Crystal and Molecular Structure of *catena*-μ-Acetato-[di-(3-aminopropyl)amine]copper(II) Perchlorate

By **B. W. Skelton** and **T. N. Waters,*** Chemistry Department, University of Auckland, New Zealand
N. F. Curtis, Chemistry Department, Victoria University of Wellington, New Zealand

The *X*-ray structural analysis of the title compound [orthorhombic, space group $Pna2_1$ or *Pnam*, *a* = 8·53(1), *b* = 18·50(2), *c* = 8·74(1) Å, *Z* = 4] reveals a polymeric complex cation in which copper has primary square-planar co-ordination with the three amino-nitrogen atoms and one oxygen atom of the acetate ion [Cu–N(1) 1·92(2), Cu–N(2)(secondary) 2·05(2), Cu–N(3) 2·02(2), and Cu–O(2) 2·02(1) Å]. The second oxygen atom of this acetate bonds more weakly in a tetragonal site of a second copper atom [Cu′–O(1) 2·29(1) Å] completing square-pyramidal co-ordination. This same oxygen is also involved in a still weaker interaction with the initial copper atom in a direction displaced *ca.* 40° from the tetragonal axis so that a distorted octahedral co-ordination geometry is present at a tertiary level [Cu–O(1) 2·74(1) Å]. The acetate group thus functions as a bridging asymmetric bidentate ligand. The amine adopts a conformation with the six-membered chelate ring including N(2) and N(3) in a chair, and the ring including N(1) and N(2) in a distorted-boat conformation. The bond angles N(1)–Cu–N(2) 83·9(9) and N(2)–Cu–N(3) 98·9(8)° are unusually divergent from the value *ca.* 92° observed for other complexes with saturated six-membered chelate rings.

The structure was solved from 1350 photographic data and refined by block-diagonal least-squares methods to *R* 0·100.

THE preparations of the compounds $[Cu(dpt)(OAc)]ClO_4$ and $[Cu(dien)(OAc)]ClO_4$ † have been reported and structures with asymmetrical bidentate co-ordination of acetate and five-co-ordination about the copper atom have been suggested on the basis of i.r. spectroscopy.[1] The compound $[Cu(dpt)(OAc)]ClO_4$ was selected for a full *X*-ray crystallographic investigation because it has a number of interesting structural features involving the co-ordination geometry about the copper ion, the mode of co-ordination of acetate, and the co-ordination geometry and chelate ring conformations of the dipropylenetriamine ligand.

The copper ion is well known for the variety of co-ordination geometries [2] it sustains and this compound complemented a series of previous studies.[3] The acetate ion as ligand has also been observed in a variety of roles, including simple unidentate co-ordination [*e.g.* as $Cu(OAc)_2(pyridine)_3$ [4]], symmetrical chelate co-ordination [*e.g.* [Ni{*C-rac*(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)}OAc]ClO_4 [5]], asymmetrical chelate co-ordination [*e.g.* $Cu(NH_3)_2(OAc)_2$ [6]], symmetrical bridging [*e.g.* $Cu_2(OAc)_4,2H_2O$ [7]], and asymmetrical chelation and bridging [$CaCu(OAc)_4,6H_2O$ [8]]. The greatest variety is observed with the copper(II) ion and further studies are desirable to determine the factors important to the adoption of particular geometries.

The tridentate ligand dipropylenetriamine can, in principle, adopt facial (' folded ') or meridional (' linear ') arrangements in complexes with octahedral co-ordination geometry, related arrangements being possible for the five-co-ordinate and tetragonally distorted octahedral structures commonly observed in copper(II) compounds. As well as this problem of co-ordination stereochemistry, the conformation adopted by the two fused chelate rings is of some interest. An isolated six-membered ring composed of tetrahedral ligand atoms is expected to take

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† dpt = Dipropylenetriamine = di-(3-aminopropyl)amine, $NH_2\cdot[CH_2]_3\cdot NH\cdot[CH_2]_3\cdot NH_2$; dien = diethylenetriamine, $NH_2\cdot[CH_2]_2\cdot NH\cdot[CH_2]_2\cdot NH_2$.

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the chair conformation and is so observed in the complexes of 1,3-diaminopropane (pn) studied.* When two rings are linked a study of models in which the metal-nitrogen bond lengths are equal at 2·0 Å suggests that the adoption of the chair conformation by both would be facilitated by facial co-ordination, although it seems likely that intramolecular repulsions between the rings would be more severe than for meridional bonding. On the other hand, meridional bonding imposes angular strain which mitigates against the adoption of a chair-chair conformation of the chelate rings. Models indicate that for metal–nitrogen distances equal at 2·0 Å a chair-twist boat conformation is probably less strained. The strain present for the chair–chair conformation is relieved if the secondary nitrogen distance is increased to *ca.* 2·3 Å, or if all the metal–nitrogen distances are increased by a smaller amount. Alternatively, an increase in the angles subtended at the metal atom will also relieve the strain imposed by the chair–chair conformation.

The geometry adopted in any particular compound will undoubtedly depend upon a number of factors. The radius of the metal ion is clearly important, but non-bonded interactions may also be significant. These may occur with additional ligands, counter-ions, or other groups in the environment as well as intermolecularly; the details or relative importance of the components depending upon details of each structure. Any one of these influences may be sufficient to dictate a particular geometry in situations of balance and further structural studies will be needed before their relative importance can be assessed.

The two structural studies of dipropylenetriamine complexes so far reported reveal two different conformations for the amine. In $[Ni(dpt)_2](ClO_4)_2$ [19] meridional co-ordination with chair–chair conformations is observed [Ni–N(primary) 2·12—2·17, Ni–N(secondary) 2·22 and 2·23 Å]. Although the central metal-ligand bond is longer than the other two, some of the strain is also taken up in the internal ring angles which vary from 111·8 to 122·4° at 'tetrahedral' centres. The same meridional co-ordination occurs in β-$[Co(dpt)(en)Cl]ZnCl_4$ [20] but this time, with the Co–N bond lengths all *ca.* 2·0 Å, only one chelate ring has the chair conformation. The other is described as having a 'distorted boat' conformation. Internal ring angles above the tetrahedral values again indicate strain. The conformations adopted by the cobalt(III) and high-spin nickel(II) complexes are those in agreement with the change in metal-ion radii, but the significance of the correspondence cannot be pressed on this restricted evidence.

EXPERIMENTAL

Blue crystals were prepared by mixing a methanolic solution of copper(II) perchlorate with one containing dipropylenetriamine and acetic acid,[1] and were recrystallised from hot methanol.

TABLE 1

Assessment of weighting scheme

F_o ranges	$\langle w\Delta^2 \rangle$	No. of data
>45	5·3	105
45—32	5·0	106
32—25	2·1	118
25—20	3·6	123
20—15	3·6	187
15—10	3·9	255
10—5	6·2	371
5—0	8·2	76

TABLE 2

Atomic positions

Atom	x/a	$\sigma(x)$ Å	y/b	$\sigma(y)$ Å	z/c	$\sigma(z)$ Å
Cu	0·2107	0·002	0·2060	0·002	0·0000	0·000
Cl	0·3530	0·004	0·3734	0·003	0·5080	0·008
N(1)	0·2185	0·018	0·2034	0·015	0·2192	0·023
N(2)	0·2549	0·016	0·0971	0·014	0·0181	0·027
N(3)	0·2268	0·014	0·2160	0·013	−0·2294	0·018
C(1)	0·3409	0·035	0·1701	0·031	0·3070	0·036
C(2)	0·3751	0·026	0·0927	0·026	0·2650	0·050
C(3)	0·2401	0·032	0·0662	0·026	0·1802	0·035
C(4)	0·3775	0·019	0·0721	0·017	−0·0868	0·031
C(5)	0·3335	0·028	0·0897	0·025	−0·2595	0·033
C(6)	0·3660	0·032	0·1680	0·029	−0·2720	0·033
C(7)	0·3233	0·011	0·3436	0·011	0·0154	0·023
C(8)	0·3259	0·017	0·4242	0·014	−0·0077	0·039
O(1)	0·4440	0·008	0·3075	0·009	−0·0199	0·013
O(2)	0·1883	0·007	0·3143	0·008	0·0129	0·018
O(3)	0·2139	0·035	0·3651	0·034	0·4350	0·039
O(4)	0·4029	0·031	0·4432	0·017	0·4473	0·023
O(5)	0·4332	0·034	0·3197	0·026	0·4230	0·035
O(6)	0·3718	0·033	0·3643	0·040	0·6575	0·027
H(1)	0·121		0·174		0·270	
H(2)	0·226		0·257		0·271	
H(3)	0·306		0·173		0·427	
H(4)	0·446		0·203		0·291	
H(5)	0·392		0·060		0·367	
H(6)	0·480		0·089		0·194	
H(7)	0·133		0·085		0·326	
H(8)	0·242		0·007		0·179	
H(9)	0·173		0·063		−0·045	
H(10)	0·391		0·014		−0·070	
H(11)	0·486		0·099		−0·054	
H(12)	0·210		0·079		−0·285	
H(13)	0·406		0·060		−0·341	
H(14)	0·400		0·179		−0·390	
H(15)	0·464		0·180		−0·197	
H(16)	0·127		0·195		−0·294	
H(17)	0·256		0·270		−0·271	
H(18)	0·327		0·454		0·091	
H(19)	0·430		0·438		−0·079	
H(20)	0·225		0·439		−0·080	

Primed atoms are at: $\frac{1}{2} + x, \frac{1}{2} - y, z$.

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* Structures of 1,3-diaminopropane complexes reported (values for N–Cu–N angles of chelate rings, where reported, in parentheses) are: $[Co(pn)_3]Br_3,H_2O$; [9] *trans*$[Co(pn)_2Cl_2]Cl,HCl,2H_2O$; [10] *trans*$[Co(pn)_2(NO_3)_2]NO_3$; [11] *cis*$[Co(pn)_2CO_3]ClO_4$; [12] *trans*$[Ni(pn)_2(H_2O)_2](NO_3)_2$; [13] $[Cu(pn)_2](NO_3)_2$ [94·9(5)°]; [14] $[Cu(pn)_2NCS]ClO_4$ (91 and 93°); [15] $Cu(pn)_2(SCN)_2$; [15] $Cu(pn)_2(NO_2)_2$ [86·8(2)°]; [16] $Cu(pn)_2(PhCO_2)_2$ [88·5(7)°]; [17] $[Cu(pn)_2]SO_4,H_2O$ and $[Cu(pn)_2]SeO_4,H_2O$ [both 93·2(8)°].[18]

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Crystal Data.—$C_8H_{20}ClCuN_3O_6$, M = 353·3, Orthorhombic, a = 8·53(1), b = 18·50(2), c = 8·74(1) Å (standard deviations from the spread of measurements), U = 1379 Å^3 D_m = 1·64, Z = 4, D_c = 1·65. Space group $Pna2_1$ or *Pnam*. Cu-K_α radiation, λ = 1·5418 Å; μ(Cu-K_α) = 41·6 cm^{-1}.

Three rod-shaped crystals were needed for data collection by Weissenberg photography because of their slow deterioration, partially prevented by a Perspex coating, during irradiation. Their dimensions were 0·54 × 0·08 × 0·14 and 0·58 × 0·07 × 0·11 mm for a axis photography (0—6hl) and 0·38 × 0·23 × 0·22 mm for c axis photography (hk0—8). No absorption corrections were made. After least-squares correlation of data 1350 independent reflexions were available.

The non-centrosymmetric space group was assumed, although initial phasing based solely on the copper atom presupposed 'non-space group' mirror symmetry perpendicular to c on the same level as the copper. This additional symmetry was reinforced by the chlorine atom which was also found to lie on a mirror plane and by the acetate group being similarly placed. The symmetry was 'broken' by selecting one set of positions for the perchlorate oxygen atoms, selection of the correct image from the two previously available for the dipropylenetriamine then being also possible. With R 0·237, least-squares refinement by block-diagonal methods was begun, but because of the strong mirror relationship still impressed on the calculation, difference-Fourier syntheses were also computed on occasions to check and guide the parameter adjustments. After inclusion of hydrogen atoms and the assumption of anisotropic thermal parameters for all other atoms, refinement converged at R 0·105, reduced subsequently to 0·100 by the removal of 9 reflexions of large amplitude which showed poor agreement. The weighting scheme, $w = [1 + (F_o - b)^2/a^2]^{-1}$, was adjusted at intervals to keep $\langle w\Delta F^2\rangle$ constant over $|F_o|$ ranges. Table 1 assesses the final values of a = 11·5, b = 8·0. Atom positions, temperature parameters, bond lengths, and bond angles are listed in Tables 2—5 together with appropriate standard deviations. The atomic numbering scheme is that of Figure 1. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20457 (5 pp., 1 microfiche).†

TABLE 3

Temperature parameters * (× 10^4)

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
Cu	86	15	100	−7	3	17
Cl	149	22	133	18	−10	4
N(1)	176	291	173	8	−34	0
N(2)	197	26	205	−14	−6	36
N(3)	129	22	111	0	4	4
C(1)	875	35	269	−12	−764	80
C(2)	170	34	640	175	−222	−10
C(3)	338	29	252	−15	−92	21
C(4)	127	17	414	−94	121	21
C(5)	259	35	303	−101	271	−29
C(6)	235	55	230	−42	249	−35
C(7)	65	20	83	22	57	−5
C(8)	161	20	242	16	−36	−9
O(1)	71	28	83	−2	35	15
O(2)	53	19	118	4	−21	−6
O(3)	536	118	609	24	−934	−175
O(4)	609	29	288	44	298	−107
O(5)	591	71	495	−72	817	107
O(6)	1273	152	151	75	−126	−262

* The scattering factor for an atom is expressed as:

$$f_o\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{23}kl + b_{13}hl + b_{12}hk)].$$

TABLE 4

Bond lengths (Å) with standard deviations in parentheses

Cu–N	1·92(2)	C(2)–C(3)	1·46(4)
Cu–N(2)	2·05(2)	C(4)–C(5)	1·59(4)
Cu–N(3)	2·02(2)	C(5)–C(6)	1·48(3)
Cu–O(1)	2·29(1)	C(7)–C(8)	1·50(2)
Cu–O(2)	2·02(1)	C(7)–O(1)	1·27(1)
Cu–O(1′)	2·74(1)	C(7)–O(2)	1·27(2)
N(1)–C(1)	1·44(4)	Cl–O(3)	1·36(3)
N(2)–C(3)	1·53(4)	Cl–O(4)	1·44(3)
N(2)–C(4)	1·47(3)	Cl–O(5)	1·40(3)
N(3)–C(6)	1·56(3)	Cl–O(6)	1·33(3)
C(1)–C(2)	1·51(4)		

TABLE 5

Bond angles (°) with standard deviations in parentheses

N(1)–Cu–N(2)	83·9(9)	Cu–N(3)–C(6)	104·1(15)
N(1)–Cu–N(3)	173·0(7)	N(1)–C(1)–C(2)	114·7(25)
N(1)–Cu–O(1)	93·2(7)	C(1)–C(2)–C(3)	106·9(25)
N(1)–Cu–O(2)	88·4(7)	C(2)–C(3)–N(2)	106·3(23)
N(1)–Cu–O(1′)	96·2(9)	N(2)–C(4)–C(5)	111·2(20)
N(2)–Cu–N(3)	98·9(8)	C(4)–C(5)–C(6)	103·1(16)
N(2)–Cu–O(1)	122·9(11)	C(5)–C(6)–N(3)	113·9(23)
N(2)–Cu–O(1′)	94·7(8)	O(1)–C(7)–C(8)	118·6(13)
N(2)–Cu–O(2)	170·8(8)	O(2)–C(7)–C(8)	115·7(11)
N(3)–Cu–O(1)	79·9(7)	O(1)–C(7)–O(2)	120·4(12)
N(3)–Cu–O(2)	88·3(6)	Cu–O(1)–C(7)	75·9(6)
N(3)–Cu–O(1′)	90·1(10)	Cu–O(2)–C(7)	109·9(7)
O(1)–Cu–O(2)	52·5(5)	Cu–O(1′)–Cu′	129·8(8)
O(1)–Cu–O(1′)	142·1(5)	O(3)–Cl–O(4)	100·6(19)
O(2)–Cu–O(1′)	91·0(5)	O(3)–Cl–O(5)	95·6(20)
Cu–N(1)–C(1)	124·7(18)	O(3)–Cl–O(6)	123·7(32)
Cu–N(2)–C(3)	114·9(16)	O(4)–Cl–O(5)	106·8(17)
Cu–N(2)–C(4)	113·0(14)	O(4)–Cl–O(6)	115·7(22)
C(3)–N(2)–C(4)	121·3(19)	O(5)–Cl–O(6)	111·7(24)

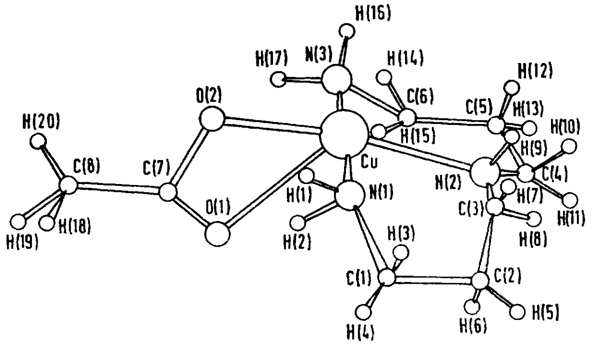

FIGURE 1 Atomic numbering system

DISCUSSION

The structure adopted by [Cu(dpt)OAc]ClO$_4$ places the copper atom in approximate square-planar co-ordination with the three nitrogen atoms of the dipropylenetriamine and an acetate oxygen atom [(2)] as donors [Table 6, plane (1)]. Bond lengths are *ca.* 2·0 Å. A fifth, weaker interaction with oxygen O(1) of a second acetate [Cu′–O(1) 2·29 Å] completes a tetragonal pyramidal co-ordination stereochemistry. This is in turn modified by a still weaker interaction at 2·74 Å with the oxygen atom O(1) of the acetate group involved

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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).

in the primary square-planar co-ordination, the overall geometry being that of a distorted octahedron. The tetragonal pyramidal co-ordination shell is regular in geometry, the copper ion being displaced 0·10 Å towards the apical donor atom, but the sixth interaction which completes the distorted octahedron is at an angle of *ca.* 50° to the basal plane, the angle O(2)–Cu–O(1) being 52·5°.

TABLE 6

Equations of planes of best fit; deviations (Å) of relevant atoms from the planes are given in square brackets

Plane (1):

N(3), N(2), O(2), N(1) $0{\cdot}989x + 0{\cdot}140y + 0{\cdot}027z + 2{\cdot}414 = 0$

[N(3) 0·006, O(2) −0·007, Cu −0·102, N(2) −0·007, N(1) 0·008]

Plane (2):

N(2), C(4), C(6), N(3) $0{\cdot}649x + 0{\cdot}558y + 0{\cdot}517z + 2{\cdot}472 = 0$

[N(2) 0·023, C(6) 0·029, Cu 0·822, C(4) −0·030, N(3) −0·022, C(5) −0·872]

Plane (3):

Cu, C(1), C(2), N(2) $-0{\cdot}910x - 0{\cdot}200y + 0{\cdot}363z - 2{\cdot}347 = 0$

[Cu −0·051, C(2) −0·083, C(1) 0·068, N(2) 0·067]

Plane (4):

Cu, N(1)—(3) $0{\cdot}9884x + 0{\cdot}1496y + 0{\cdot}0272z + 2{\cdot}4199 = 0$

[Cu −0·07, N(1) 0·04, N(2) 0, N(3) 0·03, C(4) 0·94, C(5) 0·58, C(6) 1·06, C(1) 0·99, C(2) 1·06, C(3) −0·17]

The co-ordination geometry of the acetate ion is also irregular. Although the oxygen atom O(2) is involved in normal bonding [Cu–O(2) 2·02 Å] the second atom, O(1), not only bonds to a second copper ion [Cu′–O(1) 2·29 Å] but also interacts with the first metal atom [Cu–O(1) 2·84 Å] in the ' off-axis ' manner indicated by Figure 2. The acetate ion is thus acting as an unsymmetrical bidentate chelate as inferred from the i.r. spectrum but with an additional bridging role in which it adopts the *anti–syn* geometry. As a result the complex ion is polymeric.

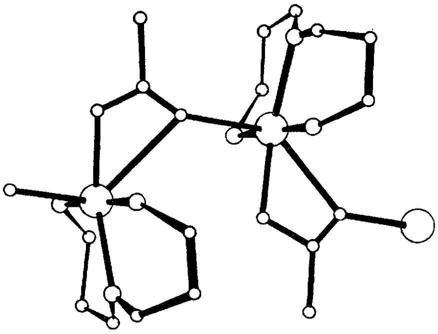

FIGURE 2 Edge-on view of the cation

An interesting feature of the structure is its relationship with other acetato-complexes of copper(II). In $Cu(NH_3)_2(OAc)_2$ [6] the two nitrogen atoms and a carboxy-oxygen atom from each acetate complete a *trans*-square-planar co-ordination array (Cu–O 2·02 Å) with a weaker interaction (Cu–O 2·74 Å) occurring between the metal atom and the second carboxy-oxygen atom located 40° off the tetragonal axis. The arrangement is thus similar to that of $[Cu(dpt)OAc]ClO_4$ but without the bridging feature. The compound $CaCu(OAc)_4,6H_2O$,[8] and its cadmium analogue, adopts a structure in which the acetate co-ordination is nearly identical with that of $[Cu(dpt)OAc]ClO_4$, each ion forming one short (1·97 Å) in-plane bond to copper with the second oxygen atom not only bonding much more weakly (2·79 Å) in a position 40° off the axis but also interacting (2·30 Å) with a calcium ion. A comparable situation to that seen in $[Cu(dpt)OAc]ClO_4$ is found in $[Cu(dien)(HCO_2)]HCO_2$,[21] the formate ion being involved in the same asymmetrical bidentate bridging [Cu–O(1) 2·030, Cu–O(2) 2·614, Cu′–O(2) 2·165 Å]. The i.r. spectrum of $[Cu(dien)OAc]ClO_4$ has similar acetate bands to the dpt analogue [1] and presumably also adopts the same mode of co-ordination.

We conclude that the structure observed for $[Cu(ptd)OAc]ClO_4$ presents a preferred mode of bonding between acetate and copper(II) ions and is not one uniquely determined by crystal packing forces and non-bonded intramolecular interactions. The strain expected when acetate functions as a symmetrical bidentate ligand, as in the nickel(II) complex already mentioned [5] where the angle O–Ni–O (62°) is relieved with copper(II) by the formation of a weak off-axial tetragonal interaction. That this bond is not of normal strength is emphasised by the fact that the oxygen atom can be simultaneously involved in a further bridging interaction without affecting the off-axial Cu–O distance.

A feature of the structure of $[Cu(dpt)OAc]ClO_4$ is the dissimilarity in conformation of the two six-membered chelate rings present. The chelate ring including N(2) and N(3) adopts a chair conformation [Table 6, planes (2) and (4)], while that including N(1) and N(2) is best described as having a distorted boat conformation, the distortion being towards a twist conformation. The atoms Cu, C(1), C(2), and N(2) form a poorly defined plane, with N(1) and C(3) on the same side of the plane as ' bowsprit ' and ' sternpost ' [Table 6, planes (3) and (4)].

The angle subtended at the copper by the N(2)–N(3) chelate ring is 98·9°, while for the N(1)–N(2) chelate ring this value is 83·9°. The angles subtended by 1,3-diaminopropane chelate rings reported cover the range 86·8—96°, obviously being sensitive to environment, but a value near 92° is most common (see footnote p. 2134). For $[Ni(dpt)_2](ClO_4)_2$ (90·5, 92·5 and 90·2, 92·4°) [19] and for $[Co(dpt)(en)Cl]ZnCl_4$ (91·1, 93·3°) [20] the values are closer to each other, and to the norm. The divergence in the values for the copper compound is attributed to the less rigid co-ordination stereochemistry of d^9 copper(II), compared with spin-paired d^6 cobalt(III) and spin-free d^8 nickel(II), evidenced by the greater variety of co-ordination geometries observed for copper(II).[2] The

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[21] M. J. Brew, R. J. Fereday, G. Davey, B. J. Hathaway, and F. S. Stephens, *Chem. Comm.*, 1970, 887; G. Davey and F. S. Stephens, *J. Chem. Soc.* (*A*), 1971, 103.

asymmetry, which can be considered as a displacement of N(2), apparently permits the chelate rings, particularly the N(2)–N(3) chelate ring, to adopt a relatively strain free conformation, as evidenced by the internal bond angles, which are closer to the tetrahedral value than those of the above cobalt and nickel complexes. The largest distortions occur near N(1) where the Cu–N(1)–C(1) bond angle (124·7°) is unusually large and the Cu–N(1) bond (1·92 Å) is unusually short. [The other two Cu–N bond lengths are similar to those reported for a variety of copper(II) amine complexes.]

TABLE 7

Intermolecular contacts (Å)

N(1) ··· O(5^{III})	3·05	C(2) ··· O(3^{V})	3·34
N(1) ··· O(5^{I})	3·34	C(3) ··· O(4^{IV})	3·29
N(2) ··· O(4^{IV})	3·21	C(4) ··· O(4^{IV})	3·39
N(3) ··· O(6^{II})	3·17	C(7) ··· O(6^{II})	3·18
C(1) ··· O(3^{V})	3·43	C(8) ··· O(4^{VI})	3·39
C(1) ··· O(5^{I})	3·05	C(8) ··· O(6^{II})	3·15

Roman numerals as superscripts refer to the equivalent positions relative to the reference molecule at x, y, z;

I x, y, z
II $x, y, z-1$
III $x-\frac{1}{2}, \frac{1}{2}-y, z$
IV $\frac{1}{2}-x, y-\frac{1}{2}, z-\frac{1}{2}$
V $x+\frac{1}{2}, \frac{1}{2}-y, z$
VI $1-x, 1-y, z-\frac{1}{2}$

TABLE 8

Hydrogen bonding details

N(1) ··· O(5^{I})	3·34 Å	N(2) ··· O(4^{IV})	3·20 Å
O(5^{I}) ··· H(2^{I})	2·5 Å	O(4^{IV}) ··· H(9^{IV})	2·3 Å
N(1)–H(2^{I})–O(5^{I})	133°	N(2)–H(9^{IV})–O(4^{IV})	139°
N(1) ··· O(5^{III})	3·05 Å	N(3) ··· O(6^{II})	3·17 Å
O(5^{III}) ··· H(1^{III})	2·1 Å	O(6^{II}) ··· H(17^{II})	2·1 Å
N(1)–H(1^{III})–O(5^{III})	145°	N(3)–H(17^{II})–O(6^{II})	165°

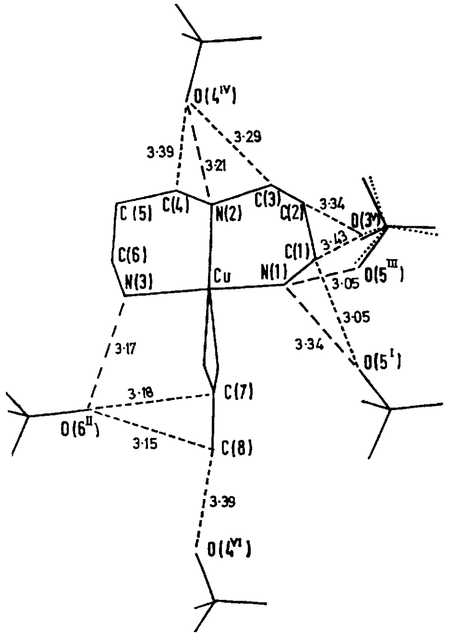

FIGURE 3 Hydrogen bonds and other close contacts. [The direction of steric and bonding pressures can be gauged by noting that O(3^{V}) and O(5^{I}) are below (beneath the page) the atoms they contact, that O(5^{III}) and O(4^{IV}) are above, and that O(6^{II}) is approximately on the same level. Dashed lines show assumed hydrogen bonds, and dotted lines other close contacts]

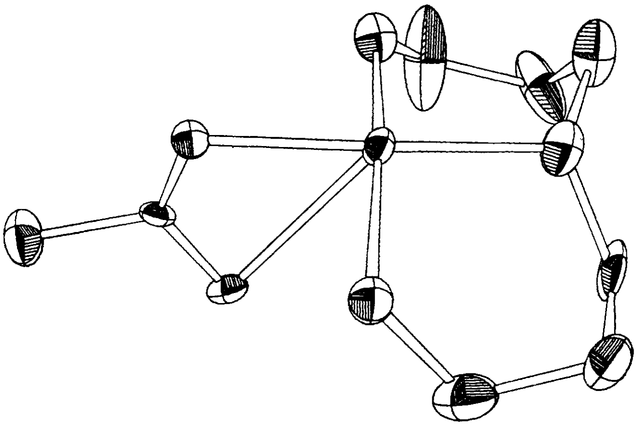

FIGURE 4 Anisotropic thermal ellipsoids of the cation

The details of the conformation adopted by the amine must be influenced by extra-ligand interactions, particularly with the perchlorate ions, which are hydrogen bonded to the amino-groups (Table 7, Figure 3), and also involved in some close contacts with carbon atoms, particularly for the 'boat' conformation chelate ring (Table 8, Figure 3). The direction of 'push' of the oxygen atom (Figure 3) is such as to favour adoption of a boat conformation.

The carbon atoms of the 'boat' conformation chelate ring, particularly C(1) and to a lesser extent C(2), are markedly anisotropic (Figure 4). If this is attributed to static or dynamic disorder, the indicated directions of motion suggest the presence of a range of conformations between the classical boat and twist-boat conformations. Since the energy barrier between these is small, experimentally for cyclohexane,[22] and theoretically for the six-membered chelate ring,[12,23] this observation is not at odds with possibility. However, it is not clear whether the range of ring conformations is present because of the small energy barrier, or because of the close contacts of C(1) and C(2) with three strongly anisotropic oxygen atoms (see later) which dictate their vibrations or equivalent static disorder.

The conformation of the dipropylenetriamine–copper(II) moiety is similar to that observed for [Co(dpt)(en)Cl]$ZnCl_4$, also described as chair–distorted boat,[20] and it is perhaps significant that the metal–amine nitrogen bond lengths are similar for the cobalt(III) and copper(II) compounds, significantly less than for high-spin [$Ni(dpt)_2$]$(ClO_4)_2$ where the chair–chair conformation is adopted.[19] For the cobalt(III) complex also, as for the copper(II) complex, the N–Co–N bond angle for the chair conformation chelate ring (93·3°) is greater than for the 'boat' conformation chelate ring (91·1°), although the difference is smaller, presumably because of the greater bond-angle rigidity of cobalt(III).

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[22] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, 'Conformational Analysis,' Wiley, New York, 1966.

[23] R. J. Gollogly and C. J. Hawkins, *Inorg. Chem.*, 1972, **11**, 156.

Large thermal motions are also indicated for the oxygen atoms of the perchlorate anion. The vibrational directions show that the motion is largely a rotary oscillation about the chlorine, confirming that a qualitative physical meaning can be placed on the derived parameters. The bond lengths in the anion, except for Cl–O(4), are somewhat shorter than normal as a consequence of the large thermal parameters. An approximate correction based on rotary oscillation of the oxygen atoms is of the order of 0·04—0·05 Å but since adjustments depend on the vibrational model assumed, and the values are not relevant to the present discussion, they are uncorrected.

Intermolecular contacts $<3{\cdot}4$ Å are listed in Table 8. Hydrogen bonding involving the oxygen atoms O(4), O(5), and O(6) of three perchlorate ions and the three amine nitrogen atoms is indicated; geometrical details are presented in Table 8 and the interactions represented in Figure 3.

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