Crystal Structure and Electronic Properties of Ammine[tris(2-aminoethyl)amine]copper(II) Diperchlorate and Potassium Penta-amminecopper(II) Tris(hexafluorophosphate)

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The crystal structure of the title compounds $[Cu(tren)(NH_3)][ClO_4]_2$ (1) and $K[Cu(NH_3)_5][PF_6]_3$ (2) have been determined by *X*-ray diffraction methods using three-dimensional diffractometer data; the structures were solved by heavy-atom techniques and successive Fourier synthesis. Compound (1) crystallises in a cubic unit cell, space group $P2_13$, with dimensions a = 11.626(3) Å and Z = 4, and (2) crystallises in the orthorhombic unit cell, space group *Imma* with dimensions, a = 14.90(1), b = 11.79(1), c = 10.57(1) Å, and Z = 4. The cation in (1) has a trigonal-bipyramidal molecular structure with strict C_3 symmetry while that in (2) has a square-based pyramidal molecular structure with strict C_{2v} symmetry. The polycrystalline and single-crystal electronic properties for these two σ-bonding CuN_5 chromophores are reported and related to the one-electron energy levels for the two stereochemistries, using extended-Hückel molecular-orbital calculations, and correlated with earlier data on high-symmetry five-co-ordinate CuN_5 chromophores.

A WEALTH of *X*-ray crystallographic data [1-5] has established the existence of the five-co-ordinate square-based pyramidal and trigonal-bipyramidal stereochemistries for the copper(II) ion in its complexes, but in general these involve mixed-ligand donors,[5] *i.e.* non-equivalent ligands and chelate ligands, which introduce the possibility of both bond-length and -angle distortions. In addition, many of the ligands, such as the halides and oxygen, introduce the complication of a possible π-bonding function for the donor atom.[6] All three effects combine in many cases to remove all elements of symmetry from the regular stereochemistries, D_{3h} for trigonal bipyramidal and C_{4v} for square pyramidal and lead to difficulties in correlating the stereochemistry and electronic properties [7-9] of these five-co-ordinate stereochemistries for the copper(II) ion. The crystal structures of ammine[tris(2-aminoethyl)amine]copper(II) diperchlorate and potassium penta-amminecopper(II) tris(hexafluorophosphate), $[Cu(tren)(NH_3)][ClO_4]_2$, (1), and $K[Cu(NH_3)_5][PF_6]_3$, (2), respectively, have been determined as representing the most regular trigonal-bipyramidal and square-pyramidal stereochemistries for a CuN_5 chromophore and involving only σ-bonding nitrogen ligands.

EXPERIMENTAL

Preparations.—Complex (1) was prepared by dissolving 1.7 g $[Cu(NH_3)_5][ClO_4]_2$ [10] in $[NH_4][OH]$ (s.g. 0.88, 40 cm³) plus tris(2-aminoethyl)amine (1 g); the resulting solution was heated, filtered, and allowed to cool in a stoppered flask (Found: C, 16.85; H, 4.85; Cl, 16.75; N, 16.3. $C_6H_{21}Cl_2CuN_5O_8$ requires C, 16.9; H, 4.95; Cl, 16.7; N, 16.45%). The copper-doped salt $[Zn(tren)(NH_3)][ClO_4]_2$ was prepared by an analogous method, using $[Zn(NH_3)_6][ClO_4]_2$ as starting material, plus an appropriate amount of $[Cu(NH_3)_5][ClO_4]_2$ (Found: C, 17.3; H, 5.15; Cl, 16.9; N, 16.4; Zn, 14.95. $C_6H_{21}Cl_2N_5O_8Zn$ requires C, 16.8; H, 4.9; Cl, 16.6; N, 16.4; Zn, 15.3%). Compound (2) was prepared as previously reported [10,11] for $[NH_4][Cu(NH_3)_5][PF_6]_3$ (Found: H, 2.45; Cu, 10.55; N, 10.95. $H_{15}CuF_{18}K_1N_5P_3$ requires H, 2.40; Cu, 10.2; N, 11.25; $H_{19}CuF_{18}N_6P_3$ requires H, 3.15; Cu, 10.55; N, 13.95%). A repeat microanalysis on the original sample also confirmed that this should be formulated as the potassium salt (Found: H, 2.45; Cu, 11.0; N, 11.3%).

TABLE 1

Crystal and refinement data

	(1)	(2)
Compound	$[Cu(tren)(NH_3)][ClO_4]_2$	$K[Cu(NH_3)_5][PF_6]_3$
M	425.54	622.74
Stoicheiometry	$C_6H_{21}Cl_2CuN_5O_8$	$H_{15}CuF_{18}KN_5P_3$
Space group	$P2_13$ (cubic)	*Imma* (orthorhombic)
a/Å	11.626(3)	14.90(1)
b/Å		11.79(1)
c/Å		10.57(1)
Z	4	4
U/Å³	1 571.41	1 857.9
D_m (flotation)/g cm⁻³	1.79(5)	2.23(5)
D_c/g cm⁻³	1.798	2.230
Radiation	Mo-K_α (0.7107)	Mo-K_α (0.7107)
F(000)	868.0	1 263.98
μ/cm⁻¹	17.02	17.25
No. of unique reflections	649	619
No. of parameters	67	81
$R = (\Sigma\Delta\|\Sigma\text{-}\|F_o\|)$	0.0401	0.0888
$R' = (\Sigma\Delta w^{\frac{1}{2}}\|\Sigma\|\text{-}F_o\|w^{\frac{1}{2}})$	0.0383	0.0943
k	1.00	2.5532
$10^4 g$	1.67	8.81
Max. final shift/e.s.d.	0.01	0.005
Residual electron density (e A⁻³)	0.35	0.85
No. of atoms anisotropic	11	9

Crystal Data.—The crystal and refinement data for (1) and (2) are summarised in Table 1. The preliminary unit-cell and space-group data for both crystals were determined from precession photographs and refined on a Philips PW1100 four-circle diffractometer. The intensity data were collected on the diffractometer using graphite-monochromatised Mo-K_α radiation; a θ—2θ scan mode was used and reflections with $3.0 < \theta < 32°$ in one quadrant were examined. A constant scan speed of 0.05° s⁻¹ and a variable scan width of (0.7 + 0.1 tan θ)° was used. With an acceptance criteria of $I > 2.50\sigma(I)$, 649 reflections were retained for (1) and 619 reflections for (2). Lorentz and polarisation corrections were applied, but no correction was made for absorption. Routine checks revealed no crystal deterioration even for (2). The structures were solved using three-dimensional Patterson and Fourier techniques; an initial solution of (2) in the space group *I2ma* proved unsatisfactory, but the alternative space group *Imma* was satisfactory. The refinement of both structures was by full-matrix least-squares analysis, initially with isotropic temperature factors, ultimately with anisotropic temperature factors for all the non-hydrogen atoms in (2) but for only a restricted number in (1). The positions of the hydrogen atoms were calculated geometrically for (1) and floated on the associated atom, assuming C–H and N–H distances of 1.08 Å and a fixed temperature factor of 0.07 Å^2. Attempts to calculate the position of the hydrogen atoms in structure (2) using the SHELX-76 facility proved unsuccessful due to the special positions occupied by the nitrogen atoms; consequently hydrogen atoms were not included in this structure. The data converged when the ratio of the maximum shift to estimated standard deviation (e.s.d.) was <0.01; with a refined weighting scheme $w = k/[\sigma^2(F_o) + g(F_o)^2]$; Table 1 lists the final *k* and *g* values for structures (1) and (2).

TABLE 2

Atomic co-ordinates (fractional × 10^4) for (1) and (2)

(1)

	x/*a*	*y*/*b*	*z*/*c*
Cu	1 955(1)	1 955(1)	1 955(1)
N(1)	951(5)	951(5)	951(1)
N(2)	2 969(3)	2 969(3)	2 969(3)
N(3)	3 012(4)	621(3)	2 510(4)
C(1)	3 678(5)	2 184(5)	3 689(5)
C(2)	3 997(5)	1 127(5)	3 054(7)
Cl(1)	5 435(1)	5 435(1)	5 435(1)
O(1)	4 729(5)	4 729(5)	4 729(5)
O(2)	5 151(6)	5 257(5)	6 588(5)
Cl(2)	7 605(1)	7 605(1)	7 605(1)
O(3)	8 310(4)	8 310(4)	8 310(4)
O(4)	6 768(3)	8 310(4)	7 023(4)

(2)

	x/*a*	*y*/*b*	*z*/*c*
K	2 500	2 500	7 500
Cu	5 000	2 500	2 663(3)
N(1)	5 000	4 188(13)	2 927(19)
N(2)	3 637(12)	2 500	2 907(17)
N(3)	5 000	2 500	589(19)
P(1)	5 000	2 500	6 583(6)
F(1′)	4 308(12)	1 750(16)	7 340(22)
F(2′)	5 000	1 557(25)	5 618(27)
F(3′)	4 290(16)	1 824(19)	5 862(25)
F(4′)	5 000	3 329(37)	7 750(43)
P(2)	2 135(3)	0	5 000
F(5)	2 144(11)	1 297(10)	5 000
F(6)	2 949(19)	−97(21)	5 879(24)
F(7)	1 497(25)	−150(28)	6 080(26)
F(5′)	2 058(36)	0	6 408(49)
F(6′)	1 101(21)	0	5 000
F(7′)	3 177(24)	0	5 000

Complex atomic scattering factors [12] were employed and the copper atom was corrected for anomalous dispersion. All calculations were carried out using the programs SHELX-76 by G. M. Sheldrick, PLUTO by S. Motherwell, and XPUB by R. Taylor on an IBM 370/138 computer. Table 2 lists the final non-hydrogen atomic co-ordinates and estimated standard deviations, Table 3 the bond lengths, Table 4 the bond angles, and Table 5 some relevant mean planes. The final observed and calculated structure factors, temperature factors, calculated hydrogen-atom positions, and selected non-bonded contacts for (1) are in Supplementary Publication No. SUP 22778 (13 pp.).* Figure 1 shows the molecular structures of (1) and (2) and the atom-numbering scheme used.

TABLE 3

Bond lengths (Å) with estimated standard deviations in parentheses

(1)		(2)	
Cu–N(1)	2.023(11)	N(1)–Cu	2.010(17)
Cu–N(2)	2.041(8)	N(2)–Cu	2.048(19)
Cu–N(3)	2.082(6)	N(3)–Cu	2.193(22)
N(2)–C(1)	1.488(7)	F(1′)–P(1)	1.577(19)
N(3)–C(2)	1.435(8)	F(2′)–P(1)	1.508(31)
C(1)–C(2)	1.481(9)	F(3′)–P(1)	1.528(21)
Cl(1)–O(1)	1.422(12)	F(4′)–P(1)	1.575(47)
Cl(1)–O(2)	1.396(6)	F(5)–P(2)	1.529(13)
Cl(2)–O(3)	1.420(10)	F(6)–P(2)	1.533(29)
Cl(2)–O(4)	1.435(5)	F(7)–P(2)	1.497(21)
		F(5′)–P(2)	1.493(53)
		F(6′)–P(2)	1.541(33)
		F(7′)–P(2)	1.553(39)

Physical Properties.—The polycrystalline and single-crystal electronic and e.s.r. spectra were determined as previously reported.[2,11] The extended-Hückel calculations were carried out using the program IKON 8,[12] involving self-consistent charge iteration, starting with a formal charge on the copper atom of +1 as suggested earlier.

Figure 2 reports the electronic reflectance spectra of (1) and (2); (1) has a maximum at 11 400 cm^{-1} and a high-energy shoulder at 15 200 cm^{-1}, while (2) has a maximum at 15 300 cm^{-1} and a low-energy shoulder at 11 000 cm^{-1}. No attempt was made to record the polarised single-crystal spectrum of (1) as the crystals are cubic; that for (2) has previously been reported [9,10] and involves a single peak at 15 000 cm^{-1} in *xy* polarisation and two less intense peaks in *z* polarisation at 14 800 and 11 400 cm^{-1}, with the latter the slightly more intense. The polycrystalline e.s.r. spectrum of (1) yields an isotropic *g* value of 2.132 and is temperature invariant. The polycrystalline e.s.r. spectrum of a 2% copper-doped [Zn(tren)(NH$_3$)][ClO$_4$]$_2$, recorded at the temperature of liquid nitrogen (77 K), is shown in

TABLE 4

Bond angles (°) with estimated standard deviations in parentheses

(1)		(2)	
N(3)–Cu–N(2)	84.9(2)	N(2)–Cu–N(1)	89.0(2)
N(3)–Cu–N(1)	95.1(2)	N(3)–Cu–N(1)	98.0(7)
N(3)–Cu–N(3′)	119.21(3)	N(3)–Cu–N(2)	97.2(6)
Cu–N(2)–C(1)	106.9(4)	F(1′)–P(1)–F(1′)	81.7(16)
C(1)–N(2)–C(1′)	111.9(4)	F(1′)–P(1)–F(2′)	86.0(13)
C(2)–C(1)–N(2)	111.5(5)	F(1′)–P(1)–F(3′)	95.3(16)
C(1)–C(2)–N(3)	111.1(6)	F(1′)–P(1)–F(4′)	87.2(14)
C(2)–N(3)–Cu	107.6(4)	F(2′)–P(1)–F(3′)	92.7(11)
O(1)–Cl(1)–O(2)	109.4(4)	F(3′)–P(1)–F(3′)	87.6(20)
O(2)–Cl(1)–O(2′)	109.5(4)	F(3′)–P(1)–F(4′)	93.9(11)
O(3)–Cl(2)–O(4)	109.8(3)	F(6)–P(2)–F(5)	93.9(12)
O(4)–Co(2)–O(4′)	109.2(3)	F(7)–P(2)–F(5)	97.1(15)
		F(6)–P(2)–F(6)	75.3(21)
		F(7)–P(2)–F(6)	91.8(20)
		F(7)–P(2)–F(7)	101.1(33)
		F(5′)–P(2)–F(5)	90.0(2)
		F(6′)–P(2)–F(5′)	85.6(21)
		F(7′)–P(2)–F(5′)	94.4(21)

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

Figure 3 and is also temperature invariant. The spectrum involves a very intense $g_\perp$ signal with clear resolution of the four copper hyperfine lines, $g_\perp = 2.176$, $A_\perp = 110.0 \times 10^{-4}$ cm^{-1}. The $g_\parallel$ spectrum is much less intense but still displays copper hyperfine lines with $g_\parallel = 2.029$ and $A_\parallel = 84 \times 10^{-4}$ cm^{-1}; as this was difficult to resolve in the polycrystalline spectra the single-crystal rotation spectrum was recorded in which improved resolution of the weak $g_\parallel$ signal confirmed the above data. The polycrystalline e.s.r. spectrum of (2) has been previously reported [10] as $g_\parallel = 2.240$ and $g_\perp = 2.053$; due to the poor morphology of the crystals of (2), attempts to record the single-crystal g factors were unsatisfactory. Extended-Hückel calculations using IKON 8 have been carried out using the molecular geometries of the CuN$_5$ chromophore of (1), (2), and [Cu(NH$_3$)$_2$][Ag(NCS)$_3$] and on the Cu(NH$_3$)$_5$ equivalents of these complexes; the results are summarised in Figure 4.

TABLE 5

Equations of planes in the form $lX' + mY' + nZ' - p = 0$ where X', Y', and Z' are a set of orthogonal axes. The deviations (Å) of the most relevant atoms from the planes are given in square brackets

(*a*) Complex (1)

	l	m	n	p
Plane (1): N(3), N(3′), N(3″)				
	0.5779	0.5784	0.5785	−4.1213
[Cu −0.1840, N(1) −2.2067, N(2) 1.8567]				
Plane (2): Cu, N(2), N(3)				
	0.6117	0.1626	−0.7742	0.0000
[C(1) −0.2923, C(2) 0.3063]				
Plane (3): Cu, N(2′), N(3′)				
	−0.1626	0.7742	−0.6117	0.0000
[C(1′) 0.2923, C(2′) −0.3063]				

(*b*) Complex (2)

	l	m	n	p
Plane (1): N(1), N(1′), N(2), N(2′)				
	0.0000	0.0000	1.0000	3.0841
[N(1) 0.0106, N(1′) −0.0106, N(2) 0.0106, N(2′) −0.0106, Cu −0.2686]				

Root mean square deviation = 0.0106 Å.

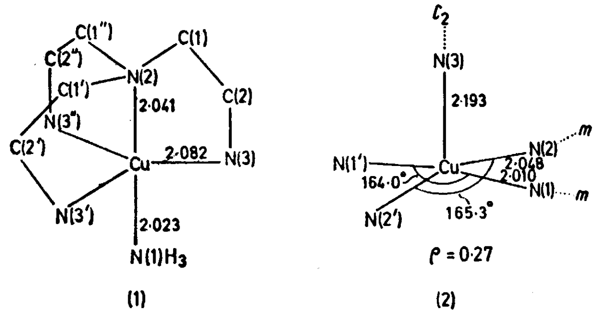

FIGURE 1 Molecular structures of (1) and (2) and the atomic numbering schemes used

RESULTS AND DISCUSSION

Description of Structures.—The structure of (1) consists of [Cu(tren)(NH$_3$)]$^{2+}$ cations and ClO$_4^-$ anions. The chlorine atoms Cl(1) and Cl(2) and one of the oxygen atoms O(1) and O(3) of each perchlorate group occupy special positions along the three-fold axis, while the remaining oxygen atoms O(2) and O(4) occupy general positions. The Cl–O bond lengths range from 1.396 to 1.435 Å (Table 3) and the O–Cl–O bond angles (Table 4) range from 109.2 to 109.8° consistent with the tetrahedral bond angle of the perchlorate anion.[13] The

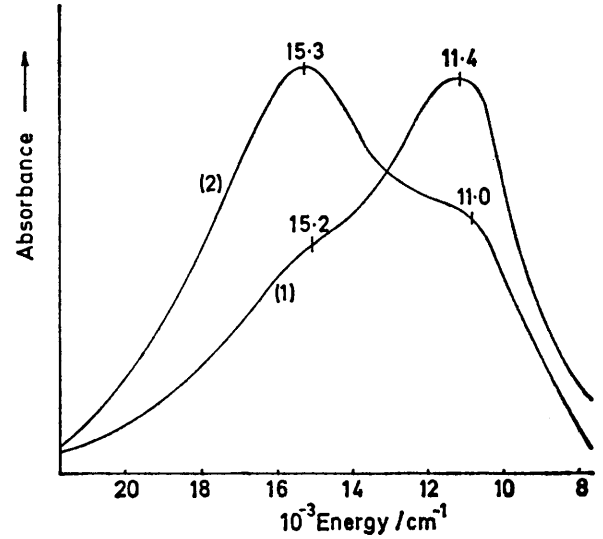

FIGURE 2 Electronic spectra of (1) and (2)

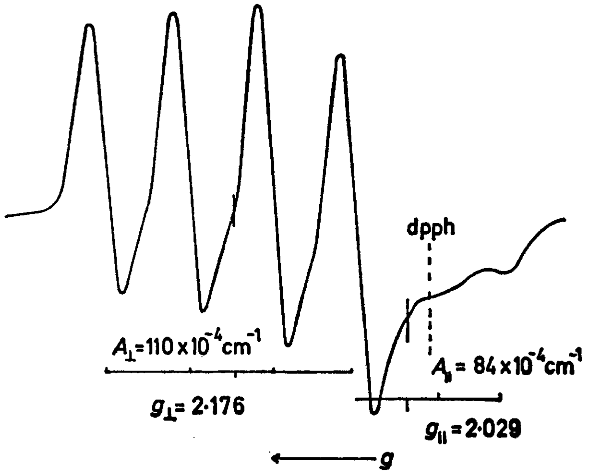

FIGURE 3 Polycrystalline e.s.r. spectrum of 2% copper-doped [Zn(tren)(NH$_3$)][ClO$_4$]$_2$ recorded at 77 K. dpph = Diphenylpicrylhydrazyl

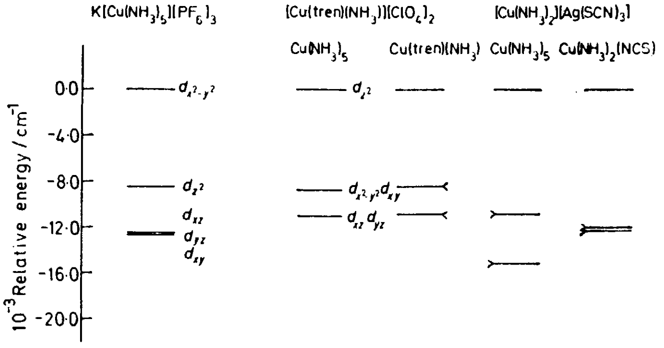

FIGURE 4 Summary of extended-Hückel calculations

Table 6

E.s.r. and electronic spectral data (in solution) for some trigonal-bipyramidal Cu(R_6tren)X_2 complexes

Complex	E.s.r. spectra					Electronic spectra (10^3 cm^{-1})
	$g_{iso.}$ (solid)	$g_\perp$	$g_\parallel$	$10^4A_\perp$/cm^{-1}	$10^4A_\parallel$/cm^{-1}	
Cu(tren)Br_2	2.110	2.210	2.00	111	67	11.2, 13.8 (sh)
Cu(tren)I_2	2.108	2.204	1.930	102	93	11.1, 14.5 (sh)
Cu(Me_6tren)Br_2 [a]	2.109	2.182	1.956	100	80	10.4, 13.4 (sh) [b]
Cu(Me_6tren)I_2 [a]	2.110	Site 1 2.226	1.895	103	97	9.8, 13.0 (sh) [b]
		Site 2 2.189	1.922	107	99	
Cu(Et_6tren)$(ClO_4)_2$	2.133	2.218	1.977	78	104	
[Cu(tren)(OH)]$^+$	2.137	2.210	2.006	111	68	
[Cu(tren)(NH_3)]$^{2+}$ [a]	2.132	2.176	2.209	110	84	114, 15.2 (sh) [b]

[a] Doped in the isomorphous zinc(II) complex. [b] As reflectance spectra.

relatively short Cl(1)–O(2) bond length of 1.396 Å (compared with the mean of the remaining Cl–O bond lengths of 1.422 Å) may be associated with some relatively short hydrogen-bond contacts to O(2) of 2.21—2.34 Å to HN(11), HN(31), and HN(32) (see SUP 22778). In the [Cu(tren)(NH_3)]$^{2+}$ cation the copper(II) ion is co-ordinated by five nitrogens with a trigonal-bipyramidal rather than a square-pyramidal stereochemistry [Figure 1(*a*)]. The Cu, N(1), and N(2) atoms all lie in special three-fold positions and the N(3), C(1), C(2), and the hydrogen atoms all lie in general positions; consequently the $CuN_5C_6H_8$ chromophore has strict C_3 molecular symmetry, rather than that of D_{3h} of a regular trigonal-bipyramidal stereochemistry, while the symmetry of the CuN′N″N_3 chromophore is C_{3v}. Consequently the N(1)–Cu–N(2) direction is perpendicular to the N(3),N(3′),N(3″) plane and the N(3)–Cu–N(3′) type angles are all equal at 119.2°. The inter-chelate bond angle, N(2)–Cu–N(3) of 84.9°, agrees [14] with that of 84.1° in [Cu(tren)(NCS)][NCS],[14] 84.2° in [Cu(Me_6tren)Br]Br,[15] and 85 and 86° in [Cu(en)$_2$][SCN]$_2$ [16] and [Cu(en)$_2$][NO_3]$_2$ [Me_6tren = tris(2-dimethylaminoethyl)amine, en = ethylenediamine],[17] respectively. The effect of the three out-of-the-plane chelate angles of 84.9° imposed by the tren ligand is that the copper(II) ion lies 0.18 Å below the N(3),N(3′),N(3″) plane (Table 6) towards the NH_3 nitrogen atom {*cf.*[15] 0.32 Å in [Cu(Me_6tren)Br]Br} and which is responsible for reducing the three N(3)–Cu–N(3′) angles to slightly below (119.2°) the regular trigonal angle of 120°. The difference between the axial Cu–N bond lengths [2.023(11) and 2.041(8) Å] is not considered significant [18] as $\Delta l/\sigma(\Delta l) = 1.32$, but that between the in-plane and out-of-plane Cu–N(tren) bond length [2.082(6) and 2.041(8) Å, a difference of ≈0.04 Å] is significant as $\Delta l/\sigma(\Delta l) = 4.1$. This difference also agrees in both magnitude (0.07 Å) and sense of difference with that observed in [Cu(Me_6tren)Br]Br [15] [Figure 5(*c*)] and in other trigonal-bipyramidal copper(II) complexes, such as [Co(NH_3)$_6$][$CuCl_5$],[19] which is consistent with the *oblate* spheroidal symmetry of the copper(II) ion due to its d^9 configuration in this stereochemistry. The axial Cu–N(2) distance in (1) of 2.041 Å is comparable to that (2.033 Å) in [Cu(tren)(NCS)][NCS],[14] despite the significant bond-length and -angle distortion of the CuN_5 chromophore of the latter (Figure 5), and may justify the suggestion that the Cu–NCS bond of 1.959 Å in this complex is significantly shortened [relative to the corresponding Cu–NH_3 bond length of 2.023 Å in (1)] possibly due to the presence of π bonding in this bond in [Cu(tren)(NCS)][NCS], even with a Cu–N–C bond angle of 163.3°. If so the linear Cu–NCS bond in [Cu(NH_3)$_2$][Ag(SCN)$_3$] [20] of 1.92 Å [Figure 5(*d*)] is exceptionally short, suggesting that the copper(II) ion has a prolate spheroidal symmetry rather than the oblate symmetry normally associated with this stereochemistry, but may be consistent with significant π bonding in this Cu–NCS equatorial bond and with the position [14] of the NCS ligand in the nephelauxetic series.[21]

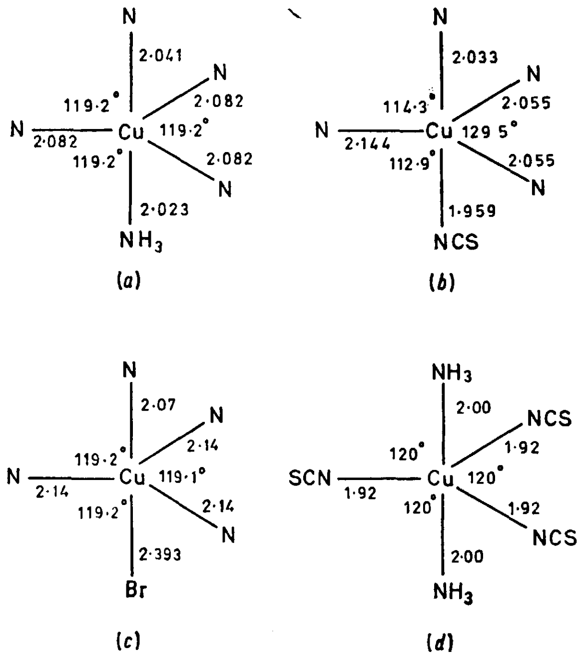

Figure 5 Local molecular structures of [Cu(tren)(NH_3)][ClO_4]$_2$ (*a*), [Cu(tren)(NCS)][NCS] (*b*), [Cu(Me_6tren)Br]Br (*c*), and [Cu(NH_3)$_2$][Ag(SCN)$_3$] (*d*)

The Cu–NH_3 axial bond length of 2.023 Å in (1) is only slightly longer than that of 2.00 Å in [Cu(NH_3)$_2$][Ag(SCN)$_3$] [20] and only slightly shorter than the equatorial bond length of 2.05 Å in the slightly distorted trigonal-bipyramidal CuN_5 chromophore of $[Cu(bipy)_2(NH_3)][BF_4]_2$ [22] (bipy = 2,2′-bipyridyl) which again emphasises the difference of $\approx$0.05 Å between the axial and equatorial bond lengths in the trigonal-bipyramidal copper(II) stereochemistry.[23]

The C–N and C–C bond lengths and bond angles of the tren ligand are consistent with the previously reported values; [14,15] all the chelate rings have the *kk* conformation (Table 5) as previously observed [14] in [Cu(tren)(NCS)][NCS] and $[Cu(Me_6tren)Br]Br$.[15]

The $[Cu(tren)(NH_3)]^{2+}$ cation may therefore be regarded as having an extremely regular trigonal-bipyramidal stereochemistry of C_3 symmetry and is the first complex isolated in this stereochemistry involving five purely σ-bonding ligands.

The crystal structure of (2) consists of K^+ and $[Cu(NH_3)_5]^{2+}$ cations and (disordered) PF_6^- anions. The copper(II) ion and one of the phosphorus atoms P(1) occupy a special position of *mm*2 (C_{2v}) symmetry, the potassium ion occupies a special position of 2/*m* symmetry (C_{2h}), while the remaining two phosphorus atoms P(2) occupy special positions of two-fold symmetry (C_2). The $[Cu(NH_3)_5]^{2+}$ cation [Figure 1(*b*)] involves a five-co-ordinate square-based pyramidal stereochemistry, with the sixth potentially bonding position occupied by a disordered fluorine atom at 3.32 Å from the copper(II) ion, a distance that is considered too great for even weak semi-co-ordination.[24] The two mirror planes of the special position associated with the copper(II) ion lie along the copper–nitrogen bonding directions which results in two independent in-plane Cu–N bond lengths [2.010(17) Å and 2.048(19) Å] and a single apical bond length [2.193(22) Å]. The two in-plane bond lengths are not considered significantly different [18] [$\Delta l/\sigma(\Delta l)$ = 1.49], but the out-of-plane bond length of 2.193 Å is considered significantly different from the in-plane bond lengths [$\Delta l/\sigma(\Delta l)$ = 5.02]. The copper(II) ion is lifted 0.27 Å above the mean plane fitted to the four in-plane nitrogen atoms (Table 6), in the direction towards the apical nitrogen atom N(3); this results in the out-of-plane angles N(1)–Cu–N(3) and N(2)–Cu–N(3) of 98.0 and 97.2°, and the corresponding basal angles N(1)–Cu–N(1′) and N(2)–Cu–N(2′) of 164 and 165.6°, values which agree closely with the predicted value [6] (extrapolated to the d^9 configuration) of 160—164° for a purely σ-bonding system. The tetragonality T^5 (defined as mean in-plane Cu–N bond distance/out-of-plane bond distance) is 0.925. The high crystallographic symmetry of the $[Cu(NH_3)_5]^{2+}$ cation, C_{2v} ($\approx C_{4v}$) is the highest symmetry square-pyramidal complex of the copper(II) ion involving five equivalent ligands, which are σ bonding only, reported to date. The nearest comparable stereochemistries are found in $[Cu(NH_3)_4(OH_2)][SO_4]$ [25] and $[Cu(en)_2(NH_3)][BF_4]_2$,[26] neither of which involves equivalent ligands, and although the latter involves purely σ-bonding ligands the chelate ligands, en, introduce significant in-plane angular distortion of the in-plane N–Cu–N angles (84.6°). Nevertheless the three complexes (Figure 6) yield comparable tetragonalities (T^5 0.87—0.92) and ρ values 0.19—0.27 Å.

All three hexafluorophosphate anions involve octahedral stereochemistries, but with appreciable disorder generated by the elements of symmetry of the two types of special positions of the P atoms, namely *mm*2 for P(1) and 2 for P(2). Within both types of disorder the occupancy is 50% and the site occupancies of the fluorine atoms are weighted at half the value appropriate to the relevant lattice positions. The bond lengths (Table 3), bond angles (Table 5), and temperature factors are in reasonable agreement with those quoted for similarly disordered systems.[27] As the three PF_6^- anions constitute a significant proportion of the electron density in the unit cell of (2), the presence of this disorder is considered primarily responsible for the relatively high final *R* value of 0.088 for this structure.

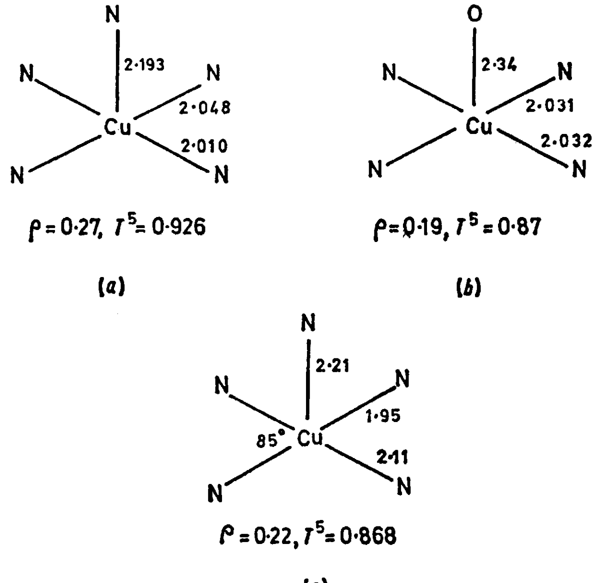

FIGURE 6 Local molecular structures of $K[Cu(NH_3)_5][PF_6]_3$ (*a*), $[Cu(NH_3)_4(OH_2)][SO_4]$ (*b*), and $[Cu(en)_2(NH_3)][BF_4]_2$ (*c*)

E.S.R. Spectra.—The isotropic e.s.r. of (1) is consistent with exchange coupling of the CuN_5 chromophores misaligned in the cubic space group $P2_13$, but yields no information on the electronic ground state. The e.s.r. of 2% copper-doped $[Zn(tren)(NH_3)][ClO_4]_2$, Figure 3, is more informative and yields *g* and *A* factors comparable with other tren-type complexes [28] which are believed to involve a trigonal-bipyramidal stereochemistry (Table 6). This comparison involves the assumption that the copper(II) ion environment is the same in (1) as in $[Zn(tren)(NH_3)][ClO_4]_2$ as a host lattice. *X*-Ray powder photographs of (1) and $[Zn(tren)(NH_3)][ClO_4]_2$ indicate that the two complexes are isomorphous. The electronic reflectance spectra of the pure copper complex (Figure 2) and the doped system show no serious changes in energy of the electronic spectra with varying concentration of the doped system (only the intensity varies) suggesting that the CuN_5 environment is the same in the concentrated and doped system. In the latter, Table 6, the g factors involve $g_\perp \gg g_\parallel \approx 2.0$ consistent with the trigonal-bipyramidal stereochemistry of the $CuN'N''N_3$ chromophore established in the solid state for (1) and $[Cu(Me_6tren)Br]Br$.[15] In 2% copper-doped $[Zn(tren)(NH_3)][ClO_4]_2$ the numerical value of $g_\parallel$ lies significantly above 2.003 6, the free-electron value, suggesting that there may be mixing of the d_{xy}, $d_{x^2-y^2}$ levels into the d_{z^2} ground state, which cannot occur by symmetry in either C_{3v} or D_{3h} [2] but can occur by vibronic coupling.[29] The occurrence of $g_\parallel < 2.00$ in the halide complexes of Table 6 has been ascribed [28] to the large effect of the spin–orbit coupling constant for the Br^- and I^- ions involved in determining the electronic ground state.

The polycrystalline e.s.r. of (2) ($g_\perp = 2.053$ and $g_\parallel = 2.240$ [10]) suggests an elongated stereochemistry for the $[Cu(NH_3)_5]^{2+}$ cations consistent with the determined structure [Figure 1(*b*)], having C_{4v} symmetry with a $d_{x^2-y^2}$ ground state. If the differences in the in-plane Cu–N bond distances are real they are only small and would only add a small in-plane rhombic component to the e.s.r. spectrum which is unlikely to be resolved in the polycrystalline e.s.r. spectrum. The inability to obtain good single-crystal e.s.r. data prevented the determination of any in-plane rhombic component, but if present it must be small. The *mm* symmetry of the copper atom does not allow a distinction to be made between a $d_{x^2-y^2}$ and a d_{xy} ground state, but the former is assumed.

Electronic Spectra.—The crystals of (1) and (2) are both bright blue and clearly absorb light in the same region of the visible spectrum; nevertheless their electronic reflectance spectra are quite different (Figure 2). While (1) has a band maximum at 11 400 cm^{-1} and a high-energy shoulder at 15 200 cm^{-1}, (2) has a band maximum at 15 300 cm^{-1} and a low-energy shoulder at 11 000 cm^{-1}. Both spectra agree with those previously reported for the $[Cu(tren)X]^{2+}$ [8] and $[Cu(NH_3)_5]^{2+}$ [10] cations respectively. The assignment of the electronic spectra of trigonal-bipyramidal copper(II) complexes has been extensively discussed in the literature [2,4,6] and in the absence of any polarised single-crystal electronic spectra for (1) it would seem reasonable to assign the intense band at 11 400 cm^{-1} as the $d_{xy}, d_{x^2-y^2} \rightarrow d_{z^2}$ transition which is allowed in C_3 and D_{3h} and the less intense shoulder at 15 000 cm^{-1} as the $d_{xy},d_{yz} \rightarrow d_{z^2}$ transition which although allowed in C_3 symmetry is forbidden in D_{3h}, but can occur weakly by a vibronic mechanism. As the relative intensities of the two observed peaks are so different this suggests that the electronic spectrum of (1) should be assigned in the higher symmetry D_{3h} rather than that of the crystallographic site symmetry of C_3. This assignment is in agreement with that suggested for other trigonal-bipyramidal copper(II) complexes [2,4,6,30,31] {excluding $[Cu(NH_3)_2][Ag(SCN)_3]$, see later}.

A tentative assignment of the polarised single-crystal electronic spectrum of $K[Cu(NH_3)_5][PF_6]_3$ has previously been suggested [4,11] before the precise stereochemistry of the $[Cu(NH_3)_5]^{2+}$ cation was known, namely the band maximum at 15 300 cm^{-1} as the $d_{xz},d_{yz} \rightarrow d_{x^2-y^2}$ transition and the shoulder at 11 000 cm^{-1} as the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition with the $d_{xy} \rightarrow d_{x^2-y^2}$ transition unobserved in the polarised single-crystal spectrum, but tentatively assigned to a weak band at $\approx$14 000 cm^{-1} in the gaussian analysis [4,11] of the reflectance spectrum. In the light of the present structure, there is no reason for changing the tentative assignment. The electronic spectrum of Figure 2 is characteristic of the ' penta-ammine effect ' type electronic spectrum [32] obtained when excess of ammonia is added to the copper(II) ion in aqueous solution, where five ammonia molecules are associated with each copper(II) ion but in addition an undetermined number of water molecules could also be involved. The present structure of (2) establishes beyond reasonable doubt that the $[Cu(NH_3)_5(OH_2)_x]^{2+}$ species in aqueous solution has a square-pyramidal, rather than a trigonal-pyramidal, CuN_5 stereochemistry, with possibly a single water molecule associated at >3.0 Å in the sixth co-ordination position.

Extended-Hückel Calculations.—The CuN_5 chromophores of (1) and (2) represent the most regular five-co-ordinate σ-bonding nitrogen-ligand complexes of the copper(II) ion yet characterised and as such represent an ideal pair of complexes involving the two alternative five-co-ordinate stereochemistries for a CuN_5 chromophore, uncomplicated by the presence of significant π bonding. The clear differences in the electronic reflectance spectra of (1) and (2) suggests that an electronic criterion of stereochemistry [9] may exist for these two stereochemistries. The relative order of the one-electron energy levels of the copper(II) ion in crystal fields of D_{3h} and C_{4v} symmetry is well established (see ref. 4, Figure 4) but is less well known using a molecular-orbital treatment.[6] For this reason extended-Hückel calculations [12] have been carried out using self-consistent charge iteration procedures, and the results for the *d*-orbital levels are illustrated in Figure 4. The calculation was carried out for the $[Cu(NH_3)_5]^{2+}$ cation using the crystallographic bond-length and -angle data of the CuN_5 chromophores and calculated hydrogen positions in both stereochemistries, and then for the $[Cu(tren)(NH_3)]^{2+}$ cation using the crystallographic co-ordinates for all the atoms. The corresponding calculation for $[Cu(NH_3)_2][Ag(SCN)_3]$ has also been carried out, first as the $Cu(NH_3)_5$ equivalent using the Cu–N bond distances of the parent complex, but then as the $Cu(NH_3)_2(NCS)_3$ equivalent, as a nearer approach to the actual environment of the CuN_5 environment in the parent complex (Figure 4).

Despite the known limitations of this type of calculation [6] in failing to calculate the total energy and the absolute energies of the *d* levels with any accuracy, the relative one-electron *d*-orbital energy levels are approximately correct and only $\approx$3 000 cm^{-1} low. The sequence of one-electron energy levels in these high-symmetry stereochemistries (which yield almost pure

d-orbital levels) are comparable (Figure 4) to those obtained in the equivalent crystal-field calculations,[4] except that the d_{xy} level in the square-pyramidal stereochemistry is slightly destabilised relative to the degenerate d_{xz},d_{yz} pair (but see ref. 6, Figure 3). Even the greater spread of the excited states of the square-pyramidal as opposed to the trigonal-bipyramidal stereochemistry is reproduced. In the $[Cu(tren)(NH_3)]^{2+}$ system there is only a small difference (<300 cm^{-1}) between the calculated energy levels using the crystallographic data and those using the simulated $Cu(NH_3)_5$ chromophore, which implies that the simulated $Cu(NH_3)_5$ chromophore is a reasonable model to describe the environment of the copper(II) ion in the $[Cu(tren)(NH_3)][ClO_4]_2$ complex. A greater effect on the energy levels is produced in the case of $[Cu(NH_3)_2][Ag(SCN)_3]$, all the levels in the simulated $Cu(NH_3)_5$ data being shifted to higher energy due to the significant shortening of the three in-plane Cu–N distances from 2.082 to 1.92 Å and the axial Cu–N distances from 2.041 to 2.00 Å, and the spread of the excited-state levels is increased, 1 400 to 3 400 cm^{-1}. In the calculation using the $Cu(NH_3)_2(NCS)_3$ simulated data the overall increase in the energy of the transitions is still present, 10 700 to 12 200 cm^{-1}, but the spread of the doubly degenerate $d_{xy},d_{x^2-y^2}$ and d_{xz},d_{yz} levels is reduced to 200 cm^{-1} with the later level still destabilised relative to the $d_{xy},d_{x^2-y^2}$ level. This near equivalence of the excited-state energy levels in $Cu(NH_3)_2(NCS)_3$ may be relevant to the assignment of the energy levels using polarised single-crystal spectra [33] which yielded a sequence $d_{z^2} > d_{xz},d_{yz} > d_{xy},d_{x^2-y^2}$, a sequence which actually reverses the order of the two degenerate levels relative to the crystal-field prediction, and is accounted for by the suggested presence of strong out-of-plane π bonding between the short-bonded (1.92 Å) thiocyanate nitrogen ligands. Despite the marked difference in the energy levels (Figure 4) between NH_3 bonded at 1.92 Å from the copper(II) ion and the nitrogen of a thiocyanate ion at this distance, there is no obvious evidence for π bonding between the thiocyanate and the copper(II) ion to account for this effect in the calculations. The largest contribution to π bonding between the copper atom and the nitrogen of the in-plane thiocyanate was $\approx 6.9\%$ in a d_{xy}–p_y bond, consequently π bonding cannot be the origin of the novel ordering of the one-electron energy levels [33] in $[Cu(NH_3)_2][Ag(SCN)_3]$ and the short Cu–N distance of 1.92 Å must be associated with the bonding properties of the nitrogen-bonded thiocyanate ion and its position in the nephelauxetic series.[21]

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