Structural, Spectral and Magnetic Investigations of Various Types of Compounds and their Isomers isolated from the System Copper(II)–C(CN)$_3^-$–Pyrazole†

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From the system Cu^{II}–C(CN)$_3^-$–Hpz (Hpz = pyrazole) the following compounds were isolated: [Cu{C(CN)$_3$}(Hpz)$_4$][C(CN)$_3$] **1**, [Cu{C(CN)$_3$}$_2$(Hpz)$_3$] **2**, α-[Cu{C(CN)$_3$}$_2$(Hpz)$_2$] **3**, β-[Cu{C(CN)$_3$}$_2$(Hpz)$_2$] **4** and [Cu{Hpz·C(CN)$_3$}$_2$] **5**. They were studied by the use of spectroscopic and cryomagnetic methods. The structures of **1** and **2** were refined to *R* values of 0.0369 and 0.0374 for 1346 and 2066 independent reflections respectively. Compound **1** crystallises in space group $P2_1/c$, with a = 9.568(4), b = 16.692(7), c = 14.957(9) Å, β = 94.05(4)° and Z = 4; **2** crystallises in space group $P\bar{1}$, with a = 7.607(4), b = 8.942(6), c = 16.027(10) Å, α = 95.95(6), β = 90.83(5), γ = 106.88(5)° and Z = 2. Both compounds show elongated pseudo-octahedral copper environments, with the Hpz molecules in the equatorial plane. In **1** one C(CN)$_3$ group bridges the Cu^{II} atoms in axial positions while the second group is anionic. Compound **2** contains mono- as well as bi-dentate bridging C(CN)$_3$ groups; the latter join the basic structure units into binuclear species. Weak ferromagnetic coupling operates between the copper(II) centres inside the dimers. Physical measurements show that compounds **3** and **4** display rhombic octahedral arrangements around Cu^{II} in which all C(CN)$_3$ groups are bridging. The α and β compounds are distortion isomers. Compound **5**, a coligand isomer with respect to **3** and **4**, contains new anionic chelate ligands, HN=C(pz)CH(CN)$_2^-$, formed by nucleophilic addition. In all these three compounds polymeric chains are present in which and between which there is magnetic interaction.

In recent papers[1–4] the preparations and basic physical properties of copper(II) complexes with non-linear pseudohalide anions and pyrazole-type ligands were presented and the main structural features deduced. It was shown that besides the normal pseudo-halide (dicyanamide or tricyanomethanide) complexes, also isomeric compounds were isolated in which nucleophilic addition had taken place between the pseudohalide and pyrazole base in the copper(II) co-ordination sphere (coligand isomers). During a study of the system Cu^{II}–C(CN)$_3^-$–Hpz (Hpz = pyrazole) such isomers were obtained[2,3] and in addition two modifications of a 1:2 adduct of pyrazole with tricyanomethanidocopper(II) as well as 1:3 and 1:4 pyrazole complexes. The last two compounds, having very unusual compositions, were obtained as single crystals suitable for X-ray crystallographic studies. All compounds prepared were investigated using spectroscopic and cryomagnetic methods.

Experimental

Preparations.—[Cu{C(CN)$_3$}(Hpz)$_4$][C(CN)$_3$] **1**. A solution of Cu(NO$_3$)$_2$ (2 mmol) in water (2.5 cm^3) and a solution of K[C(CN)$_3$] (4 mmol) in water (5 cm^3) were poured into a solution of pyrazole (10 mmol) in water (5 cm^3). The water used for dissolution was heated to 70 °C and the reaction ran at *ca.* 40 °C. From the resulting solution, blue crystals were separated and dried in a desiccator placed in a refrigerator. The compound is stable only at low temperature, loosing pyrazole at room temperature to give α-[Cu{C(CN)$_3$}$_2$(Hpz)$_2$].

[Cu{C(CN)$_3$}$_2$(Hpz)$_3$] **2**. Solutions of Cu(NO$_3$)$_2$ (2 mmol) in water (4 cm^3), K[C(CN)$_3$] (4 mmol) in water (4 cm^3), and pyrazole (5 mmol) in water (4 cm^3) all heated to 50 °C were mixed. From the turbid, dark green solution, emerald-green crystals were separated.

α-[Cu{C(CN)$_3$}$_2$(Hpz)$_2$] **3**. Cooled solutions of Cu(NO$_3$)$_2$ (2.7 mmol) in water (5 cm^3) and K[C(CN)$_3$] (7 mmol) in water (5 cm^3) were poured into a solution of pyrazole (7 mmol) in water (5 cm^3). An oily suspension was formed from which a grass-green microcrystalline material was separated.

β-[Cu{C(CN)$_3$}$_2$(Hpz)$_2$] **4**. Solutions of Cu(NO$_3$)$_2$ (2 mmol) in water (5 cm^3) and K[C(CN)$_3$] (4 mmol) in water (7 cm^3) were poured into a solution of pyrazole (5 mmol) in methanol (7.5 cm^3) at room temperature. From the resulting solution, after cooling in a refrigerator, yellow-green crystals were isolated.

The X-ray diffraction patterns for the α and β isomeric compounds showed considerable differences.

[Cu{HN=C(pz)CH(CN)$_2$}$_2$] **5**. On recrystallisation of all tricyanomethanidocopper(II) complexes of pyrazole from hot methanol, on prolonged standing of the 1:2 complexes, and also from the mother-liquors obtained after separating these complexes, an olive-green powder was formed.

Elemental analyses were carried out on a C, H, N analyzer (Carlo Erba); copper was determined chelatometrically. The analytical data are summarised in Table 1.

Crystallographic Data Collection.—The initial space-group data were determined from Weissenberg and oscillation photographs and refined on a Syntex P2$_1$ four-circle diffractometer from least-squares fits of 12 for **1** and 15 for **2** automatically centred reflections distributed over reciprocal space. Final cell

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† *Supplementary data available* (No. SUP 56824, 8 pp.): magnetic susceptibilities and moments. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Analytical and characteristic IR (cm^{-1}) data for the compounds

		Analysis (%)[a]						
Compound	Colour	C	H	N	Cu	ν(C≡N)	γ(C–C≡N)	ν(Cu–N)
1	Blue	45.70 (46.55)	3.25 (3.20)	37.65 (38.00)	12.00 (12.30)	2190vs, 2181vs, 2169vs	569vs	278vs, 242w
2	Emerald green	45.00 (45.60)	2.80 (2.70)	37.15 (37.55)	14.05 (14.20)	2253ms, 2209vs, 2195vs, 2176vs, 2165vs	571s 566s	290(sh), 286vs, 243mw
3	Grass green	44.20 (44.30)	2.20 (2.10)	36.80 (36.90)	16.60 (16.70)	2247ms, 2193vs	566s	292s, 229ms, 221ms
4	Pale yellow-green	43.85 (44.30)	2.25 (2.10)	36.40 (36.90)	16.50 (16.70)	2247ms, 2193vs, 2174vs, 2162vs	566s	291vs, 230(sh), 221ms
5[b]	Olive green	43.80 (44.30)	2.15 (2.10)	36.35 (36.90)	16.60 (16.70)	2208vs, 2187vs		344s, 306ms, 264m

[a] Calculated values are given in parentheses. [b] ν(C=N) 1576vs, ν_{asym}(NCC) 1412s, ν(C–N) 1224 ms and 1209m cm^{-1}.

constants, as well as other pertinent data, are given in Table 2. The details of the data collection were similar, except as noted below. For compound **1** the Laue symmetry was $2/m$ and an inspection of the complete data set revealed systematic absences of $0k0$, $k = 2n + 1$; and $h0l$, $l = 2n + 1$, which are consistent with the space group $P2_1/c$. For **2** the preliminary X-ray photographic data indicated that the space group was $P\bar{1}$ or $P1$. The former was assumed throughout the structure analysis and confirmed by the successful refinement.

All data were corrected for Lorentz and polarisation effects. An empirical absorption correction based on reflection intensity measurements at different azimuthal angles was applied. A θ–2θ scan mode with a variable scan rate ranging from 4.88 to 29.30° min^{-1} was used. Two standard reflections were remeasured after every 98. They showed a considerable decrease in intensity during data collection (about 25% for **1** and about 32% for **2**), and the data were rescaled to be correct for this.

Structure determination and refinement. Both structures were solved by Patterson and Fourier techniques and refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were located from difference syntheses in positions consistent with those expected on geometrical grounds (C–H 1.080 Å, sp^2 hybridisation). The refinement converged when the ratio of the maximum shift to estimated standard deviation (e.s.d.) was 0.019 and 0.051, respectively, using a refined weighting scheme $w^{-1} = k[\sigma^2(F_o) + gF_o^2]$ (see Table 2 for the final values of k and g). Scattering factors and anomalous-dispersion corrections were used from ref. 5. All calculations were carried out using the SHELX 76 program[6] for solution and refinement of the structure, PARST[7] for the geometrical description of the structure and ORTEP[8] for the structure drawings.

The final non-hydrogen atomic coordinates are given in Tables 3 and 4 and selected bond distances and angles in Tables 5 and 6. The ORTEP plots for compounds **1** and **2** are presented in Figs. 1 and 2, and projections of the units cell in Figs. 3 and 4.

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

Physical Measurements.—Infrared,[9] far-infrared,[10] and electronic spectra,[11] as well as magnetic susceptibilities in the temperature range 4.5–295 K[12] were obtained as described. ESR spectra at room temperature, 77, and 4.2 K were recorded as reported.[9]

Results and Discussion

Description of the Structures.—The structure of compound **1** consists of polymeric one-dimensional chains, formed from $[Cu(Hpz)_4]^{2+}$ cations linked together by one bridging tricyanomethanide anion. The second tricyanomethanide anion is not bonded to this chain. The Cu^{II} is pseudo-octahedrally co-ordinated by four pyrazole molecules in the equatorial plane and axially by two atoms N(1*) and N(2) from two symmetrically equivalent tricyanomethanide anions. The Cu–N distances in the equatorial plane are in the range 1.979(7)–2.007(5) Å. Two of them in *trans* positions are significantly longer, *viz.* 2.002(6) and 2.007(5) Å, than the others [1.979(7) and 1.987(6) Å]. The lengths of the Cu–N axial interactions are considerably different [2.373(7) and 2.500(7) Å]. The four equatorial nitrogens are coplanar within +0.008(7) Å with the Cu^{II} atom displaced by 0.036(2) Å from their mean plane towards the N(1*) atom of the tricyanomethanide ligand.

The structure of compound **2** consists of discrete dimeric species formed by two complex molecules related by a centre of symmetry and bridged by one tricyanomethanide anion. The Cu^{II} atom is pseudo-octahedrally co-ordinated by three pyrazole molecules and one nitrogen atom N(1) of a bridging tricyanomethanide anion in the equatorial plane. The axial position is completed by a second nitrogen atom N(2*) of another, symmetrically equivalent, tricyanomethanide anion and the nitrogen atom N(5) of a second, terminally bonded, tricyanomethanide anion. The Cu–N distances in the equatorial plane are in the range 1.981(4)–1.987(3) Å and may be considered equivalent, while the axial interactions are different [2.420(4) and 2.472(4) Å]. The four equatorial nitrogens are coplanar within +0.005(5) Å with the Cu^{II} atom displaced by 0.048(3) Å from their mean plane towards the N(5) atom of the tricyanomethanide ligand.

In both structures the pyrazole rings are planar [distances to the least-squares planes not exceeding 0.012(9) Å for **1** and 0.003(6) Å for **2**], as are the tricyanomethanide anions [0.019(7) and 0.047(5) Å, respectively]. The tricyanomethanide ligand is rather rigid and a correlation may be seen between the Cu–N$_{ax}$ axial distances and the angle Cu–N$_{ax}$–C for both crystal structures.

Compound	N$_{ax}$	Cu–N$_{ax}$ (Å)	Cu–N$_{ax}$–C(°)
1	N(2)	2.373(7)	173.7(7)
2	N(5*)	2.420(4)	156.6(4)
2	N(2*)	2.472(4)	151.6(4)
1	N(5)	2.500(7)	148.9(6)

There are some strong hydrogen bonds (see Tables 5 and 6) between the nitrogens of the tricyanomethanide anion and the pyrazole hydrogens H(12), H(22), H(32) and H(42) in compound **1** and H(12), H(22) and H(32) in **2**, which stabilise the crystal structure.

Infrared Spectra.—The frequencies of characteristic IR ligand vibrations of the compounds studied are presented in Table 1. In

Table 2 Summary of crystal and refinement data for $[Cu\{C(CN)_3\}(Hpz)_4][C(CN)_3]$ and $[Cu\{C(CN)_3\}_2(Hpz)_3]$[a]

	1	2
Formula	$C_{20}H_{16}CuN_{14}$	$C_{17}H_{12}CuN_{12}$
M	515.82	447.74
Crystal system	Monoclinic	Triclinic
a/Å	9.568(4)	7.607(4)
b/Å	16.692(7)	8.942(6)
c/Å	14.957(9)	16.027(10)
α/°		95.95(6)
β/°	94.05(4)	90.83(5)
γ/°		106.88(5)
U/Å^3	2383(2)	1036(1)
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
Z	4	2
D_m/g cm^{-3}	1.43(1)[b]	1.41(1)[b]
F(000)	1052	454
μ(Cu-Kα)/mm^{-1}	1.54	1.67
Dimensions/mm	0.5 × 0.2 × 0.1	0.4 × 0.2 × 0.4
T_{min}, T_{max}[c]	0.825, 1.001	0.643, 0.996
hkl ranges	0–13, −19 to 19, −17 to 17	0–9, −11 to 11, −18 to 18
Total data	3650	2857
Data with $I > 3\sigma(I)$	1346	2066
Total variables	381	320
R	0.0369	0.0374
R'	0.0321	0.0390
$\Delta\rho$/e Å^{-3}	−0.20, 0.20	−0.36, 0.32
k	0.8730	0.3494
g	0.000942	0.001233

[a] In each case: Cu-Kα (graphite-monochromated radiation, λ = 1.54178 Å); D_c = 1.44 g cm^{-3}; $(\sin\theta/\lambda)_{max}$ 0.53. [b] CCl_4–C_6H_6. [c] Transmission factors.

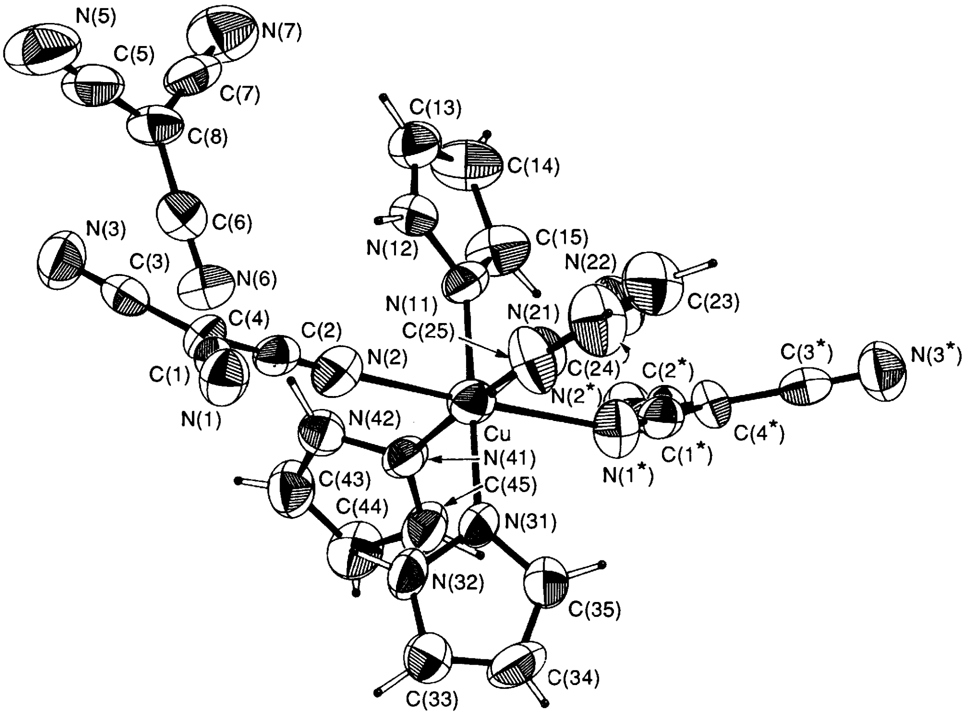

Fig. 1 ORTEP drawing of the molecular structure of $[Cu\{C(CN)_3\}(Hpz)_4][C(CN)_3]$. The thermal ellipsoids are drawn at the 50% probability level

the case of **1**, two low-lying ν(CN) frequencies originate in the ionic $C(CN)_3$ group, while the highest ν(CN) value is due to the axially bridging $C(CN)_3$ group. For **2**, ν(CN) bands are found which may be assigned to the bi- as well as mono-dentate $C(CN)_3$ groups. The isomers **3** and **4** exhibit ν(CN) bands attributable only to the bidentate $C(CN)_3$ ligands;[13] for **4**, however, some additional splitting occurs.

The IR pattern of compound **5** indicates[2] that this compound is a coligand isomer of **3** and **4**, containing new chelate ligands, *viz.* $HN{=}C(pz)CH(CN)_2^-$ anions. This ligand is formed by nucleophilic addition of the pyrazole imine nitrogen to the cyanide carbon of the $C(CN)_3^-$ anion in the copper(II) co-ordination sphere, as in related systems.[1–4,14–16]

In the FIR region (to 200 cm^{-1}) three or exceptionally two bands corresponding to the Cu–N stretching modes were identified for all the compounds (Table 1). The considerable shift of all the Cu–N stretches to higher energies for **5**, in comparison with compound **3**, suggests a strengthening of these bonds in the

Table 3 Atomic coordinates (× 10^4) for $[Cu\{C(CN)_3\}(Hpz)_4][C(CN)_3]$

Atom	*x*	*y*	*z*
Cu	831(1)	2311(1)	3513(1)
N(1)	712(7)	3815(4)	7408(4)
N(2)	1016(6)	3356(4)	4590(4)
N(3)	2159(7)	5763(4)	5685(4)
N(5)	5365(7)	6409(5)	4729(5)
N(6)	2024(7)	4884(4)	3279(4)
N(7)	5975(8)	5304(4)	2154(5)
N(11)	2674(5)	2624(3)	3053(4)
N(12)	3607(7)	3088(3)	3525(4)
C(13)	4680(9)	3269(5)	3047(7)
C(14)	4484(9)	2923(6)	2265(7)
C(15)	3227(9)	2523(5)	2271(6)
N(21)	1742(6)	1570(3)	4408(5)
N(22)	2645(7)	1002(5)	4243(5)
C(23)	3063(10)	588(5)	4968(9)
C(24)	2387(12)	893(6)	5645(6)
C(25)	1614(10)	1493(5)	5275(7)
N(31)	−1041(6)	1995(4)	3918(4)
N(32)	−1927(7)	2508(3)	4263(4)
C(33)	−3160(8)	2179(5)	4366(5)
C(34)	−3086(9)	1429(5)	4063(6)
C(35)	−1766(10)	1335(5)	3810(5)
N(41)	−1810(6)	3000(4)	2598(4)
N(42)	8(6)	3792(4)	2530(4)
C(43)	−913(10)	4098(5)	1926(6)
C(44)	−1717(9)	3515(6)	1563(5)
C(45)	1231(8)	2837(5)	2002(5)
C(1)	977(7)	4062(4)	6719(7)
C(2)	1139(7)	3802(5)	5161(6)
C(3)	1755(7)	5127(5)	5771(4)
C(4)	1278(7)	4334(4)	5880(5)
C(5)	4913(8)	6014(5)	4164(6)
C(6)	3084(9)	5185(4)	3368(5)
C(7)	5270(9)	5402(4)	2733(6)
C(8)	4418(8)	5537(4)	3431(6)

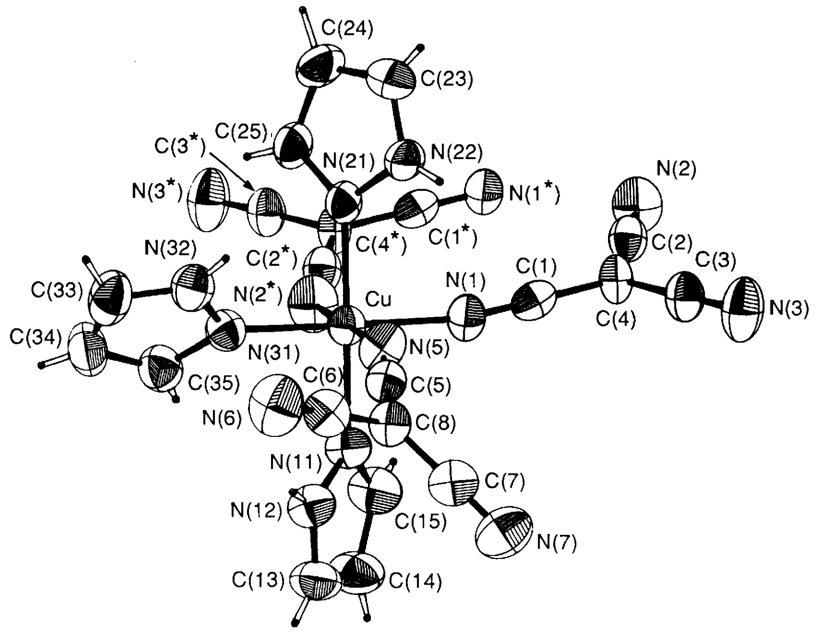

Fig. 2 ORTEP drawing of the molecular structure of $[Cu\{C(CN)_3\}_2(Hpz)_3]$. The thermal ellipsoids are drawn at the 50% probability level

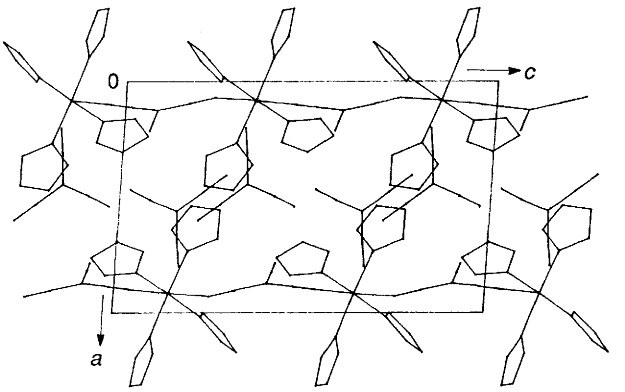

Fig. 3 Projection of the crystal structure of $[Cu\{C(CN)_3\}(Hpz)_4]$-$[C(CN)_3]$ down the *b* axis

chelate systems present. In the case of **5**, a band at 104 cm^{-1} (with a shoulder at 87 cm^{-1}) can be assigned to the axial Cu–N vibration.[1]

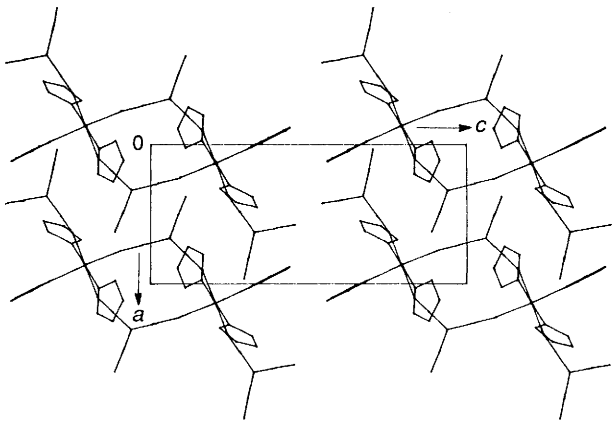

Fig. 4 Projection of the crystal structure of $[Cu\{C(CN)_3\}_2(Hpz)_3]$ down the *b* axis

Electronic Spectra.—The wavenumbers of the band maxima in the electronic spectra of the compounds are given in Table 7.

Table 4 Atomic coordinates (× 10^4) for $[Cu\{C(CN)_3\}_2(Hpz)_3]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu	1340(1)	1854(1)	2214(1)	C(24)	−2675(7)	3874(6)	1485(3)
N(1)	2377(5)	1892(4)	1084(2)	C(25)	−2107(6)	2783(6)	1882(3)
N(2)	981(6)	588(4)	−1604(2)	N(31)	195(4)	1749(4)	3321(2)
N(3)	6269(6)	4035(5)	−805(2)	N(32)	−147(5)	2990(4)	3759(2)
N(5)	3654(5)	4242(4)	2783(2)	C(33)	−997(7)	2601(7)	4456(3)
N(6)	5781(6)	7358(5)	5128(3)	C(34)	−1213(7)	1067(8)	4485(3)
N(7)	9641(6)	6115(5)	3433(3)	C(35)	−461(6)	565(6)	3775(3)
N(11)	2894(5)	554(4)	2538(2)	C(1)	2786(5)	2034(4)	404(3)
N(12)	3757(5)	704(4)	3286(2)	C(2)	2014(6)	1298(5)	−1080(3)
C(13)	4511(7)	−434(6)	3342(3)	C(3)	4925(6)	3194(5)	−624(2)
C(14)	4135(8)	−1380(6)	2619(3)	C(4)	3265(5)	2182(4)	−432(2)
C(15)	3137(7)	−741(5)	2140(3)	C(5)	4860(6)	5008(5)	3217(3)
N(21)	−308(4)	3051(4)	1859(2)	C(6)	6010(6)	6715(5)	4504(3)
N(22)	267(5)	4331(4)	1443(2)	C(7)	8138(7)	6033(5)	3559(3)
C(23)	−1132(8)	4812(6)	1220(3)	C(8)	6329(6)	5949(5)	3746(2)

Table 5 Selected bond lengths (Å) and angles (°) with e.s.d.s for $[Cu\{C(CN)_3\}(Hpz)_4][C(CN)_3]$

Cu–N(1^{I})	2.500(7)	N(3)–C(3)	1.140(6)
Cu–N(2)	2.373(7)	N(5)–C(5)	1.133(114)
Cu–N(11)	2.007(5)	N(6)–C(6)	1.131(106)
Cu–N(21)	1.979(6)	N(7)–C(7)	1.146(120)
Cu–N(31)	2.002(6)	N(2)–C(2)	1.133(107)
Cu–N(41)	1.987(6)	N(3)–C(3)	1.140(106)
N(1)–C(1)	1.155(18)		
N(1^{I})–Cu–N(2)	177.9(2)	N(1^{I})–Cu–N(11)	88.2(2)
N(1^{I})–Cu–N(21)	88.6(2)	N(1^{I})–Cu–N(31)	90.1(2)
N(1^{I})–Cu–N(41)	89.0(2)	N(2)–Cu–N(11)	91.0(2)
N(2)–Cu–N(21)	89.6(3)	N(2)–Cu–N(31)	90.8(2)
N(2)–Cu–N(41)	93.0(3)	N(11)–Cu–N(21)	92.3(2)
N(11)–Cu–N(31)	177.6(3)	N(11)–Cu–N(41)	90.6(3)
N(21)–Cu–N(31)	89.6(3)	N(21)–Cu–N(41)	176.2(3)
N(31)–Cu–N(41)	87.5(3)		

Hydrogen bonds and short interionic contacts

X–H ··· Y	X ··· Y	H ··· Y	X–H ··· Y
N(42)–H(42) ··· N(6)	2.83(7)	2.03(6)	150(6)
N(12)–H(12) ··· N(5^{II})	2.85(1)	2.09(6)	137(5)
N(22)–H(22) ··· N(7^{III})	2.80(1)	2.04(7)	145.7(6)
N(32)–H(32) ··· N(3^{IV})	2.90(1)	2.09(6)	151(6)

Symmetry code: I $x, \frac{1}{2} - y, -\frac{1}{2} + z$; II $1 - x, 1 - y, 1 - z$; III $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$; IV $-x, 1 - y, 1 - z$.

Table 6 Selected bond lengths (Å) and angles (°) with e.s.d.s for $[Cu\{C(CN)_3\}_2(Hpz)_3]$

Cu–N(1)	1.985(4)	N(3)–C(3)	1.141(6)
Cu–N(2^{I})	2.472(4)	N(5)–C(5)	1.146(5)
Cu–N(5)	2.420(4)	N(6)–C(6)	1.142(7)
Cu–N(11)	1.981(4)	N(7)–C(7)	1.147(7)
Cu–N(21)	1.981(4)	N(1)–C(1)	1.147(6)
Cu–N(31)	1.987(3)	N(2)–C(2)	1.143(5)
N(1)–Cu–N(11)	89.8(2)	N(1)–Cu–N(21)	89.7(2)
N(1)–Cu–N(31)	177.4(2)	N(1)–Cu–N(2^{I})	85.6(2)
N(1)–Cu–N(5)	93.1(2)	N(2^{I})–Cu–N(11)	88.5(2)
N(2^{I})–Cu–N(21)	88.4(2)	N(2^{I})–Cu–N(31)	92.0(2)
N(5)–Cu–N(2^{I})	178.7(1)	N(5)–Cu–N(11)	91.2(2)
N(5)–Cu–N(21)	91.8(2)	N(5)–Cu–N(31)	89.4(2)
N(11)–Cu–N(21)	176.9(2)	N(11)–Cu–N(31)	91.0(2)
N(21)–Cu–N(31)	89.4(2)	Cu–N(1)–C(1)	169.5(4)
Cu–N(2^{I})–C(2^{I})	151.6(4)	Cu–N(5)–C(5)	156.6(4)

Hydrogen bonds and short interionic contacts

X–H ··· Y	X ··· Y	H ··· Y	X–H ··· Y
N(12)–H(12) ··· N(6^{I})	2.88(1)	2.15(5)	151(5)
N(22)–H(22) ··· N(3^{II})	2.88(1)	2.17(5)	159(5)
N(32)–H(32) ··· N(7^{III})	3.22(2)	2.62(2)	119.3(8)
C(3)–H(3) ··· N(10^{III})	2.94(6)	2.22(6)	144(5)

Symmetry code: I $1 - x, 1 - y, 1 - z$; II $1 - x, 1 - y, - z$; III $- 1 + x, y, z$.

The d–d band maxima of **1** and **2** conform to axially elongated pseudo-octahedral CuN_6 chromophores having a medium-strong tetragonality[17] (≈ 0.8). The differences in the electronic spectra of **3** and **4**, compared with that of **2**, can be rationalised in terms of rhombic octahedral or square-pyramidal molecular structures.[18] The former structure of the *trans*-$Cu\{2C(CN)_3\}_{eq}(2Hpz)_{eq}\{2C(CN)_3\}_{ax}$ type is consistent with all $C(CN)_3$ groups being bridging. The difference in the d–d spectra of the α and β isomers indicate different distortions of their donor arrangements, so that we are dealing with distortion isomers.[19] The spectrum of compound **5** reveals a pseudo-octahedral configuration showing a moderate tetragonal distortion,[20,21] apparently achieved by bonding interactions between adjacent structural units.

ESR Spectra.—The room-temperature ESR spectra (Table 7) of compounds **1** and **2** show broad pseudo-isotropic lines in the region of 300 mT with bulges at $g = 2.45$; the spectra at low temperatures are similar. These spectra are affected by exchange coupling between the four structural units in the unit cell or among the dimeric units.[20] Both modifications **3** and **4** exhibit normal orthorhombic spectra at all temperatures, while **5** has an axial spectrum. The spectra are in agreement with the structures proposed for the respective compounds from the electronic and IR spectra. The considerably lower $\bar{g}$ value for **5** might be caused by increasing covalency in the chelate bonding system.[22]

In the spectra of compounds **2** and **5** at 77 K recorded with great amplification (*ca.* 10^4), weak signals at about 165 mT appear which can be assigned to the forbidden $\Delta M_S = \pm 2$ transitions in the exchange-coupled copper(II) systems.[23]

Magnetism.—The $(\chi_M^{corr})^{-1}$ and $\chi_M^{corr}T$ values for compounds **2** and **3** are plotted *versus* temperature in Fig. 5. The temperature dependence of $(\chi_M^{corr})^{-1}$ for **2** exhibits a Curie–Weiss behaviour and a least-squares analysis yields the C and θ constants for two temperature ranges (Table 7). In the region 25–295 K, the C value is practically unchanged but the θ value is considerably higher than that in the temperature range 4.2–295 K. A slow increase in $\chi_M^{corr}T$ from 0.398 at 295 to 0.562 cm^3 K mol^{-1} at 6 K is characteristic of ferromagnetic coupling of the copper centres in binuclear systems. Below 6 K the $\chi_M^{corr}T$ *vs.* T curve falls steeply, indicating a long-range antiferromagnetic three-dimensional ordering. A sharp maxi-

Table 7 Electronic and ESR spectral data and Curie–Weiss parameters for the compounds

Compound	$\nu_{max}/10^3$ cm^{-1}	g_1 or $g_\perp$	g_2	g_3 or $g_\parallel$	$\bar{g}$[a]	C[b]/cm^3 K mol^{-1}	θ/K
1	16.3, *ca.* 25.5(sh)				2.06[c]		
2	15.7,[d] 26.5				2.08[c]	0.389[e] 0.392[f]	4.7[e] 3.3[f]
3	14.8, *ca.* 16.9(sh), 24.1	2.043	2.119	2.280	2.150	0.359	6.6
4	14.6, *ca.* 16.3(sh), 24.7	2.044	2.117	2.302	2.157	0.363	4.0
5	*ca.* 10.0(sh), *ca.* 14.8(sh), 16.0, *ca.* 22.0(sh)	2.050		2.169	2.090	0.325	1.2

[a] $\bar{g} = [\frac{1}{3}(g_1{}^2 + g_2{}^2 + g_3{}^2)]^{\frac{1}{2}}$ or $[\frac{1}{3}(2g_\perp{}^2 + g_\parallel{}^2)]^{\frac{1}{2}}$. [b] Temperature range 50–295 K. [c] Isotropic g value. [d] An unresolved shoulder occurs to lower wavenumbers. [e] At 25–295 K. [f] At 4.2–295 K.

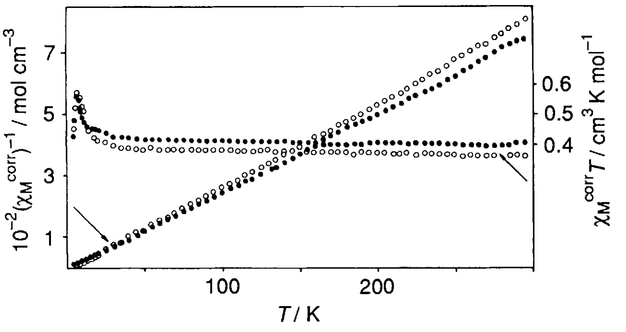

Fig. 5 Temperature dependence of the inverse molar susceptibility and $\chi_M^{corr}T$ for $[Cu\{C(CN)_3\}_2(Hpz)_3]$ (●) and α-$[Cu\{C(CN)_3\}_2(Hpz)_2]$ (○)

mum at 6 K then suggests a phase transition to a magnetically ordered state.

The magnetic behaviour of compounds **3**–**5** is consistent with the Curie–Weiss law, with the θ constants at high temperatures (> 50 K) between *ca.* 1 and 6.5 K. Complex **3** exhibits a very slow increase in $\chi_M^{corr}T$ with decreasing temperature, from 0.357 at 295 to 0.399 cm^3 K mol^{-1} at 30 K, respectively. At lower temperatures this product increases rapidly, to reach its maximum of 0.571 cm^3 K mol^{-1} at 7 K and from where it decreases. The product $\chi_M^{corr}T$ for **4** increases with temperature decrease less than for **3**; the maximum value is 0.540 cm^3 K mol^{-1} at 7 K. The $\chi_M^{corr}T$ *vs.* T function of **5** is similar to that observed in the latter case and the temperature of its maximum (0.431 cm^3 K mol^{-1}) is the same.

The crystal structures of complexes **3**–**5** are assumed to be composed of polymeric chains of the type $[\{Cu[C(CN)_3]_2(Hpz)_2\}_x]$ or $[\{Cu[HN{=}C(pz)CH(CN)_2]_2\}_x]$ which are magnetically non-isolated from the rest of the structure. Hence, besides the magnetic intramolecular interactions among the copper centres inside the chains, there should be intermolecular interactions between the chains.

Since below the temperature of the $\chi_M^{corr}T$ maximum the molar susceptibility is independent of the field strength and the relation between the magnetisation and field strength is linear, the maxima are most likely associated with structural phase transitions.[24]

The results of this study confirm that in tricyanomethanide[9,25] (and also dicyanamide[1,9,25]) complexes of Cu^{II} the bridging pseudo-halide groups act as media for magnetic exchange between the copper centres. Furthermore, the $(CN)_2CCN$ chains of the chelate $HN{=}CH(pz)C(CN)_2{}^-$ ligands connecting adjacent Cu^{II} atoms appear to be also available for spin transmission between them.

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