(5)	114·2(4)
N(1)–Cu–N(3)	94·4(3)	C(10)–N(4)–Cu	125·8(6)
N(1)–Cu–N(5)	92·2(2)	C(6)–N(4)–Cu	113·3(6)
N(1)–Cu–N(6)	92·4(2)	Cu–N(2)–C(11)	120·1(5)
N(1)–Cu–N(2)	165·6(2)	Cu–N(2)–C(15)	119·8(5)
N(2)–Cu–N(3)	91·6(3)	C(20)–N(5)–Cu	124·6(5)
N(2)–Cu–N(4)	94·0(3)	C(16)–N(5)–Cu	102·4(5)
N(2)–Cu–N(6)	101·6(2)	Cu–N(3)–C(21)	121·1(6)
N(3)–Cu–N(4)	174·2(2)	Cu–N(3)–C(25)	116·4(7)
N(3)–Cu–N(5)	99·1(3)	C(30)–N(6)–Cu	128·4(6)
N(4)–Cu–N(5)	83·6(3)	C(26)–N(6)–Cu	109·6(6)
N(4)–Cu–N(6)	99·5(3)		

TABLE 4

Bond lengths (Å) and angles (°) in the ligand rings and perchlorate ions with estimated standard deviations in parentheses

(*a*) Bond lengths (i) N(1),N(4) system

N(1)–C(1)	1·362(11)	C(6)–N(4)	1·351(10)
C(1)–C(2)	1·407(12)	C(6)–C(7)	1·425(16)
C(2)–C(3)	1·383(19)	C(7)–C(8)	1·403(12)
C(3)–C(4)	1·398(14)	C(8)–C(9)	1·373(13)
C(4)–C(5)	1·407(11)	C(9)–C(10)	1·419(16)
C(5)–N(1)	1·332(13)	C(10)–N(4)	1·358(10)
C(5)–C(6)	1·466(11)		

(ii) N(2),N(5) system

N(2)–C(11)	1·358(10)	C(16)–N(5)	1·328(8)
C(11)–C(12)	1·424(10)	C(16)–C(17)	1·389(12)
C(12)–C(13)	1·387(13)	C(17)–C(18)	1·415(12)
C(13)–C(14)	1·389(13)	C(18)–C(19)	1·411(11)
C(14)–C(15)	1·407(10)	C(19)–C(20)	1·404(13)
C(15)–N(2)	1·334(10)	C(20)–N(5)	1·347(11)
C(15)–C(16)	1·499(11)		

(iii) N(3),N(6) system

N(3)–C(21)	1·341(14)	C(25)–C(26)	1·481(16)
C(21)–C(22)	1·438(18)	C(26)–N(6)	1·361(12)
C(22)–C(23)	1·388(14)	C(26)–C(27)	1·414(12)
C(23)–C(24)	1·352(18)	C(27)–C(28)	1·367(18)
C(24)–C(25)	1·431(16)	C(28)–C(29)	1·409(16)
C(25)–N(3)	1·337(10)	C(29)–C(30)	1·409(13)
		C(30)–N(6)	1·344(15)

(iv) Perchlorate containing Cl(1)

Cl(1)–O(1)	1·432(8)	Cl(1)–O(2′)	1·434(17)
Cl(1)–O(2)	1·471(21)	Cl(1)–O(3′)	1·373(23)
Cl(1)–O(3)	1·452(16)	Cl(1)–O(4′)	1·431(18)
Cl(1)–O(4)	1·431(19)		

(v) Perchlorate containing Cl(2)

Cl(2)–O(5)	1·454(9)	Cl(2)–O(7)	1·420(9)
Cl(2)–O(6)	1·424(9)	Cl(2)–O(8)	1·417(7)

(b) Bond angles (i) N(1),N(4) system

C(1)–N(1)–C(5)	120·3(6)	C(5)–C(6)–C(7)	122·9(7)
N(1)–C(1)–C(2)	121·1(10)	C(5)–C(6)–N(4)	115·0(8)
C(1)–C(2)–C(3)	117·7(8)	C(7)–C(6)–N(4)	117·6(7)
C(2)–C(3)–C(4)	121·7(8)	C(6)–C(7)–C(8)	116·5(8)
C(3)–C(4)–C(5)	116·9(11)	C(7)–C(8)–C(9)	121·9(11)
C(4)–C(5)–N(1)	122·3(8)	C(8)–C(9)–C(10)	118·3(8)
C(4)–C(5)–C(6)	122·1(10)	C(9)–C(10)–N(4)	121·1(7)
N(1)–C(5)–C(6)	115·6(7)	C(10)–N(4)–C(6)	120·0(8)

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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. supplied in full size copies.)

TABLE 4 (*Continued*)

(ii) N(2),N(5) system			
C(11)–N(2)–C(15)	120·2(6)	C(15)–C(16)–C(17)	120·8(6)
N(2)–C(11)–C(12)	120·2(7)	C(15)–C(16)–N(5)	114·8(7)
C(11)–C(12)–C(13)	118·8(8)	N(5)–C(16)–C(17)	124·4(7)
C(12)–C(13)–C(14)	120·6(7)	C(16)–C(17)–C(18)	117·7(7)
C(13)–C(14)–C(15)	117·5(8)	C(17)–C(18)–C(19)	118·4(9)
C(14)–C(15)–N(2)	122·8(7)	C(18)–C(19)–C(20)	118·5(8)
C(14)–C(15)–C(16)	121·0(7)	C(19)–C(20)–N(5)	122·4(6)
N(2)–C(15)–C(16)	116·1(6)	C(20)–N(5)–C(16)	118·6(7)
(iii) N(3),N(6) system			
C(21)–N(3)–C(25)	122·4(7)	C(25)–C(26)–C(27)	124·3(9)
N(3)–C(21)–C(22)	119·7(8)	C(25)–C(26)–N(6)	115·1(7)
C(21)–C(22)–C(23)	116·4(12)	N(6)–C(26)–C(27)	120·6(10)
C(22)–C(23)–C(24)	124·2(12)	C(26)–C(27)–C(28)	119·6(10)
C(23)–C(24)–C(25)	116·4(9)	C(27)–C(28)–C(29)	120·3(9)
C(24)–C(25)–N(3)	120·9(10)	C(28)–C(29)–C(30)	117·1(11)
C(24)–C(25)–C(26)	121·5(8)	C(29)–C(30)–N(6)	122·8(10)
N(3)–C(25)–C(26)	117·6(9)	C(30)–N(6)–C(26)	119·6(7)
(iv) Cl(1) Perchlorate			
O(1)–Cl(1)–O(2)	113·6(7)	O(3)–Cl(1)–O(4)	108·1(10)
O(1)–Cl(1)–O(3)	114·2(6)	O(3)–Cl(1)–O(2′)	132·9(9)
O(1)–Cl(1)–O(4)	108·2(8)	O(3)–Cl(1)–O(3′)	60·4(12)
O(1)–Cl(1)–O(2′)	112·9(8)	O(3)–Cl(1)–O(4′)	49·4(11)
O(1)–Cl(1)–O(3′)	102·3(7)	O(4)–Cl(1)–O(2′)	55·1(12)
O(1)–Cl(1)–O(4′)	107·6(7)	O(4)–Cl(1)–O(3′)	149·3(9)
O(2)–Cl(1)–O(3)	104·7(11)	O(4)–Cl(1)–O(4′)	64·0(10)
O(2)–Cl(1)–O(4)	107·7(10)	O(2′)–Cl(1)–O(3′)	109·5(13)
O(2)–Cl(1)–O(2′)	55·2(12)	O(2′)–Cl(1)–O(4′)	114·1(10)
O(2)–Cl(1)–O(3′)	55·1(11)	O(3′)–Cl(1)–O(4′)	109·7(11)
O(2)–Cl(1)–O(4′)	138·2(9)		
(v) Cl(2) Perchlorate			
O(5)–Cl(2)–O(6)	107·0(5)	O(6)–Cl(2)–O(7)	110·0(5)
O(5)–Cl(2)–O(7)	111·2(6)	O(6)–Cl(2)–O(8)	109·4(6)
O(5)–Cl(2)–O(8)	109·4(4)	O(7)–Cl(2)–O(8)	109·8(4)

of equal length, mean 2·031 Å. The remaining two Cu–N bonds are of unequal length: Cu$^{\text{II}}$–N(5) 2·450 and Cu$^{\text{II}}$–N(6) 2·226 Å. This inequality in the long bond lengths is also unexpected, as many complexes of copper(II) which exhibit a static Jahn–Teller distortion of this type have two long bonds of equal length.

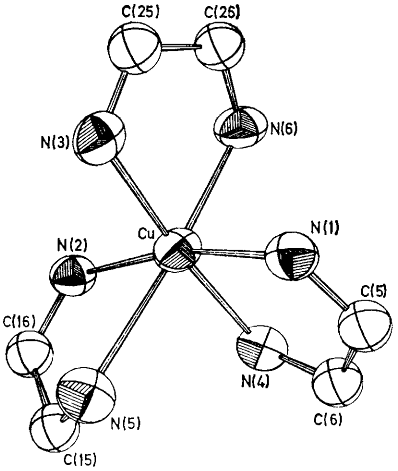

FIGURE 1 The co-ordination geometry about Cu$^{\text{II}}$; only the two nitrogen atoms and connecting carbon atoms of each ligand are shown

The whole of the co-ordination geometry for Cu(bipy)$_3^{2+}$ represents a considerable departure from the D_3 symmetry found for complex ions such as Cu(en)$_3^{2+}$. Apart from the bond-length distortions, large deviations in the expected bond angles N–Cu$^{\text{II}}$–N′ are also found.

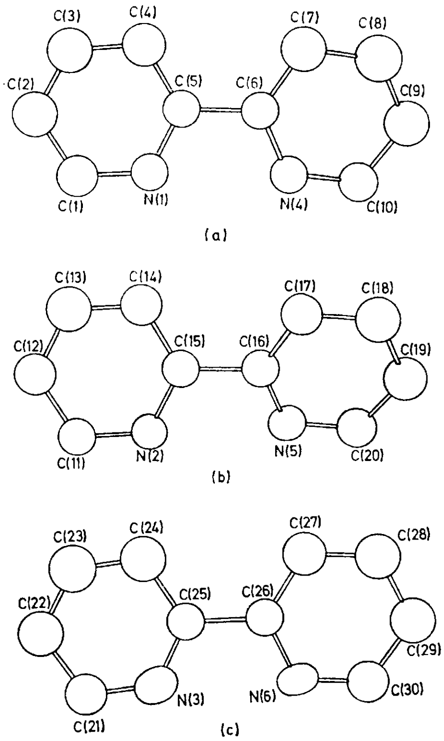

FIGURE 2 The labelling of the bipyridyl ligands

As the only other tris(bidentate) complex of copper(II) involving three identical ligands which co-ordinate only through nitrogen, the non-distorted complex ion Cu(en)$_3^{2+}$ may serve as a basis for comparison with the results of this study. As mentioned earlier, this ion has been found to possess D_3 symmetry,[1] which, although a trigonal distortion of O_h, is not sufficient to remove the Jahn–Teller degeneracy.[7] In Cu(en)$_3^{2+}$, the six equal Cu–N bond lengths were 2·150(2) Å. The mean of the six Cu–N distances in Cu(bipy)$_3^{2+}$ is 2·133(7) Å. In the tris(ethylenediamine) complex ion, the N–Cu–N′ angle for two nitrogens of the same ligand molecule is 80·9°. In the bipyridyl complex, the angle N(1)–Cu–N(4) involving the ligand molecule with two nitrogen atoms at equal distances from the copper(II) ion is 80·4(3)°. The angle N(3)–Cu–N(6), which involves an intermediate lengthening of one of the Cu–N bonds, is significantly less at 78·2(3)°, and for the angle N(2)–Cu–N(5), involving the very long Cu–N(5) bond, the angle is further decreased to 73·9(2)°. Other angles of the type N–Cu–N′ vary (Table 3) for nitrogen atoms mutually *cis* from 83·6(3) to 101·6(2)°, mean 94·5°. In the case of Cu(en)$_3^{2+}$, angles of this type were either 92·8° for atoms related by the three-fold rotation axis, or 94·2° for the other *cis*-angles. The angles N–Cu–N′ for mutually *trans* nitrogen atoms range from 165·6(2) to 174·8(2)°.

Results from other structural studies involving the bipyridyl ligand and the copper(II) ion may also be compared. In bisnitrito-(2,2′-bipyridyl)copper(II), Cu–N is 1·98 Å, the angle N–Cu–N′ being 81·3°;[16] Cu–N bond lengths are 1·96—2·10 Å with N–Cu–N′ 82° in $[Cu(bipy)_2I]I$,[17] Cu–N 1·998 Å in $Cu(hfacac)_2(bipy)$,[18] and Cu–N 1·98—2·10 Å and N–Cu–N′ 81·1 and 80·3° in $[Cu(bipy)_2(ONO)]NO_3$.[19]

The configurations of the ligands themselves are as expected from earlier results on uncomplexed 2,2′-bipyridyl,[20] which show mean C–N bond lengths to be 1·36 Å, and mean C–C bond lengths in the rings to be 1·39 Å. The C–C bond length between the rings is 1·50 Å. In the present study the mean C–N bond length is 1·35(1) Å, and mean C–C bond length in the rings 1·40(2) Å. The largest spread of values and the largest standard deviations are found in the N(3),N(6) ligand system. Inter-ring C–C bond lengths average 1·48(2) Å.

Best least-squares planes through selected sets of atoms were calculated, with the copper(II) ion given a weight of five relative to carbon and nitrogen atoms. The individual pyridine rings are satisfactorily planar, while the bipyridyl ligands are not. The dihedral angle between the pyridine rings of the N(1),N(4) ligand is 13·6° and for the N(3),N(6) ligand is 11·2°. The N(2),N(5) ligand, with the abnormally long Cu–N(5) distance, exhibits a dihedral angle between the two pyridine rings of 31·3°. The first two values must be considered normal in view of other results from copper(II)–bipyridyl systems of *ca.* 11°.[17,19] Planar bipyridyl ligands are also found in copper(II) systems.[16,17] It appears from this that the Cu–N(5) bond has been abnormally lengthened and the N(5) pyridine group twisted away from the copper(II) ion. For the N(1),N(4) ligand system as a whole, the maximum deviation of a ring atom from the best plane through the N(1) pyridine ring is 0·005 Å, with the copper(II) ion 0·15 Å out of this plane, with corresponding values of 0·02 and −0·45 Å for the N(4) half of this ligand. In the N(2),N(5) ligand system, there are corresponding values of 0·004 Å maximum deviation and 0·001 Å copper displacement for the N(2) ring, and 0·009 and 1·52 Å for the N(5) ring; in the N(3),N(6) system there are values of 0·010 Å maximum deviation and 0·09 Å copper displacement for the N(3) ring and 0·008 and 0·61 Å for the N(6) ring. The least-squares best planes through copper and each bipyridyl ligand were also calculated, and the dihedral angles between these planes were 119° between the system involving Cu and the N(1),N(4) ring system and the Cu–N(2)–N(5) system, 96° between the Cu–N(1)–N(4) system and the Cu–N(3)–N(6) system, and 87° between the Cu–N(2)–N(5) system and the Cu–N(3)–N(6) system.

The results for the perchlorate anions are also satisfactory, despite the disorder found to be present in one of the ions. The mean for all the Cl–O bond lengths is 1·43 Å, and for all tetrahedral angles 109·4° for the disordered Cl(1) perchlorate ion and 109·5° for the Cl(2) perchlorate ion. The bond length values are to be compared with those for the Cl–O bond in the perchlorate ion in $HClO_4,H_2O$ of 1·43 Å.[21]

TABLE 5

Root-mean-square displacements (Å) on the principal axes of thermal ellipsoids for anisotropically refined atoms

Atom	Axis (1)	Axis (2)	Axis (3)
Cu^{II}	0·17	0·20	0·24
N(1)	0·20	0·21	0·23
N(2)	0·19	0·21	0·23
N(3)	0·18	0·22	0·28
N(4)	0·20	0·21	0·24
N(5)	0·20	0·24	0·26
N(6)	0·19	0·23	0·26

The root-mean-square displacements along the principal axes of the thermal ellipsoids of the copper(II) ion and the six co-ordinating nitrogen atoms are given in Table 5. The orientations of these ellipsoids can be seen in Figure 1, and there is little evidence for any abnormal vibration along the directions of the copper–nitrogen bonds, such as would have been expected had there been a tendency toward a dynamic Jahn–Teller distortion, as has been suggested for this complex in earlier work.[7,9] Thus, it would seem unlikely that the static distortion found in the present work would be converted to a purely dynamic Jahn–Teller distortion at slightly higher temperatures.

There is no apparent reason for the inequality of the bond lengths for the long Cu–N bonds. A calculation designed to find significant intra- and inter-ionic contacts of the van der Waals type failed to reveal any crystal packing or steric effects which could explain the unusual distortion present in this complex. Although crystal packing must remain the most likely source for the inequality of the long bond lengths, the previously mentioned near equality of the average Cu–N bond length in this complex [2·133(7) Å] and in the tris(ethylenediamine)-complex [2·150(2) Å] is very striking. Also, the two long Cu–N bonds in $[Cu(phen)_3]^{2+}$, which are of equal length, are 2·33(1) Å,[10] and the mean of the two long bonds in $[Cu(bipy)_3]^{2+}$ (Table 3) is 2·338(7) Å. This suggests that the extent of the unequal distortion of bond lengths may still be controlled by the electronic structure of the complex ion.

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