Synthesis, Properties and Molecular Structures of Iron(III), Cobalt(II), Nickel(II), Copper(II), Copper(I) and Zinc(II) Complexes with *N,N*-Bis(pyrazol-1-ylmethyl)benzylamine†

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A newly prepared ligand, *N,N*-bis(pyrazol-1-ylmethyl)benzylamine (L) reacted with metal ions to form [FeLCl$_3$], [NiL(NCS)$_2$(MeOH)], [MLX$_2$] (M = Co^{II}, Cu^{II} or Zn^{II}, X = Cl$^-$, Br$^-$ or NCS$^-$) and [(CuLI)$_2$]. The crystallographically determined structures of [CoLCl$_2$] and [CoL(NCS)$_2$] reveal the co-ordination sphere of cobalt(II) to be intermediate between distorted tetrahedral and trigonal bipyramidal. In [NiL(NCS)$_2$(MeOH)] the co-ordination sphere of nickel(II) ion is distorted octahedral while that of copper(II) in [CuLCl$_2$] is distorted square pyramidal. The complex [(CuLI)$_2$] displays distorted tetrahedral geometry around copper(I), and [ZnLBr$_2$] shows distorted tetrahedral geometry around zinc(II).

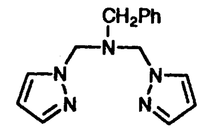
Polyfunctional ligands derived from pyrazole,[1-5] imidazole[6-9] and pyridazine[10-12] form transition-metal complexes in which metal atoms are brought into proximity because of N-donor sites that co-ordinate to metals in the systems. Structural characterizations of these molecules are vigorously pursued in many laboratories because these compounds serve as potential models for biological dimetallic sites.[13-15] Some dicopper(II) complexes with pyrazolyl ligands are potential models for haemocyanin.[16]

In an effort to develop new polynuclear complexes, we were interested in metal complexation of polyfunctional pyrazole ligands. The previously prepared 4-methyl-2,6-bis(pyrazol-1-ylmethyl)phenol[17] ligand, reacted with Zn^{II} to give a binuclear complex. 1,3,5-Tri(pyrazol-1-ylmethyl)benzene[18] reacted with Cu^{II} to give polymeric bis(μ-chloro) copper(II) complexes. Other novel ligands, 1,2-bis(pyrazol-1-ylmethyl)benzene[19] and 5-methyl-1,3-bis(pyrazol-1-ylmethyl)benzene,[20] were prepared and their abilities to complex with Cu^{II} and Co^{II} were reported. Here, we report an investigation of complexing properties of the pyrazolyl ligand *N,N*-bis(pyrazol-1-ylmethyl)benzylamine L, which is a tridentate ligand with two N-donor sites of pyrazolyl rings and one N-donor site of benzylamine. The spectral properties and crystal structures of cobalt(II), nickel(II), copper(II), zinc(II) and copper(I) complexes of *N,N*-bis(pyrazol-1-ylmethyl)benzylamine are described.

Experimental

Chemicals.—All reagents and solvents were purchased from commercial sources and used as received unless noted otherwise. *N*-Hydroxymethylpyrazole was prepared according to the literature method.[21]

Physical Methods.—Melting points were obtained in open capillaries with a Thomas–Hoover capillary apparatus and are uncorrected. Proton NMR spectra were recorded on a Bruker AM-300WB instrument at 300 MHz using CDCl$_3$ and (CD$_3$)$_2$SO as solvents. EPR spectra were recorded on a Bruker ESP 300 X-band instrument with diphenylpicrylhydrazyl (dpph) as standard. Magnetic susceptibilities were measured with the Faraday method on a CAHN 200 instrument with Hg[Co(SCN)$_4$] as standard; diamagnetic corrections were made using Pascal's parameters. Infrared spectra were recorded on a Perkin-Elmer 983G and Bomem DA8 FTIR instrument (far-IR spectra) and elemental analyses were obtained using a Perkin-Elmer 2400 analyser. The ultraviolet spectra were recorded on a Hitachi U-3210 spectrophotometer and solid-state electronic spectra were measured on a Shimadzu UV-2101PC UV/VIS scanning spectrophotometer (200–800 nm) in the diffusion reflectance mode with BaO as a reference.



L

Syntheses.—N,N-*Bis(pyrazol-*1*-ylmethyl)benzylamine* L. *N*-Hydroxymethylpyrazole (1.96 g, 20 mmol) and benzylamine (1.07 g, 10 mmol) in acetonitrile (50 cm^3) were stirred in a closed vessel at room temperature for 4 d. The acetonitrile layer was dried from the water produced by treatment with anhydrous MgSO$_4$ and was filtered; the solvent was removed on a rotatory evaporator, yielding a slightly yellow liquid, which was used without further purification. Yield 1.92 g (72%) (Found: C, 67.00; H, 6.30; N, 26.45. Calc. for C$_{15}$H$_{17}$N$_5$: C, 67.40; H, 6.40; N, 26.20%). ^{1}H NMR(CDCl$_3$): δ 3.71 (2 H, s, aryl CH$_2$N), 4.95 (4 H, s, CH$_2$), 6.25 (2 H, t, *J* 2.1, pyrazolyl C^{4}H), 7.25–7.29 (5 H, m, aryl H), 7.45 (2 H, d, *J* 2.1, pyrazolyl C^{5}H) and 7.53 (2 H, d, *J* 2.1 Hz, pyrazolyl C^{3}H). IR: ν_{max}/cm^{-1} 3107m, 3029m, 1596m, 1507m, 1447m, 1390s, 1083s, 1044s, 961m, 748s, 699m and 617m.

[FeLCl$_3$] 1. Iron(III) chloride hexahydrate (270 mg, 1 mmol) in absolute ethanol (15 cm^3) was added to a solution (15 cm^3) of L in absolute ethanol (267 mg, 1 mmol). The yellow precipitate was filtered off, washed successively with ethanol and diethyl ether, and dried in air. Yield 0.36 g (82%), m.p. 158–159 °C (decomp.) (Found: C, 41.20; H, 4.00; N, 15.70. Calc. for C$_{15}$H$_{17}$Cl$_3$FeN$_5$·0.5H$_2$O: C, 41.05; H, 4.10; N, 15.95%). IR:

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: $\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}.

ν_{max}/cm^{-1} 3414 (br), 3130m, 1517m, 1456m, 1400s, 1281s, 1068s, 993m, 769m, 702m and 606m. λ_{max}/nm (MeOH) 355 (ε 3406 dm^3 mol^{-1} cm^{-1}), 252 (5468) and 209 (22 336).

[CoLCl$_2$] **2**. Cobalt(II) chloride hexahydrate (238 mg, 1 mmol) in methanol (15 cm^3) was added to a methanolic solution (10 cm^3) of L (267 mg, 1 mmol). The mixture was stirred for 10 min at room temperature and filtered. The blue crystalline product was obtained by slow diffusion of diethyl ether into the mixture. M.p. 180–181 °C (Found: C, 45.60; H, 4.10; N, 17.20. Calc. for $C_{15}H_{17}Cl_2CoN_5$: C, 45.35; H, 4.30; N, 17.65%). IR: ν_{max}/cm^{-1} 3440 (br), 3122m, 1507m, 1448m, 1398s, 1354m, 1277m, 1206m, 1091m, 1062s, 980m, 772s, 754s and 645s. λ_{max}/nm (MeOH) 258 (ε 342 dm^3 mol^{-1} cm^{-1}) and 209 (12 497).

[CoL(NCS)$_2$] **3**. Cobalt(II) nitrate hexahydrate (291 mg, 1 mmol) in methanol (15 cm^3) was added to a methanolic solution (10 cm^3) of L (267 mg, 1 mmol) and a methanolic solution (10 cm^3) of NaSCN (162 mg, 2 mmol) was added. The mixture was allowed to stand at room temperature. A violet crystalline product was filtered off, washed successively with methanol and diethyl ether and dried in air. Yield 0.27 g (61%). M.p. 186–187 °C (decomp.) (Found: C, 45.35; H, 3.80; N, 21.80. Calc. for $C_{17}H_{17}CoN_7S_2{\cdot}0.5H_2O$: C, 45.25; H, 4.00; N, 21.75%). IR: ν_{max}/cm^{-1} 3123m, 2077s, 2060s, 1519m, 1400m, 1278m, 1066m and 764m. λ_{max}/nm (MeCN) 579 (ε 705 dm^3 mol^{-1} cm^{-1}), 323 (5425) and 225 (11 572).

[NiL(NCS)$_2$(MeOH)] **4**. The complex was prepared as described for complex **3**. A blue crystalline product was filtered off, washed successively with methanol and diethyl ether and dried in air. Yield 0.32 g (68%). M.p. 199–200 °C (decomp.) (Found: C, 45.60; H, 4.50; N, 19.85. Calc. for $C_{18}H_{21}N_7NiOS_2$: C, 45.60; H, 4.45; N, 20.70%). IR: ν_{max}/cm^{-1} 3334 (br), 3112m, 2088s, 1519m, 1446m, 1397m, 1273m, 1202m, 1093m, 1056m, 977m, 773m, 744m, 702m and 651m. λ_{max}/nm (MeCN) 294 (ε 1332 dm^3 mol^{-1} cm^{-1}) and 219 (12 284).

[CuLCl$_2$] **5**. The complex was prepared as described for complex **2**. M.p. 155–156 °C (Found: C, 44.85; H, 4.15; N, 17.55. Calc. for $C_{15}H_{17}Cl_2CuN_5$: C, 44.85; H, 4.25; N, 17.45%). IR: ν_{max}/cm^{-1} 3443 (br), 3125m, 1507m, 1461m, 1410s, 1397s, 1270s, 1202m, 1140m, 1093m, 1065s, 978m, 763m, 737s, 703s and 645m. λ_{max}/nm (MeOH) 718 (ε 95 dm^3 mol^{-1} cm^{-1}), 265 (3397) and 209 (18 994).

[(CuLI)$_2$] **6**. Copper(I) iodide (190 mg, 1 mmol) in acetonitrile (20 cm^3) was bubbled with N_2 for 10 min and added to an acetonitrile solution (20 cm^3) of L (267 mg, 1 mmol). The mixture was allowed to stand at room temperature. Colourless crystals were filtered off, washed successively with acetonitrile and diethyl ether and dried in air. Yield 0.34 g (37%). M.p. 159–160 °C (decomp.) [Found: C, 39.35; H, 3.55; N, 15.10. Calc. for $(C_{15}H_{17}CuIN_5)_2$: C, 39.35; H, 3.70; N, 15.30%]. IR: ν_{max}/cm^{-1} 3104m, 1508m, 1392m, 1374m, 1241s, 1150s, 1100m, 1085s, 1053s, 981m, 962m and 748s. ^{1}H NMR [$(CD_3)_2SO$]: δ 3.84 (2 H, s), 5.20 (4 H, s), 6.44 (2 H, s), 7.28–7.38 (5 H, m), 7.75 (2 H, s) and 7.88 (2 H, s)

[ZnLBr$_2$] **7** *and* [ZnL(NCS)$_2$] **8**. These complexes were prepared as described for complex **3**, above, with appropriate anions substituted for Br$^-$ and NCS$^-$. Colourless crystals were filtered, washed successively with methanol and diethyl ether and dried in air. Yield 0.19 g (39%) for complex **7** (m.p. 176–178 °C) and 0.42 g (92%) for complex **8** (m.p. 149–151 °C) [Found: C, 36.45; H, 3.4; N, 14.65. Calc. for $C_{15}H_{17}Br_2N_5Zn$ (**7**): C, 36.60; H, 3.50; N, 14.20%]. IR: ν_{max}/cm^{-1} 3105m, 1523m, 1407m, 1381m, 1259m, 1150m, 1072s, 986m, 781m, 755m and 612m. ^{1}H NMR [$(CD_3)_2SO$]: δ 3.72 (2 H, s), 5.07 (4 H, s), 6.31 (2 H, s), 7.20–7.33 (5 H, m), 7.54 (2 H, s) and 7.76 (2 H, s). λ_{max}/nm (MeCN) 342 (ε 190 dm^3 mol^{-1} cm^{-1}) and 212 (7334) [Found: C, 45.45; H, 3.75; N, 22.20. Calc. for $C_{17}H_{17}N_7S_2Zn$ (**8**): C, 45.50; H, 3.80; N, 21.85%]. IR: ν_{max}/cm^{-1} 3092m, 2083s, 1523m, 1404m, 1065m, 766m, 706m and 614m. ^{1}H NMR [$(CD_3)_2SO$]: δ 3.71 (2 H, s), 5.05 (4 H, s), 6.31 (2 H, s), 7.22–7.32 (5 H, m), 7.53 (2 H, s) and 7.76 (2 H, s). λ_{max}/nm (MeCN) 342 (ε 123 dm^3 mol^{-1} cm^{-1}) and 218 (7928).

[ZnLCl$_2$] **9**. Zinc(II) chloride (136 mg, 1 mmol) in methanol (15 cm^3) was added to a solution of L (267 mg, 1 mmol) in methanol (15 cm^3). The mixture was allowed to stand at room temperature. Colourless crystals were filtered off, washed successively with methanol and diethyl ether and dried in air. Yield 0.36 g (89%). M.p. 191–192 °C (Found: C, 44.80; H, 4.05; N, 17.00. Calc. for $C_{15}H_{17}Cl_2N_5Zn$: C, 44.65; H, 4.25; N, 17.35%). IR: ν_{max}/cm^{-1} 3104m, 1507m, 1402s, 1379m, 1301m, 1259s, 1149s, 1100m, 1073s, 986s, 931m, 782s and 757m. ^{1}H NMR [$(CD_3)_2SO$]: δ 3.72 (2 H, s), 5.09 (4 H, s), 6.31 (2 H, d), 7.20–7.30 (5 H, m), 7.55 (2 H, d) and 7.77 (2 H, d). λ_{max}/nm (MeOH) 258 (ε 400 dm^3 mol^{-1} cm^{-1}) and 208 (11 550).

Structural Determinations.—Suitable crystals of complexes **2**–**7** were chosen. Intensity data were collected at room temperature on a CAD-4 diffractometer using monochromatic Mo-Kα radiation (λ 0.7107 Å). The unit-cell parameters were derived from a least-squares refinement of 25 setting reflections for complexes **5** and **7** and 24 setting reflections for complexes **2**–**4** and **6**. The θ–2θ scan technique and a variable scan speed were used to obtain integrated intensities. Three reference reflections were monitored throughout the measurement; the decay of the intensities was less than 2% in all cases. Absorption corrections were applied according to an experimental ψ rotational curve. Other details of crystal data are given in Table 1.

The structures were solved by the heavy-atom method; subsequent Fourier syntheses based on the heavy-atoms revealed the positions of all non-hydrogen atoms. Least-squares refinement including anisotropic thermal parameters for all non-hydrogen atoms was performed; the final results are given Tables 2–7. For these complexes a weighting scheme of the form $1/[\sigma^2(F_o) + k(F_o)^2]$, $k = 0.000\,02$ for complex **4** and $k = 0$ for complexes **2**, **3** and **5**–**7**, was used. All hydrogen-atom parameters were calculated according to ideal geometries and were not refined. The structural analyses were made on a Microvax III computer using NRCVAX programs.[22] Atomic scattering factors were taken from ref. 23.

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 *N*,*N*-bis(pyrazol-1-ylmethyl)benzylamine (L), which possesses three nitrogen donor sites, was prepared using a modification of the literature method.[21] Reactions of metal ions and ligand (L), which possesses two potential nitrogen donor sites from the pyrazolyl rings and one nitrogen donor site from benzylamine, result in the formation of complexes [FeLCl$_3$], [CoLCl$_2$], [CoL(NCS)$_2$], [NiL(NCS)$_2$(MeOH)], [CuLCl$_2$], [(CuLI)$_2$], [ZnLBr$_2$], [ZnL(NCS)$_2$] and [ZnLCl$_2$].

Molecular Structures of [CoLCl$_2$] **2** *and* [CoL(NCS)$_2$] **3**.—These structures are shown in Figs. 1 and 2; selected bond distances and angles are presented in Table 8.

In complex **2**, the cobalt(II) ion is surrounded by two pyrazolyl nitrogen atoms at Co–N(1) 2.014(4) Å and Co–N(3) 2.001(3) Å, and two chloride ions at Co–Cl(1) 2.320(2) Å and Co–Cl(2) 2.249(2) Å. Some angles between co-ordination bonds of cobalt(II), which range from 95.9(1) to 123.7(1)°, deviate substantially from ideal tetrahedral angles. Bonding may also occur from Co to the amine N as the Co–N(3) distance is 2.510(4) Å. While the Co–N(amine) distance is longer than that found in [CoL′$_2$][NO$_3$]$_2$ [2.229(5) Å] [L′ = bis(1-pyrazolylmethyl)amine],[24] in which the Co–N bond is described as bonding, it is much shorter than that of [Co(bdmpab)Cl$_2$] [3.854(2) Å] [bdmpab = *N*,*N*-bis(3,5-dimethylpyrazol-1-ylmethyl)aminobenzene] ,[5] in which the cobalt ion is described as having a distorted tetrahedral configuration. The geometry of

Table 1 Crystallographic data for [CoLCl$_2$] **2**, [CoL(NCS)$_2$] **3**, [NiL(NCS)$_2$(MeOH)] **4**, [CuLCl$_2$] **5**, [(CuLI)$_2$] **6** and [ZnLBr$_2$] **7**

Complex	**2**	**3**	**4**	**5**	**6**	**7**
Formula	$C_{15}H_{17}Cl_2CoN_5$	$C_{17}H_{17}CoN_7S_2$	$C_{18}H_{21}N_7NiOS_2$	$C_{15}H_{17}Cl_2CuN_5$	$C_{30}H_{34}Cu_2I_2N_{10}$	$C_{15}H_{17}Br_2N_5Zn$
M	397.34	442.42	474.24	401.78	915.57	492.52
Crystal size/mm	0.20 × 0.30 × 0.35	0.20 × 0.25 × 0.30	0.30 × 0.30 × 0.25	0.20 × 0.30 × 0.30	0.20 × 0.15 × 0.20	0.20 × 0.20 × 0.30
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	Cc	$P2_1/c$	$P\bar{1}$	$P2_1/c$
Z	2	4	4	4	2	4
a/Å	7.337(8)	9.820(5)	7.288(2)	7.921(2)	9.856(6)	8.603(2)
b/Å	9.841(7)	17.751(10)	34.899(20)	32.971(2)	10.282(6)	14.305(4)
c/Å	13.361(4)	11.896(7)	8.548(5)	7.178(2)	17.468(6)	15.809(3)
α/°	70.35(4)				74.07(5)	
β/°	87.60(7)	106.08(4)	99.26(3)	114.04(2)	84.03(5)	93.137(20)
γ/°	71.61(9)				86.01(5)	
U/Å^3	860.0(12)	1992.5(18)	2145.8(19)	1712.0(12)	1691.3(17)	1820.9(7)
F(000)	406	908	986	820	896	968
D_c/Mg m^{-3}	1.534	1.475	1.468	1.599	1.798	1.797
μ/mm^{-1}	1.17	1.08	1.11	1.59	0.68	5.73
$2\theta_{max}$/°	45.0	45.0	45.0	45.0	45.0	45.0
Ranges of h, k, l	−7 to 7, 0–10, −13 to 14	−10 to 10, 0–19, 0–12	0–7, −37 to 37, −9 to 9	−8 to 7, 0–35, 0–7	−10 to 10, 0–11, −17 to 18	−8 to 8, 0–15, 0–16
Scan parameter	2 (0.90 + 0.35 tan θ)	2 (0.75 + 0.35 tan θ)	2 (0.90 + 0.35 tan θ)	2 (0.60 + 0.35 tan θ)	2 (0.80 + 0.35 tan θ)	2 (0.75 + 0.35 tan θ)
Total number of reflections	2237	2602	1401	2237	4407	2370
Reflections with $I > 2\sigma(I)$	1816	1547	1167	1850	3103	1852
R	0.031	0.050	0.071	0.034	0.033	0.030
R'*	0.026	0.037	0.071	0.032	0.024	0.022
S*	2.01	2.43	3.91	2.07	1.85	2.01

* $R = \Sigma|F_o - F_c|/\Sigma|F_o|$, $R' = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{\frac{1}{2}}$, $S = [\Sigma w(F_o - F_c)^2/(N_o - N_v)]^{\frac{1}{2}}$, where N_o is number of observations and N_v is the number of variables.

Table 2 Final atomic positional parameters of non-hydrogen atoms for [$CoLCl_2$] **2**

Atom	*x*	*y*	*z*
Co	0.824 81(8)	0.939 32(7)	0.273 89(5)
Cl(1)	0.630 98(16)	0.823 77(13)	0.390 33(9)
Cl(2)	0.685 76(18)	1.021 61(14)	0.108 23(9)
N(1)	1.056 1(5)	0.750 6(4)	0.304 7(3)
N(2)	1.230 6(5)	0.759 1(4)	0.271 4(3)
N(3)	0.839 9(5)	1.078 0(4)	0.351 41(25)
N(4)	0.995 2(5)	1.124 2(4)	0.349 11(25)
N(5)	1.105 4(5)	1.030 8(4)	0.208 68(25)
C(1)	1.091 0(6)	0.607 8(5)	0.369 9(3)
C(2)	1.284 0(7)	0.524 9(5)	0.378 1(4)
C(3)	1.368 6(6)	0.626 2(5)	0.314 4(4)
C(4)	0.715 9(6)	1.154 0(5)	0.405 0(3)
C(5)	0.790 8(7)	1.247 5(5)	0.436 3(3)
C(6)	0.971 0(7)	1.224 2(5)	0.400 4(3)
C(7)	1.240 8(6)	0.898 6(5)	0.189 4(3)
C(8)	1.165 2(6)	1.051 2(5)	0.302 1(3)
C(9)	1.082 8(6)	1.165 4(5)	0.108 8(3)
C(10)	0.972 3(7)	1.314 7(5)	0.120 5(3)
C(11)	1.068 7(7)	1.408 0(6)	0.134 1(3)
C(12)	0.967 2(11)	1.549 9(7)	0.139 0(4)
C(13)	0.771 7(11)	1.599 8(6)	0.129 3(5)
C(14)	0.674 8(8)	1.508 3(6)	0.115 5(4)
C(15)	0.773 4(7)	1.366 6(5)	0.110 7(4)

Table 3 Final atomic positional parameters of non-hydrogen atoms for [$CoL(NCS)_2$] **3**

Atom	*x*	*y*	*z*
Co	0.236 60(13)	0.163 13(7)	0.072 81(10)
S(1)	0.143 3(3)	0.101 90(15)	0.429 18(21)
S(2)	0.721 4(3)	0.211 99(16)	0.211 03(22)
N(1)	0.214 2(6)	0.092 7(3)	−0.066 4(5)
N(2)	0.095 2(6)	0.099 4(3)	−0.156 1(5)
N(3)	0.209 6(7)	0.272 5(4)	0.030 1(5)
N(4)	0.077 1(7)	0.300 2(3)	−0.014 4(5)
N(5)	−0.008 9(6)	0.175 1(3)	−0.040 9(5)
N(6)	0.170 6(6)	0.136 6(4)	0.209 1(5)
N(7)	0.449 4(7)	0.161 4(4)	0.136 4(6)
C(1)	0.282 0(9)	0.032 9(5)	−0.090 5(8)
C(2)	0.207 4(10)	0.001 7(5)	−0.194 8(7)
C(3)	0.092 6(10)	0.044 5(5)	−0.233 6(7)
C(4)	0.294 1(9)	0.330 9(5)	0.024 9(7)
C(5)	0.217 3(11)	0.393 8(5)	−0.019 8(8)
C(6)	0.081 8(10)	0.373 1(5)	−0.043 0(8)
C(7)	0.008 3(8)	0.164 5(4)	−0.158 6(6)
C(8)	−0.043 6(9)	0.252 5(4)	−0.017 1(7)
C(9)	−0.104 9(8)	0.118 9(4)	−0.011 3(6)
C(10)	−0.251 4(8)	0.114 3(4)	−0.099 4(6)
C(11)	−0.282 5(10)	0.056 3(5)	−0.177 1(8)
C(12)	−0.411 2(11)	0.053 6(6)	−0.257 7(8)
C(13)	−0.509 0(10)	0.108 6(6)	−0.259 6(8)
C(14)	−0.480 2(9)	0.165 4(6)	−0.181 7(8)
C(15)	−0.351 9(8)	0.168 4(5)	−0.100 9(7)
C(16)	0.157 1(8)	0.121 9(4)	0.300 7(7)
C(17)	0.563 6(8)	0.182 8(5)	0.165 3(7)

Table 4 Final atomic positional parameters of non-hydrogen atoms for [$NiL(NCS)_2(MeOH)$] **4**

Atom	*x*	*y*	*z*
Ni	0.479 16	0.896 57(7)	0.721 23
S(1)	0.743 0(8)	0.814 24(17)	0.377 2(7)
S(2)	−0.066 1(8)	0.947 43(25)	0.418 0(9)
N(1)	0.324 4(20)	0.848 2(4)	0.741 4(18)
N(2)	0.406 3(19)	0.821 5(4)	0.835 4(18)
N(3)	0.413 6(19)	0.923 8(5)	0.913 0(17)
N(4)	0.515 4(20)	0.914 7(5)	1.054 1(19)
N(5)	0.655 7(19)	0.866 7(4)	0.929 6(17)
C(1)	0.187 4(24)	0.829 7(6)	0.645 3(22)
C(2)	0.189(3)	0.792 9(7)	0.685(3)
C(3)	0.331(3)	0.788 1(6)	0.807(3)
C(4)	0.278(3)	0.946 5(5)	0.957 9(24)
C(5)	0.292(3)	0.949 5(6)	1.121(3)
C(6)	0.449(3)	0.929 1(6)	1.187 7(22)
C(7)	0.539 9(24)	0.833 5(6)	0.975 9(23)
C(8)	0.683 0(25)	0.893 7(5)	1.052 6(23)
C(9)	0.830 4(23)	0.850 9(5)	0.877 0(21)
C(10)	0.970 3(24)	0.831 1(5)	1.011 3(22)
C(11)	0.982(3)	0.793 0(6)	1.019 6(24)
C(12)	1.112(3)	0.774 3(7)	1.137(3)
C(13)	1.223(3)	0.799 0(6)	1.244 4(24)
C(14)	1.209(3)	0.836 4(6)	1.235 0(22)
C(15)	1.084(3)	0.854 1(6)	1.123(3)
N(6)	0.594 9(19)	0.868 5(5)	0.549 4(17)
C(16)	0.657 3(22)	0.845 2(5)	0.476 7(20)
N(7)	0.280 1(23)	0.924 1(6)	0.573 2(20)
C(17)	0.141(3)	0.933 0(6)	0.505 8(21)
O	0.686 8(18)	0.938 9(3)	0.708 3(17)
C(18)	0.653(4)	0.975 4(6)	0.716(3)

Table 5 Final atomic positional parameters of non-hydrogen atoms for [$CuLCl_2$] **5**

Atom	*x*	*y*	*z*
Cu	0.027 20(8)	0.145 876(19)	0.028 25(9)
Cl(1)	0.166 81(18)	0.201 72(4)	−0.088 87(19)
Cl(2)	−0.192 76(19)	0.113 33(5)	−0.233 92(21)
N(1)	−0.136 3(6)	0.180 18(12)	0.107 5(6)
N(2)	−0.048 7(5)	0.199 16(12)	0.287 7(6)
N(3)	0.235 2(5)	0.109 52(12)	0.064 3(6)
N(4)	0.389 0(5)	0.116 98(12)	0.234 5(6)
N(5)	0.196 0(5)	0.153 59(11)	0.353 4(5)
C(1)	−0.315 3(7)	0.190 49(17)	0.043 0(8)
C(2)	−0.337 6(7)	0.216 67(17)	0.181 0(10)
C(3)	−0.165 9(8)	0.221 44(16)	0.335 9(9)
C(4)	0.275 3(7)	0.077 98(16)	−0.023 1(7)
C(5)	0.454 6(8)	0.065 88(18)	0.087 3(8)
C(6)	0.523 7(7)	0.091 05(18)	0.252 7(8)
C(7)	0.152 9(6)	0.195 54(15)	0.390 2(7)
C(8)	0.385 3(6)	0.150 63(15)	0.364 6(7)
C(9)	0.160 5(7)	0.125 69(15)	0.495 1(7)
C(10)	0.147 4(7)	0.081 43(15)	0.434 4(8)
C(11)	0.292 7(8)	0.055 07(18)	0.529 8(8)
C(12)	0.274 6(9)	0.014 76(20)	0.473 8(11)
C(13)	0.114 8(11)	0.000 98(20)	0.319 3(12)
C(14)	−0.029 4(9)	0.026 83(20)	0.224 0(10)
C(15)	−0.013 4(7)	0.066 82(17)	0.281 6(8)

the cobalt ion environment can thus also be described as intermediate between tetrahedral and trigonal bipyramidal.

The Co–N(pyrazole) distances [2.037(6) Å and 2.006(6) Å] of complex **3** are similar to those of complex **2**, but the Co–N(amine) distance [2.425(6) Å] is even smaller than that of complex **2** [2.510(4) Å] and the Co–N(amine) bonding interaction is thus stronger in complex **3**. Some of the angles between co-ordination bonds deviate significantly from ideal tetrahedral angles [range 99.2(3)–122.6(3)°] and as in complex **2** the geometry of the cobalt(II) environment can be described as intermediate between tetrahedral and trigonal bipyramidal. Two thiocyanate ions are bonded to the cobalt(II) ion [Co–N(6) 1.963(6) Å, Co–N(7) 2.016(7) Å]. The co-ordination angles of the thiocyanates to the metal ion deviates from linearity to a moderate degree [167.7(6) and 159.4(7)°].

Molecular Structure of [$NiL(NCS)_2(MeOH)$] **4**.—This structure is shown in Fig. 3; selected bond distances and angles are presented in Table 8.

The nickel(II) ion is six-coordinate with the ligand bound in a facial manner [Ni–N(1) 2.052(15), Ni–N(3) 2.018(15) and Ni–N(5) 2.276(14) Å]. Two isocyanate ions [Ni–N(6) 2.056(15) and Ni–(7) 2.009(15) Å] and one oxygen from methanol [Ni–O 2.130(13) Å] occupy the remaining facial site. Distortion from

Table 6 Final atomic positional parameters of non-hydrogen atoms for $[(CuLI)_2]$ **6**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
I(1)	0.591 42(5)	0.975 61(5)	0.133 44(3)	C(14)	1.475 4(8)	0.374 2(8)	0.119 1(5)
I(2)	0.836 54(5)	0.783 11(6)	0.331 30(3)	C(15)	1.401 1(8)	0.494 4(7)	0.096 0(4)
Cu(1)	0.821 34(10)	0.844 18(10)	0.170 59(6)	N(6)	0.448 7(6)	0.759 8(6)	0.348 0(3)
Cu(2)	0.595 10(10)	0.896 37(10)	0.291 14(6)	N(7)	0.311 8(6)	0.776 6(6)	0.344 9(3)
N(1)	0.985 5(5)	0.970 1(6)	0.126 2(3)	N(8)	0.557 3(5)	1.042 8(6)	0.349 9(3)
N(2)	1.102 8(5)	0.949 7(5)	0.080 6(3)	N(9)	0.441 9(6)	1.117 5(6)	0.355 5(3)
N(3)	0.852 7(5)	0.674 4(6)	0.133 7(3)	N(10)	0.237 5(6)	1.015 4(6)	0.328 5(3)
N(4)	0.971 3(5)	0.597 8(5)	0.138 2(3)	C(21)	0.467 6(8)	0.635 9(8)	0.397 3(4)
N(5)	1.180 6(5)	0.710 8(5)	0.093 0(3)	C(22)	0.342 8(8)	0.575 3(7)	0.424 8(4)
C(1)	1.006 6(8)	1.082 6(7)	0.146 0(4)	C(23)	0.246 3(8)	0.667 9(8)	0.391 3(5)
C(2)	1.131 2(8)	1.133 3(7)	0.115 1(4)	C(24)	0.633 3(7)	1.073 3(7)	0.399 5(4)
C(3)	1.190 3(7)	1.046 6(7)	0.074 6(4)	C(25)	0.566 7(8)	1.164 6(8)	0.437 3(4)
C(4)	0.772 9(7)	0.609 9(8)	0.099 7(5)	C(26)	0.445 7(8)	1.192 2(7)	0.407 1(4)
C(5)	0.839 5(8)	0.499 7(9)	0.081 5(5)	C(27)	0.249 2(7)	0.903 1(7)	0.295 7(4)
C(6)	0.965 1(8)	0.494 7(7)	0.106 3(5)	C(28)	0.333 7(7)	1.120 3(7)	0.302 5(4)
C(7)	1.121 6(7)	0.834 4(7)	0.045 7(4)	C(29)	0.147 0(7)	1.009 8(7)	0.400 7(4)
C(8)	1.090 0(7)	0.643 7(7)	0.163 2(4)	C(30)	0.066 7(7)	1.141 7(7)	0.395 2(4)
C(9)	1.318 2(7)	0.723 0(7)	0.113 3(4)	C(31)	−0.019 0(8)	1.187 3(9)	0.335 7(5)
C(10)	1.392 8(6)	0.587 7(7)	0.141 0(4)	C(32)	−0.086 5(10)	1.307 7(10)	0.327 6(6)
C(11)	1.459 9(7)	0.556 3(7)	0.208 5(4)	C(33)	−0.077 5(10)	1.387 4(9)	0.377 4(7)
C(12)	1.535 6(8)	0.436 4(9)	0.231 4(4)	C(34)	0.005 9(10)	1.337 2(10)	0.438 2(6)
C(13)	1.544 4(8)	0.345 6(8)	0.185 9(5)	C(35)	0.078 2(8)	1.215 8(9)	0.447 2(5)

Table 7 Final atomic positional parameters of non-hydrogen atoms for $[ZnLBr_2]$ **7**

Atom	*x*	*y*	*z*
Zn	0.970 60(7)	0.247 34(4)	0.071 05(4)
Br(1)	0.829 21(7)	0.391 43(4)	0.069 84(4)
Br(2)	0.854 16(7)	0.130 82(4)	−0.022 97(4)
N(1)	0.965 3(5)	0.197 1(3)	0.189 8(3)
N(2)	1.037 3(5)	0.117 4(3)	0.218 61(24)
N(3)	1.196 9(4)	0.275 7(3)	0.031 00(25)
N(4)	1.323 1(5)	0.214 7(3)	0.022 3(3)
N(5)	1.279 7(5)	0.114 0(3)	0.138 37(25)
C(1)	0.878 5(6)	0.228 4(4)	0.253 2(3)
C(2)	0.892 1(7)	0.168 6(4)	0.321 4(3)
C(3)	0.996 1(7)	0.098 5(4)	0.297 9(3)
C(4)	1.245 8(6)	0.356 3(4)	−0.002 1(3)
C(5)	1.401 9(7)	0.345 7(4)	−0.032 6(4)
C(6)	1.448 5(6)	0.255 3(4)	−0.016 4(3)
C(7)	1.140 5(6)	0.060 5(3)	0.164 0(3)
C(8)	1.308 0(6)	0.117 9(3)	0.050 8(3)
C(9)	1.425 4(6)	0.122 5(4)	0.198 4(3)
C(10)	1.521 9(6)	0.032 7(3)	0.213 3(3)
C(11)	1.486 0(6)	−0.026 3(4)	0.277 1(3)
C(12)	1.571 3(7)	−0.108 5(4)	0.290 5(4)
C(13)	1.697 5(7)	−0.131 8(4)	0.240 7(4)
C(14)	1.736 7(6)	−0.072 8(4)	0.177 0(4)
C(15)	1.649 8(6)	0.009 4(4)	0.162 7(3)

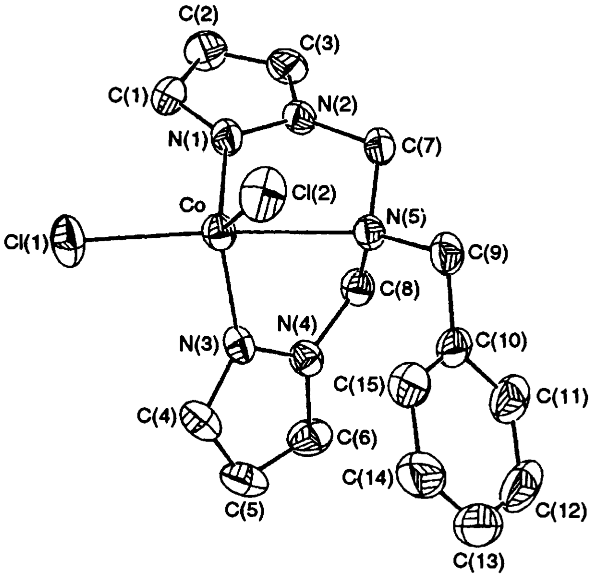

Fig. 1 Molecular structure of $[CoLCl_2]$ **2** with 50% probability ellipsoids for non-hydrogen atoms

octahedral symmetry is fairly substantial considering that the relevant angles lie between 76.0(3) and 96.6(7)°. The Ni–N(amine) bond which is *trans* to the NCS^- is longer than that found in $[NiL'_2][BF_4]_2$ [2.182(9) Å].[25] The co-ordination angles of the thiocyanates to the metal ion deviate from linearity [163.4(16) and 162.4(19)°].

Molecular Structure of $[CuLCl_2]$ **5**.—This structure is shown in Fig. 4; selected bond distances and angles are presented in Table 8.

In complex **5**, the copper(II) ion is co-ordinated by a benzylamine nitrogen atom at Cu–N(5) 2.182(4) Å, and two pyrazolyl nitrogen atoms at Cu–N(1) 1.970(4) and Cu–N(3) 1.968(4) Å, and two chloride ions at Cu–Cl(1) 2.465(2) and Cu–Cl(2) 2.248(2) Å. Addison *et al.*[26] defined the τ parameter (τ = 0, square-pyramidal geometry; τ = 1, trigonal-bipyramidal geometry) to distinguish between these geometries. The τ value for complex **5** is 0.10, indicating that the co-ordination sphere of copper(II) is better described as distorted square pyramidal rather than distorted trigonal bipyramidal. The geometry and the Cu–N distances are similar to those of $[Cu(ddae)Cl_2]$ {ddae = bis[2-(3,5-dimethylpyrazol-1-yl)ethyl]ethylamine}[27] in which the ligand forms six-membered chelate rings upon co-ordination. The basal plane involves N(1), N(5), N(3) and Cl(2) while Cl(1) occupies the apical position; the Cu^{II} ion lies 0.418(2) Å above the basal plane.

Molecular Structure of $[(CuLI)_2]$ **6**.—This structure is shown in Fig. 5; selected bond distances and angles are presented in Table 8.

The copper(I) ion is surrounded by two nitrogen atoms at Cu(1)–N(1) 2.092(6) and Cu(1)–N(3) 2.015(6) Å and by two bridging iodide ions at Cu(1)–I(1) 2.604(2) and Cu(1)–I(2) 2.721(2) Å. Two copper(I) ions and two bridging iodide ions form a planar Cu_2I_2 four-membered ring. The Cu(1) ··· Cu(2) distance at 3.028(2) Å, is larger than that in other known

Table 8 Selected bond distances (Å) and angles (°) for [CoLCl$_2$] **2**, [CoL(NCS)$_2$] **3**, [NiL(NCS)$_2$(MeOH)] **4**, [CuLCl$_2$] **5**, [(CuLI)$_2$] **6** and [ZnLBr$_2$] **7**. For the atomic numbering see Figs. 1–6

[CoLCl$_2$] **2**			
Co–N(1)	2.014(4)	Co–Cl(1)	2.320(2)
Co–N(3)	2.001(3)	Co–Cl(2)	2.249(2)
Co–N(5)	2.510(4)		
N(1)–Co–N(3)	113.98(15)	Cl(1)–Co–N(3)	96.02(11)
N(1)–Co–N(5)	74.12(14)	Cl(1)–Co–N(5)	159.66(9)
N(3)–Co–N(5)	72.98(23)	Cl(2)–Co–N(1)	113.36(13)
Cl(1)–Co–Cl(2)	107.57(8)	Cl(2)–Co–N(3)	123.74(11)
Cl(1)–Co–N(1)	95.90(12)	Cl(2)–Co–N(5)	92.72(10)
[CoL(NCS)$_2$] **3**			
Co–N(1)	2.037(6)	Co–N(3)	2.006(6)
Co–N(5)	2.425(6)	Co–N(6)	1.963(6)
Co–N(7)	2.016(7)		
N(1)–Co–N(3)	114.3(3)	N(1)–Co–N(5)	74.54(22)
N(1)–Co–N(6)	122.6(3)	N(1)–Co–N(7)	99.4(3)
N(3)–Co–N(5)	74.49(22)	N(3)–Co–N(6)	113.0(3)
N(3)–Co–N(7)	99.2(3)	N(5)–Co–N(6)	88.68(23)
N(5)–Co–N(7)	167.86(24)	N(6)–Co–N(7)	103.4(3)
Co–N(6)–C(16)	167.7(6)	Co–N(7)–C(17)	159.4(7)
[NiL(NCS)$_2$(MeOH)] **4**			
Ni–N(1)	2.052(15)	Ni–N(3)	2.018(15)
Ni–N(5)	2.276(14)	Ni–N(6)	2.056(15)
Ni–N(7)	2.009(15)	Ni–O	2.130(13)
N(1)–Ni–N(3)	96.5(6)	N(1)–Ni–N(3)	78.9(6)
N(1)–Ni–N(6)	87.8(6)	N(1)–Ni–N(7)	95.4(7)
N(1)–Ni–O	168.3(5)	N(3)–Ni–N(5)	76.0(5)
N(3)–Ni–N(6)	169.4(5)	N(3)–Ni–N(7)	92.6(7)
N(3)–Ni–O	88.8(6)	N(5)–Ni–N(6)	95.5(6)
N(5)–Ni–N(7)	166.4(6)	N(5)–Ni–O	92.4(5)
N(6)–Ni–N(7)	96.6(7)	N(6)–Ni–O	85.2(6)
N(7)–Ni–O	94.8(7)	Ni–N(6)–C(16)	163.4(19)
Ni–N(7)–C(17)	162.4(19)		
[CuLCl$_2$] **5**			
Cu–N(1)	1.970(4)	Cu–Cl(1)	2.465(2)
Cu–N(3)	1.968(4)	Cu–Cl(2)	2.248(2)
Cu–N(5)	2.182(4)		
N(1)–Cu–N(3)	157.77(16)	Cl(1)–Cu–N(3)	91.83(12)
N(1)–Cu–N(5)	79.03(15)	Cl(1)–Cu–N(5)	96.26(10)
N(3)–Cu–N(5)	79.52(15)	Cl(2)–Cu–N(1)	98.00(13)
Cl(1)–Cu–Cl(2)	111.92(6)	Cl(2)–Cu–N(3)	98.12(12)
Cl(1)–Cu–N(1)	96.23(13)	Cl(2)–Cu–N(5)	151.81(11)
[(CuLI)$_2$] **6**			
Cu(1)–N(1)	2.092(6)	Cu(1)–I(2)	2.721(2)
Cu(1)–N(3)	2.015(6)	Cu(2)–I(1)	2.653(2)
Cu(2)–N(6)	2.064(6)	Cu(2)–I(2)	2.650(2)
Cu(2)–N(8)	2.037(6)	Cu(1) · · · Cu(2)	3.028(2)
Cu(1)–I(1)	2.604(2)		
Cu(1)–I(1)–Cu(2)	70.34(6)	N(1)–Cu(1)–N(3)	109.67(22)
Cu(1)–I(2)–Cu(2)	68.62(6)	I(1)–Cu(2)–I(2)	110.63(6)
I(1)–Cu(1)–I(2)	109.93(6)	I(1)–Cu(2)–N(6)	113.83(16)
I(1)–Cu(1)–N(1)	110.54(16)	I(2)–Cu(2)–N(8)	116.57(16)
I(1)–Cu(1)–N(3)	114.00(16)	I(2)–Cu(2)–N(6)	107.73(16)
I(2)–Cu(1)–N(1)	102.31(16)	I(2)–Cu-(2)–N(8)	105.61(16)
I(2)–Cu(1)–N(3)	109.75(17)	N(6)–Cu(2)–N(8)	101.67(23)
[ZnLBr$_2$] **7**			
Zn–Br(1)	2.355(1)	Zn–Br(2)	2.391(1)
Zn–N(1)	2.013(4)	Zn–N(3)	2.005(4)
Zn–N(5)	3.270(4)		
Br(1)–Zn–Br(2)	115.57(4)	Br(1)–Zn–N(1)	106.57(11)
Br(1)–Zn–N(3)	105.58(11)	Br(2)–Zn–N(1)	107.64(11)
Br(2)–Zn–N(3)	106.15(11)	N(1)–Zn–N(3)	115.66(16)

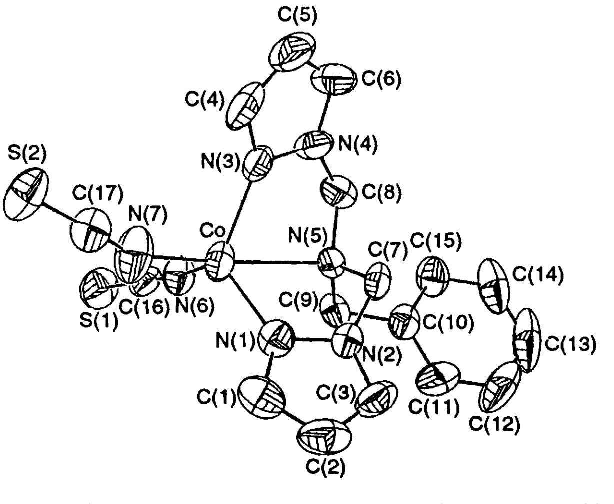

Fig. 2 Molecular structure of [CoL(NCS)$_2$] **3** with 50% probability ellipsoids for non-hydrogen atoms

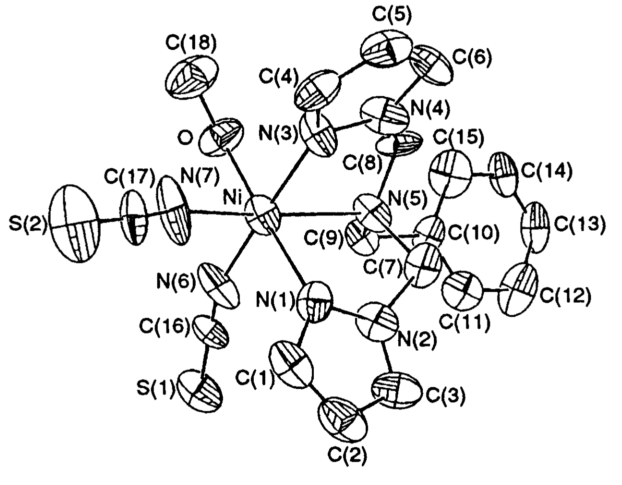

Fig. 3 Molecular structure of [NiL(NCS)$_2$(MeOH)] **4** with 50% probability ellipsoids for non-hydrogen atoms

structural examples of isolated planar Cu$_2$X$_2$ rhombohedra: [{CuI(AsPPh$_3$)(MeCN)$_2$}$_2$] [2.779(1) Å][28] and [{Cu(Pr^{i}HNCH$_2$CH$_2$NHPr^i)I}$_2$] [2.733(1) Å],[29] but a little smaller than that found in [{CuI(C$_9$H$_7$N)}$_2$] (C$_9$H$_7$N = quinoline) [3.364(5) Å].[30] The Cu(1)–I(1)–Cu(2) bridging angle is 70.34(6)° and the I(1)–Cu(1)–I(2) angle is 109.93(6)°. The benzylamine nitrogen–copper distances are 3.950(6) and 3.702(6) Å which are too long to be regarded as bonding. The co-ordination of copper(I) can be described as distorted tetrahedral with angles from 102.31(16) to 110.54(16)° for Cu(1) and from 101.67(23) to 116.57(16)° for Cu(2).

The structure of complex **6** is very similar to that of [Cu(aebd)I] [aebd = *N*,*N*-bis(3,5-dimethylpyrazol-1-ylmethyl)aminoethane][31] which is mononuclear and complex **6** can be regarded as being formed from two copper(I) moieties like [Cu(aebd)I]. However as for [{Cu(aebp)Cl}$_2$] [aebp = *N*,*N*-bis(pyrazol-1-ylmethyl)aminoethane][32] formation of a bridge occurs in complex **6** because there is no ligand steric hindrance in contrast to aebd where methyl groups prevent association of the [Cu(aebd)I] moieties.

Molecular Structure of [ZnLBr$_2$] **7**.—This structure is shown in Fig. 6; selected bond distances and angles are presented in Table 8.

In complex **7**, the zinc(II) ion is surrounded by two pyrazolyl nitrogen atoms at Zn–N(1) 2.013(4) and Zn–N(3) 2.005(4) Å, and two bromide ions at Zn–Br(1) 2.355(1) and Zn–Br(2) 2.391(1) Å. The benzylamine nitrogen–zinc distance is 3.270(4) Å [Zn–N(5)] which is too long to be considered as a bonding interaction. The co-ordination sphere of zinc(II) can be described as only slightly distorted from tetrahedral with angles ranging from 105.58(11) to 115.66(16)°.

Comparison of the structures of complexes **2**–**7** indicates that *N*,*N*-bis(pyrazol-1-ylmethyl)benzylamine is a flexible ligand. The cobalt(II) (d^7) and zinc(II) (d^{10}) ions favour tetrahadral geometry. In complexes **2** and **3** the amine rotates toward the Co ion, but away from the Zn ion in complex **7**. This results in Co–N(amine) distances being shorter than that of Zn–N(amine). The shorter Co–N distances in **2** and **3** leads to some interaction between Co and N(amine) and to deviation from tetrahedral toward trigonal-bipyramidal geometry. The Ni–N(amine) bond in complex **4** can be described as bonding for nickel(II) (d^8) which prefers octahedral geometry. In the d^{10} copper(I) and zinc(II) complexes **6** and **7**, the metal ion can be regarded as tetrahedral and the ligand is bidentate. For the octahedral nickel(II) complex **4** and square-pyramidal copper(II) in complex **5** the ligand is tridentate and the M–N(amine) distances are within the range observed for other complexes.[16–20] In all the complexes, the pyrazole rings are planar and the methyl carbons are coplanar with the respective pyrazole ring; the pyrazole rings are not mutually coplanar and there is no stacking between the aromatic rings with crystal packing determined by normal van der Waals contacts.

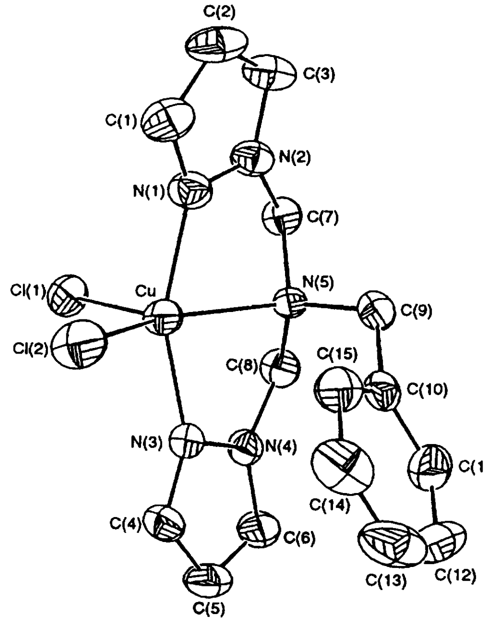

Fig. 4 Molecular structure of [CuLCl$_2$] **5** with 50% probability ellipsoids for non-hydrogen atoms

Spectroscopy.—In the IR spectra the C–H and C=N stretching vibrations of the pyrazolyl groups of the complexes are similar to those of the free ligand at 3107 and 1507 cm^{-1}. There are new strong features at 2077 and 2060 cm^{-1} (complex **3**), 2088 cm^{-1} (complex **4**) and 2083 cm^{-1} (complex **8**) arising from N-co-ordinated NCS$^-$ groups. Complex **4** shows a broad absorption at 3334 cm^{-1} due to ν(OH) from co-ordinated methanol.

The far-IR spectra of [CoLCl$_2$] **2** shows bands at 308 and 278 cm^{-1} characteristic of ν(Co–Cl)[5,33,34] while ν(Cu–Cl) in [CuLCl$_2$] **5** is located as one strong band at 258 cm^{-1}. The chloro and bromo zinc complexes show very similar IR spectra except for absorptions at 284 and 223 cm^{-1} due to ν(Zn–Cl) and ν(Zn–Br) respectively; these values being characteristic for a tetrahedral structure.[33] The ligand-field spectra of complexes **2**–**5** are reported in Table 9.

The ^1H NMR signals of complex **6** showed a large positive chemical shift of the methylene bridge protons at δ 5.20, pyrazolyl C^5H at δ 7.75 and pyrazolyl C^3H at δ 7.88 relative to that of the free ligand (δ 4.95, 7.45 and 7.53). The ^1H NMR signals of the zinc(II) complexes **7**–**9** also showed large positive chemical shifts of the methylene bridge protons at δ 5.07, 5.05 and 5.09, pyrazolyl C^5H at δ 7.54, 7.53 and 7.55, and pyrazolyl C^3H at δ 7.76, 7.76 and 7.77 relative to that of the ligand (δ 4.95, 7.45 and 7.53). Upon co-ordination most of the pyrazolyl proton signals were merged and broadened.

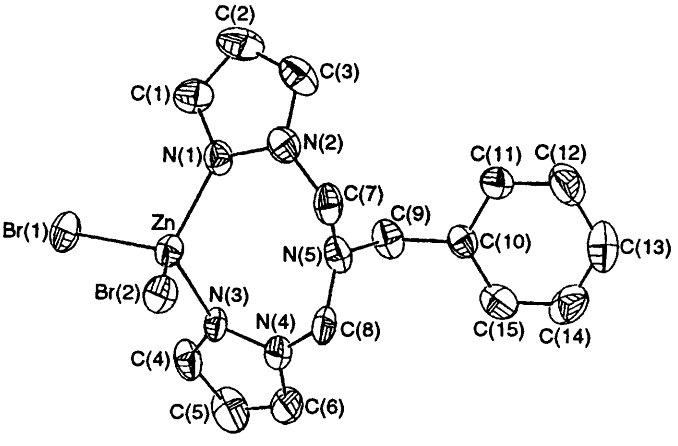

Fig. 6 Molecular structure of [ZnLBr$_2$] **7** with 50% probability ellipsoids for non-hydrogen atoms

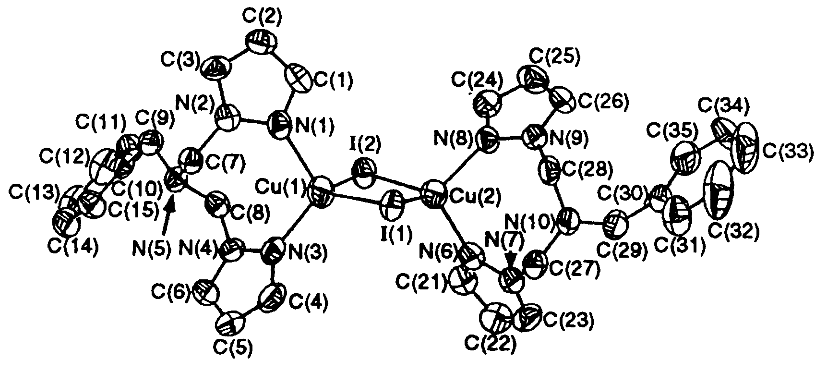

Fig. 5 Molecular structure of [(CuLI)$_2$] **6** with 50% probability ellipsoids for non-hydrogen atoms

Table 9 Electronic absorption maxima of co-ordination compounds of L

Compound	Ligand-field bands (cm^{-1})
[CoLCl$_2$]	17 667, 16 667
[CoL(NCS)$_2$]	17 123
[NiL(NCS)$_2$(MeOH)]	27 778, 13 405, 12 771
[CuLCl$_2$]	25 906, 16 233, 12 987

The X-band EPR spectra and magnetic moments of the polycrystalline complexes were measured at 298 K. The EPR spectrum of complex **5** is similar to that of [{Cu(bmdhp)(H$_2$O)(ClO$_4$)}$_2$][26] [bmdhp = 1,7-bis(*N*-methylbenzimidazol-2-yl)-2,6-dithiaheptane] and shows an axial signal.[35] The *g* values ($g_{\parallel} = 2.243$, $g_{\perp} = 2.130$) of complex **5** are consistent with a square-pyramidal co-ordination sphere for copper(II) and the single unpaired electron is located in an essentially d$_{x^2-y^2}$ orbital. The g_{iso} value is 2.150 in MeOH–MeCN solution at 77 K. The EPR spectra of complexes **2** and **3** at 298 K show no signal, but do show broad isotropic signals at 77 K, with *g* values of 3.307 and 3.552. The magnetic moments (μ_{eff}) of complexes **1**–**5** are 5.98, 4.55, 4.40, 3.19 and 1.94 μ_B, respectively. These values indicate that the octahedral iron(III) ion (d^5 configuration) has high spin ($S = \frac{5}{2}$) for complex **1** and the tetrahedral cobalt(II) ion (d^7 configuration) has high spin ($S = \frac{3}{2}$)[36] for complexes **2** and **3**.

Acknowledgements

We thank the National Science Council of the Republic of China for support.

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Received 16*th June* 1995; *Paper* 5/03919C