Crystal and Molecular Structure of the Five-co-ordinate, $S=1$, Macrocyclic Complex of Cobalt(III), $[Co(C_{22}H_{22}N_4)I]\cdot CHCl_3$: 7,16-Dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetra-azacyclotetradecinato(iodo)cobalt(III) Iodide

By MARVIN C. WEISS and VIRGIL L. GOEDKEN*

(*Department of Chemistry, University of Chicago, Chicago, Illinois* 60637)

Summary The *X*-ray crystal structure and its implications in chemical reactivity of a novel five-co-ordinate macrocyclic complex of cobalt(III), $[Co(C_{22}H_{22}N_4)I].CHCl_3$, having an $S=1$ ground state are described.

WHILST most cobalt(III) complexes are low-spin, diamagnetic, and six-co-ordinate, some exceptions do exist. Most notable are some five-co-ordinate cobalt-alkyls,[1] which are diamagnetic. The paramagnetic anomalies are the bis-dithiolenes (square planar),[2] the $[Co(PEt_3)_2X_3]$ series,[3] and the five-co-ordinate complexes formed from dianionic open-chain tetradentate ligands and halide ion.[4]

Oxidation of the low-spin four co-ordinate complex $[Co(C_{22}H_{22}N_4)]$ with I_2 (2:1 molar ratio in cold chloroform) yields the title complex, $[Co(C_{22}H_{22}N_4)I]$, for which $\mu =$ 2·85 B.M. The resulting species reacts with nitriles and acetylenes in a four-centre reaction to yield pentadentate ligand complexes with addition of the nitrile or acetylene to the macrocycle, and with oxygen to incorporate a carbonyl function into the pentane-2,4-diiminato part of the chelate ring.[5]

Crystal data: $Co(C_{22}H_{22}N_4)I\cdot CHCl_3$; $M = 647·66$; orthorhombic, space group *Pnma*; $a = 8·311(1)$, $b = 13·902(3)$, $c = 21·405(5)$ Å, $U = 2473·03$ Å^3, $D_m = 1·74$ g cm^{-3}, $D_c = 1·739$ g cm^{-3} for $Z = 4$, (thus constraining the molecule to lie on a crystallographic mirror plane). Intensity data were collected on an automated diffractometer and corrected for absorption. The structure was solved by Patterson and Fourier techniques and refined by full-matrix least-squares analysis varying positional and anisotropic thermal parameters for nonhydrogen atoms and including hydrogen atoms as fixed contributions. At convergence conventional and weighted *R* values were 0·052 and 0·050 respectively for **2929** independent reflections with $F > 3\sigma(F)$.

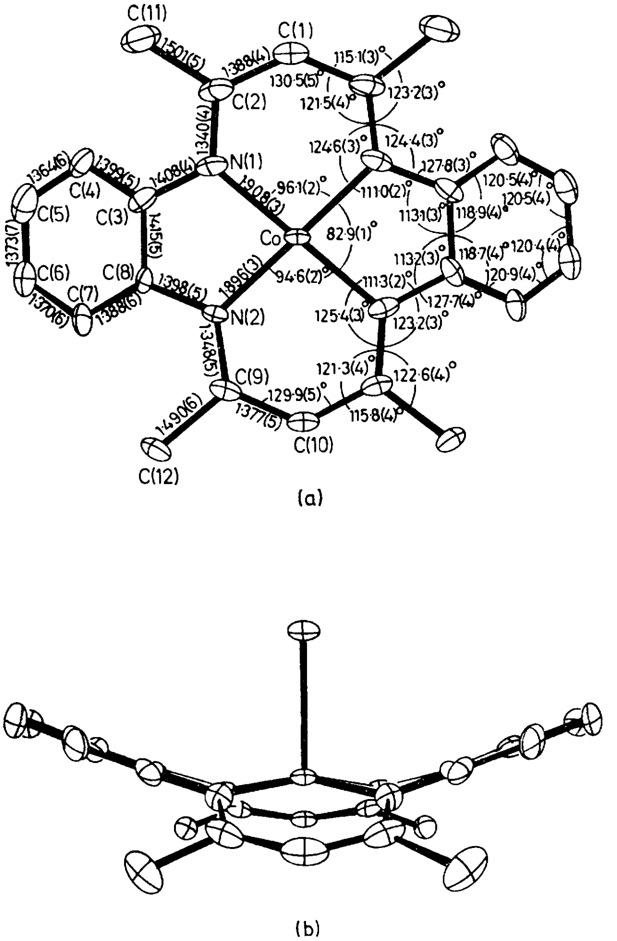

FIGURE. (a) Projection down the Co–I bond axis in $[Co(C_{22}H_{22}N_4)I]$ showing bond distances and angles, with estimated standard deviations in parentheses; (b) side view of the molecule illustrating the saddle shape of the ligand.

The bond distances and angles within the macrocyclic moiety are given in the Figure and are very similar to those, reported for the Fe^{III}–phenyl complex, $[Fe(C_{22}H_{22}N_4)(Ph)]$, of the same ligand.[6] The Co–I distance is long, 2·557 Å consistent with the $S = 1$ spin configuration with an electron occupying the d_{z^2} orbital. The Co^{III} atom is displaced by 0·234 Å out of the N_4 donor plane towards the I atom.

A number of aspects associated with the structure of this complex contribute to its remarkable reactivity. First, the complex is five-co-ordinate thus possessing a vacant co-ordination site capable of interacting with a sixth ligand. Secondly, the consequences of the steric interactions of the methyl groups with the benzenoid rings are considerable. They produce large dihedral angles between planes defined by atoms C(4)–C(3)–N(1) and C(3)–N(1)–C(2) (i), and between planes defined by C(3)–N(1)–C(2) and N(1)–C(2)–C(11) (ii), of 28·5 and 12·0° respectively, leading to high reactivity. A non-planar, saddle-shaped ligand (Figure) containing an activated ligand centre results. The torsion described by dihedral angle (ii) decreases the overlap between the p–π orbitals of the C–N linkages and results in a redistribution of the electron density within the pentane-2,4-diiminato chelate rings. A correlation of these C–N and C–C bond lengths within the 6-membered rings with the magnitude of the dihedral angle (ii) in a series of related structures (Table),† as well as reactivity studies, indicate that the electron density increases on C(1) and C(10). The combination of an exposed positively charged metal centre and an activated electron-rich ligand centre provides unusually favourable circumstances for reactivity with suitable substrates.

TABLE

Data for pentane-2,4-diiminato rings for three closely related structures[a]

Complex	'Twist angle' (ii)	Average C–N bond length[b]	Average C–C bond length[b]
$[Co(C_{22}H_{22}N_4)I]$ ..	12·1	1·344(4)	1·382(4)
$[Fe(C_{22}H_{22}N_4)Cl]$ ..	3·2	1·331(3)	1·404(4)
$[Mn(C_{22}H_{22}N_4)N(C_2H_5)_3]$	1·6	1·327(4)	1·406(5)

[a] M. C. Weiss, B. Bursten, S-M. Peng, and V. Goedken, *J. Amer. Chem. Soc.*, submitted for publication. [b] Numbers in parentheses refer to estimated standard deviations for the individual, unaveraged bond lengths.

The parameters of the inner co-ordination sphere may be compared with those of the five-co-ordinate Co^{III} porphyrin complex, [Co(TPP)(NO)], which has an $S = 0$ ground state, however.[7] The average Co–N distance (in-plane) is 1·902 Å for our complex as opposed to 1·978 Å for the [Co(TPP)-(NO)] complex and the Co atom is displaced only 0·094 Å from the N_4 plane in the porphyrin complex. These differences arise chiefly from the approximate planarity and the larger radius associated with 16-membered ring porphyrin ligands.

The paramagnetism of $[Co(C_{22}H_{22}N_4)I]\cdot CHCl_3$ arises because of the low symmetry and anisotropy of the ligand field, as is documented by the structure. A $d_{xz}{}^2$, $d_{yz}{}^2$, $d_{xy}{}^1$, $d_{z^2}{}^1$ configuration has been proposed as the ground (or thermally accessible) state configuration.[4]

The support of this research by a U.S. National Institutes of Health grant is gratefully acknowledged. M. C. W. is an M.S.T.P. trainee supported by a U.S. Public Health Service training grant from the N.I.G.M.S.

(*Received*, 23*rd March* 1976; *Com.* 307.)

---

† The C–N bond lengths increase and the C–C bond lengths decrease as the dihedral angles involving the C–N linkage defined in the text increase.

[1] V. L. Goedken, S-M. Peng, and Y-A. Park, *J. Amer. Chem. Soc.*, 1974, **96**, 284.
[2] R. Williams, E. Billing, J. H. Waters, and H. B. Gray, *J. Amer. Chem. Soc.*, 1966, **88**, 43.
[3] K. A. Jensen, P. H. Nielsen, and C. Th. Pederson, *Acta Chem. Scand.*, 1963, **17**, 1115.
[4] M. Gerloch, B. M. Higson, and E. D. McKenzie, *Chem. Comm.*, 1971, 1149.
[5] M. Weiss and V. Goedken, *J. Amer. Chem. Soc.*, 1976, **98**, 3389.
[6] V. Goedken, S-M. Peng, and Y-A. Park, *J. Amer. Chem. Soc.*, 1974, **96**, 284.
[7] W. R. Scheidt and J. Hoard, *J. Amer. Chem. Soc.*, 1973, **95**, 8281.