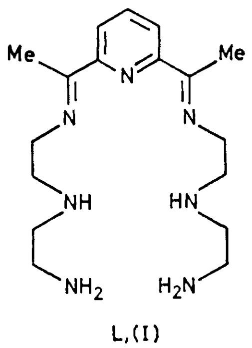
Synthesis of some Pentagonal-bipyramidal Complexes of Manganese(II), Iron(II), Cobalt(II), Nickel(II), Copper(II), and Zinc(II) with a Heptadentate Schiff-base Ligand and the Crystal and Molecular Structures of a Copper-(II) Complex

By **Michael G. B. Drew,*** Department of Chemistry, The University, Reading RG6 2AD
Jane Nelson, The Open University, Milton Keynes MKT 6AA
S. Martin Nelson,* Department of Chemistry, Queen's University, Belfast BT9 5AG, N. Ireland

Complexes of the type $[ML]X_2.xH_2O$, where M is a divalent metal ion (Mn, Fe, Co, Ni, Cu, Zn), X = ClO_4^- or BPh_4^-, x = 0 or 1, and L is a potentially heptadentate Schiff base derived from the condensation of one molecule of 2,6-diacetylpyridine with two molecules of diethylenetriamine, are reported. The complexes were prepared by metal exchange from corresponding alkaline-earth metal complexes. By means of a single-crystal *X*-ray analysis of $[CuL][ClO_4]_2$, comparisons of *X*-ray powder patterns, and various physical properties it is shown that the complexes have a pentagonal-bipyramidal structure in the solid state and also, nickel(II) complexes excepted, in acetonitrile solution. Crystals of $[CuL][ClO_4]_2$ are monoclinic, with a = 12.18(1), b = 13.78(1), c = 14.92(1) Å, β = 98.3(1)°, Z = 4, space group $P2_1/n$. 1 486 Reflections above background have been measured by diffractometer and refined by full-matrix least squares to R 0.079. The three nitrogen atoms of the trimethine group together with the two secondary amine nitrogen atoms define the equatorial plane of a distorted pentagonal bipyramid, the primary amine nitrogen atoms occupying the axial positions. The $Cu-N_{ax.}$ bonds [1.993(19), 1.997(20) Å] are notably shorter than the $Cu-N_{eq.}$ bonds (average 2.356 Å). The transition-metal complexes are all high spin. Electronic spectra are reported, as well as the e.s.r. spectrum of $[CuL][BPh_4]_2$.

FOLLOWING the first report by Hoard and co-workers [1] of some anionic ethylenediaminetetra-acetic acid complexes of Mn^{II} and Fe^{III} there has been a growing number of examples of seven-co-ordinate complexes among transition-metal ions of the first row.† While seven-co-ordination is now established for all the metals scandium to zinc in one or more oxidation state, it remains true that this is a rare co-ordination number.†,[2] By far the greatest number of examples are pentagonal-bipyramidal complexes in which the equatorial plane is made up of the five donor atoms of a quinquedentate ligand. Since most such quinquedentate ligands are either macrocyclic [3] and/or contain a conjugated planar segment [4] the adoption of the pentagonal-bipyramidal co-ordination geometry can logically be traced to preferred ligand conformation. In continuation of our studies on complexes of high co-ordination number [3a,5] and on the influence of the d^n configuration of a metal ion on its response,[6,7] in properties and reactions as well as structure, to multidentate ligands having an unusual preferred disposition of donor atoms we now report on some complexes of the potentially heptadentate Schiff-base ligand L, (I), with the metal ions Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}.



L,(I)

RESULTS AND DISCUSSION

The complexes under consideration are listed in Table 1 along with analytical and physical data pertaining to them. They were prepared by a two stage procedure starting from 2,6-diacetylpyridine and diethylenetriamine. In the first stage the diketone was treated with a two- to three-fold excess of the amine in methanol at room temperature in the presence of one equivalent of the diperchlorate of Ca^{II}, Sr^{II}, or Ba^{II} to yield the complexes $[ML][ClO_4]_2.xH_2O$ (M = Ca^{II}, Sr^{II}, or Ba^{II}; x = 0 or 1). After isolation, treatment of the alkaline-earth metal complexes in methanol with an excess of the perchlorate salt of the transition metal ions gave crystalline complexes $[ML][ClO_4]_2$ in good yield [M = Mn, Fe, Co, Cu, or Zn] (see Experimental section for details). Tetraphenylborate salts were obtained by metathesis. In the case of M = Ni^{II} there are two reaction products, one green, the other brown. Only the brown form (shown in the following paper to be an isomerisation product of the green complex) [8] could be isolated as the perchlorate. Pure crystals of the green form were obtained by fractional crystallisation of the impure tetraphenylborate from acetonitrile, the green form separating first.

The ligand L, in its complexes with the alkaline-earth metals ions, has previously been shown [9] from analytical, i.r., and ^1H n.m.r. data to have the structure (I). However, because of the possibility of facile intramolecular nucleophilic additions of primary and secondary amine groups to co-ordinated azomethine centres [7,9,10] it cannot be assumed that a Schiff-base ligand such as L will remain unaltered on replacement of one metal ion by

---

† For a comprehensive review of seven-co-ordination covering publications up to 1976 see M. G. B. Drew, *Progr. Inorg. Chem.*, 1977, **23**, 67; see also refs. 3 and 4 for some later papers.

another. In the present case it is shown below that the ligand L does, in fact, retain the structure (I) on transmetallation and, further, that the co-ordination geometry around the transition-metal ions is pentagonal bipyramidal.

The i.r. spectra of the complexes show strong similarities to one another. All exhibit three to four bands in the 3 150—3 350 cm^{-1} region attributable to ν(NH) of both primary and secondary amine groups, a medium intensity absorption at 1 620—1 650 cm^{-1} due to ν(C=N) (Table 1), as well as various features characteristic of the pyridine ring. The mull spectra of several of the perchlorates indicated the presence of H_2O and/or MeOH in the lattice. No absorption at *ca.* 1 700 cm^{-1} was observed attesting to the absence of hydrolysis during the transmetallation. The ν_3 and ν_4 vibrations of $[ClO_4]^-$ showed some broadening (ν_3) or splitting (ν_4) suggesting some reduction from the T_d symmetry expected for ionic $[ClO_4]^-$. This is accounted for not by co-ordination to the metal ion but by hydrogen bonding with NH groups in the lattice as shown by *X*-ray analysis of $[CuL][ClO_4]_2$. The complexes are all 2 : 1 electrolytes in MeCN (Table 1). The lower conductance values found for the $[BPh_4]^-$ salts compared with the $[ClO_4]^-$ salts is a generally observed phenomenon due, presumably, to a lower ionic mobility of $[BPh_4]^-$.

TABLE 1

Analytical, i.r. spectroscopic, and physical data for the complexes

	Analysis (%)						I.r. bands/cm^{-1}			
	Found [a]			Calc.						
Complex	C	H	N	C	H	N	ν(NH)	ν(C=N)	$\mu_{eff.}$ [b]/ B.M.	Λ [c]/ S cm^2 mol$^-$
$[MnL][ClO_4]_2 \cdot MeOH$	35.2	5.4	15.5	35.0	5.7	15.8	3 342, 3 334, 3 292	1 642	5.85	338
$[MnL][BPh_4]_2$	76.0	7.2	9.5	76.0	7.0	9.5	3 320, 3 288, 3 280	1 642		
$[FeL][ClO_4]_2 \cdot H_2O$	33.5	5.1	16.1	33.7	5.5	16.2	3 344, 3 298, 3 230	1 640, 1 632	5.22	297
$[FeL][BPh_4]_2$	75.3	6.9	9.5	76.0	7.0	9.5	3 304, 3 260, 3 240 (sh)	1 626		226
$[CoL][ClO_4]_2 \cdot H_2O(MeOH)$	34.1	5.6	15.3	33.7	5.8	15.3	3 342, 3 336, 3 254, 3 230	1 640	4.41	281
$[CoL][BPh_4]_2$	75.7	6.7	9.4	75.7	6.9	9.5	3 342, 3 336, 3 294, 3 230	1 640		215
$[NiL][BPh_4]_2$	75.7	7.0	9.6	75.7	6.9	9.5	3 310, 3 264, 3 160	1 648	3.10	
$[CuL][ClO_4]_2$	33.1	5.4	16.2	34.2	5.0	16.4	3 332, 3 274, 3 194	1 658, 1 642	1.92	335
$[CuL][BPh_4]_2$	75.1	7.0	9.2	75.4	6.9	9.4	3 322, 3 302, 3 280, 3 262	1 640		234
$[ZnL][ClO_4]_2$	34.3	5.4	15.8	34.2	5.2	16.4	3 338, 3 282, 3 230	1 652		310
$[ZnL][BPh_4]_2$	74.5	7.0	8.8	75.3	6.9	9.4	3 338, 3 316, 3 270	1 644		252

[a] The inclusion of H_2O and/or MeOH in the formula of some of the crystalline complexes was based on mull i.r. spectra and the best fit to the analytical data. [b] At 20 °C, corrected for diamagnetism of ligands. [c] For 10^{-3} mol dm^{-3} solutions in MeCN at 25 °C.

The ^1H n.m.r. spectrum of $[ZnL][ClO_4]_2$ in MeCN consisted of a multiplet at 8.22, a triplet at 3.72, a triplet at 3.15, a multiplet at 2.58, and a singlet at 2.45 p.p.m. Integrated relative intensities were in the ratio 3 : 4 : 4 : 8 : 6 in agreement with the assignment of the resonances to the pyridine protons, the CH_2–C=N groups, the adjacent CH_2 groups, the remaining CH_2 groups linking the NH and NH_2 functions, and the methyl groups, respectively. In addition, a strong singlet occurred at 2.16 p.p.m. This resonance shifted downfield on addition of D_2O and is assigned to the NH protons in rapid exchange with the protons of water present in the solvent.

The formulation of the complexes as salts of the complex cations $[ML]^{2+}$ in which all seven potential nitrogen donor atoms are available for co-ordination (molecular models) suggested by these properties was confirmed for the case of $[CuL][ClO_4]_2$ by a single-crystal *X*-ray diffraction study.

Crystal Data.—$[CuL][ClO_4]_2$, $C_{17}H_{31}Cl_2CuN_7O_8$, M = 595, Monoclinic, $a = 12.18(1)$, $b = 13.78(1)$, $c = 14.92(1)$ Å, $\beta = 98.3(1)°$, $U = 2\,478.0$ Å^3, $D_m = 1.59$ g cm^{-3}, $Z = 4$, $D_c = 1.60$ g cm^{-3}, $F(000) = 1\,236$, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, $\mu = 11.9$ cm^{-1}. Space group $P2_1/n$ from systematic absences $h0l$, $h = 2n + 1$, $0k0$, $k = 2n + 1$.

A single crystal of approximate size 0.33 × 0.40 × 0.80 mm was mounted with the (1 0 1) planes perpendicular to the instrument axis of a General Electric XRD5 diffractometer. This was used to measure cell dimensions by refinement of high-angle data and intensities by the stationary-crystal–stationary-counter method. 2 317 Independent reflections were measured of which 1 486 with $I > 2\sigma(I)$ were used in subsequent calculations. Neither an absorption nor an extinction correction was applied.

Structure Determination.—The position of the copper atom was located from a Patterson map and the positions of the remaining atoms in the cation from Fourier maps. Hydrogen atoms were fixed in the appropriate trigonal or tetrahedral positions and given thermal parameters equivalent to those of the atom to which they are bonded. Only one of the perchlorate anions, around Cl(1), was disordered. We approximated the disorder by three tetrahedra with relative occupancies $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{4}$. These were refined as rigid groups but isotropic thermal parameters of individual atoms were allowed to refine. For Cl(2) the oxygen atoms were refined anisotropically. In the cation the copper atoms were given anisotropic and carbon and nitrogen atoms isotropic thermal parameters. The structure was refined by full-matrix least squares to R 0.079. The weighting scheme used in the

TABLE 2

Atomic co-ordinates ($\times 10^4$) for $[CuL][ClO_4]_2$ with estimated standard deviations in parentheses

Atom	X	Y	Z
Cu	2 217(3)	2 280(3)	194(2)
Cl(1)	6 513(6)	2 011(6)	1 685(5)
O(11)	5 767(28)	2 706(25)	1 271(25)
O(12)	6 213(31)	1 497(25)	2 406(22)
O(13)	7 464(31)	2 592(32)	2 081(30)
O(14)	6 861(38)	1 463(30)	992(25)
O(21)	7 365(41)	1 930(45)	2 410(35)
O(22)	6 935(51)	2 016(49)	868(31)
O(23)	5 777(40)	1 211(32)	1 665(42)
O(24)	5 881(41)	2 845(31)	1 829(41)
O(32)	6 070(51)	2 959(28)	1 702(47)
O(33)	6 018(49)	1 512(42)	921(29)
O(34)	7 664(27)	2 048(42)	1 770(40)
Cl(2)	2 804(6)	3 581(5)	3 622(5)
O(41)	3 102(21)	4 283(14)	4 270(13)
O(42)	3 479(17)	2 770(14)	3 858(16)
O(43)	3 012(18)	3 910(15)	2 761(13)
O(44)	1 712(16)	3 332(22)	3 560(18)
N(1)	3 335(17)	2 347(16)	1 308(14)
C(2)	3 231(24)	1 512(21)	1 887(20)
C(3)	2 022(25)	1 360(23)	1 980(20)
N(4)	1 386(18)	1 314(17)	1 076(15)
C(5)	171(23)	1 523(19)	1 060(20)
C(6)	−72(24)	2 560(19)	1 309(20)
N(7)	653(19)	3 168(17)	839(15)
C(8)	788(22)	4 058(20)	997(18)
C(9)	1 601(23)	4 567(20)	540(19)
N(10)	2 222(17)	3 970(14)	88(14)
C(11)	2 976(23)	4 348(20)	−374(19)
C(12)	3 679(22)	3 630(20)	−812(18)
N(13)	3 560(17)	2 780(17)	−602(14)
C(14)	4 194(25)	2 030(20)	−999(20)
C(15)	4 052(25)	1 058(22)	−572(21)
N(16)	2 926(20)	863(18)	−459(17)
C(17)	2 156(26)	734(24)	−1 337(22)
C(18)	1 018(24)	1 082(20)	−1 234(20)
N(19)	1 098(17)	2 093(14)	−910(14)
C(20)	156(25)	4 582(22)	1 657(20)
C(21)	1 738(26)	5 561(23)	495(22)
C(22)	2 507(25)	5 944(24)	29(20)
C(23)	3 128(26)	5 350(23)	−417(22)
C(24)	4 397(27)	3 980(24)	−1 464(21)

refinement was $w^{\frac{1}{2}} = 1$ for $F_o < 120$ and $w^{\frac{1}{2}} = 120/F_o$ for $F_o > 120$. This gave similar values of $w\Delta^2$ for ranges of F_o and $(\sin\theta)/\lambda$. Calculations were done using SHELX-76 (ref. 11) at the University of Manchester Computer Centre. Scattering factors were taken from International Tables.[12] In the final cycle of refinement, shifts were less than 0.1σ and a difference-Fourier gave no significant peaks. Reflections given zero weight gave no serious discrepancies. Positional parameters are given in Table 2 and bond lengths and angles in Table 3. Thermal parameters and hydrogen atom positions are given in Supplementary Publication No. SUP 23051 (14 pp.).*

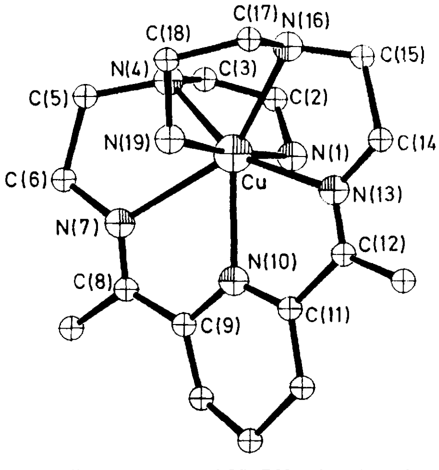


FIGURE 1 The structure of $[CuL]^{2+}$ showing the atomic numbering scheme

TABLE 3

Molecular dimensions, distances (Å) and angles (°), for $[CuL][ClO_4]_2$* with estimated standard deviations in parentheses

Cu–N(1)	1.994(19)	Cu–N(13)	2.263(23)
Cu–N(4)	2.217(24)	Cu–N(16)	2.398(26)
Cu–N(7)	2.565(24)	Cu–N(19)	1.997(19)
Cu–N(10)	2.335(20)		
N(1)–Cu–N(4)	81.3(8)	N(4)–Cu–N(16)	88.5(8)
N(1)–Cu–N(7)	96.9(8)	N(7)–Cu–N(16)	150.6(8)
N(4)–Cu–N(7)	68.7(8)	N(10)–Cu–N(16)	141.3(8)
N(1)–Cu–N(10)	90.1(8)	N(13)–Cu–N(16)	72.9(8)
N(4)–Cu–N(10)	130.2(8)	N(1)–Cu–N(19)	175.3(8)
N(7)–Cu–N(10)	63.8(8)	N(4)–Cu–N(19)	95.5(8)
N(1)–Cu–N(13)	88.0(8)	N(7)–Cu–N(19)	85.1(8)
N(4)–Cu–N(13)	157.1(8)	N(10)–Cu–N(19)	94.7(7)
N(7)–Cu–N(13)	133.1(8)	N(13)–Cu–N(19)	93.8(8)
N(10)–Cu–N(13)	69.6(8)	N(16)–Cu–N(19)	78.6(8)
N(1)–Cu–N(16)	97.7(8)		
N(1)–C(2)	1.46(3)	C(11)–C(12)	1.52(4)
C(2)–C(3)	1.51(4)	C(11)–C(23)	1.40(4)
C(3)–N(4)	1.46(3)	C(12)–N(13)	1.23(3)
N(4)–C(5)	1.51(3)	C(12)–C(24)	1.48(4)
C(5)–C(6)	1.52(3)	N(13)–C(14)	1.47(3)
C(6)–N(7)	1.47(3)	C(14)–C(15)	1.50(4)
N(7)–C(8)	1.26(3)	C(15)–N(16)	1.43(4)
C(8)–C(9)	1.46(4)	N(16)–C(17)	1.51(3)
C(8)–C(20)	1.52(4)	C(17)–C(18)	1.50(4)
C(9)–N(10)	1.36(3)	C(18)–N(19)	1.47(3)
C(9)–C(21)	1.38(4)	C(21)–C(22)	1.35(4)
N(10)–C(11)	1.33(3)	C(22)–C(23)	1.35(4)
Cu–N(1)–C(2)	110.5(16)	N(10)–C(11)–C(12)	116.3(23)
N(1)–C(2)–C(3)	109.4(22)	N(10)–C(11)–C(23)	121.1(26)
C(2)–C(3)–N(4)	108.4(24)	C(12)–C(11)–C(23)	122.5(26)
Cu–N(4)–C(3)	107.2(17)	C(11)–C(12)–N(13)	114.6(25)
Cu–N(4)–C(5)	114.1(16)	C(11)–C(12)–C(24)	119.7(24)
C(3)–N(4)–C(5)	113.4(22)	N(13)–C(12)–C(24)	125.6(27)
N(4)–C(5)–C(6)	113.7(21)	Cu–N(13)–C(12)	123.1(19)
C(5)–C(6)–N(7)	105.7(23)	Cu–N(13)–C(14)	117.4(17)
Cu–N(7)–C(8)	116.9(19)	C(12)–N(13)–C(14)	118.8(24)
Cu–N(7)–C(6)	115.9(16)	N(13)–C(14)–C(15)	111.0(25)
C(6)–N(7)–C(8)	122.7(25)	C(14)–C(15)–N(16)	112.8(24)
N(7)–C(8)–C(9)	117.5(26)	Cu–N(16)–C(15)	107.6(17)
N(7)–C(8)–C(20)	121.4(26)	Cu–N(16)–C(17)	103.5(17)
C(9)–C(8)–C(20)	121.1(24)	C(15)–N(16)–C(17)	114.0(24)
C(8)–C(9)–N(10)	113.9(23)	N(16)–C(17)–C(18)	110.0(26)
C(8)–C(9)–C(21)	126.4(27)	C(17)–C(18)–N(19)	108.6(23)
N(10)–C(9)–C(21)	119.6(27)	Cu–N(19)–C(18)	113.4(15)
Cu–N(10)–C(9)	124.2(17)	C(9)–C(21)–C(22)	121(3)
Cu–N(10)–C(11)	115.7(17)	C(21)–C(22)–C(23)	120(3)
C(9)–N(10)–C(11)	119.7(22)	C(11)–C(23)–C(22)	119(3)

* Dimensions of the perchlorates are given in the Supplementary Publication.

Discussion of the Structure.—The cation $[CuL]^{2+}$ is shown in Figure 1. The copper atom is bonded to all seven nitrogen atoms of the ligand, providing a distorted pentagonal-bipyramidal environment. The trimethine group, together with the two secondary amine nitrogen atoms, make up the approximately planar equatorial

---

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

girdle while the two terminal (primary) amine nitrogens occupy the axial positions.

The Cu–$N_{ax.}$ bonds [1.993(19), 1.997(20) Å] are notably shorter than the Cu-$N_{eq.}$ bonds [average 2.356 Å]. It is difficult to disentangle electronic and steric effects in high co-ordination number complexes of this type; relatively short axial bonds are a fairly common feature of pentagonal bipyramids (see footnote on title page) as they are less crowded than equatorial bonds. However, steric effects alone are unlikely to account for the large difference observed. In $[Cu(dapsc)(OH_2)_2][NO_3]_2\cdot3H_2O$ [H_2dapsc = 2,6-diacetylpyridine bis(semicarbazone)] a similar disparity in axial and equatorial bond lengths has been observed[13] with Cu–$O_{ax.}$ 1.922 Å, and average Cu–$O_{eq.}$ 2.305 Å and average Cu–$N_{eq.}$ 2.260 Å, whereas in $[Ni(dapsc)(OH_2)_2][NO_3]_2\cdot3H_2O$ the corresponding average distances are 2.069, 2.347, and 2.130 Å. Wester and Palenik[13] have related these effects to the different *d*-electron configurations of Cu^{II} $[(d_{xy}, d_{x^2-y^2})^4, (d_{z^2})^1]$ and Ni^{II} $[(d_{xy}, d_{x^2-y^2})^3, (d_{z^2})^1]$ in D_{5h} symmetry.

The Cu–N(7), Cu–N(10), and Cu–N(13) bond lengths of the copper–trimethine moiety, respectively, 2.56(2), 2.33(2), and 2.26(2) Å, are considerably longer, and more unequal, than are found in other copper(II) complexes[14] containing the same trimethine group. This is probably a consequence of the strain inherent in the accommodation of the seven-co-ordinate ligand to a pentagonal bipyramid. Thus, in five-co-ordinate $[CuL^2]^{2+}$, where L^2 is a 17-membered macrocycle having an N_3S_2 donor set, the Cu–N distances are 2.02(1), 1.93(1), and 2.08(1) Å. The disparity in bond length, in the present complex, between N(7) and N(13) is compensated by a similar difference between Cu-N(4) [2.216(24) Å] and Cu–N(16) [2.396(26) Å].

TABLE 4

Torsion angles (°) in the ligand for $[CuL][ClO_4]_2$; standard deviations are *ca.* 1°

C(11)–C(12)–N(13)–C(14)	179.3
C(12)–N(13)–C(14)–C(15)	172.6
N(13)–C(14)–C(15)–N(16)	43.6
C(14)–C(15)–N(16)–C(17)	67.3
C(15)–N(16)–C(17)–C(18)	−148.4
N(16)–C(17)–C(18)–N(19)	55.1
N(1)–C(2)–C(3)–N(4)	52.9
C(2)–C(3)–N(4)–C(5)	−159.3
C(3)–N(4)–C(5)–C(6)	66.8
N(4)–C(5)–C(6)–N(7)	42.5
C(5)–C(6)–N(7)–C(8)	−169.3
C(6)–N(7)–C(8)–C(9)	175.0

Despite these Cu–N inequivalences, the torsion angles (Table 4) show that the ligand does keep to approximate C_2 symmetry. The major differences in torsion angles are C(5)–C(6)–N(7)–C(8) −169.3 *versus* C(12)–N(13)–C(14)–C(15) 172.6°, and C(15)–N(16)–C(17)–C(18) −148.4 *versus* C(2)–C(3)–N(4)–C(5) −159.3°. These latter two angles, and N(4)–C(5)–C(6)–N(7), N(13)–C(14)–C(15)–N(16) at 42.5, 43.6°, further reflect the considerable strain imposed on the ligand. The two five-membered chelate rings containing N(4), N(7) and N(13), N(16) also have an unusual conformation in that, in each case, both carbon atoms are on the same side of the CuN_2 plane, one by a small amount (0.12, 0.22 Å), the other by a large amount (0.63, 0.73 Å) (see Table 5, Planes 3 and 5). The other two five-membered rings, containing the terminal NH_2 groups, have the more usual asymmetric puckered conformation with the carbon atoms on either side of the plane (−0.50, 0.17; −0.57, 0.11 Å) (Planes 2 and 4 in Table 5). The CuN_5 girdle is approximately planar with an average deviation of a contributing atom of 0.19 Å. The $N_{ax.}$–Cu–$N_{eq.}$ angles are all within 12° of 90°, the most disparate being N(19)–Cu–N(16) at 78.6(8)°. The most striking deviation in the observed $N_{eq.}$–Cu–$N_{eq.}$ angles from the ideal ' pentagonal ' value of 72° is that of N(4)–Cu–N(16) at 88.5(8)° and it is caused by the need for N(1) and N(19) to reach relatively unstrained axial positions. The metal atom sits 0.20 Å out of the plane of the pyridine ring, this being a commonly observed means of relieving steric strain in this type of ligand.[14] The root mean square deviation of this observed CuN_7 polyhedron from the ideal pentagonal bipyramid is 0.13 Å, a small enough value for a complex of a seven-co-ordinate ligand (see footnote on title page). There are no equivalent fits to the other ideal seven-co-ordinate polyhedra.

TABLE 5

Least-squares planes in $[CuL][ClO_4]_2$†

Plane 1	Cu 0.04, N(4) 0.33, N(7) −0.29, N(10) 0.06, N(13) 0.15, N(16) −0.29
Plane 2	Cu 0.00, N(1) 0.00, N(4) 0.00, C(2) * 0.50, C(3) * −0.17
Plane 3	Cu 0.00, N(13) 0.00, N(16) 0.00, C(14) * 0.12, C(15) * 0.63
Plane 4	Cu 0.00, N(16) 0.00, N(19) 0.00, C(17) * −0.11, C(18) * 0.57
Plane 5	Cu 0.00, N(4) 0.00, N(7) 0.00, C(5) * 0.73, C(6) * 0.22
Plane 6	C(9) 0.01, N(10) −0.01, C(11) 0.00, C(21) −0.01, C(22) 0.01, C(23) −0.00, C(20) * 0.20, C(24) * −0.15, C(12) * 0.07, N(13) * 0.27, C(8) * −0.04, N(7) * −0.25, N(16) * 0.10, N(4) * 0.64, Cu * 0.21

† Distances in Å of relevant atoms from the planes are quoted. Atoms not contributing to the calculation of the plane are marked with an asterisk.

There is an intermolecular hydrogen bond between N(4) and O(41) [O(41) · · · N(4) 2.93 Å, ($\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$); O(41) · · · H(4)–N(4) 156°]. This accounts for the splitting in the i.r. bands of ClO_4^- and may also be responsible for some of the distortion from C_2 symmetry observed in the cation. There are several other short intermolecular distances; those less than 3.4 Å are listed in the Supplementary Publication.

X-Ray powder diffraction patterns of the tetraphenylborate salts of the complexes of all the divalent metal ions [Mn, Fe, Co, Ni, Cu, Zn] were determined. With the exception of the cobalt(II) complex, the complexes are isomorphous. Some physical properties of the complexes are described below which support the conclusion that all the complexes, including the cobalt(II) complexes, have a basically similar pentagonal-bipyramidal co-ordination geometry.

Magnetic, E.S.R., and Mössbauer Measurements.—Magnetic moments of the solids measured at 20 °C are given in Table 1. The values obtained for the perchlorate complexes of Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, and Cu^{II} show that the metal ions are high spin with $S = \frac{5}{2}, 2, \frac{3}{2}, 1$, and $\frac{1}{2}$ ground states, respectively. While low- or intermediate-spin ground states are, in theory, possible for several of these ions in D_{5h} symmetry this has never yet been observed. Except for the cobalt(II) complex the magnitudes of the magnetic moments fall within the ranges associated with the high-spin ions in octahedral fields and consequently magnetic measurements are unlikely to be of value in discriminating between these metal ions in weak O_h and D_{5h} fields. This is because, Co^{II} excepted, no major difference in the orbital contribution to the magnetic moment is expected. For high-spin d^7, however, the ground state is orbitally non-degenerate (^4A) in D_{5h} whereas in O_h it is orbitally triply degenerate ($^4T_{2g}$). Thus, notably smaller orbital contributions are to be expected for Co^{II} in D_{5h} (as in D_{3h} or T_d) symmetry as found in the present case ($\mu_{\text{eff.}} = 4.41$ B.M.*). A few magnetic data [5,15,16] are available for other pentagonal-bipyramidal cobalt(II) complexes for comparison. In these cases the moments fall within the range 4.1—4.6 B.M. at 293 K with small temperature dependence in the range 90—293 K.

FIGURE 2 The powder e.s.r. spectrum of [CuL][BPh$_4$]$_2$

The Mössbauer spectra of [FeL][ClO$_4$]$_2$·H$_2$O confirm the high-spin ($S = 2$) nature of Fe^{II} in this complex. The isomer shifts (relative to iron foil) at 293 K and 77K are respectively 0.97 and 1.08 mm s^{-1} while the quadrupole splittings are 2.88 and 3.09 mm s^{-1}, respectively, at the same two temperatures. While these parameters have values similar to those found for some other pentagonal-bipyramidal iron(II) complexes [17] they do not distinguish between high-spin Fe^{II} in D_{5h} and fields of other symmetry.

Room temperature e.s.r. powder spectra of [CuL][ClO$_4$]$_2$ and [CuL][BPh$_4$]$_2$ and of the latter complex doped into the isomorphous [ZnL][BPh$_4$]$_2$ and [NiL][BPh$_4$]$_2$ complexes have been measured at X-band frequency. All gave essentially the same axial type spectrum although the spectrum of [CuL][ClO$_4$]$_2$ showed no hyperfine splitting. The powder spectrum of [CuL][BPh$_4$]$_2$ is shown in Figure 2. The values of $g_{\parallel}$ and $g_{\perp}$ are, respectively, 2.02 and 2.22 while the hyperfine splittings $A_{\parallel}$ and $A_{\perp}$ are 124 and 52 G, respectively. The occurrence of $g_{\parallel}$ at lower values than $g_{\perp}$ is the effect expected for a ground-state Cu^{2+} ion in which the d_{z^2} orbital is singly occupied.[18] We believe this to be the first reported e.s.r. spectrum of a pentagonal-bipyramidal copper(II) complex.

TABLE 6

Electronic spectral data for the complexes in MeCN

	Band positions [a]/10^3 cm^{-1}
[MnL][ClO$_4$]$_2$·MeOH	25.0 (166)
[FeL][ClO$_4$]$_2$·H$_2$O	*ca.* 28.0 (sh), 15.7 (430)
[CoL][ClO$_4$]$_2$·H$_2$O(MeOH)	24.2 (310), 21.4 (170), 15.3 (5), 6.90 (4)
[NiL][BPh$_4$]$_2$ [b]	16.2, *ca.* 10.0 (sh), 6.5
[CuL][ClO$_4$]$_2$	27.6 (152), 13.4 (44), 8.2 (32)

[a] ϵ (dm^3 mol^{-1} cm^{-1}) in parentheses. [b] Mull spectrum of the solid.

Electronic Spectra of the Complexes.—Spectra were recorded for the divalent metal complexes (Mn, Fe, Co, Ni, Cu) in the solid state and in acetonitrile solution in the range 5 000—30 000 cm^{-1}. Good correspondence of the spectra in the two phases was observed, with one exception, supporting earlier conclusions that the complexes dissolve without gross stereochemical rearrangement of the complex cations. The exception is [NiL][BPh$_4$]$_2$ which changed colour from green to yellow-green and subsequently to brown on dissolution. As will be described in the following paper [8] this complex isomerises in solution to a six-co-ordinate complex of the intramolecularly rearranged ligand. Solutions of all the other complexes are stable except those of Cu^{II} in the presence of water. Separate experiments showed that these are susceptible to hydrolysis to yield products having C=O groups.

These exceptions apart, all the spectra exhibited one or more strong bands in the 24 000—30 000 cm^{-1} region which are probably due to charge-transfer and/or co-ordinated ligand transitions (Table 1). No spin-allowed d–d transitions are possible for the manganese(II) complexes and no absorption at lower energies was observed. The iron(II) complexes exhibited a fairly intense band (ε_{M} *ca.* 430 dm^3 mol^{-1} cm^{-1}) at 15 700 cm^{-1}. This is attributed to a charge-transfer transition from the occupied d_{xz}, d_{yz} orbitals of the metal to the unoccupied $p_{\pi}{}^*$ orbitals of the trimethine segment of the ligand. Charge-transfer bands of this type ($t_{2g}{}^6 \longrightarrow p_{\pi}{}^*$, in this case) are well known for low spin ($S = 0$) six-co-ordinate complexes of unsaturated nitrogen ligands. Here, much higher intensities (ε_{M} *ca.* 10 000 dm^3 mol^{-1} cm^{-1}) are observed. However, the occurrence of the transitions appears not to be restricted to low-spin Fe^{II} since exactly similar bands of

---

* Throughout this paper: 1 B.M. = 0.927×10^{-23} A m^2; 1 G = 10^{-4} T.

comparable intensity to those found here for $[FeL]^{2+}$ have previously been reported for several high-spin pentagonal-bipyramidal complexes of Fe^{II} of macrocyclic ligands containing the same trimethine moiety.[17] No other bands could be discerned in the spectra of the iron(II) complexes attributable to the two expected spin-allowed *d–d* transitions from the $^5E_1''$ ground state; presumably they are masked by the more intense charge-transfer band.

The spectra of $[CuL][ClO_4]_2$ exhibited two well resolved bands at 13 400 cm^{-1} and 8 200 cm^{-1} which we assign to the transitions $^2A_1' \longrightarrow {}^2E_1''$ and $^2A \longrightarrow {}^2E_2'$, respectively, in D_{5h} symmetry.

The spectra of the complexes of Co^{II} and Ni^{II} each comprise three to five bands below 24 000 cm^{-1}. As expected, they are quite different from those of these metal ions in more common stereochemical environments. The spectrum of the nickel(II) complex is similar to that observed [6] for the pentagonal-bipyramidal $[Ni(dapsc)(OH_2)_2][NO_3]_2 \cdot H_2O$; [13] a noteworthy feature of both is a band at 6 500 cm^{-1}. A discussion of the spectra (over a narrower wavelength range) of this complex [19] and of two pentagonal-bipyramidal cobalt(II) complexes [16] of the same ligand have appeared. However, we defer attempting assignments for the spectra of the present complexes until a larger number of complexes can be considered collectively.

EXPERIMENTAL

Preparation of the Complexes.—The complexes $[ML][ClO_4]_2 \cdot xH_2O$ [M = Mn^{II}, Fe^{II}, Co^{II}, Cu^{II}, or Zn^{II}] were prepared from the corresponding alkaline-earth metal complexes described previously [9] *via* metal exchange. The complexes $[ML][ClO_4]_2 \cdot xH_2O$ [M = Ca^{II}, Sr^{II}, or Ba^{II}] (0.01 mol) in methanol (*ca.* 200 cm^3) were treated with a *ca.* 20% deficit of the transition-metal perchlorate and refluxed for 5—10 min. On cooling and standing (2—8 h), crystals of the product complexes started to separate. Yields were in the range 50—80% depending on the nature of the metal ion being replaced as well as on the in-coming metal ion.

Tetraphenylborate salts were obtained by metathesis from the diperchlorates in acetonitrile solution.

$[NiL][BPh_4]_2$ was prepared by fractional crystallisation of the crude material obtained when excess of $Na[BPh_4]$ was added to a methanol or acetonitrile solution of $[CaL][ClO_4]_2$ and $Ni[ClO_4]_2 \cdot 6H_2O$, followed by fairly rapid concentration.

Physical Measurements.—E.s.r. spectra of polycrystalline powders were measured with a Decca XI spectrometer operated at 9 270 MHz with a magnetic field modulation of 100 kHz.

Other physical measurements were carried out as described in earlier papers.[17]

[0/1928 *Received*, 15*th December*, 1980]

REFERENCES

[1] S. Richards, B. Pedersen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, 1964, **3**, 27; M. D. Lind, M. J. Hamor, T. A. Hamor, and J. L. Hoard, *Inorg. Chem.*, 1964, **3**, 32.

[2] R. Hoffmann, B. F. Beier, E. L. Mutterties, and A. R. Rossi, *Inorg. Chem.*, 1977, **16**, 511.

[3] See for example, (*a*) M. G. B. Drew, A. H. vin Othman, S. G. McFall, P. D. A. McIlroy, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1977, 1173; (*b*) N. W. Alcock, D. C. Liles, M. McPartlin, and P. A. Tasker, *J. Chem. Soc., Chem. Commun.*, 1974, 727; (*c*) M. M. Bishop, J. Lewis, T. D. O'Donoghue, P. R. Raithby, and J. N. Ramsden, *J. Chem. Soc., Dalton Trans.*, 1980, 1390.

[4] See for example, (*a*) G. Palenik and D. W. Wester, *Inorg. Chem.*, 1978, **17**, 864; (*b*) T. J. Giordano, G. J. Palenik, R. C. Palenik, and D. A. Sullivan, *Inorg. Chem.*, 1979, **18**, 2445; (*c*) N. Nardelli, C. Pelizzi, and G. Pelizzi, *Transition Met. Chem.*, 1977, **2**, 40.

[5] M. G. B. Drew, J. Cabral, M. F. Cabral, F. S. Esho, and S. M. Nelson, *J. Chem. Soc., Chem. Commun.*, 1979, 1033.

[6] C. Cairns, S. G. McFall, S. M. Nelson, and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1979, 446.

[7] S. M. Nelson, F. S. Esho, M. G. B. Drew, and P. Bird, *J. Chem. Soc., Chem. Commun.*, 1979, 1035.

[8] M. G. B. Drew, J. Nelson, and S. M. Nelson, following paper.

[9] M. G. B. Drew, J. Nelson, and S. M. Nelson, preceding paper.

[10] S. M. Nelson, M. McCann, C. V. Knox, and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1981, 1669.

[11] G. M. Sheldrick, personal communication.

[12] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.

[13] D. W. Wester and G. J. Palenik, *J. Am. Chem. Soc.*, 1974, **96**, 7564.

[14] M. G. B. Drew, C. Cairns, S. M. Nelson, and J. Nelson, *J. Chem. Soc., Dalton Trans.*, 1981, 942.

[15] C. Cairns and S. M. Nelson, unpublished results.

[16] M. Gerloch, I. Morgenstern-Badarau, and J.-P. Audiere, *Inorg. Chem.*, 1979, **18**, 3220.

[17] M. G. B. Drew, J. Grimshaw, P. D. A. McIlroy, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1976, 1388.

[18] Adams and Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 135.

[19] M. Gerloch and I. Morgenstern-Badarau, *Inorg. Chem.*, 1979, **18**, 3225.