Inorganica Chimica Acta, 41 (1980) 213–219

The Crystal Structures of Iron(II) and Cobalt(II) Complexes of a 30-membered Macrocyclic Ligand: Observation of Jahn–Teller Distortion in a Six-Coordinate Low-spin Cobalt(II) Complex

M. G. B. DREW

Department of Chemistry, The University, Whiteknights, Reading RG6 2AD, U.K.

M. McCANN and S. M. NELSON

Department of Chemistry, Queen's University, Belfast BT9 5AG, U.K.

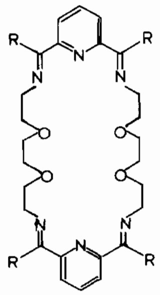
Received January 12, 1980

The crystal structures of the complexes [ML] $[ClO_4]_2 \cdot H_2O$, where M = Fe(II) or Co(II) and L is a 30-membered macrocyclic Schiff base ligand having an 'N_6O_4' donor set, have been determined. Crystal data: for M = Fe(II), a = *11.305(7),* b = *18.165(12),* c = *35.695(14)* Å, Z = *8, orthorhombic, space group* Pcab. *The Co(II) complex is isomorphous with* a = *11.387(5),* b = *18.253(5),* c = *35.694(8)* Å. *Both structures have been refined by full-matrix least squares to give* R *values of 0.0685 and 0.083 for 1854 and 1391 independent reflections above background, respectively. In both structures the metal ions have a distorted octahedral environment comprised of the six nitrogen donors, the four oxygen atoms being uncoordinated. In the low-spin Fe(II) complex the bond lengths are Fe–N(pyridine) 1.865(10), 1.867(10)* Å*; Fe–N(imino) 1.992(9), 1.994(10), 1.980(10), 1.979(10)* Å*. In the low spin Co(II) complex, on the other hand, two of the mutually* trans *Co–N(imino) bonds are* ca. *0.09* Å *longer than the other pair [Co–N(pyridine) 1.864(15), 1.907(14); Co–N(imino) 2.034(13), 2.021(15), 2.117(14), 2.121(15)* Å*]. The differences in metal–nitrogen bond lengths in the two complexes are attributed to Jahn–Teller effects in the Co(II) complex arising from the presence of a single electron in the anti-bonding e_g orbital set.*

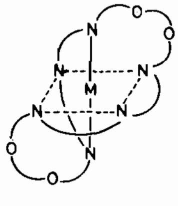
Introduction

The preparation of a di-lead(II) complex $[Pb_2L(SCN)_4]$ of the 30-membered macrocyclic Schiff base L has been reported [1].

Although L has not been isolated in the uncomplexed state it is possible to prepare complexes of L of other metal ions *via* metal exchange reactions in solution [2, 3]. The coordination mode of L is dependent on the nature of the metal ion. In $[Pb_2L(SCN)_4]$ each metal ion is bonded to three nitrogen and two oxygen atoms of L, as well as to two thiocyanate sulphur atoms, giving an overall 7-coordinate geometry [1]. In $[Cu_2L(N_3)_3][ClO_4]$ each (5-coordinate) Cu(II) ion is bonded to three nitrogens of L and to two azide ions (one terminal, one bridging), the oxygen atoms of L being uncoordinated [2]. In reactions of $[Pb_2L(SCN)_4]$ with Fe(II), Co(II) and Ni(II), on the other hand, only mononuclear 6-coordinate $[ML]^{2+}$ complexes are obtained in which, once again, only the six nitrogen donors are bonded to the metal, as shown in structure I [3].



(L)



(I)

Since the Fe(II) and Co(II) complexes are low-spin the preference of all three metal ions for the mononuclear 6-coordinate structure can be understood in terms of the substantial crystal field stabilization advantage which this geometry confers over other 5- or 7-coordinate alternatives.

The magnetic moment of $[CoL][ClO_4]_2 \cdot H_2O$ is 1.98 B.M. and is temperature independent; it is thus virtually completely in the low-spin form at ambient temperatures [3]. This is a rather uncommon situation [4] though several 6-coordinate Co(II) complexes of α-diimine and related ligands are known to exhibit temperature dependent moments attributable to a thermal equilibrium between doublet and quartet spin states [5]. Since the octahedral low-spin Co(II) ion has a $t_{2g}^6 e_g^1$ electron configuration *i.e.* one having an unsymmetrical occupancy of the e_g orbital set, it is expected to be subject to ground state Jahn–Teller distortion [6]. Such distortion has been demonstrated crystallographically [7] at 233 K for the low-spin complex $K_2Ba[Co(NO_2)_6]$ which shows an elongation along one axis, the three independent Co–N distances in the centrosymmetric complex anion being 1.93(6)*, 1.91(2) and 2.12(2) Å. Axial distortion in the same ion has also been detected by e.s.r. measurements in solution [8].

The recognition of Jahn–Teller distortion in complexes other than those containing only monodentate ligands of the same kind is rendered difficult by the effects of ligand inequivalence and, in chelate complexes, of distortions due to constraints in the ligand. For this reason we have determined the crystal and molecular structures of the isomorphous pair of complexes $[FeL][ClO_4]_2 \cdot H_2O$ and $[CoL][ClO_4]_2 \cdot H_2O$. Since the Fe(II) complex has a spherically symmetrical (t_{2g}^6) d-orbital occupancy we might reasonably expect differences in the molecular dimensions of the Co(II) complex to be directly attributable to the presence of the single e_g electron in this case.

Crystal Data

Crystal were prepared using the method of ref. 3. $[FeL][ClO_4]_2 \cdot H_2O$, I, $C_{30}H_{44}O_{13}N_6Cl_2Fe$, M = 823.1, orthorhombic, a = 11.305(7), b = 18.165(12), c = 35.695(14) Å, U = 7330.0 Å^3, D_m = 1.50, D_c = 1.49 g cm^{-3}, Z = 8, λ(MoKα) = 0.7107 Å, μ = 6.43 cm^{-1}, F(000) = 3440. $[CoL][ClO_4]_2 \cdot H_2O$, II, $C_{30}H_{44}O_{13}N_6Cl_2Co$, M = 826.2, orthorhombic, a = 11.387(5), b = 18.253(5), c = 35.694(8) Å, U = 7418.9 Å^3, D_m = 1.50, D_c = 1.48 g cm^{-3}, Z = 8, λ(CuKα) = 1.54178 Å, μ = 42.9 cm^{-1}, F(000) = 3448.

Both crystals belong to space group *Pcab* (No. 61), with systematic absences hk0, k = 2n + 1, h0l, h = 2n + 1, 0kl, l = 2n + 1.

Crystals of I of approximate size 0.3 × 0.3 × 0.8 mm, and of II 0.45 × 0.25 × 1.0 mm, were mounted on an Enraf-Nonius CAD4 diffractometer; data were measured by the $\theta/2\theta$ scan technique. For I 6986 independent reflections were measured with $2\theta < 50°$; for II 7856 independent reflections were measured for $2\theta < 140°$. Intensity data for both crystals were weak and for I 1854 reflections with $I > 2.5\ \sigma(I)$, and for II 1391 reflections with $I > 3\ \sigma(I)$, were used in subsequent refinement. Absorption and extinction corrections were not considered necessary.

The structures were determined by the Patterson and Fourier methods. For both compounds the metal atom, the two chlorine atoms and the oxygen atoms of the ordered perchlorate group were refined anisotropically, with the remaining atoms isotropically. Hydrogen atoms were placed in trigonal or tetrahedral positions and they contributed to the structure factor calculation but their parameters were not refined. Both structures contained a disordered perchlorate group which was described by two independent tetrahedra (of occupancy 0.5) of oxygen atoms. The Cl–O and O...O distances were fixed in each case. (Oxygen atoms in the ordered perchlorate were allowed to refine independently).

Refinement was carried out using the Shelx-76 package [9] at the University of Manchester Computer Centre. Both compounds were weighted according to the formula w = $1/\sigma^2(F) + 0.002(F*F)$ a scheme which gave constant values of wΔ^2 for ranges of F_0 and $\sin\theta/\lambda$. Scattering factors were taken from International Tables [10]. In the final refinement shift/error ratios were less than 0.2. A final difference Fourier map showed no significant peaks. Final atomic parameters are given in Tables I and II, bond lengths and angles in Table III. The anisotropic thermal parameters and structure factors can be obtained from the Editor.

TABLE I. Atomic Coordinates (*10**4) with Estimated Standard Deviations in Parentheses; I.

Atom	X	Y	Z
FE	824(1)	−18(1)	1249(0)
CL(1)	1474(5)	1009(3)	4466(2)
O(111)	1150(29)	276(14)	4515(10)
O(121)	628(24)	1495(15)	4588(8)
O(132)	1856(34)	1139(17)	4111(7)
O(142)	2603(25)	1157(17)	4706(9)
O(112)	1305(25)	311(12)	4656(9)
O(122)	861(30)	1514(17)	4705(9)
O(131)	666(41)	994(23)	4124(10)
O(141)	2562(33)	1214(23)	4370(15)
CL(2)	4901(5)	1321(4)	1889(2)
O(21)	3815(10)	1580(9)	2035(4)
O(22)	5678(19)	1854(10)	1877(8)
O(23)	4794(16)	968(13)	1556(5)
O(24)	5373(19)	816(12)	2131(6)
O(100)	1027(14)	639(9)	3292(5)
N(1A)	−121(9)	−942(5)	1270(3)
C(2A)	130(11)	−1437(6)	1028(3)
C(3A)	1140(10)	−1252(6)	795(3)
N(4A)	1548(9)	−565(5)	871(3)
C(5A)	2472(12)	−260(7)	679(4)
C(6A)	2728(12)	466(7)	826(4)
N(7A)	2042(9)	707(5)	1085(3)

(Continued on facing page)

---

*This high standard deviation is due to the peculiar nature of the structure (see ref. 7 for details).

TABLE I. *(Continued)*

C(8A)	−463(12)	−2173(7)	957(4)
C(9A)	1689(12)	−1666(8)	523(4)
C(10A)	2660(13)	−1370(9)	337(4)
C(11A)	3053(14)	−669(8)	406(4)
C(12A)	3764(14)	906(9)	663(5)
N(1B)	−516(8)	415(5)	969(3)
C(2B)	−1265(11)	772(7)	1165(4)
C(3B)	−921(12)	874(7)	1549(4)
N(4B)	94(9)	522(5)	1629(3)
C(5B)	568(11)	524(7)	1975(4)
C(6B)	1649(11)	80(7)	1988(3)
N(7B)	1882(9)	−239(5)	1676(3)
C(8B)	−2401(14)	1118(8)	1025(5)
C(9B)	−1469(13)	1297(7)	1833(4)
C(10B)	−986(13)	1313(8)	2183(4)
C(11B)	47(13)	932(8)	2251(4)
C(12B)	2341(12)	46(8)	2351(4)
C(21)	−1088(11)	−1051(7)	1539(3)
C(22)	−635(12)	−1339(7)	1901(4)
O(23)	−169(8)	−2062(5)	1832(3)
C(24)	505(13)	−2377(10)	2137(4)
C(25)	1783(15)	−2397(9)	2068(4)
O(26)	2260(9)	−1658(6)	2026(3)
C(27)	2694(14)	−1500(8)	1674(4)
C(28)	2967(13)	−679(7)	1648(4)
C(31)	2181(12)	1422(7)	1259(4)
C(32)	1304(13)	1961(8)	1119(4)
O(33)	1595(10)	2127(6)	737(3)
C(34)	736(16)	2558(10)	555(5)
C(35)	174(16)	2142(9)	251(5)
O(36)	−532(9)	1548(6)	402(3)
C(37)	−56(14)	836(7)	328(4)
C(38)	−746(12)	294(7)	576(4)

TABLE II. Atomic Coordinates (*10**4) with Estimated Standard Deviations in Parentheses; II.

Atom	x	y	z
CO	865(2)	−32(2)	1244(1)
CL(1)	1482(7)	1011(4)	4459(2)
O(111)	1221(49)	273(19)	4516(15)
O(121)	599(30)	1475(19)	4583(10)
O(132)	1830(43)	1134(22)	4097(9)
O(142)	2593(31)	1168(22)	4686(11)
O(112)	1319(31)	325(16)	4647(11)
O(122)	941(35)	1534(19)	4698(10)
O(131)	633(42)	959(23)	4127(10)
O(141)	2535(36)	1160(27)	4329(16)
CL(2)	4925(8)	1335(6)	1892(2)
O(21)	3835(18)	1600(12)	2034(6)
O(22)	5706(26)	1851(14)	1869(9)
O(23)	4835(19)	968(15)	1554(7)
O(24)	5383(29)	847(16)	2140(8)
O(100)	1103(17)	619(11)	3307(5)
N(1A)	−87(12)	−973(7)	1269(4)
C(2A)	184(15)	−1453(10)	1016(5)
C(3A)	1167(15)	−1253(10)	786(5)
N(4A)	1603(13)	−577(8)	870(4)
C(5A)	2515(16)	−273(9)	681(5)
C(6A)	2792(18)	463(11)	816(6)
N(7A)	2096(13)	692(8)	1074(4)
C(8A)	−425(16)	−2200(10)	952(5)
C(9A)	1784(18)	−1692(11)	518(5)
C(10A)	2698(19)	−1364(12)	336(6)
C(11A)	3099(19)	−678(12)	411(6)
C(12A)	3839(21)	871(13)	650(6)
N(1B)	−572(12)	432(8)	953(4)
C(2B)	−1263(16)	779(10)	1172(5)
C(3B)	−890(17)	866(9)	1549(5)
N(4B)	130(12)	528(7)	1629(4)
C(5B)	588(16)	522(9)	1965(5)
C(6B)	1712(17)	109(9)	2006(5)
N(7B)	1968(13)	−231(7)	1712(4)
C(8B)	−2457(18)	1088(12)	1046(6)
C(9B)	−1418(18)	1279(10)	1831(5)
C(10B)	−976(20)	1309(12)	2187(6)
C(11B)	69(18)	934(11)	2256(6)
C(12B)	2330(18)	111(11)	2371(5)
C(21)	−1057(16)	−1097(10)	1534(5)
C(22)	−565(18)	−1355(10)	1903(5)
O(23)	−115(11)	−2086(7)	1830(4)
C(24)	557(19)	−2375(13)	2128(6)
C(25)	1795(22)	−2398(14)	2054(7)
O(26)	2320(13)	−1660(9)	2039(4)
C(27)	2775(19)	−1474(11)	1703(6)
C(28)	3057(18)	−662(10)	1693(6)
C(31)	2228(18)	1408(10)	1245(6)
C(32)	1364(17)	1958(10)	1115(5)
O(33)	1618(14)	2098(8)	730(4)
C(34)	723(23)	2534(15)	562(6)
C(35)	152(23)	2137(15)	262(7)
O(36)	−586(13)	1565(9)	398(4)
C(37)	−97(17)	865(10)	323(6)
C(38)	−831(18)	345(11)	559(5)

Discussion of the Structures

In both structures the asymmetric unit contains discrete $[ML]^{2+}$ cations, two independent perchlorate anions and one water molecule. In each case the metal ion is bonded to the six nitrogen atoms of the

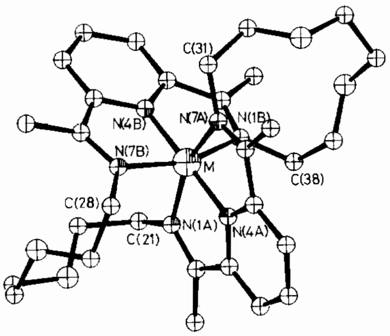


Fig. 1. The structure of $[ML]^{2+}$. Hatched circles: large = iron or cobalt, small = nitrogen. Crossed circles: medium = oxygen, small = carbon.

TABLE III. Molecular Dimensions in I (M = Fe) and II (M = Co).

(a) Metal Coordination Spheres:

	I	II
M–N(1A)	1.992(9)	2.034(13)
M–N(4A)	1.865(10)	1.864(15)
M–N(7A)	1.994(10)	2.021(15)
M–N(1B)	1.980(10)	2.117(14)
M–Ni(4B)	1.867(10)	1.907(14)
M–Ni(7B)	1.979(10)	2.121(15)
N(1A)–M–N(4A)	79.3(4)	79.7(6)
N(1A)–M–N(7A)	159.9(4)	159.4(6)
N(1A)–M–N(1B)	86.8(4)	87.0(5)
N(1A)–M–N(4B)	100.3(4)	100.8(6)
N(1A)–M–N(7B)	97.2(4)	97.9(6)
N(4A)–M–N(7A)	80.6(4)	79.7(6)
N(4A)–M–N(1B)	100.5(4)	102.2(6)
N(4A)–M–N(4B)	179.6(4)	179.2(6)
N(4A)–M–N(7B)	100.6(4)	101.9(6)
N(7A)–M–N(1B)	96.7(4)	97.3(6)
N(7A)–M–N(4B)	99.8(4)	99.7(6)
N(7A)–M–N(7B)	86.7(4)	86.4(6)
N(1B)–M–N(4B)	79.6(4)	78.4(6)
N(1B)–M–N(7B)	158.9(4)	155.9(6)
N(4B)–M–N(7B)	79.3(4)	77.5(6)

b) Dimensions in Unsaturated Fragment:

	I A	I B	II A	II B
N(1)–C(2)	1.28(1)	1.27(2)	1.30(2)	1.28(2)
C(2)–C(3)	1.45(2)	1.44(2)	1.44(2)	1.42(2)
C(2)–C(8)	1.52(2)	1.52(2)	1.55(2)	1.54(3)
C(3)–C(9)	1.38(2)	1.41(2)	1.43(3)	1.39(2)
C(3)–N(4)	1.36(1)	1.34(2)	1.36(2)	1.35(2)
N(4)–C(5)	1.37(2)	1.35(2)	1.36(2)	1.31(2)
C(5)–C(6)	1.45(2)	1.46(2)	1.46(3)	1.49(2)
C(5)–C(11)	1.39(2)	1.37(2)	1.38(3)	1.41(3)
C(6)–N(7)	1.28(2)	1.28(2)	1.28(3)	1.25(2)
C(6)–C(12)	1.53(2)	1.51(2)	1.52(3)	1.48(2)
C(9)–C(10)	1.39(2)	1.36(2)	1.37(3)	1.37(3)
C(10)–C(11)	1.37(2)	1.38(2)	1.36(3)	1.40(3)
M–N(1)–C(2)	116.6(8)	115.7(9)	114.4(12)	112.0(12)
N(1)–C(2)–C(3)	113.5(10)	114.1(11)	114.4(16)	116.8(16)
N(1)–C(2)–C(8)	129.3(11)	126.4(13)	126.3(15)	123.2(16)
C(3)–C(2)–C(8)	117.1(10)	119.4(12)	119.3(15)	120.0(16)
C(2)–C(3)–N(4)	111.4(10)	111.9(11)	112.8(15)	114.1(16)
C(2)–C(3)–C(9)	129.2(11)	129.4(12)	128.5(17)	128.0(17)
N(4)–C(3)–C(9)	119.3(11)	118.7(12)	118.3(16)	117.8(16)
M–N(4)–C(3)	119.0(8)	118.2(9)	118.4(12)	118.2(12)
M–N(4)–C(5)	118.8(8)	119.5(8)	118.9(12)	118.8(11)
C(3)–N(4)–C(5)	122.1(10)	122.2(11)	122.6(15)	122.8(15)
N(4)–C(5)–C(6)	109.9(11)	111.1(11)	112.2(16)	115.8(15)
N(4)–C(5)–C(11)	119.7(12)	119.4(12)	119.7(16)	120.1(17)
C(6)–C(5)–C(11)	130.2(13)	129.4(13)	128.0(18)	123.8(16)
C(5)–C(6)–N(7)	116.8(12)	113.1(11)	113.7(17)	111.6(16)
C(5)–C(6)–C(12)	119.3(12)	118.7(11)	119.3(18)	119.5(16)
N(7)–C(6)–C(12)	123.9(12)	128.1(12)	127.0(18)	128.8(17)
M–N(7)–C(6)	113.8(8)	116.9(8)	115.5(13)	115.9(12)
C(3)–C(9)–C(10)	118.8(13)	119.5(13)	116.5(18)	122.3(19)
C(9)–C(10)–C(11)	121.9(14)	119.3(13)	124.5(20)	117.3(20)
C(5)–C(11)–C(10)	117.9(13)	120.7(13)	117.9(19)	119.2(19)

(c) Saturated Ring Dimensions:

	I	II
N(1A)–C(21)	1.47(2)	1.47(2)
N(7A)–C(31)	1.45(2)	1.45(2)
N(1B)–C(38)	1.44(2)	1.45(2)
N(7B)–C(28)	1.46(2)	1.47(2)
M–N(1A)–C(21)	122.5(8)	124.0(10)
M–N(7A)–C(31)	122.8(8)	122.4(12)
M–N(1B)–C(38)	124.6(8)	126.2(12)
M–N(7B)–C(28)	124.3(8)	123.7(12)
C(2A)–N(1A)–C(21)	120.8(10)	121.6(14)
C(6A)–N(7A)–C(31)	123.3(11)	115.5(13)
C(2B)–N(1B)–C(38)	119.4(11)	121.6(15)
C(6B)–N(7B)–C(28)	118.5(11)	120.0(16)
N(1A)–C(21)–C(22)	111.1(10)	109.3(15)
N(7A)–C(31)–C(32)	112.1(11)	114.2(16)
N(1B)–C(38)–C(37)	111.8(11)	111.0(16)
N(7B)–C(28)–C(27)	111.0(11)	110.1(16)

	I (n = 2)	I (n = 3)	II (n = 2)	II (n = 3)
C(n1)–C(n2)	1.49(2)	1.48(2)	1.51(3)	1.48(3)
C(n2)–O(n3)	1.44(2)	1.43(2)	1.45(2)	1.43(2)
O(n3)–C(n4)	1.45(2)	1.41(2)	1.41(2)	1.42(3)
C(n4)–C(n5)	1.47(2)	1.47(2)	1.43(3)	1.44(3)
C(n5)–O(n6)	1.45(2)	1.45(2)	1.47(3)	1.43(3)
O(n6)–C(n7)	1.38(2)	1.43(2)	1.35(3)	1.42(2)
C(n7)–C(n8)	1.53(2)	1.54(2)	1.52(3)	1.52(3)
C(n1)–C(n2)–O(n3)	107.4(11)	107.8(12)	105.2(14)	106.8(16)
C(n2)–O(n3)–C(n4)	115.2(11)	113.4(12)	113.5(15)	111.1(16)
O(n3)–C(n4)–C(n5)	113.8(12)	110.7(14)	113.9(19)	110.7(21)
C(n4)–C(n5)–O(n6)	111.1(13)	110.3(14)	112.2(20)	112.3(20)
C(n5)–O(n6)–C(n7)	114.7(11)	113.5(11)	114.7(17)	111.3(17)
O(n6)–C(n7)–C(n8)	109.3(12)	106.4(11)	110.4(17)	104.0(16)

d) Dimensions in the Ordered Perchlorate*

	I	II
Cl(2)–O(21)	1.41(1)	1.42(2)
Cl(2)–O(22)	1.31(2)	1.30(2)
Cl(2)–O(23)	1.36(2)	1.38(2)
Cl(2)–O(24)	1.37(2)	1.36(2)
O(21)–Cl(2)–O(22)	110(1)	112(2)
O(21)–Cl(2)–O(23)	114(1)	114(2)
O(21)–Cl(2)–O(24)	109(1)	109(2)
O(22)–Cl(2)–O(23)	112(2)	110(2)
O(22)–Cl(2)–O(24)	105(1)	105(2)
O(23)–Cl(2)–O(24)	106(1)	106(2)

*In the disordered perchlorate around Cl(1), tetrahedral symmetry was imposed on the two sets of four oxygen atoms.

30-membered macrocycle as illustrated in Fig. 1. together with the numbering scheme. The two pyridine nitrogens [N(4A), N(4B)] are exactly *trans* to each other but the two distal imino nitrogens [N(1A), N(7A) and N(1B), N(7B)] of a given trimethine moiety are not, the N–M–N angles all being less than 160° [159.9(4), 158.9(4) Å in I, 159.4(6), 155.9(6) Å in II]. These deviations from 180°, which arise from the structure of the trimethine unit, lead to an approximate D_{2d}, rather than O_h, symmetry for the two coordination spheres. The two trimethine units about each metal (themselves planar, see Table V) intersect at angles of 81.1°, and 80.0° in I and II, respectively; a consequence is that the N(7A)–M–N(1B) and N(1A)–M–N(7B) angles are greater than 90° [96.7(4)° and 97.2(4)° in I, 97.3(6)° and

TABLE IV. Torsion Angles (°).

	I (n = 2)	I (n = 3)	II (n = 2)	II (n = 3)
N–C(n1)–C(n2)–O(n3)	−65.5	−69.5	−69.1	−67.0
C(n1)–C(n2)–O(n3)–C(n4)	169.2	171.9	170.1	170.9
C(n2)–O(n3)–C(n4)–C(n5)	−106.9	−114.4	−107.1	−117.6
O(n3)–C(n4)–C(n5)–O(n6)	62.7	68.0	69.1	72.2
C(n4)–C(n5)–O(n6)–C(n7)	−114.2	−110.6	−116.5	−108.7
C(n5)–O(n6)–C(n7)–C(n8)	170.3	167.9	168.2	167.5
O(n6)–C(n7)–C(n8)–N	−65.5	−66.5	−66.6	−71.4

TABLE V. Distances (Å) of Atoms from Least Squares Planes. Atoms not Contributing to the Planes are Marked*.

	Plane contains atoms M, N(1), C(2), C(3), N(4), C(5), C(6), N(7), C(8), C(9), C(10), C(11), C(12)
(IA)	0.03, 0.06, −0.00, 0.01, −0.00, −0.04, −0.01, −0.03, −0.07, 0.02, 0.04, −0.01, 0.01, C(21)* 0.12, C(31)* −0.01
(IB)	0.01, 0.09, −0.02, −0.01, 0.02, −0.01, −0.02, −0.06, −0.07, 0.02, 0.01, 0.02, 0.02, C(28)* −0.02, C(38)* 0.04
(IIA)	0.03, 0.08, −0.01, −0.03, 0.01, −0.03, −0.02, −0.04, −0.07, 0.05, 0.02, 0.00, 0.02, C(21)* 0.14, C(31)*−0.03
(IIB)	0.00, 0.11, 0.01, 0.00, 0.03, −0.02, −0.01, −0.08, −0.12, 0.04, 0.01, 0.01, 0.02, C(28)* −0.06, C(38)*, 0.20

Angles between planes (IA) and (IB), 81.1°; (IIA) and (IIB), 80.0°.

97.9(6)° in II]. Possibly, the increases of these angles from 90° arise from a need to ensure that the 11-membered rings N(1A)–C(21)–C(22)····C(28)–N(7B) and N(1B)–C(38)–C(37)····(C31)–N(7A) are unstrained. However, we note that in the complex bis(2,6-diacetylpyridinedihydrazone)cobalt(II) diiodide monohydrate, III, the two, independent planar trimethine units intersect at a similar angle (83°) [11].

The torsion angles in the 11-membered rings are given in Table IV. They show, as do the bond angles in Table III, that the 11-membered rings are relatively stable being without eclipsed conformations. All torsion angles are close to 60° or 120° with the exception of those around two of the C–O bonds which are *ca.* 180°. They further show, as does Fig. 1, that there is a two-fold axis through the metal atom and the mid-points of C(24)–C(25) and C(34)–C(35).

Despite the close similarity in the structures of the two cations there are distinct and significant differences in the M–N bond distances in the two cases. In both structures the metal–N(pyridine) distances are the shortest (Table III), a consequence, as noted above, of the rigid nature of the trimethine unit, which does not accommodate ideally to three corners of a square. In the Fe(II) complex, however, the four metal–N(imino) distances are equivalent at 1.986(10) Å (mean). In the Co(II) complex, on the other hand, two mutually *trans* Co–N(imino) bonds [2.117(14), 2.121(15) Å] are 0.091 Å (mean) longer than the other pair [2.034(13), 2.021(15) Å]. Thus, for the Co(II) complex there are three distinct, mutually near perpendicular, sets of Co–N distance, as compared to two sets of metal–nitrogen distance in the Fe(II); complex. At least one pair of mutually *trans* Co–N bonds is expected to be elongated, relative to the situation in the Fe(II) complex, because of the single electron occupancy of the (sigma antibonding) e_g orbital set. Since two pairs of mutually *trans* Co–N bonds are elongated, to different extents, and since ligand imposed distortions also occur, it is difficult to assign the e_g electron positively to either the d_{z^2} or to the $d_{x^2-y^2}$ orbital.

It is noteworthy that a similar, though less marked, pattern of Co–N bond length variation occurs in the closely related (mainly low-spin) Co(II) complex III referred to above [11]. It therefore seems likely that Jahn–Teller effects are operative here also. It is possible that the apparently smaller distortion in III may be related to the occurrence of a proportion of the cobalt(II) ions in the high-spin configuration [12].

In neither structure is the water molecule 0(100) involved in hydrogen bonding in any obvious way, no distances between the water oxygen atom and the perchlorate or macrocycle oxygen atoms of less than 3.00 Å being observed.

Acknowledgements

We thank A. W. Johans for assistance with the crystallographic investigations, and the Science Research Council and the Department of Education of N. Ireland for support.

References

1 M. G. B. Drew, A. Rodgers, M. McCann and S. M. Nelson, *Chem. Commun.*, 415 (1978).
2 M. G. B. Drew, M. M. McCann and S. M. Nelson, *Chem. Commun.*, 481 (1979).
3 S. M. Nelson, M. McCann, C. Stevenson and M. G. B. Drew, *J. Chem. Soc. Dalton*, 1477 (1979).
4 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', 3rd edition, Interscience, New York (1972).
5 J. S. Judge and W. A. Baker, *Inorg. Chim. Acta, 1*, 58 (1967); E. K. Barefield, D. H. Busch and S. M. Nelson, *Quart. Rev.*, 457 (1966).
6 H. A. Jahn and E. Teller, *Proc. Roy. Soc. London, 161*, 200 (1937).
7 J. A. Bertrand, D. A. Carpenter and A. R. Kalyanaraman, *Inorg. Chim. Acta, 5*, 113 (1971).
8 N. Katoaka and H. Kon, *J. Am. Chem. Soc., 90*, 2978 (1968).
9 'Shelx-76' G. M. Sheldrick, Cambridge University, Private Communications.
10 International Tables for X-ray Crystallography Vol. IV, Kynoch Press, Birmingham (1974).
11 B. N. Figgis, E. S. Kucharski and A. H. White, *Austral. J. Chem., 31*, 737 (1978).
12 J. D. Curry, M. A. Robinson and D. H. Busch, *Inorg. Chem., 6*, 1570 (1967).