Crystal and Molecular Structure of Tris-(1,10-phenanthroline)copper(II) Perchlorate

By Oren P. Anderson,† Institute of Chemistry, University of Bergen, Bergen, Norway

The crystal and molecular structures of the title compound have been determined from three-dimensional single-crystal *X*-ray diffraction data, collected by counter techniques. Crystals are monoclinic, space group *C*2/*c*, with $Z = 8$ in a unit cell of dimensions: $a = 35{\cdot}98(5)$, $b = 15{\cdot}97(3)$, $c = 12{\cdot}20(3)$ Å, and $\beta = 101{\cdot}7(3)°$. The structure was solved by Patterson and Fourier methods and refined by least-squares methods on alternate sets of atoms to *R* 0·133 for 2662 observed reflections. The monomeric complex cations exhibit a distorted octahedral configuration about copper(II), with equal distortions of the axial Cu–N bonds; mean Cu–N(eq) 2·04(1), mean Cu–N(ax) 2·33(1) Å.

THE structural information currently available for trisbidentate chelates of copper(II) shows an interesting diversity. On the one hand, in complexes such as tris-(ethylenediamine)copper(II) sulphate[1] and tris(octamethylpyrophosphoramide)copper(II) perchlorate[2] the complex ions have been found at sites requiring 32 (D_3) site-symmetry. This ability to occupy a site which requires higher symmetry than the Jahn–Teller theorem allows for copper(II) has been rationalized by postulating the existence of a disordering effect. Such an effect would take the form of a dynamic Jahn–Teller distortion or random trapping of statically distorted ions, but experimental evidence for such disorder from *X*-ray structural studies has not been clear. On the other hand, two recent structural studies, on tris-(2,2′-bipyridyl)copper(II) perchlorate,[3] and on the tris(hexafluoroacetylacetonato)cuprate(II) anion,[4] have shown that these types of system may also exhibit the type of distortion expected from the Jahn–Teller theorem. In these two cases, however, the axial ligand atoms were at unequal distances from the metal ion. No example has yet been found of a trisbidentate chelate of copper(II) possessing the co-ordination geometry which has become considered normal for six-co-ordinate copper(II) complexes, *i.e.* four short metal–ligand bonds in an equatorial plane, with two equally long axial bonds to give the tetragonally distorted octahedral system.

The results of an earlier e.s.r. study of the complex cation $[\mathrm{Cu(phen)_3}]^{2+}$ (phen = 1,10-phenanthroline) doped into the corresponding zinc(II) complex have been interpreted in terms of a statically distorted system at 77 K, and a dynamic Jahn–Teller distortion at slightly above room temperature,[5] so that *X*-ray experiments at room temperature should indicate the complex to be essentially undistorted. However, *X*-ray results for tris-(bipyridine)copper(II) perchlorate[3] did not confirm the undistorted nature of that complex cation, which had also been claimed on the basis of e.s.r.[6] and single-crystal polarized electronic[7] spectra. We now report the determination of the structure of another example of this type of complex, carried out in order to reveal either another example of an 'undistorted' complex, or to give more information on the type of static Jahn–Teller distortion to which these complexes are subject.

EXPERIMENTAL

Crystal Data.—$\mathrm{C_{36}H_{24}N_6Cl_2CuN_6O_8}$, $M = 803{\cdot}1$, Monoclinic, $a = 35{\cdot}98(5)$, $b = 15{\cdot}97(3)$, $c = 12{\cdot}20(3)$ Å, $\beta = 101{\cdot}7(3)°$, $U = 6864$ Å^3, $D_m = 1{\cdot}62$, $Z = 8$, $D_c = 1{\cdot}55$, $F(000) = 3256$. Space group *C*2/*c* (No. 15). Mo-$K_{\alpha 1}$ radiation, $\lambda = 0{\cdot}70926$ Å; $\mu(\text{Mo-}K_\alpha) = 8{\cdot}8$ cm^{-1}.

Crystals were grown as small, dark blue, multifaceted polyhedra from aqueous solutions of copper(II) perchlorate with a slightly greater than stoicheiometric amount of 1,10-phenanthroline.

Preliminary oscillation and Weissenberg photographs showed systematic absences: $h + k = 2n$ for hkl and $l = 2n$ for $h0l$, consistent with monoclinic space groups *Cc* (No. 9) or *C*2/*c* (No. 15). The latter was chosen arbitrarily, and shown by subsequent successful solution and refinement to be correct. The crystal chosen for data collection was mounted along the *b* axis and placed on the Siemens automatic four-circle diffractometer with this axis nearly coincident with the ϕ axis of the instrument. Unit-cell constants were calculated by a least-squares procedure from values of 2θ for 9 high-order reflections.

Diffractometer data were obtained as described in ref. 3. Scan-width was 0·3° for the bottom half and $(0{\cdot}3 + 0{\cdot}34 \tan\theta_{\text{max.}})°$ for the upper half of the scan. The intensities of two reference reflections were measured throughout data collection, and their intensities used to scale the various data groups.

The data set comprised all reflections in a unique quadrant of the sphere of reflection, with $1° < \theta < 25°$ for hkl reflections and $1° < \theta < 20°$ for $\bar{h}kl$ reflections. 3895 Reflections were obtained, of which 2662 (68·4%) having $I > 2\sigma(I)$ were considered observed [where $\sigma(I)$ is defined as the square root of the total number of counts during the five-value measurement]. For unobserved reflections, the measured intensity was replaced by 2σ, with a label to indicate that these reflections were unobserved.

Lorentz and polarization corrections were applied, but no absorption correction because of the small size of the crystal used (*ca.* $0{\cdot}15 \times 0{\cdot}20 \times 0{\cdot}25$ mm). A sample calculation of $\exp(-\mu d)$ for maximum and minimum path

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† *Present address:* Department of Chemistry, University of Michigan, Ann Arbor, Michigan, U.S.A.

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lengths d through the crystal indicated a deviation for the relative transmission coefficients of *ca.* 0·5% about a mean value.

The computer programs used are listed in ref. 3.

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 remaining 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. 8, and for chloride ion and atomic nitrogen, carbon, and oxygen from ref. 9. For copper, corrections for anomalous dispersion ($\Delta f'$ and $\Delta f''$) were taken from ref. 10, and included by letting f equal the magnitude of the complex scattering factor.

The perchlorate oxygen atoms proved very difficult to treat in an adequate fashion because of disorder. The Cl(1) perchlorate ion was finally treated as a freely rotating single unit,* for which only the centre could be refined. Two other perchlorate ions were independently situated on two-fold axes in the unit cell. For the Cl(3) perchlorate ion, one of the Cl–O axes coincided with this crystallographic two-fold axis, which implied rotational disorder about this bond. The ring of electron density generated by this rotation was approximated by six one-half oxygen atoms, fixed in positions determined from the known structure of the perchlorate ion.[11]

The final refinement steps were carried out in alternate cycles, because of program limitations. In one cycle the overall scale-factor, together with the positions and thermal parameters of all atoms except the three refinable oxygen atoms, were refined. The next cycle was similar, with three of the carbon atoms replaced by the three refinable oxygen atoms. Thermal parameters for copper(II), nitrogen, and chlorine were anisotropic, with all others isotropic. After two repetitions of this process, R had reached its final value of 0·133 (observed reflections only, 0·139 all reflections). This relatively high value may be explained, at least in part, by the drastic, but necessary, approximations taken to the disorder in the perchlorate ions. The refinement program 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, was set equal to $1/\sigma^2(F_o)$, where $\sigma(F_o)$, the standard deviation in the observed structure factor, is evaluated from counting statistics.

On the last pair of cycles, positional shifts for most atoms were $<0{\cdot}1\sigma$, with a few carbon atoms and one oxygen atom showing positional shifts of up to $0{\cdot}5\sigma$. Observed and calculated structure factors for strong reflections showed an extinction correction to be unnecessary, and no attempt was made to locate hydrogen atoms. A final difference-Fourier map showed no peak higher than 1·8 eÅ^{-3}, and no depression lower than −0·9 eÅ^{-3}. Furthermore, these extreme cases are found in the region immediately surrounding the severely disordered perchlorate ions. In the area occupied by the copper(II) complex cation, the highest peak was 0·7 eÅ^{-3}, and the lowest −0·5 eÅ^{-3}. Observed and calculated structure factors are listed in Supplementary Publication No. SUP20683 (3 pp., 1 microfiche).† Atomic positions and isotropic thermal parameters are listed in Table 1, and anisotropic thermal parameters in Table 2.

TABLE 1

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

Atom	x	y	z	U/Å^2
Cu(II)	0·37790(6)	0·27591(13)	0·12258(19)	
N(1)	0·3509(4)	0·3546(9)	0·2150(11)	
N(2)	0·3962(3)	0·2055(7)	0·0063(11)	
N(3)	0·3928(4)	0·3886(7)	0·0605(10)	
N(4)	0·3717(4)	0·1739(8)	0·2127(11)	
N(5)	0·3249(3)	0·2689(9)	−0·0236(12)	
N(6)	0·4300(3)	0·2832(9)	0·2697(11)	
C(1)	0·3289(5)	0·3320(12)	0·2892(16)	0·066(6)
C(2)	0·3115(5)	0·3981(13)	0·3461(16)	0·073(6)
C(3)	0·3166(5)	0·4780(12)	0·3206(16)	0·074(6)
C(4)	0·3397(5)	0·5018(12)	0·2432(15)	0·062(6)
C(5)	0·3479(6)	0·5848(13)	0·2141(17)	0·083(7)
C(6)	0·3719(6)	0·6061(13)	0·1417(18)	0·083(7)
C(7)	0·3866(5)	0·5386(11)	0·0857(14)	0·054(5)
C(8)	0·4086(6)	0·5507(13)	0·0064(17)	0·081(6)
C(9)	0·4231(5)	0·4861(12)	−0·0451(15)	0·059(5)
C(10)	0·4127(5)	0·4026(11)	−0·0145(15)	0·051(5)
C(11)	0·3787(5)	0·4533(11)	0·1091(15)	0·051(5)
C(12)	0·3564(5)	0·4341(12)	0·1907(14)	0·051(5)
C(13)	0·4306(5)	0·1729(11)	0·0204(15)	0·055(5)
C(14)	0·4444(5)	0·1264(12)	−0·0641(16)	0·066(6)
C(15)	0·4199(6)	0·1194(12)	−0·1647(17)	0·072(6)
C(16)	0·3841(5)	0·1535(11)	−0·1849(15)	0·064(5)
C(17)	0·3573(6)	0·1481(13)	−0·2972(17)	0·081(6)
C(18)	0·3216(6)	0·1808(12)	−0·3059(17)	0·075(6)
C(19)	0·3093(5)	0·2208(12)	−0·2180(15)	0·062(5)
C(20)	0·2720(6)	0·2614(13)	−0·2251(17)	0·077(6)
C(21)	0·2632(6)	0·3021(12)	−0·1404(17)	0·075(6)
C(22)	0·2903(5)	0·3042(11)	−0·0364(15)	0·058(5)
C(23)	0·3356(5)	0·2288(11)	−0·1105(14)	0·048(5)
C(24)	0·3723(5)	0·1973(10)	−0·0937(14)	0·047(5)
C(25)	0·3416(6)	0·1179(13)	0·1848(17)	0·073(6)
C(26)	0·3346(6)	0·0532(13)	0·2579(17)	0·076(6)
C(27)	0·3590(6)	0·0456(13)	0·3575(17)	0·078(6)
C(28)	0·3909(5)	0·0997(12)	0·3918(16)	0·065(6)
C(29)	0·4176(6)	0·0938(12)	0·4969(16)	0·073(6)
C(30)	0·4459(5)	0·1485(12)	0·5268(16)	0·070(6)
C(31)	0·4523(5)	0·2181(12)	0·4513(15)	0·062(5)
C(32)	0·4800(5)	0·2768(14)	0·4805(16)	0·075(6)
C(33)	0·4832(5)	0·3419(12)	0·4060(16)	0·072(6)
C(34)	0·4574(5)	0·3411(12)	0·2987(16)	0·065(5)
C(35)	0·4269(5)	0·2207(12)	0·3457(14)	0·052(5)
C(36)	0·3958(5)	0·1637(10)	0·3163(15)	0·048(5)
Cl(1)O$_4$	0·2630(2)	0·0180(4)	0·4480(5)	
Cl(2) †	0·0	0·0887(5)	0·25	
Cl(3) †	0·50	0·0475(5)	0·25	
O(5)	0·0053(6)	0·0380(14)	0·3512(19)	0·186(9)
O(6)	0·0312(5)	0·1382(12)	0·2483(15)	0·141(6)
O(31) †	0·500	0·1376(17)	0·250	0·134(9)
O(32) †	0·494	0·017	0·355	0·150
O(33) †	0·535	0·017	0·232	0·150
O(34) †	0·471	0·017	0·162	0·150

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

RESULTS AND DISCUSSION

Bond lengths and angles involving the copper(II) ion are in Table 3, those within the ligands and the perchlorate ions in Table 4. The standard deviations 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

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* By use of a scattering factor curve calculated for a freely rotating perchlorate ion by Dr. B. Dawson, Division of Chemical Physics, C.S.R.O.

† For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

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Table 2

Anisotropic thermal parameters (Å^2)

Atom	10^4U_{11}	10^4U_{22}	10^4U_{33}	10^4U_{12}	10^4U_{23}	10^4U_{13}
Cu(II)	481(12)	384(12)	528(13)	47(12)	−17(13)	101(10)
N(1)	456(85)	685(103)	508(95)	88(77)	70(80)	4(74)
N(2)	330(73)	256(80)	749(101)	7(61)	97(71)	78(70)
N(3)	543(88)	380(82)	484(89)	50(69)	−16(71)	115(73)
N(4)	552(91)	466(85)	530(93)	99(73)	−22(76)	259(75)
N(5)	383(79)	541(88)	790(110)	−10(76)	168(87)	−17(76)
N(6)	398(80)	561(89)	632(98)	−55(77)	−99(84)	95(73)
$Cl(1)O_4$	759(41)	1266(55)	812(43)	−82(39)	0(41)	30(35)
Cl(2)	770(54)	776(54)	648(54)	0	0	−99(43)
Cl(3)	956(59)	620(52)	851(59)	0	0	87(47)

* In the form exp $[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots)]$. Standard deviations in the least significant digits are given in parentheses, unless the parameter was not refined.

Table 3

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

(*a*) Bond lengths

Cu–N(1)	2·059(14)	Cu–N(4)	2·003(13)
Cu–N(2)	2·022(13)	Cu–N(5)	2·335(12)
Cu–N(3)	2·065(12)	Cu–N(6)	2·321(11)

(*b*) Bond angles

N(1)–Cu–N(3)	81·6(5)	N(5)–Cu–N(6)	179·2(5)
N(2)–Cu–N(5)	76·6(5)	Cu–N(1)–C(12)	111(1)
N(4)–Cu–N(6)	77·2(5)	Cu–N(1)–C(1)	127(1)
N(1)–Cu–N(2)	168·6(5)	C(10)–N(3)–Cu	129(1)
N(1)–Cu–N(4)	94·5(6)	C(11)–N(3)–Cu	111(1)
N(1)–Cu–N(5)	92·5(5)	Cu–N(2)–C(13)	124(1)
N(1)–Cu–N(6)	86·7(5)	Cu–N(2)–C(24)	117(1)
N(2)–Cu–N(3)	94·7(5)	C(22)–N(5)–Cu	131(1)
N(2)–Cu–N(4)	91·2(5)	C(23)–N(5)–Cu	107·5(9)
N(2)–Cu–N(6)	104·2(5)	Cu–N(4)–C(25)	124(1)
N(3)–Cu–N(4)	167·5(5)	Cu–N(4)–C(36)	118(1)
N(3)–Cu–N(5)	89·6(5)	C(34)–N(6)–Cu	132(1)
N(3)–Cu–N(6)	90·6(5)	C(35)–N(6)–Cu	108·7(9)
N(4)–Cu–N(5)	102·4(5)		

Table 4

Bond lengths (Å) and angles (°) in the ligand rings and perchlorate ions, with standard deviations in parentheses unless one of the atoms was not refined

(*a*) Bond lengths

N(1)–C(1)	1·37(3)	C(19)–C(20)	1·48(3)
C(1)–C(2)	1·47(3)	C(20)–C(21)	1·31(3)
C(2)–C(3)	1·34(3)	C(21)–C(22)	1·44(2)
C(3)–C(4)	1·43(3)	C(22)–N(5)	1·35(2)
C(4)–C(12)	1·45(3)		
C(12)–N(1)	1·33(2)	N(4)–C(25)	1·39(2)
C(4)–C(5)	1·42(3)	C(25)–C(26)	1·42(3)
C(5)–C(6)	1·40(3)	C(26)–C(27)	1·35(3)
C(6)–C(7)	1·43(3)	C(27)–C(28)	1·43(3)
C(7)–C(11)	1·43(2)	C(28)–C(36)	1·41(3)
C(11)–C(12)	1·43(3)	C(36)–N(4)	1·39(2)
C(7)–C(8)	1·38(3)	C(28)–C(29)	1·44(2)
C(8)–C(9)	1·37(3)	C(29)–C(30)	1·34(3)
C(9)–C(10)	1·46(3)	C(30)–C(31)	1·49(3)
C(10)–N(3)	1·29(2)	C(31)–C(35)	1·42(2)
N(3)–C(11)	1·34(2)	C(35)–C(36)	1·43(2)
		C(31)–C(32)	1·36(3)
N(2)–C(13)	1·32(2)	C(32)–C(33)	1·40(3)
C(13)–C(14)	1·44(3)	C(33)–C(34)	1·44(2)
C(14)–C(15)	1·36(3)	C(34)–N(6)	1·35(2)
C(15)–C(16)	1·37(3)	N(6)–C(35)	1·38(2)
C(16)–C(24)	1·45(3)		
C(24)–N(2)	1·35(2)	Cl(2)–O(5)	1·46(2)
C(16)–C(17)	1·51(3)	Cl(2)–O(6)	1·38(2)
C(17)–C(18)	1·37(3)	Cl(3)–O(31)	1·44(3)
C(18)–C(19)	1·40(3)	Cl(3)–O(32)	1·43
C(19)–C(23)	1·46(2)	Cl(3)–O(33)	1·41
C(23)–C(24)	1·39(2)	Cl(3)–O(34)	1·42
C(23)–N(5)	1·36(2)		

Table 4 (*Continued*)

(*b*) Bond angles

C(1)–N(1)–C(12)	122(2)	C(15)–C(16)–C(24)	118(2)
N(1)–C(1)–C(2)	119(2)	C(16)–C(24)–N(2)	121(1)
C(1)–C(2)–C(3)	119(2)	N(2)–C(24)–C(23)	121(2)
C(2)–C(3)–C(4)	122(2)	C(23)–C(24)–C(16)	119(1)
C(3)–C(4)–C(12)	116(2)	C(15)–C(16)–C(17)	123(2)
C(3)–C(4)–C(5)	126(2)	C(24)–C(16)–C(17)	119(2)
C(5)–C(4)–C(12)	117(2)	C(16)–C(17)–C(18)	118(2)
C(4)–C(12)–N(1)	121(2)	C(17)–C(18)–C(19)	124(2)
N(1)–C(12)–C(11)	119(2)	C(18)–C(19)–C(23)	119(2)
C(4)–C(12)–C(11)	119(2)	C(18)–C(19)–C(20)	126(2)
C(4)–C(5)–C(6)	125(2)	C(20)–C(19)–C(23)	116(2)
C(5)–C(6)–C(7)	117(2)	C(19)–C(23)–C(24)	122(2)
C(6)–C(7)–C(11)	121(2)	C(24)–C(23)–N(5)	118(1)
C(6)–C(7)–C(8)	123(2)	C(19)–C(23)–N(5)	120(1)
C(11)–C(7)–C(8)	116(2)	C(19)–C(20)–C(21)	122(2)
N(3)–C(11)–C(7)	122(2)	C(20)–C(21)–C(22)	119(2)
C(7)–C(11)–C(12)	120(2)	C(21)–C(22)–N(5)	123(2)
N(3)–C(11)–C(12)	117(2)	C(22)–N(5)–C(23)	121(1)
C(7)–C(8)–C(9)	123(2)		
C(8)–C(9)–C(10)	116(2)	O(5)–Cl(2)–O(6)	111(1)
C(9)–C(10)–N(3)	123(2)	O(31)–Cl(3)–O(32)	110
C(10)–N(3)–C(11)	120(1)	O(31)–Cl(3)–O(33)	110
		O(31)–Cl(3)–O(34)	110
C(13)–N(2)–C(24)	119(1)	O(32)–Cl(3)–O(33)	109
N(2)–C(13)–C(14)	124(1)	O(32)–Cl(3)–O(34)	110
C(13)–C(14)–C(15)	116(2)	O(33)–Cl(3)–O(34)	108
C(14)–C(15)–C(16)	123(2)		

link together the two co-ordinating nitrogen atoms of each phenanthroline ligand. Figure 2 shows the labelling of the individual ligand ring systems.

The results reported here are not those expected on the basis of earlier e.s.r. work,[5] which predicted the presence of a dynamic Jahn–Teller distortion at room temperature and above. The $[Cu(phen)_3]^{2+}$ complex cation possesses the co-ordination geometry of four short and two long bonds, which are considered typical for static Jahn–Teller distortion in six-co-ordinate copper(II) systems. If the four short bonds are assumed equal, the mean Cu–N is 2·037(13) Å. In fact, there may be three sets of Cu–N bond distances. The shortest Cu–N distances are Cu–N(2) and Cu–N(4) [2·022(13) and 2·003(13) Å]. In both cases, the nitrogen atom belongs to a ligand in which the Cu–N bond is very long. In the N(1),N(3) ligand, which does not exhibit a very long Cu–N bond, the two equal Cu–N bond lengths are 2·059(14) and 2·065(12) Å. Application of the usual statistical test suggests that these bonds are significantly longer than the first quoted. Finally, the complex also exhibits two much longer axial bonds which are equal: Cu–N(5) and Cu–N(6) [2·335(12) and 2·321(11) Å], giving a mean axial bond length of 2·328(12) Å. The mean of all six metal–nitrogen bond distances is 2·134(12) Å. This complex is the first trisbidentate chelate system of copper(II) found to possess this 'normal' Jahn–Teller distortion, with four equal short bonds and two equal longer bonds.

The bond angles subtended at the metal ion by an individual ligand vary according to whether the ligand is distorted. A lengthening of one of the metal–nitrogen bonds would be expected to decrease the angle N–Cu–N′, and this is found. In the ligand in which no distortion is present, the angle N(1)–Cu–N(3) is 81·6(5)°. In the two ligands which show the long Cu–N bonds, the angles are considerably reduced [N(2)–Cu–N(5) 76·6(5), N(4)–Cu–N(6) 77·2(5)°]. These last two are equal, as would be expected from the equality of the metal–nitrogen bond lengthening for these two ligands.

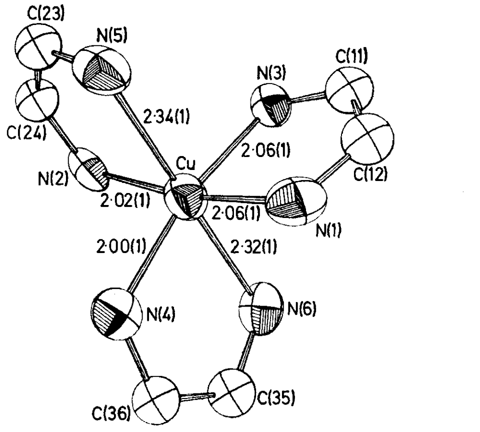

FIGURE 1 The co-ordination geometry about Cu^{II}; only the two nitrogen atoms and connecting carbon atoms of each ligand are shown

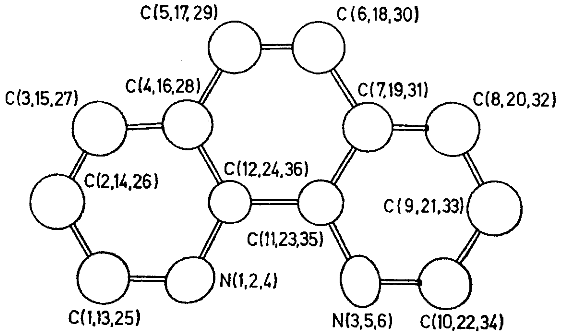

FIGURE 2 The labelling of the phenanthroline ligands

These structural parameters may best be compared with the results available for the complex cations $[Cu(en)_3]^{2+}$ (en = ethylenediamine), found to be non-distorted,[1] and $[Cu(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridyl), found to be statically distorted and to exhibit two unequal long Cu–N bonds.[3] In the latter complex, the four short equatorial bonds were experimentally equal, mean 2·031(6) Å. As noted earlier, the mean of the four short Cu–N bonds in $[Cu(phen)_3]^{2+}$ is 2·037(13) Å. In $[Cu(bipy)_3]^{2+}$, the mean of the unequal long bonds [2·226(7) and 2·450(7) Å] is 2·338(7) Å, which is the same as that found in the present study for the two equal long Cu–N bonds. Furthermore, the undistorted $[Cu(en)_3]^{2+}$ ion, in which all six Cu–N bonds were required to be equal, gave Cu–N 2·150(2) Å. The mean of all six Cu–N bonds for tris(bipyridyl)copper(II) cation is 2·133(7) Å, and for tris(phenanthroline)copper(II) is 2·134(12) Å. These striking similarities once again suggest that the total extent of possible distortion is constant, and may be controlled by the electronic structure of the complex.

The bond angles N–Cu–N′ in $[Cu(bipy)_3]^{2+}$ are also found to vary with the amount of distortion present, from 80·4(3)° for the ligand forming two short Cu–N bonds, to 78·2(3)° in the intermediate case, and to 73·9(2)° for the ligand involving the very large distortion. Since the long bonds in the tris(phenanthroline) system fall in between the two long bonds of $[Cu(bipy)_3]^{2+}$, the angles are expected to fall between these latter two values, as indeed they do. The corresponding angle for $[Cu(en)_3]^{2+}$ is 80·9(1)°. All these comparisons of geometry indicate that the present results for the co-ordination geometry about Cu^{II} are reasonable.

The geometries of the individual ligands are in agreement with those from earlier studies.[12] The mean C–C bond distance for all three ligands is 1·41(3) Å, as found earlier; mean C–N is 1·35(2) Å. The best plane through each ligand has been calculated by least-squares techniques (Table 5). The individual ligands are planar, as expected, with the standard deviation from the plane of the atoms defining the plane being 0·03 for ligands (1) and (2), and 0·04 Å for ligand (3). The deviations of the copper ion from ligands (1)—(3) are 0·06, 0·19, and 0·19 Å. These last two large deviations from planarity with the

TABLE 5

(*a*) Deviations (Δ/Å) of atoms from least-squares planes through ligand atoms

Ligand (1)		Ligand (2)		Ligand (3)	
Atom	Δ	Atom	Δ	Atom	Δ
N(1)	0·05	N(2)	0·03	N(4)	0·02
N(3)	−0·01	N(5)	−0·03	N(6)	0·05
C(1)	0·03	C(13)	0·03	C(25)	−0·01
C(2)	0·00	C(14)	−0·02	C(26)	−0·06
C(3)	−0·05	C(15)	−0·02	C(27)	−0·04
C(4)	−0·03	C(16)	0·00	C(28)	0·01
C(5)	−0·03	C(17)	0·04	C(29)	0·03
C(6)	0·06	C(18)	0·00	C(30)	0·02
C(7)	0·02	C(19)	−0·04	C(31)	0·02
C(8)	0·01	C(20)	0·00	C(32)	−0·04
C(9)	0·00	C(21)	0·04	C(33)	−0·09
C(10)	−0·05	C(22)	0·00	C(34)	−0·01
C(11)	−0·01	C(23)	−0·03	C(35)	0·06
C(12)	0·01	C(24)	0·01	C(36)	0·03
Cu^{II}	0·06	Cu^{II}	0·19	Cu^{II}	−0·19

(*b*) Equations of planes in the form $PX + QY + RZ = S$ where X, Y, and Z are fractional co-ordinates

Ligand	P	Q	R	S
(1)	24·59	0·03	7·03	10·11
(2)	14·91	13·74	−4·56	8·68
(3)	24·85	−9·48	−6·64	6·16

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[12] G. P. Khare and R. Eisenberg, *Inorg. Chem.*, 1970, **9**, 2211; C. G. Pierpont and R. Eisenberg, *ibid.*, p. 2218.

ligands making the two long Cu–N bonds, confirm the tendency [3] for bond lengthening to be accompanied by a twisting away of the ligand to reduce its bonding ability still further.

The configurations of the refinable portions of the perchlorate ions are also satisfactory. For the three refinable oxygen atoms, the mean of the Cl–O bond lengths is 1·43(2) Å, which may be compared with 1·43 Å for Cl–O in $HClO_4,H_2O$.[11] The value of the O(5)–Cl(2)–O(6) angle [111(1)°] is close to the tetrahedral.

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 were calculated and their orientations (Figure 1) show little evidence for abnormal vibration along the directions of the copper–nitrogen bonds, as would have been expected had there been a tendency toward dynamic Jahn–Teller distortion, as has been established for this complex ion in other crystalline matrices.

It is now clear that trisbidentate chelates of the copper(II) ion exhibit much the same range of structures found in other systems involving six-co-ordinate copper(II). The co-ordination geometry may range from a straightforward tetragonal distortion, through less symmetric distortions, to cases which apparently involve no Jahn–Teller distortion at all.

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