

Syntheses and Molecular Structures of Copper(II) Complexes with 1,3,5-Tris(pyrazol-1-ylmethyl)benzene†

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A new trifunctional ligand, 1,3,5-tris(pyrazol-1-ylmethyl)benzene (L), has been prepared. It reacts with 1 equivalent of copper(II) perchlorate to form the complex $[\text{CuL}_2(\text{ClO}_4)_2(\text{H}_2\text{O})_2]$ **1** and with 1.5 equivalents of copper(II) chloride to form $[\{\text{Cu}_3\text{L}_2\text{Cl}_6(\text{H}_2\text{O})_2\}_n]$ **3**. The macromolecular complex $[\{\text{Cu}_2\text{L}_2\text{Cl}_2(\text{ClO}_4)_2(\text{H}_2\text{O})_4\}_n]$ **2** was formed by the reaction of **1** with 1 equivalent of CuCl_2 . Complex **3** can also be prepared from **2** with 1 equivalent of CuCl_2 or from **1** with 2 equivalents of CuCl_2 . The mixed-metal complex $[\{\text{Cu}_2\text{CoL}_2\text{Cl}_6(\text{H}_2\text{O})_3\}_n]$ **4** was prepared from **2** with cobalt(II) chloride. The molecular structures of complexes **1**, **2** and **4** have been characterized by X-ray diffraction: **1**, monoclinic, space group $P2_1$, $a = 10.255(1)$, $b = 20.218(3)$, $c = 10.316(2)$ Å, $\beta = 106.21(1)^\circ$, $Z = 2$; **2**, monoclinic, space group $P2_1/c$, $a = 11.288(2)$, $b = 13.633(3)$, $c = 15.173(3)$ Å, $\beta = 104.635(15)^\circ$, $Z = 2$; **4**, monoclinic, space group $C2/c$, $a = 7.473(3)$, $b = 22.137(7)$, $c = 28.155(10)$ Å, $\beta = 96.21(3)^\circ$, $Z = 4$. The co-ordination sphere of copper(II) in **1** and **2** is distorted square pyramidal and **2–4** have polymeric structures.

The chemistry of polynuclear complexes containing copper or copper mixed with other metal ions has been the subject of much interest in chelate systems.^{1–16} Some dicopper complexes were prepared as models for copper proteins in the hope that they would mimic the active site of biological systems.^{17–19}

For example, the ligand 2,6-bis(acetylacetyloxymethyl)pyridine reacts with Cu^{II} and Pd^{II} to form $\text{Cu}^{\text{II}}\text{Pd}^{\text{II}}\text{Cu}^{\text{II}}$ trinuclear complexes,¹¹ ethylenediamine Schiff-base derivatives of *o*-acetoacetylphenol react with Cu^{II} and Ni^{II} to form $\text{Cu}^{\text{II}}\text{Ni}^{\text{II}}$ binuclear complexes^{12–14} and some of the copper–metal complexes were synthesised by use of macrocyclic ligands.^{15,16} The mixed copper–metal complexes were studied as representations of the metal-containing sites in metallobiomolecules^{16,20–22} and for their relevance to versatile catalytic systems in synthetic processes.^{11,23–26}

In an effort to develop new polynuclear complexes, we were interested in studying the metal complexation of polyfunctional pyrazole ligands. We prepared previously the 4-methyl-2,6-bis(pyrazol-1-ylmethyl)phenol ligand, which reacted with Zn^{II} to give a binuclear complex.²⁷ In this paper we report the synthesis and structure of mono-, bi- and tri-nuclear complexes of 1,3,5-tris(pyrazol-1-ylmethyl)benzene with Cu^{II} and Co^{II} .

Experimental

Chemicals.—All reagents and solvents were purchased from commercial sources and used as received unless noted otherwise. 1,3,5-Tris(bromomethyl)benzene was prepared according to the literature.²⁸

Physical Methods.—Melting points were obtained with a Thomas Hoover capillary apparatus in open capillaries and are uncorrected. Proton NMR spectra were recorded on a Bruker AM-200WB instrument at 200 MHz using CDCl_3 as solvent and ESR spectra on a Bruker ESP 300 X-band instrument using diphenylpicrylhydrazyl (dpph) as standard. Magnetic susceptibilities were measured using the Faraday method on a CAHN 2000 instrument with $\text{Hg}[\text{Co}(\text{SCN})_4]$ as standard and

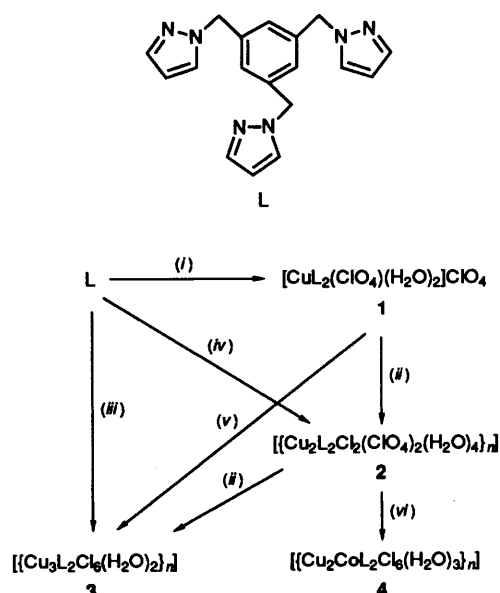
diamagnetic corrections were made using Pascal's constants. Mass spectra were recorded on a Finnigan MAT TSQ-46C instrument, infrared spectra on a Perkin Elmer 983G spectrometer using KBr as support, and ultraviolet–visible spectra on a Hewlett-Packard 8452A diode-array spectrometer using MeOH as solvent. Elemental analyses were obtained using a Hitachi CHN-O-Rapid Analyser instrument.

Syntheses.—1,3,5-Tris(pyrazol-1-ylmethyl)benzene (L). Pyrazole (2.04 g, 30 mmol) and sodium carbonate (3.18 g, 30 mmol) were dissolved in benzene (20 cm³) then 1,3,5-tris(bromomethyl)benzene (3.57 g, 10 mmol) in benzene (20 cm³) was added. After refluxing for 3 h the solvents were removed under reduced pressure and the residue was washed by acetone. The product was purified by column chromatography (silica gel 60) using ethyl acetate–hexane (1 : 1) ($R_f = 0.33$) as eluent. After solvent evaporation the crude product was crystallized from a mixture of ethyl acetate and hexane to obtain a white solid (yield 1.3 g, 40%), m.p. 60–61 °C (Found: C, 67.50; H, 5.70; N, 26.30. Calc. for $\text{C}_{18}\text{H}_{18}\text{N}_6$: C, 67.90; H, 5.65; N, 26.40%). Mass spectrum: m/z 318, 250, 182 and 114. ¹H NMR (CDCl_3): δ 5.22 (6 H, s, aryl CH_2N), 6.24 (3 H, t, J 2.0, pyrazolyl C^4H), 6.89 (3 H, s, aryl H), 7.32 (3 H, d, J 1.0, pyrazolyl C^5H) and 7.50 (3 H, d, J 1.0 Hz, pyrazolyl C^3H). Infrared: ν_{max} 3115m, 1604m, 1511m, 1431m, 1397s, 1055s and 752s cm^{-1} .

$[\text{CuL}_2(\text{ClO}_4)_2(\text{H}_2\text{O})_2]$ **1**. Copper(II) perchlorate hexahydrate (370 mg, 1 mmol) and L (318 mg, 1 mmol) were dissolved in methanol (10 cm³). The mixture was stirred for 5 min at room temperature and filtered. Blue crystals were obtained by slow diffusion of diethyl ether into the mixture (Found: C, 46.00; H, 4.35; N, 17.95. Calc. for $\text{C}_{36}\text{H}_{40}\text{Cl}_2\text{CuN}_{12}\text{O}_{10}$: C, 46.25; H, 4.30; N, 17.95%). Infrared: ν_{max} 3115m, 1606m, 1512m, 1286s, 1089s, 747s and 625s cm^{-1} . λ_{max} (MeOH) 223 (11 763), 269 (sh, 1952) and 318 nm (sh, ϵ 488 dm³ mol⁻¹ cm⁻¹).

$[\{\text{Cu}_2\text{L}_2\text{Cl}_2(\text{ClO}_4)_2(\text{H}_2\text{O})_4\}_n]$ **2**. (a) Copper(II) chloride dihydrate (170 mg, 1 mmol) and L (318 mg, 1 mmol) were dissolved in methanol (10 cm³). This solution was treated with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (370 mg, 1 mmol), stirred for 5 min at room temperature and filtered. Greenish blue crystals were obtained by slow diffusion of diethyl ether into the mixture (Found: C, 38.55; H, 4.00; N, 14.95. Calc. for $\text{C}_{36}\text{H}_{44}\text{Cl}_4\text{Cu}_2\text{N}_{12}\text{O}_{12}$: C, 39.10; H, 4.00; N, 15.20%). Infrared: ν_{max} 3541 (br), 3481 (br),

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



Scheme 1 (i) 1 equivalent $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, MeOH; (ii) 1 equivalent $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, MeOH; (iii) 1.5 equivalents $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, MeOH; (iv) 1 equivalent $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, MeOH; (v) 2 equivalents $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, MeOH; (vi) 1 equivalent $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, MeOH

3119m, 1607m, 1515m, 1150s, 1074s, 1051s, 770s and 626s cm^{-1} . $\lambda_{\text{max}}(\text{MeOH})$ 224 (14.946), 268 (6.250) and 322 nm (sh, ϵ 0.815 $\text{dm}^3 \text{g}^{-1} \text{cm}^{-1}$).

(b) Complex 1 (93.5 mg, 0.1 mmol) in methanol (10 cm^3) was added to a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (17 mg, 0.1 mmol) in methanol (5 cm^3) and the solution was filtered. Slow diffusion of diethyl ether into the mixture gave greenish blue crystals. Infrared: ν_{max} 3540 (br), 3479 (br), 3118m, 1607m, 1515m, 1151s, 1074s, 1051s, 770s and 626s cm^{-1} .

$[(\text{Cu}_3\text{L}_2\text{Cl}_6(\text{H}_2\text{O})_2)_n]$ 3 (a) Copper(II) chloride dihydrate (25.5 mg, 0.15 mmol) and L (31.8 mg, 0.1 mmol) were dissolved in methanol (20 cm^3). The mixture was stirred for 5 min at room temperature and filtered. The pale green product 3 was obtained by slow diffusion of diethyl ether into the mixture (Found: C, 40.30; H, 3.80; N, 15.60. Calc. for $\text{C}_{36}\text{H}_{40}\text{Cl}_6\text{Cu}_3\text{N}_{12}\text{O}_2$: C, 40.20; H, 3.75; N, 15.60%). Infrared: ν_{max} 3519 (br), 3116m, 1608m, 1514m, 1412s, 1280m, 1073s and 760s cm^{-1} . $\lambda_{\text{max}}(\text{MeOH})$ 241 (16.749), 270 (10.409) and 322 nm (sh, 3.346 $\text{dm}^3 \text{g}^{-1} \text{cm}^{-1}$).

(b) Complex 1 (93.5 mg, 0.1 mmol) in methanol (15 cm^3) was added to a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (34 mg, 0.2 mmol) in methanol (5 cm^3) and the solution was filtered. Slow diffusion of diethyl ether into the mixture gave a pale green product. Infrared: ν_{max} 3456 (br), 3111m, 1608m, 1515m, 1416s, 1277m, 1071s and 759s cm^{-1} .

(c) Complex 2 (110 mg, 0.1 mmol) in methanol (15 cm^3) was added to a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (17 mg, 0.1 mmol) in methanol (5 cm^3) and the solution was filtered. Slow diffusion of diethyl ether into the mixture gave a pale green product. Infrared: ν_{max} 3424 (br), 3111m, 1608m, 1514m, 1415s, 1277m, 1071s and 759s cm^{-1} .

$[(\text{Cu}_2\text{CoL}_2\text{Cl}_6(\text{H}_2\text{O})_3)_n]$ 4. Complex 2 (110 mg, 0.1 mmol) in methanol (15 cm^3) was added to a solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (23.8 mg, 0.1 mmol) in methanol (5 cm^3) and the solution was filtered. Slow diffusion of diethyl ether into the mixture gave green crystals (Found: C, 40.20; H, 3.75; N, 15.70. Calc. for $\text{C}_{36}\text{H}_{42}\text{Cl}_6\text{CoCu}_2\text{N}_{12}\text{O}_3$: C, 39.70; H, 3.90; N, 15.45%). Infrared: ν_{max} 3444 (br), 3127m, 1609m, 1513m, 1417s, 1290m, 1070s and 759s cm^{-1} . $\lambda_{\text{max}}(\text{MeOH})$ 238 (15.351), 267 (7.897) and 320 nm (sh, 3.321 $\text{dm}^3 \text{g}^{-1} \text{cm}^{-1}$).

Structure Determination.—Suitable crystals of complexes 1, 2

and 4 were chosen. Intensity data were collected at room temperature on a CAD-4 diffractometer using monochromated Mo-K α radiation ($\lambda = 0.71069 \text{ \AA}$). The unit-cell constants were derived from a least-squares refinement of 25 setting reflections. The θ - 2θ scan technique and a variable scan speed were used to obtain the integrated intensities. Three reference reflections were monitored throughout the measurement; the variation of the intensities was less than 2% for complexes 2 and 4, and there was a total decay of 7% for complex 1. Absorption corrections were applied according to an experimental ψ rotation curve. Other details of the crystal data are given in Table 1.

The structures were solved by the heavy-atom method. The atomic parameters were obtained from subsequent Fourier syntheses and least-squares refinement. The final results for all the non-hydrogen are given in Table 3. For all the crystals a weighting scheme of the form $1/[\sigma^2(F_o) + k(F_o)^2]$, $k = 0.0001$ in complexes 1 and 2 and $k = 0$ in 4, was used. All the hydrogen-atom parameters were calculated according to the ideal geometry and were not refined. The structural analyses were carried out on a MicroVaxIII computer using NRCVAX programs.²⁹ Atomic scattering factors were taken from ref. 30.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Synthesis.—The ligand 1,3,5-tris(pyrazol-1-ylmethyl)benzene (L) was prepared as follows. First the bromination²⁸ of 1,3,5-trimethylbenzene gives 1,3,5-tris(bromomethyl)benzene, which is then treated with pyrazole and sodium carbonate in benzene to produce the ligand, an air-stable white substance. Reactions of metal(II) ions and the ligand (L), which possesses three potential nitrogen donor sites in the pyrazolyl rings, result in formation of complexes 1–4. The 1:1 reaction of the ligand and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ gives complex 1 in which only one N atom co-ordinates to copper(II). Complex 1 continues to react with 1 equivalent of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ to form complex 2. In this case the second free N atom co-ordinates to copper(II), and polymerization occurs. Complex 2 also can be synthesised by the reaction of the ligand with 1 equivalent of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 1 equivalent of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. It reacts with 1 equivalent of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ to give complex 3 or with 1 equivalent of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ to give 4, involving coordination of the third free N atom of 2 and polymerization. Also complex 3 can be synthesised by the reaction of the ligand with 1.5 equivalents of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and of complex 1 with 2 equivalents of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. All synthetic sequences are shown in Scheme 1.

Molecular Structure of $[\text{CuL}_2(\text{ClO}_4)_2(\text{H}_2\text{O})_2]\text{ClO}_4$ 1.—The molecular structure is shown in Fig. 1, selected bond distances and angles in Table 2.

Complex 1 is a monocopper(II) compound. The copper(II) ion is co-ordinated by two pyrazolyl nitrogen atoms at Cu–N(1A) 2.019(4) and Cu–N(1B) 1.988(4) Å, and two water oxygen atoms at Cu–O(1) 1.924(4) and Cu–O(2) 1.901(4) Å. Only one oxygen atom O(3) of the perchlorate ligand is co-ordinated [Cu–O(3) 2.411(3) Å] and another perchlorate anion is not co-ordinated. The co-ordination sphere of copper(II) can be described as distorted square pyramidal³¹ with two oxygen atoms, O(1) and O(2), of the water molecules and two nitrogen atoms, N(1A) and N(1B), of the pyrazolyl rings of the ligand, in the square plane and O(3) at the apical position. The O(1)–Cu–O(2) angle is 178.76(15)°, which is near to the theoretical value of 180°. The N(1A)–Cu–O(3) [92.11(15)], N(1B)–Cu–O(3) [97.78(14)], O(1)–Cu–O(3) [85.69(15)] and O(2)–Cu–O(3) [95.03(17)°] angles show distortion from the ideal value of 90° in the perfectly square-pyramidal geometry.

Molecular Structure of $[\text{Cu}_2\text{L}_2\text{Cl}_2(\text{H}_2\text{O})_2][\text{ClO}_4]_2 \cdot 2\text{H}_2\text{O}$ 2.—Selected bond distances and angles are shown in Table 2

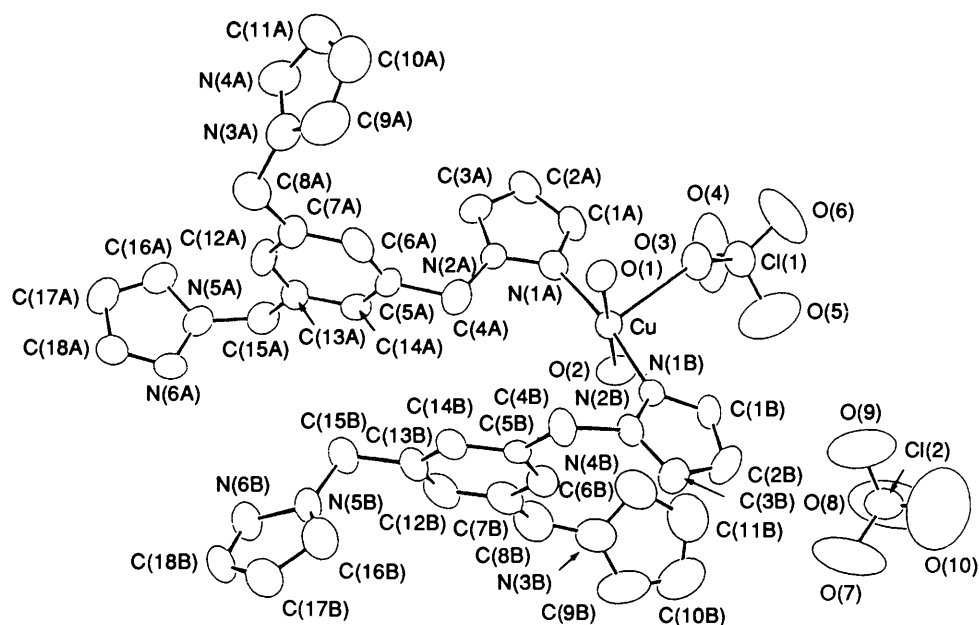


Fig. 1 The molecular structure of complex 1

Table 1 Crystallographic data for the complexes

Complex	1	2	4
Formula	$[\text{CuL}_2(\text{ClO}_4)(\text{H}_2\text{O})_2]\text{ClO}_4$	$[\text{Cu}_2\text{L}_2\text{Cl}_2(\text{H}_2\text{O})_2][\text{ClO}_4]_2 \cdot 2\text{H}_2\text{O}$	$[\text{Cu}_2\text{CoL}_2\text{Cl}_6] \cdot 3\text{H}_2\text{O}$
<i>M</i>	935.2	1105.7	1080.3
Crystal size/mm	0.35 × 0.40 × 0.50	0.15 × 0.30 × 0.50	0.15 × 0.20 × 0.20
Crystal symmetry	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1/c$	$C2/c$
<i>a</i> /Å	10.255(1)	11.288(2)	7.474(3)
<i>b</i> /Å	20.218(3)	13.633(3)	22.137(7)
<i>c</i> /Å	10.316(2)	15.173(3)	28.155(10)
β /°	106.21(1)	104.635(15)	96.21(3)
<i>U</i> /Å ³	2053.8(5)	2259.2(8)	4630(3)
<i>Z</i>	2	2	4
<i>F</i> (000)	946	1132	2211
<i>D_c</i> /Mg m ⁻³	1.516	1.625	1.550
μ /mm ⁻¹	0.73	1.25	1.66
2 θ range/°	2–50	2–45	2–45
Scan parameters	1.3 + 0.7 tan θ	1.8 + 0.7 tan θ	1.4 + 0.7 tan θ
Total number of reflections	3707 (3309 > 2 σ)	2947 (2220 > 2 σ)	3018 (1923 > 2 σ)
<i>R</i> , <i>R'</i>	0.038, 0.043	0.055, 0.062	0.062, 0.053
<i>S</i>	2.21	2.98	3.81

and the repeating unit in Fig. 2. The co-ordination sphere of copper(II) in this polymeric structure is distorted square pyramidal³¹ with one bridging chloride ion Cl(1), one oxygen atom O(1) of the water and two nitrogen atoms, N(1) and N(3), of the pyrazolyl rings of the ligands in the equatorial and another bridging chloride ion Cl(1') at the apical position. Two Cu–N distances at 2.009(5) and 2.025(6) Å and the Cu–N distances of complexes 1 and 4 are within the ranges observed for other complexes.^{2,5,9,32–36}

Each copper(II) ion is bridged by two ligands and two chloride ions to form a polymeric structure. In the dicopper unit, two copper(II) ions and two bridging chloride ions form a centrosymmetric planar four-membered ring. Long [Cu–Cl(1') 2.6847(19) Å] and short distances [Cu–Cl(1) 2.2764(22) Å] can be distinguished in this ring and the Cu–Cl–Cu' angle is 87.31(6)° [giving a value of 92.69(7)° for the Cl(1)–Cu–Cl(1') angle].³ The Cu...Cu' distance is 3.437(2) Å. One oxygen atom of the water molecule is co-ordinated to each copper(II) and the Cu–O(1) distance is 1.978(5) Å. There are two water molecules of crystallization and two perchlorate counter anions in each dicopper unit of the complex.

Molecular Structure of $[\text{Cu}_2\text{CoL}_2\text{Cl}_6] \cdot 3\text{H}_2\text{O}$ 4.—Complex 4 is a mixed-metal chain compound, involving two copper(II) and one cobalt(II) ion in the trinuclear unit. Selected bond distances and angles are shown in Table 2, the repeating unit in Fig. 3.

Complex 4 was synthesised from 2 with cobalt(II) chloride and there are three water molecules in the formula unit. The structure contains a copper part and a cobalt part. In the former the co-ordination sphere around each individual copper(II) is intermediate between square pyramidal and trigonal bipyramidal.^{9,31} Consideration of the distortion from an idealized square-pyramidal geometry illustrates this point. The equatorial plane is defined by two nitrogen atoms N(1), N(4) of the ligands and two chloride atoms, non-bridging Cl(2) and bridging Cl(3''), while another bridging chloride ion Cl(3) occupies the apex of the co-ordination pyramid. Although the N(1)–Cu–N(4) [176.4(4)°] angle is near to the ideal value of 180° and the Cl(3)–Cu–Cl(3'') [92.61(11)], Cl(3)–Cu–N(1) [91.7(3)] and Cl(3)–Cu–N(4) [91.0(3)°] angles are closer to the expected 90°, Cl(2)–Cu–Cl(3'') [156.64(14)] (ideally 180°) and Cl(2)–Cu–Cl(3) [110.62(13)°] (ideally 90°) show marked differences from the

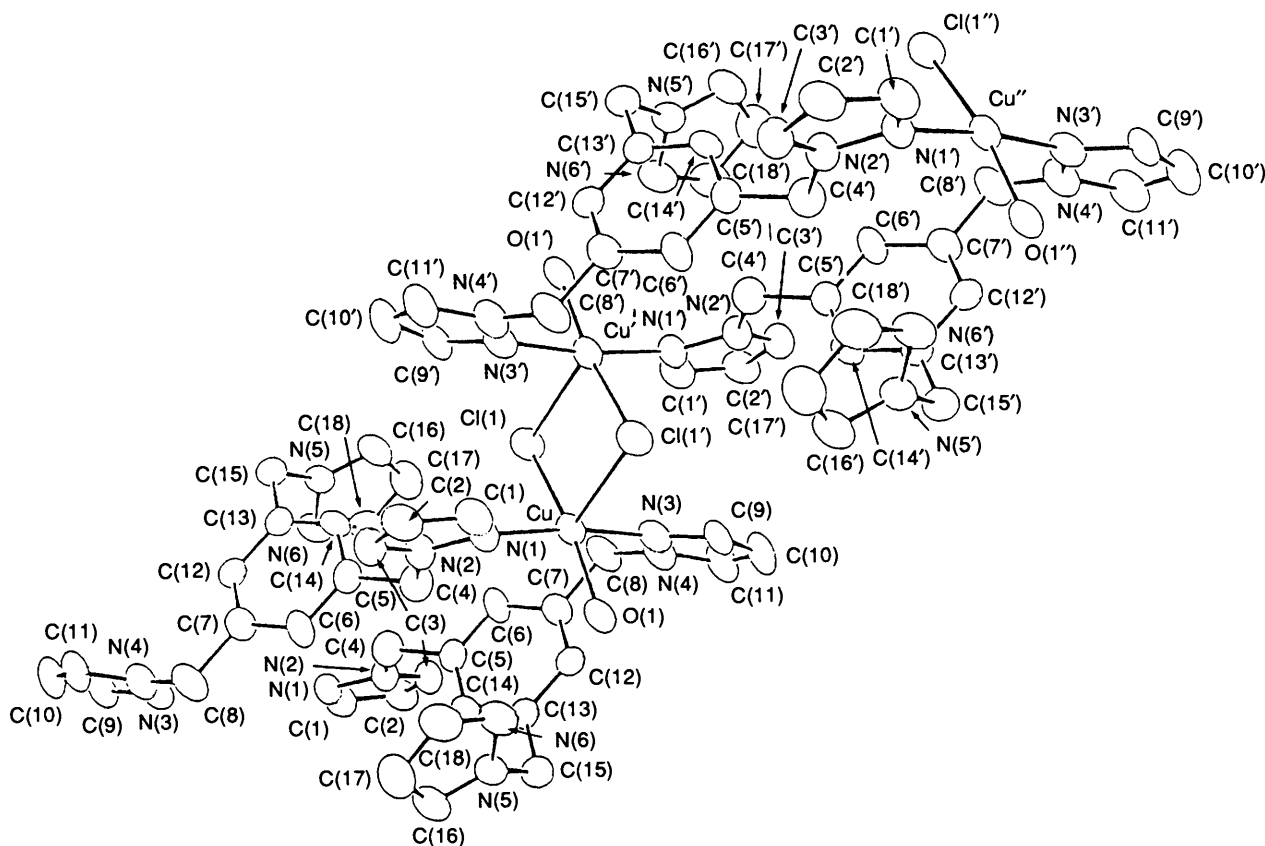


Fig. 2 The repeat unit of complex 2

Table 2 Selected bond distances (Å) and angles (°)

Complex 1			
Cu–N(1A)	2.019(4)	Cu–O(1)	1.924(4)
Cu–N(1B)	1.988(4)	Cu–O(2)	1.901(4)
Cu–O(3)	2.411(3)		
N(1A)–Cu–N(1B)	169.89(16)	N(1A)–Cu–O(1)	89.62(16)
N(1A)–Cu–O(2)	91.37(17)	N(1A)–Cu–O(3)	92.11(15)
N(1B)–Cu–O(1)	89.05(16)	N(1B)–Cu–O(2)	89.85(17)
N(1B)–Cu–O(3)	97.78(14)	O(1)–Cu–O(2)	178.76(15)
O(1)–Cu–O(3)	85.69(15)	O(2)–Cu–O(3)	95.03(17)
Complex 2			
Cu...Cu'	3.437(2)	Cu–Cl(1)	2.2764(22)
Cu–Cl(1')	2.6847(19)	Cu–N(1)	2.009(5)
Cu–N(3)	2.025(6)	Cu–O(1)	1.978(5)
Cl(1)–Cu–Cl(1')	92.69(7)	Cu–Cl(1)–Cu'	87.31(6)
Cl(1)–Cu–N(1)	91.30(17)	Cl(1)–Cu–N(3)	93.55(18)
Cl(1)–Cu–O(1)	171.73(14)	Cl(1')–Cu–N(1)	92.93(16)
Cl(1')–Cu–N(3)	92.05(16)	Cl(1')–Cu–O(1)	95.06(14)
N(1)–Cu–N(3)	172.87(23)	N(1)–Cu–O(1)	85.42(21)
N(3)–Cu–O(1)	89.07(22)		
Complex 4			
Co–Cl(1)	2.211(4)	Co–N(6)	1.989(11)
Cu...Cu''	3.450(3)	Cu–Cl(2)	2.270(4)
Cu–Cl(3'')	2.390(3)	Cu–Cl(3)	2.599(3)
Cu–N(1)	1.995(9)	Cu–N(4)	1.997(9)
Cl(1)–Co–Cl(1')	124.12(23)	Cl(1)–Co–N(6)	111.4(3)
Cl(1')–Co–N(6)	103.7(3)	N(6)–Co–N(6')	100.1(4)
Cl(2)–Cu–Cl(3')	156.64(14)	Cl(2)–Cu–Cl(3)	110.62(13)
Cl(2)–Cu–N(1)	89.0(3)	Cl(2)–Cu–N(4)	87.9(3)
Cl(3)–Cu–Cl(3'')	92.61(11)	Cl(3)–Cu–N(1)	91.7(3)
Cl(3)–Cu–N(4)	91.0(3)	Cl(3'')–Cu–N(1)	92.9(3)
Cl(3'')–Cu–N(4)	89.3(3)	N(1)–Cu–N(4)	176.4(4)
Cu–Cl(3)–Cu''	87.39(11)		

ideal square-pyramidal geometry. A similar comparison can be made for an idealized trigonal-bipyramidal geometry assuming N(1), N(4) to be the 'axial' donors and Cl(2), Cl(3), Cl(3') to form the 'equatorial' plane. Two Cu–N distances [Cu–N(1) 1.995(9) and Cu–N(4) 1.997(9) Å] are shorter than those of complex 2. Each copper(II) is bridged by two chloride ions and two ligands. The bridging Cu₂Cl₂ unit is similar to that of complex 2, the short distance Cu–Cl(3'') 2.390(3) Å being longer than Cu–Cl(1) 2.2764(22) Å in 2 but the long distance Cu–Cl(3) 2.599(3) Å is shorter than Cu–Cl(1') 2.6847(19) Å in 2. The Cu...Cu'' distance is 3.450(3) Å, longer than Cu...Cu' 3.437(2) Å of complex 2. The Cu–Cl(3)–Cu'' angle is 87.39(11) and Cl(3)–Cu–Cl(3'') is 92.61(11)°; Cu, Cu'', Cl(3) and Cl(3'') are in the same plane.

In the cobalt part the co-ordination sphere around each individual cobalt(II) can be described as distorted tetrahedral. The cobalt(II) is co-ordinated by two pyrazolyl nitrogen atoms of the ligands and two non-bridging chloride ions. The two Co–N distances are 1.989(11) Å and the two Co–Cl distances are 2.211(4) Å. The Cl(1)–Co–Cl(1') [124.12(23)] and N(6)–Co–N(6') [100.1(4)°] angles differ from tetrahedral geometry (ideally 109.5°), signifying C₂ symmetry of the cobalt(II) centre.

In complex 4 each ligand possesses three donor sites, N(1), N(4) and N(6), of the pyrazolyl rings and all are co-ordinated to metal(II) ions, N(1) and N(4) to copper(II) and N(6) to cobalt(II). Also each copper(II) is co-ordinated by two bridging chloride ions, Cl(3) and Cl(3''), and one non-bridging chloride Cl(2) and each cobalt(II) is co-ordinated by two non-bridging chlorides, Cl(1) and Cl(1'). Complex 4 is a mixed trinuclear Cu^{II}Cu^ICo^{II} infinite network.

Structure of [Cu₃L₂Cl₆].2H₂O 3.—The tricopper(II) unit structure of complex 3 [Cu₃L₂Cl₆].2H₂O was believed to be similar to complex 4 [CoCu₂L₂Cl₆].3H₂O. Complexes 3 and 4 are prepared in a similar way from 2 and different metal (II) ions (see Scheme 2). When the IR, UV and elemental analysis properties of these complexes are compared it is concluded that the structure of 3 is similar to that of 4.

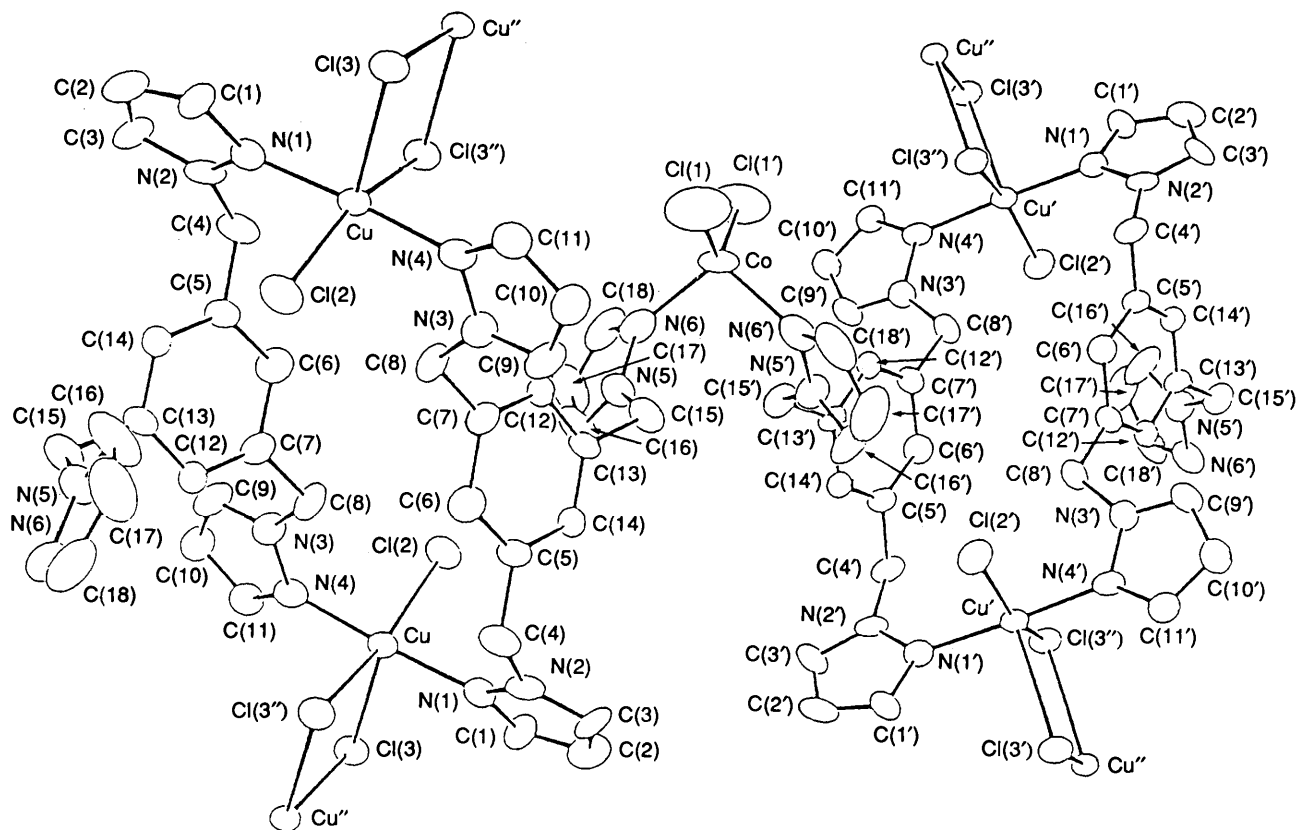
Table 3 Final atomic positional parameters of non-hydrogen atoms

Atom	x	y	z	Atom	x	y	z
Complex 1							
Cu	0.299 23(5)	0.500 00	0.211 88(5)	C(1B)	0.468 1(5)	0.397 2(3)	0.387 1(6)
N(1A)	0.188 5(4)	0.556 49(23)	0.059 1(4)	C(2B)	0.503 0(6)	0.371 6(3)	0.516 9(6)
N(2A)	0.091 9(4)	0.601 05(21)	0.062 9(4)	C(3B)	0.440 1(6)	0.411 4(3)	0.589 3(5)
N(3A)	-0.022 8(4)	0.866 04(24)	0.225 8(5)	C(4B)	0.273 6(4)	0.503 2(4)	0.531 7(5)
N(4A)	-0.034 8(5)	0.898 7(3)	0.112 1(5)	C(5B)	0.128 0(5)	0.482 07(23)	0.467 5(5)
N(5A)	-0.559 8(4)	0.694 35(24)	0.041 7(4)	C(6B)	0.099 3(5)	0.419 9(3)	0.408 9(5)
N(6A)	-0.590 1(5)	0.686 64(25)	0.160 0(5)	C(7B)	-0.031 6(5)	0.402 5(3)	0.345 0(5)
C(1A)	0.211 8(5)	0.564 5(3)	-0.061 2(5)	C(8B)	-0.058 6(7)	0.336 9(4)	0.269 2(7)
C(2A)	0.132 0(5)	0.614 5(3)	-0.131 5(5)	C(9B)	0.092 2(9)	0.247 4(3)	0.392 2(9)
C(3A)	0.056 6(5)	0.636 2(3)	-0.050 9(6)	C(10B)	0.213 5(12)	0.225 7(4)	0.397 7(13)
C(4A)	0.040 6(6)	0.605 1(3)	0.182 8(5)	C(11B)	0.251 8(9)	0.259 6(4)	0.297 0(9)
C(5A)	-0.074 9(5)	0.653 7(3)	0.162 9(5)	C(12B)	-0.136 8(5)	0.445 8(4)	0.346 0(5)
C(6A)	-0.052 6(5)	0.717 8(3)	0.208 3(5)	C(13B)	-0.111 3(5)	0.506 3(4)	0.405 0(5)
C(7A)	-0.158 5(6)	0.761 9(3)	0.192 9(6)	C(14B)	0.023 6(5)	0.525 4(3)	0.466 9(5)
C(8A)	-0.138 1(6)	0.831 3(3)	0.248 0(7)	C(15B)	-0.227 4(6)	0.553 1(4)	0.399 4(6)
C(9A)	0.105 6(7)	0.865 7(4)	0.305 9(7)	C(16B)	-0.189 0(5)	0.551 4(4)	0.652 7(6)
C(10A)	0.179 6(7)	0.900 1(4)	0.236 1(9)	C(17B)	-0.268 8(6)	0.563 8(4)	0.736 3(5)
C(11A)	0.090 9(7)	0.918 7(4)	0.117 2(7)	C(18B)	-0.395 2(5)	0.574 5(3)	0.647 4(6)
C(12A)	-0.288 1(5)	0.740 4(3)	0.128 0(6)	O(1)	0.387 8(3)	0.578 30(18)	0.300 4(3)
C(13A)	-0.315 1(5)	0.676 0(3)	0.083 2(5)	O(2)	0.211 7(4)	0.421 87(22)	0.128 1(4)
C(14A)	-0.205 9(5)	0.632 6(3)	0.102 4(5)	O(3)	0.485 0(6)	0.493 27(23)	0.111 8(3)
C(15A)	-0.457 1(6)	0.653 5(3)	0.010 6(6)	O(4)	0.427 2(6)	0.441 8(5)	-0.093 0(5)
C(16A)	-0.617 4(6)	0.748 1(3)	-0.023 8(6)	O(5)	0.549 2(9)	0.387 0(3)	0.090 9(7)
C(17A)	-0.690 5(6)	0.777 7(3)	0.054 0(7)	O(6)	0.649 5(6)	0.467 0(3)	0.005 7(7)
C(18A)	-0.669 3(6)	0.737 1(3)	0.165 2(6)	O(7)	0.619 1(9)	0.199 0(4)	0.514 1(7)
N(1B)	0.383 8(4)	0.448 79(21)	0.378 7(4)	O(8)	0.666 8(9)	0.163 9(4)	0.326 9(6)
N(2B)	0.371 0(4)	0.456 98(22)	0.505 3(4)	O(9)	0.704 0(11)	0.271 0(3)	0.391 6(11)
N(3B)	0.054 1(6)	0.293 5(3)	0.296 1(5)	O(10)	0.824 7(8)	0.193 1(8)	0.492 2(14)
N(4B)	0.154 9(6)	0.302 9(3)	0.236 9(6)	Cl(1)	0.526 09(15)	0.447 66(8)	0.022 86(15)
N(5B)	-0.265 0(4)	0.554 75(24)	0.525 1(4)	Cl(2)	0.699 68(16)	0.208 74(8)	0.428 53(14)
N(6B)	-0.395 3(4)	0.570 3(3)	0.520 8(4)				
Complex 2							
Cu	0.890 85(7)	0.086 63(7)	0.003 98(6)	C(10)	1.096 6(7)	0.221 2(7)	0.240 6(5)
Cl(1)	0.895 73(16)	-0.074 81(14)	0.043 06(13)	C(11)	1.010 9(7)	0.177 1(7)	0.275 8(4)
N(1)	0.792 0(5)	0.056 4(4)	-0.122 9(4)	C(12)	0.697 1(6)	0.186 0(5)	0.125 0(4)
N(2)	0.677 4(5)	0.016 9(4)	-0.147 4(3)	C(13)	0.419 7(6)	-0.215 9(5)	-0.074 2(4)
N(3)	0.975 3(5)	0.130 6(5)	0.131 9(4)	C(14)	0.517 0(6)	-0.151 3(5)	-0.065 0(4)
N(4)	0.938 7(5)	0.122 6(5)	0.210 1(4)	C(15)	0.435 4(6)	-0.312 2(5)	-0.025 2(4)
N(5)	0.466 2(5)	-0.297 4(4)	0.072 6(4)	C(16)	0.576 3(7)	-0.295 7(6)	0.131 2(5)
N(6)	0.379 0(5)	-0.265 2(5)	0.112 9(4)	C(17)	0.562 5(8)	-0.262 1(7)	0.212 6(5)
C(1)	0.827 4(6)	0.063 0(6)	-0.200 1(5)	C(18)	0.438 9(7)	-0.244 6(6)	0.197 7(5)
C(2)	0.737 8(7)	0.028 2(6)	-0.272 5(5)	O(1)	0.860 9(4)	0.225 8(4)	-0.031 5(3)
C(3)	0.641 8(6)	0.001 3(6)	-0.236 5(5)	Cl(2)	0.253 45(20)	0.422 11(18)	0.064 04(15)
C(4)	0.604 5(6)	0.014 8(6)	-0.080 1(5)	O(2)	0.250 1(10)	0.325 5(6)	0.040 2(9)
C(5)	0.500 3(6)	-0.058 7(5)	-0.101 7(4)	O(3)	0.348 7(12)	0.441 5(12)	0.131 5(9)
C(6)	0.385 2(6)	-0.028 0(6)	-0.150 1(4)	O(4)	0.282 7(12)	0.466 6(8)	-0.003 3(7)
C(7)	0.714 2(6)	0.096 4(5)	0.162 9(4)	O(5)	0.157 7(9)	0.456 2(10)	0.086 8(9)
C(8)	0.838 5(6)	0.059 9(6)	0.218 4(5)	O(6)	0.917 0(6)	0.382 8(5)	0.081 3(5)
C(9)	1.071 1(6)	0.191 3(6)	0.151 0(5)				
Complex 4							
Co	$\frac{1}{2}$	0.380 98(11)	$\frac{1}{4}$	C(6)	0.105 8(14)	0.201 0(5)	0.050 1(4)
Cu	-0.022 21(21)	0.433 42(7)	-0.031 93(5)	C(7)	0.133 9(15)	0.264 5(5)	0.060 3(4)
Cl(1)	0.270 7(7)	0.427 77(23)	0.209 50(17)	C(8)	0.060 1(18)	0.310 5(6)	0.023 3(4)
Cl(2)	-0.169 3(5)	0.366 88(15)	-0.083 67(12)	C(9)	-0.223 6(17)	0.320 0(6)	0.064 4(4)
Cl(3)	-0.209 0(4)	0.531 83(13)	-0.027 06(11)	C(10)	-0.354 3(17)	0.363 8(6)	0.065 8(4)
N(1)	0.398 4(12)	0.033 7(4)	0.085 7(3)	C(11)	-0.299 0(15)	0.408 5(5)	0.037 4(4)
N(2)	0.234 1(13)	0.048 4(4)	0.099 6(3)	C(12)	0.216 3(16)	0.282 0(5)	0.104 2(4)
N(3)	-0.103 5(13)	0.339 4(4)	0.036 8(3)	C(13)	0.273 7(15)	0.237 4(5)	0.138 8(4)
N(4)	-0.147 0(12)	0.395 5(4)	0.019 8(3)	C(14)	0.244 9(14)	0.177 8(5)	0.127 7(4)
N(5)	0.549 1(12)	0.270 9(4)	0.188 4(3)	C(15)	0.355 5(16)	0.256 5(6)	0.187 5(4)
N(6)	0.617 0(13)	0.323 3(5)	0.208 9(3)	C(16)	0.672 3(18)	0.234 9(7)	0.175 1(5)
C(1)	0.467 3(18)	-0.004 3(5)	0.119 1(4)	C(17)	0.833 5(18)	0.263 6(8)	0.183 5(5)
C(2)	0.348 2(21)	-0.013 9(6)	0.153 2(4)	C(18)	0.792 6(19)	0.316 9(7)	0.204 1(4)
C(3)	0.204 0(19)	0.020 5(6)	0.140 3(4)	O(1)	$\frac{1}{2}$	0.123 4(9)	$\frac{1}{4}$
C(4)	0.120 9(16)	0.093 3(5)	0.072 5(4)	O(2)	0.793(4)	0.082 3(12)	0.217 2(8)
C(5)	0.160 1(15)	0.158 8(5)	0.084 0(4)				

Table 4 Values of τ for selected copper(II) complexes

Complex ^a	$\beta/^\circ$	$\alpha/^\circ$	τ	Geometry ^b	Ref.
[Cu(bbes)(acac)] ⁺	171.4	170.8	0.01	SPY	36
[Cu ₂ L ₂ Cl ₂ (H ₂ O) ₂] ²⁺	172.87	171.73	0.02	SPY	This work
[Cu(pdto)(ClO ₄)] ⁺	170.1	162.8	0.12	SPY	34
[CuL ₂ (ClO ₄) ₂ (H ₂ O) ₂] ⁺	178.76	169.89	0.15	SPY	This work
[Cu(tpea)Cl] ⁺	171.1	159.8	0.19	SPY	35
[Cu(bbes)(MeOH)(H ₂ O)] ²⁺	174.6	158.6	0.27	SPY	36
[Cu(fptc)(bipy)] ⁺	174.9	156.9	0.3	SPY, TBPY ^c	9
[Cu ₂ CoL ₂ Cl ₆]	176.4	156.64	0.33	SPY, TBPY	This work
[Cu(bbdh)Cl]	165.9	142.18	0.39	TBPY	37
[Cu(teen)Cl ₂] ₂	174.91	145.69	0.49	TBPY	2
[Cu(bbtb)(H ₂ O)] ²⁺	175.2	136.8	0.64	TBPY	38
[Cu(bipy) ₂ (tu)] ²⁺	169.6	119.9	0.83	TBPY	39
[CuCl ₅] ³⁻	180	120	1.00	TBPY	40

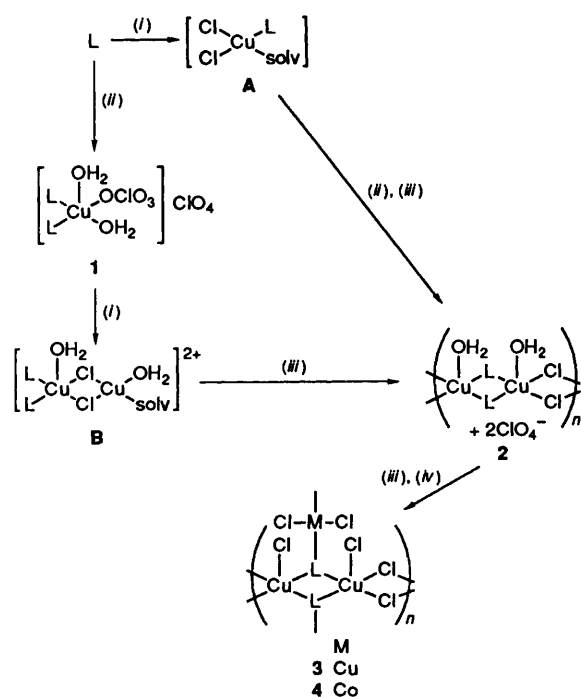
^a bbdh = 1,6-Bis(benzimidazol-2-yl)-2,5-dithiahexane; teen = *N,N,N'*-triethylethylenediamine; bbtb = 1,2-bis(benzimidazol-2-ylmethylthio)benzene; tu = thiourea. ^b The co-ordination geometry of the copper centre; SPY = square pyramidal, TBPY = trigonal bipyramidal. ^c The geometry is between SPY and TBPY.

**Fig. 3** The repeat unit of complex 4

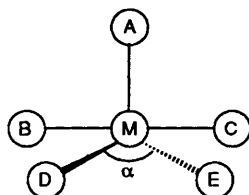
As complexes 1, 2 and 4 comprise a series which contains a range of structural types intermediate between the idealized square-pyramidal and trigonal-bipyramidal extremes it seems desirable to systematize these geometries by using a structural index. In a five-co-ordinate system such as that represented on the following page, ideally square-pyramidal geometry is associated with $\alpha = \beta = 180^\circ$, for A as the axial ligand (β is the greater of the basal angles, B–M–C). For perfectly trigonal-bipyramidal geometry, $\alpha = 120^\circ$ and B–M–C is the principal axis. The geometric parameter $\tau = (\beta - \alpha)/60$, 0 for a C_{4v} and 1 for a D_{3h} co-ordination polyhedron, as defined by Addison *et al.*³²

Table 4 shows complexes 1, 2 and 4 to have τ values of 0.15, 0.02 and 0.33, and compares these values with structural results for complexes with related geometries. For [Cu(bbes)(acac)]⁺ [bbes = bis(2-benzimidazolylethyl) sulfide, acac =

acetylacetonate],³⁶ $\tau = 0.01$, so the geometry is very close to being perfectly square pyramidal, and [CuCl₅]³⁻,⁴⁰ $\tau = 1.00$, is perfectly trigonal bipyramidal. The other τ values are in the range 0.01–1.00 which reveals the 'distortion' of their geometries. For complex 2, [Cu₂L₂Cl₂(H₂O)₂]²⁺, τ is very small (0.02) and the geometry is slightly distorted square pyramidal. The complex [Cu(pdto)(ClO₄)]⁺ [pdto = 1,8-bis-(2-pyridyl)-3,6-dithiaoctane],³⁴ [CuL₂(ClO₄)₂(H₂O)₂]⁺ 1 and [Cu(tpea)Cl]⁺ {tpea = tris[2-(2-pyridyl)ethyl]amine}³⁵ are about 10–20% distorted toward the trigonal-bipyramidal state as judged by the τ values. Complex 4, [Cu₂CoL₂Cl₆], has a larger τ value (0.33), however the value of α [156.64°, the angle Cl(2)–Cu–Cl(3'')] is between 180 (ideal square pyramidal) and 120° (ideal trigonal bipyramidal) which shows that the geometry is similar to that of [Cu(fptc)(bipy)]⁺ (Hfptc = 2-formylpyridine thiosemicarbazone, bipy = 2,2'-bipyridine).⁹



Scheme 2 solv = Solvent. (i) CuCl_2 ; (ii) $\text{Cu}(\text{ClO}_4)_2$; (iii) polymerization; (iv) MCl_2 (M = Cu or Co)



Spectroscopy.—In the IR spectra the C–H stretching vibrations of the pyrazolyl groups in complexes 1–4 are at 3115, 3119, 3116 and 3127 cm^{-1} , and the C=N stretching vibrations at 1512, 1515, 1514 and 1513 cm^{-1} , respectively. Complex 2 shows a strong peak at 1074 cm^{-1} for the perchlorate ion which has a regular tetrahedral structure and belongs to the point group T_d . Complex 1 has two perchlorate ions. One is a counter anion with a peak at 1089 cm^{-1} . The other is bonded through one oxygen (O^*) and the original T_d symmetry is lowered to C_{3v} , with two strong absorption peaks at 1150 (Cl– O^*) and 1051 cm^{-1} (ClO_3).⁴¹

In the UV spectra the pyrazolyl group absorption maxima are at 223, 224, 241 and 238 nm,⁴² those of the benzene group are at 269, 268, 270 and 267 nm and there is a shoulder at about 318, 332, 322 and 320 nm for complexes 1–4 (see Experimental section).

The X-band polycrystalline ESR spectra and magnetic moments of the complexes were measured at room temperature. The ESR spectrum of complex 1 is similar to that of $[\text{Cu}(\text{bmdhp})(\text{H}_2\text{O})(\text{ClO}_4)_2]^{32}$ [bmdhp = 1,7-bis(*N*-methylbenzimidazol-2-yl)-2,6-dithiaheptane] and complex 2 shows an axial signal.⁴³ The g values ($g_{\parallel} = 2.297$, $g_{\perp} = 2.066$ for complex 1, $g_{\parallel} = 2.304$, $g_{\perp} = 2.056$ for 2) are consistent with a square-pyramidal co-ordination sphere for the copper(II) and the single unpaired electron is located in an essentially $d_{x^2-y^2}$ orbital. The magnetic moment of complex 1 ($\mu_{\text{eff}} = 1.87$) can be regarded as normal and 2 has a value ($\mu_{\text{eff}} = 1.86$ per copper), relatively near to the spin-only value of 1.73 for the free copper(II) ion.⁴³ This indicates the absence of antiferro-

magnetic coupling between the two copper(II) ions of the bridging CuCl_2Cu unit.⁴⁴ The ESR spectra of complexes 3 and 4 show rhombic signals with three g values⁴³ ($g_1 = 2.050$, $g_2 = 2.112$, $g_3 = 2.200$ for 3 and $g_1 = 2.054$, $g_2 = 2.128$, $g_3 = 2.262$ for 4). The magnetic moments are low ($\mu_{\text{eff}} = 3.30$ per unit of 3, 3.81 per unit of 4). The total magnetic moments of complexes 3 and 4 can be obtained by the equation: χ_M' (per unit) = χ_M' [non-bridged metal(II) (Cu,Co)] + χ_M' [bridged copper(II) (CuCl_2Cu)]. Because the CuCl_2Cu units of complexes 3 and 4 are similar to that of complex 2, χ_M' for 2 can be substituted for the term χ_M' [bridged copper(II) (CuCl_2Cu)] in each. Values of χ_M' (and μ_{eff}) for non-bridged metal(II) (Co, Cu) can thus be found. For complex 3, μ_{eff} for the non-bridged copper(II) is ≈ 1.90 , in accord with a d^9 configuration.⁴⁴

Non-bridged Co^{II} (d^7 configuration) can show two spin states, high spin ($S = \frac{3}{2}$) for which μ_{eff} is in the range 4.1–5.2⁴⁵ and low spin ($S = \frac{1}{2}$) for which μ_{eff} is similar to that of $[\text{Co}(\text{NO})\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3]\text{BPh}_4$ ($\mu_{\text{eff}} = 1.98$),⁴⁶ $[\text{Co}(\text{dman})_2\text{I}]\text{I}$ [dman = 1,8-bis(dimethylarsino)naphthalene] ($\mu_{\text{eff}} = 2.06$), $[\text{Co}(\text{dman})_2\text{I}]\text{ClO}_4$ ($\mu_{\text{eff}} = 1.97$),⁴⁷ $[\text{Co}(\text{NCS})_2(\text{PMe}_3)_2]$ ($\mu_{\text{eff}} = 2.15$) and $[\text{CoBr}_2(\text{PMe}_3)_3]$ ($\mu_{\text{eff}} = 2.20$).⁴⁸ In complex 4 $\mu_{\text{eff}} = 2.47$ for Co^{II} *i.e.* towards the low spin regime.

Acknowledgements

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