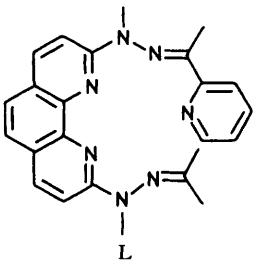
The Stabilisation of Low Oxidation State Transition Metal Complexes. Preparation and Electrochemistry of Cobalt(II) Unsaturated Macrocyclic Complexes and the Stabilisation of a Cobalt(I) Derivative. Crystal and Molecular Structures of $[Co^{II}(L)(CH_3OH)_2][BF_4]_2$ and $[Co^{I}(L)\{P(OCH_3)_3\}][BF_4]$ †

By **Christopher W. G. Ansell, Jack Lewis,* Michael C. Liptrot, Paul R. Raithby,** and **Martin Schröder,** University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

A series of seven cobalt(II) complexes $[Co^{II}(L)X_2]^{2+}$, based on the planar macrocyclic ligand L derived from 2,9-di(1-methylhydrazino)-1,10-phenanthroline and 2,6-diacetylpyridine have been prepared with varying axial ligands X [X=H_2O, pyridine (py), 4-aminopyridine (apy), 4-cyanopyridine (cpy), 4-dimethylaminopyridine (dap), imidazole (im), 1-methylimidazole (mim), quinoline (quin), pyrazine (pyz), or 1,4-diazabicyclo[2.2.2]octane (dabco)]. The single-crystal *X*-ray structure of the bis-methanol adduct $[Co^{II}(C_{23}H_{21}N_7)(CH_3OH)_2][BF_4]_2$, which crystallises in space group $P2_1/n$ with a = 12.110(8), b = 17.205(9), c = 15.411(8) Å, β = 112.62(3)°, and Z = 4, was solved by a combination of Patterson and Fourier techniques, and refined by blocked full-matrix least squares to R = 0.088 for 1 754 observed diffractometer data. The structure confirms the seven-co-ordinate geometry for this complex with the cobalt ion in the plane of the macrocyclic ligand. Cyclic voltammetry of the complexes in acetonitrile at a platinum microsphere shows a reversible reduction wave near $E_{\frac{1}{2}}$ = −1.4 V which may be tentatively assigned to the initial formation of a highly unstable cobalt(II) ligand radical species. Addition of $P(OCH_3)_3$ to a solution of $[Co(L)(H_2O)_2][BF_4]_2$ in acetonitrile shifts the reversible reduction wave from $E_{\frac{1}{2}}$ = −1.43 to −1.19 V; electrochemical reduction of such a solution by controlled potential electrolysis yields the metal-reduced cobalt(I) complex $[Co^{I}(C_{23}H_{21}N_7)\{P(OCH_3)_3\}][BF_4]$. The single-crystal *X*-ray structure shows it to crystallise in space group $P2_1/n$ with a = 10.745(4), b = 10.721(5), c = 24.722(8) Å, β = 92.57(2)°, and Z = 4. The structure was solved by a combination of Patterson and Fourier-difference techniques, and refined by blocked-cascade least squares to R = 0.069 for 2 519 observed diffractometer data. The cobalt ion is displaced out of the plane of the five donor nitrogen atoms by 0.36 Å towards the phosphorus atom. The macrocyclic ligand is not planar but has the shape of a shallow dome, the distortion being away from the axial ligand. The stabilisation of the metal-reduced cobalt(I) complex is attributed to the combined π-acceptor properties of the unsaturated macrocyclic ligand and the axial $P(OCH_3)_3$ ligand.

We have previously reported the preparation of Mn^{II},[1,2] Fe^{II},[3,4] Zn^{II},[5,6] Cd^{II},[5,6] and Hg^{II} [5,6] complexes of the planar, quinquedentate macrocyclic ligand L. These complexes were prepared by the template condensation



L

of 2,6-diacetylpyridine with 2,9-di(1-methylhydrazino)-1,10-phenanthroline in the presence of the corresponding metal dichloride. Transition metal complexes of 2,6-di-iminopyridine [7-10] and related di-imino-species,[11-15] and those of aromatic heterocyclic ligands such as 2,2'-bipyridyl and 1,10-phenanthroline,[16-20] exhibit rich redox chemistry. Metal complexes of the unsaturated macrocyclic ligand L should likewise be expected to undergo redox processes, and in particular due to the likely strong π-acceptor properties of L,[21] the stabilisation of low oxidation state transition metal complexes might be attained.

We have therefore investigated the redox chemistry, particularly with regard to reduction, of transition metal complexes of L in the presence of a series of axial ligands to determine whether reduced-metal species are formed or whether reduction occurs at the ligand site *via* occupation of ligand π* orbital(s) to give a metal stabilised ligand radical complex. In this paper we report the preparation and electrochemistry of a series of seven-co-ordinate cobalt(II) complexes, $[Co^{II}(L)X_2]^{2+}$, and in particular the stabilisation and *X*-ray structural determination of the corresponding cobalt(I) complex $[Co^{I}(L)\{P(OMe)_3\}][BF_4]$.

RESULTS AND DISCUSSION

The cobalt(II) macrocyclic complex $[Co^{II}(L)(H_2O)_2][BF_4]_2$ was prepared by a template condensation of 2,6-diacetylpyridine and 2,9-di(1-methylhydrazino)-1,10-phenanthroline in the presence of cobalt(II) dichloride in refluxing water.[22] Addition of several drops of dilute mineral acid was found to hasten the reaction, the yield of orange cobalt(II) complex being *ca.* 80%. Reaction of $[Co^{II}(L)(H_2O)_2][BF_4]_2$ with excess of X {X = pyridine (py), 4-aminopyridine (apy), 4-cyanopyridine (cpy), 4-dimethylaminopyridine (dap), imidazole (im), 1-methylimidazole (mim), quinoline (quin), pyrazine (pyz), or 1,4-diazabicyclo[2.2.2]octane (dabco)} in refluxing methanol yielded on addition of diethyl ether the corresponding

† (2,6-Diacetylpyridine *NN'*-dimethyl-*NN'*-1,10-phenanthroline-2,9-diyldihydrazone)-bis(methanol)cobalt(II) bis(tetrafluoroborate) and -(trimethyl phosphite) cobalt(I) tetrafluoroborate. An alternative name for the macrocyclic ligand, L is: 1,3,10,12-tetramethyl-1,2,11,12-tetra-aza[3](2,6)pyridino[3](2,9)-1,10-phenanthrolinophan-2,10-diene. (F. Vögtle and P. Neumann, *Tetrahedron*, 1970, **26**, 5847.)

complexes $[Co^{II}(L)X_2][BF_4]_2$. Completion of reaction could be determined by the absence of the two water ν(O–H) resonances in the i.r. spectrum near 3 500 cm^{-1} assigned to the di-aquo starting material. Analytical data for these complexes are listed in Table 1. The complexes appear to be stable at room temperature in air. Electrical conductance measurements in nitromethane confirm the complexes to be 2 : 1 electrolytes, while magnetic moments recorded at room temperature (293 K) are typical for high spin cobalt(II) d^7 systems, the value of 4.2 B.M.* for the complex $[Co^{II}(L)(mim)_2][BPh_4]_2$ being typical. The e.s.r. spectra of the complexes as glasses in acetonitrile at 77 K or in the solid state at 77 K all show very undefined, broad signals, $g_{av.} = 2.920$. No clear hyperfine coupling was observed under these conditions.

* Throughout this paper: 1 B.M. = 9.27×10^{-24} A m^2.

Recrystallisation of $[Co^{II}(L)(H_2O)_2][BF_4]_2$ from methanol and diethyl ether yielded crystals of the corresponding bis-methanol adduct $[Co^{II}(L)(CH_3OH)_2][BF_4]_2$, a single-crystal *X*-ray structural determination of which was undertaken.

TABLE 1

Analytical and conductivity data for cobalt(II) complexes

Compound	Analyses (%) Found C	H	N	Calculated C	H	N	Λ/ S cm^2 mol^{-1}
$[Co(L)(H_2O)_2][BF_4]_2$[22]	41.4	3.7	15.1	41.6	3.8	14.8	67.2 [a]
$[Co(L)(im)_2][PF_6]_2 \cdot 0.5H_2O$	38.9	3.3	17.3	39.1	3.4	17.3	172 [b]
$[Co(L)(quin)_2][BF_4]_2 \cdot 2H_2O$	53.4	4.2	13.9	53.4	4.2	13.7	
$[Co(L)(apy)_2][BF_4]_2$	48.4	4.3	19.1	48.5	4.0	18.9	154 [b]
$[Co(L)(cpy)_2][BF_4]_2 \cdot 0.5H_2O$	49.8	3.7	18.2	49.7	3.6	18.2	167 [b]
$[Co(L)(py)_2][BF_4]_2 \cdot H_2O$	49.1	4.1	15.9	49.2	4.1	15.7	
$[Co(L)(dap)_2][BF_4]_2$	50.4	4.9	17.6	50.9	4.7	17.7	174 [b]
$[Co(L)(mim)_2][PF_6]_2 \cdot 2.5H_2O$	39.7	3.8	16.2	39.8	4.0	16.5	
$[Co(L)(im)_2][BF_4]_2$	45.4	4.2	20.1	45.5	3.8	20.1	
$[Co(L)(mim)_2][BF_4]_2 \cdot H_2O$	74.2	6.0	11.7	74.4	5.9	12.1	161 [b]
$[Co(L)(pyz)(H_2O)][BF_4]_2$	44.4	3.7	17.7	44.6	3.7	17.4	166 [b]
$[Co(L)(dabco)(H_2O)][BF_4]_2 \cdot H_2O$	44.7	4.3	15.9	44.8	4.8	16.2	

[a] Measured in $(CH_3)_2SO$. [b] Measured in nitromethane.

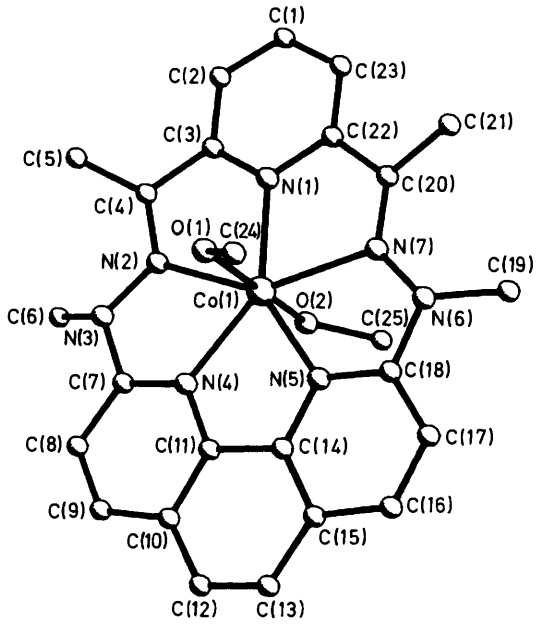


FIGURE 1 The molecular structure of $[Co^{II}(L)(CH_3OH)_2][BF_4]_2$ and atom-numbering scheme used. Hydrogen atoms have been omitted for clarity

The crystal structure of $[Co(L)(CH_3OH)_2][BF_4]_2$ is illustrated in Figure 1 along with the numbering scheme adopted. The hydrogen atoms and the tetrafluoroborate anions have been omitted for clarity. Tables 2, 3, and 4 list bond lengths, interbond angles, and details of least-squares planes, respectively. The co-ordination geometry of the cobalt atom is a pentagonal bipyramid with the two axial positions being occupied by the methanol ligands. The N_5 donor set of atoms forming the pentagon are essentially coplanar (the maximum deviation from this plane being <0.07 Å), with the cobalt atoms sitting in this plane. The pyridine ring makes an angle

TABLE 2

Bond lengths (Å) for $[Co^{II}(L)(CH_3OH)_2][BF_4]_2$ with estimated standard deviations in parentheses

N(1)–Co(1)	2.091(13)	N(2)–Co(1)	2.257(12)
N(4)–Co(1)	2.121(12)	N(5)–Co(1)	2.099(13)
N(7)–Co(1)	2.266(12)	O(1)–Co(1)	2.211(9)
O(2)–Co(1)	2.182(10)	C(2)–C(1)	1.380(23)
C(3)–C(2)	1.395(26)	C(3)–N(1)	1.344(21)
C(4)–C(3)	1.477(21)	C(5)–C(4)	1.502(24)
N(2)–C(4)	1.323(21)	N(3)–N(2)	1.406(17)
C(6)–N(3)	1.450(21)	C(7)–N(3)	1.388(23)
C(8)–C(7)	1.428(23)	C(9)–C(8)	1.351(27)
C(10)–C(9)	1.450(23)	C(11)–C(10)	1.408(23)
C(12)–C(10)	1.399(28)	N(4)–C(7)	1.327(19)
N(4)–C(11)	1.355(22)	C(13)–C(12)	1.309(24)
C(14)–C(11)	1.430(20)	C(15)–C(13)	1.437(25)
C(15)–C(14)	1.399(26)	N(5)–C(14)	1.367(19)
C(16)–C(15)	1.410(23)	C(17)–C(16)	1.361(25)
C(18)–C(17)	1.409(24)	C(18)–N(5)	1.334(17)
C(18)–N(6)	1.393(19)	C(19)–N(6)	1.456(19)
N(7)–N(6)	1.369(19)	C(20)–N(7)	1.295(19)
C(21)–C(20)	1.538(19)	C(22)–C(20)	1.478(23)
C(22)–N(1)	1.389(18)	C(23)–C(22)	1.386(25)
C(23)–C(1)	1.367(24)	C(24)–O(1)	1.361(23)
C(25)–O(2)	1.454(24)	F(1A)–B(1)	1.389(27)
F(1B)–B(1)	1.368(29)	F(1C)–B(1)	1.351(24)
F(1D)–B(1)	1.314(27)	F(2A)–B(2)	1.360(16)
F(2B)–B(2)	1.385(19)	F(2C)–B(2)	1.367(19)
F(2D)–B(2)	1.363(27)	F(2A′)–B(2)	1.361(32)
F(2B′)–B(2)	1.372(22)	F(2C′)–B(2)	1.387(28)
F(2D′)–B(2)	1.360(24)		

of 2.7° with the N_5 plane while the angle between the phenanthroline (phen) plane and the N_5 plane is 0.8°. Interatomic distances indicate that the BF_4 anions are unco-ordinated. The Co–N bond distances which lie within the range 2.09—2.27 Å fall into two distinct sets. The long Co–N(hydrazino) bonds are 2.266 and 2.257 Å with the shorter Co–N(phen) bonds being 2.121 and 2.099 Å and the Co–N(pyridine) bond 2.091 Å. The angles subtended by adjacent nitrogen donor atoms with the cobalt atom fall in the region 69—76°, the N(phen)–Co–N(hydrazino) bond angles being less than 70°. The macrocyclic ligand is rigid and accounts for the longer Co–N(hydrazino) bond lengths and also the low N(phen)–Co–N(hydrazino) bond angles. As a result of this rigidity, there is thus likely to be a fair amount of strain imposed upon the ligand. Strain is observed in the deviation of the N(3)–C(7)–N(4) and N(5)–C(18)–N(6) bond angles from 120° as would be expected for sp^2 hybridisation, their respective values being 116.4 and 116.1°. Some strain in the ligand is relieved by the skewing of the methyl groups, the imine methyl groups being displaced to one side of the N_5 plane and the displacement of the hydrazino-methyl groups being on the opposite side.

TABLE 3

Bond angles (°) for $[Co^{II}(L)(CH_3OH)_2][BF_4]_2$ with estimated standard deviations in parentheses

N(2)–Co(1)–N(1)	72.7(5)	C(3)–N(1)–Co(1)	120.3(10)
N(4)–Co(1)–N(1)	141.5(5)	C(22)–N(1)–Co(1)	119.8(10)
N(4)–Co(1)–N(2)	69.0(5)	C(22)–N(1)–C(3)	119.7(14)
N(5)–Co(1)–N(1)	142.5(4)	N(3)–N(2)–Co(1)	119.1(10)
N(5)–Co(1)–N(2)	144.7(5)	C(4)–N(2)–Co(1)	117.2(9)
N(5)–Co(1)–N(4)	75.6(5)	N(3)–N(2)–C(4)	122.2(12)
N(7)–Co(1)–N(1)	73.4(5)	C(6)–N(3)–N(2)	122.2(14)
N(7)–Co(1)–N(2)	146.0(5)	C(7)–N(3)–N(2)	110.7(11)
N(7)–Co(1)–N(4)	144.9(5)	C(7)–N(3)–C(6)	118.3(12)
N(7)–Co(1)–N(5)	69.3(5)	C(7)–N(4)–Co(1)	124.4(11)
N(1)–Co(1)–O(1)	85.8(4)	C(11)–N(4)–Co(1)	116.4(9)
N(2)–Co(1)–O(1)	90.6(4)	C(11)–N(4)–C(7)	119.0(13)
N(4)–Co(1)–O(1)	90.3(4)	C(14)–N(5)–Co(1)	117.6(9)
N(5)–Co(1)–O(1)	90.1(4)	C(18)–N(5)–Co(1)	124.1(10)
N(7)–Co(1)–O(1)	89.8(4)	C(18)–N(5)–C(14)	118.3(13)
N(1)–Co(1)–O(2)	91.7(4)	N(7)–N(6)–C(18)	111.6(11)
N(2)–Co(1)–O(2)	86.0(4)	N(7)–N(6)–C(19)	121.1(14)
N(4)–Co(1)–O(2)	89.9(4)	C(19)–N(6)–C(18)	119.1(12)
N(5)–Co(1)–O(2)	93.5(4)	N(6)–N(7)–Co(1)	118.8(9)
N(7)–Co(1)–O(2)	92.2(4)	C(20)–N(7)–Co(1)	115.7(10)
O(2)–Co(1)–O(1)	176.2(4)	C(20)–N(7)–N(6)	123.6(12)
C(23)–C(1)–C(2)	120.5(18)	C(3)–C(2)–C(1)	119.9(16)
C(2)–C(3)–N(1)	120.1(14)	C(4)–C(3)–N(1)	116.1(15)
C(4)–C(3)–C(2)	123.7(15)	C(5)–C(4)–C(3)	119.9(14)
N(2)–C(4)–C(3)	111.9(13)	N(2)–C(4)–C(5)	127.8(14)
N(4)–C(7)–N(3)	116.4(13)	N(4)–C(7)–C(8)	122.3(16)
C(8)–C(7)–N(3)	121.2(14)	C(9)–C(8)–C(7)	116.6(15)
C(10)–C(9)–C(8)	124.6(16)	C(11)–C(10)–C(9)	111.9(16)
C(12)–C(10)–C(9)	128.6(16)	C(12)–C(10)–C(11)	119.4(15)
N(4)–C(11)–C(10)	125.4(14)	C(14)–C(11)–C(10)	118.5(16)
C(14)–C(11)–N(4)	116.0(14)	C(13)–C(12)–C(10)	121.9(18)
C(15)–C(13)–C(12)	122.2(19)	C(15)–C(14)–C(11)	120.6(14)
N(5)–C(14)–C(11)	114.3(14)	N(5)–C(14)–C(15)	125.0(13)
C(14)–C(15)–C(13)	117.2(14)	C(16)–C(15)–C(13)	128.4(18)
C(16)–C(15)–C(14)	114.3(16)	C(17)–C(16)–C(15)	121.7(18)
C(18)–C(17)–C(16)	119.8(15)	N(5)–C(18)–C(17)	120.8(14)
N(6)–C(18)–C(17)	123.0(12)	N(6)–C(18)–N(5)	116.1(13)
C(21)–C(20)–N(7)	128.0(15)	C(22)–C(20)–N(7)	115.3(12)
C(22)–C(20)–C(21)	116.6(13)	C(20)–C(22)–N(1)	113.3(14)
C(23)–C(22)–N(1)	121.1(14)	C(23)–C(22)–C(20)	125.6(13)
C(22)–C(23)–C(1)	118.6(14)	C(24)–O(1)–Co(1)	127.9(10)
F(1B)–B(1)–F(1A)	104.8(20)	F(1C)–B(1)–F(1A)	104.7(15)
F(1D)–B(1)–F(1A)	109.2(18)	F(1C)–B(1)–F(1B)	110.3(19)
F(1D)–B(1)–F(1B)	112.4(15)	F(1D)–B(1)–F(1C)	114.8(22)
F(2B)–B(2)–F(2A)	108.2(13)	F(2C)–B(2)–F(2A)	109.9(14)
F(2D)–B(2)–F(2A)	111.0(14)	F(2C)–B(2)–F(2B)	109.0(13)
F(2D)–B(2)–F(2B)	109.2(14)	F(2D)–B(2)–F(2C)	109.4(15)
F(2B′)–B(2)–F(2A′)	110.0(20)	F(2C′)–B(2)–F(2A′)	108.5(22)
F(2D′)–B(2)–F(2A′)	111.1(21)	F(2C′)–B(2)–F(2B′)	108.7(22)
F(2D′)–B(2)–F(2B′)	109.9(17)	F(2D′)–B(2)–F(2C′)	108.7(19)

This skewing minimises the non-bonded interactions between the methyl groups. The sums of the bond angles at N(3) and N(6) are 351.2 and 351.8°, the deviations from 360° for sp^2 hybridisation being due to the methyl interactions. The bond angle O(1)–Co(1)–O(2) is 176.2°, showing a slight deviation from linearity, with the Co–O bond distances similar for those found in $[Co^{II}(L)(H_2O)_2][BF_4]_2$.[22]

Electrochemistry.—The electrochemistry of the seven-co-ordinate cobalt(II) macrocyclic complexes was investigated in acetonitrile with 0.1 mol dm^{-3} of $[NBu^n_4]^+[BF_4]^-$ as base electrolyte. The cyclic voltammetric data

are listed in Table 5. All the complexes show a reversible or quasi-reversible reduction near −1.4 V *versus* a Ag–$AgNO_3$ reference electrode (Table 5). Controlled potential electrolysis of the above complexes in acetonitrile at −1.4 V led to a darkening of the orange solutions. The e.s.r. spectra of the reduced solutions at

TABLE 4

Equations of least-squares planes * with selected atomic deviations (Å) shown in square brackets

Plane 1: N(1), N(2), N(4), N(5), N(7)

$9.83x - 6.05y + 1.82z = 8.20$

[Co(1) −0.024, N(1) 0.063, N(2) −0.054, N(4) 0.024, N(5) 0.015, N(7) −0.048, C(5) 0.622, C(6) −0.603, C(19) −0.561, C(21) 0.650]

Plane 2: Pyridine ring

$9.61x - 5.78y + 2.51z = 8.33$

[Co(1) −0.192, N(1) −0.010, N(2) −0.222, N(7) −0.156, C(4) 0.046, C(5) 0.519, C(6) −0.837, C(19) −0.669, C(20) 0.130, C(21) 0.651]

Plane 3: Phenanthroline ring

$9.75x - 6.25y + 1.90z = 8.09$

[Co(1) −0.018, N(3) 0.040, N(4) 0.038, N(5) −0.004, N(6) −0.012, C(5) 0.688, C(6) −0.541, C(19) −0.612, C(21) 0.623]

Interplanar angles (°)	Plane	3	2
	1	0.8	2.7
	2	2.8	

* x, y, and z are fractional atomic co-ordinates.

77 K as acetonitrile glasses showed a very broad signal near $g_{av.} = 2.920$ which we assign to a high spin d^7 configuration of a cobalt(II) species. The i.r. spectrum of the dark brown product derived from the reduction of $[Co^{II}(L)(H_2O)_2][BF_4]_2$ showed broad bands in the range 3 500—3 200 cm^{-1} which we assign to N–H stretching

TABLE 5

Cyclic voltammetry data of cobalt(II) complexes in acetonitrile with 0.1 mol dm^{-3} $[NBu^n_4]^+[BF_4]^-$ as base electrolyte [a]

Compound	$E_{\frac{1}{2}}$/V [b]	$E_1 - E_2$/mV
$[Co(L)(H_2O)_2][BF_4]_2$	−1.43	60
$[Co(L)(im)_2][PF_6]_2$	−1.42	67
$[Co(L)(mim)_2][PF_6]_2$	−1.42	56
$[Co(L)(dap)_2][BF_4]_2$	−1.40	56
$[Co(L)(py)_2][BF_4]_2$	−1.39	70
$[Co(L)(apy)_2][BF_4]_2$	−1.38	70
$[Co(L)(cpy)_2][BF_4]_2$	−1.37	98
$[Co(L)(quin)_2][BF_4]_2$	−1.37	63.5

[a] Measured on 10^{-3}—10^{-4} mol dm^{-3} solutions relative to Ag–$AgNO_3$ standard electrode, $E_{\frac{1}{2}}$(ferrocene–ferrocenium) = +0.19 V. [b] In solution, equilibria of the type $[Co(L)X_2]^{2+} \rightleftharpoons [Co(L)X(CH_3CN)]^{2+} \rightleftharpoons [Co(L)(CH_3CN)_2]^{2+}$ would be expected. Addition of excess of ligand X to solutions of $[Co(L)X_2]^{2+}$ in acetonitrile did not markedly alter the values of $E_{\frac{1}{2}}$ obtained.

vibrations, ν(N–H). We believe this product to be derived from an intermediate cobalt(II)–ligand radical complex which, by hydrogen transfer from co-ordinated water, yields a cobalt(II) hydroxy species with a reduced macrocyclic ligand. In the strict absence of water, the cobalt(II)–ligand radical complex could only be detected by e.s.r. spectroscopy [g = 2.926 (Co^{II}), 2.002] as a highly reactive, transient species. That the reversible reduction near −1.4 V is indeed a reduction on the macrocyclic ligand is also suggested by the similar $E_{\frac{1}{2}}$ values obtained for all the complexes listed in Table 5, the variation of $E_{\frac{1}{2}}$ on varying the axial ligand being slight. No cobalt(I) species were detected in these experiments.

Cyclic voltammetry of $[Co^{II}(L)(H_2O)_2][BF_4]_2$ in acetonitrile at a platinum microsphere showed a quasi-reversible reduction wave at −1.43 V; on addition of one equivalent or an excess of $P(OCH_3)_3$, the reduction wave shifted to $E_{\frac{1}{2}}$ = −1.19 V (Figure 2). Controlled

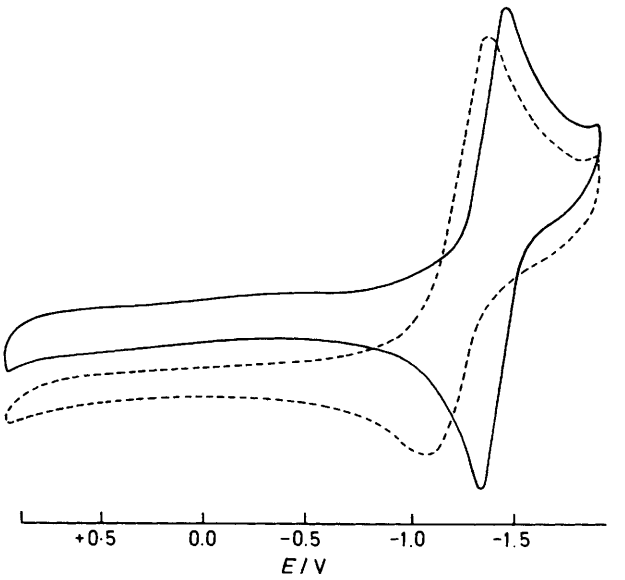


FIGURE 2 Cyclic voltammograms in acetonitrile of $[Co^{II}(L)(H_2O)_2][BF_4]_2$ (——) and $[Co^{II}(L)(H_2O)_2][BF_4]_2$ (– – – –) treated with excess of $P(OCH_3)_3$

potential electrolysis of $[Co^{II}(L)(H_2O)_2][BF_4]_2$ in acetonitrile in the presence of excess of $P(OCH_3)_3$ at −1.2 V led to the reduction of the cobalt(II) species with concomitant change of colour from orange to dark green. The reduction was followed by e.s.r. spectroscopy measured at 77 K, which showed the gradual loss of signal $g_{av.}$ = 2.920 assigned to high spin d^7 cobalt(II); on completion of reduction no e.s.r. signal could be observed at 77 K as an acetonitrile glass. This is consistent with the formation of a high spin d^8 cobalt(I) species with a high zero-field splitting.[23] The visible spectrum of the paramagnetic reduced species in acetonitrile showed a band near 800 nm (ε = 900 dm^3 mol^{-1} cm^{-1}) and a broad shoulder near 450 nm ($\varepsilon \simeq 5\,100$) which we may assign to d–d transition and cobalt(I)→ligand charge-transfer bands respectively. This is not inconsistent with previously reported data for cobalt(I) macrocyclic systems.[24,25] The visible spectrum of the starting material $[Co^{II}(L)(H_2O)_2][BF_4]_2$ in acetonitrile shows only d–d transitions at 670 nm (ε = 5).

The ^1H n.m.r. spectrum (measured at 400 MHz) of a 2 : 1 mixture of $P(OCH_3)_3$ and $[Co^{II}(L)(H_2O)_2][BF_4]_2$ in C^2H_3CN shows two singlets at δ 3.72 and 3.26 p.p.m. of equal intensity which we assign to a co-ordinated and

non-co-ordinated phosphite ligand. This is consistent with the formation, in solution, of a 1 : 1 cobalt(II) phosphite macrocyclic complex; attempts to isolate this adduct in the solid state have so far failed, although the cyclic voltammetry data (Figure 2) in acetonitrile indicate the complete formation of a cobalt(II) phosphine complex, no reduction wave at $E_{\frac{1}{2}} = -1.43$ V being detected in the presence of excess of $P(OCH_3)_3$.

The stabilisation of cobalt(I) species by synthetic *N*-donor macrocyclic ligands has been reported,[26] but relatively few examples have been isolated in the solid state, and to our knowledge, only one has been characterised crystallographically.[14] A single-crystal *X*-ray structural determination was therefore undertaken.

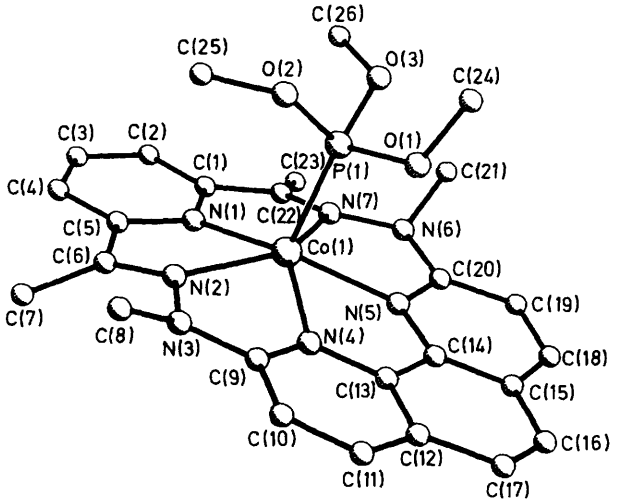


FIGURE 3 The molecular structure of $[Co^I(L)\{P(OCH_3)_3\}][BF_4]$ and atom-numbering scheme used. Hydrogen atoms have been omitted for clarity

The crystal structure of $[Co^I(L)\{P(OCH_3)_3\}][BF_4]$ is illustrated in Figure 3, along with the numbering scheme adopted. The hydrogen atoms and the tetrafluoroborate anion have been omitted for clarity. The associated bond lengths and interbond angles and details of least-squares planes are given in Tables 6, 7, and 8, respectively. The co-ordination geometry of the cobalt atom is a slightly distorted pentagonal pyramid with the phosphite ligand in the axial position. The N_5 donor set of atoms, which form the pentagon, are approximately coplanar (the maximum deviation from the least-squares plane being 0.18 Å) and the cobalt atom is displaced 0.36 Å from this plane towards the phosphorus. An angle of 6.2° is formed between the direction of the Co–P bond and the normal to this plane. The macrocycle is not planar but assumes the shape of a shallow dome, the direction being away from the phosphorus atom.

The pyridine ring makes an angle of 6.5° with the N_5 plane while the angle between the phenanthroline ring system and the same N_5 plane is 4.7°. Interatomic distances indicated that the BF_4^- anion is unco-ordinated. The Co–N distances lie within the range 2.04—2.24 Å and fall into three distinct sets; the Co–N

TABLE 6

Bond lengths (Å) for $[Co^I(L)\{P(OCH_3)_3\}][BF_4]$ with estimated standard deviations in parentheses

Co(1)–N(1)	2.042(5)	Co(1)–N(2)	2.236(5)
Co(1)–N(4)	2.124(5)	Co(1)–N(5)	2.149(5)
Co(1)–N(7)	2.222(6)	Co(1)–P(1)	2.284(2)
N(1)–C(1)	1.364(9)	N(1)–C(5)	1.390(9)
C(1)–C(2)	1.401(10)	C(1)–C(22)	1.467(10)
C(2)–C(3)	1.380(12)	C(3)–C(4)	1.367(12)
C(4)–C(5)	1.391(11)	C(5)–C(6)	1.430(10)
C(6)–C(7)	1.507(11)	C(6)–N(2)	1.320(9)
N(2)–N(3)	1.384(8)	N(3)–C(8)	1.474(10)
N(3)–C(9)	1.374(9)	C(9)–C(10)	1.404(10)
C(9)–N(4)	1.346(9)	C(10)–C(11)	1.359(11)
C(11)–C(12)	1.416(11)	C(12)–C(13)	1.399(9)
C(12)–C(17)	1.443(10)	C(13)–N(4)	1.374(8)
C(13)–C(14)	1.423(9)	C(14)–N(5)	1.375(8)
C(14)–C(15)	1.390(9)	C(15)–C(16)	1.426(10)
C(16)–C(17)	1.335(11)	C(15)–C(18)	1.403(10)
C(18)–C(19)	1.347(10)	C(19)–C(20)	1.434(10)
C(20)–N(5)	1.318(9)	C(20)–N(6)	1.377(9)
N(6)–C(21)	1.467(10)	N(6)–N(7)	1.404(8)
N(7)–C(22)	1.296(9)	C(22)–C(23)	1.513(11)
P(1)–O(1)	1.577(6)	O(1)–C(24)	1.455(12)
P(1)–O(2)	1.592(7)	O(2)–C(25)	1.406(11)
P(1)–O(3)	1.598(6)	O(3)–C(26)	1.372(12)
B(1)–F(1)	1.329(12)	B(1)–F(2)	1.326(11)
B(1)–F(3)	1.345(11)	B(1)–F(4)	1.339(11)

TABLE 7

Bond angles (°) for $[Co^I(L)\{P(OCH_3)_3\}][BF_4]$ with estimated standard deviations in parentheses

N(1)–Co(1)–N(2)	72.0(2)	Co(1)–N(1)–C(1)	120.5(4)
N(1)–Co(1)–N(4)	134.9(2)	Co(1)–N(1)–C(5)	121.3(4)
N(2)–Co(1)–N(4)	69.0(2)	C(1)–N(1)–C(5)	117.4(5)
N(1)–Co(1)–N(5)	133.9(2)	N(1)–C(1)–C(2)	122.3(6)
N(2)–Co(1)–N(5)	140.7(2)	N(1)–C(1)–C(22)	114.2(6)
N(4)–Co(1)–N(5)	73.5(2)	C(2)–C(1)–C(22)	123.4(7)
N(1)–Co(1)–N(7)	72.8(2)	C(1)–C(2)–C(3)	118.3(7)
N(2)–Co(1)–N(7)	144.8(2)	C(2)–C(3)–C(4)	121.2(8)
N(4)–Co(1)–N(7)	140.9(2)	C(3)–C(4)–C(5)	118.9(8)
N(5)–Co(1)–N(7)	68.2(2)	N(1)–C(5)–C(4)	121.9(6)
N(1)–Co(1)–P(1)	111.2(2)	N(1)–C(5)–C(6)	114.6(6)
N(2)–Co(1)–P(1)	99.5(2)	C(4)–C(5)–C(6)	123.5(7)
N(4)–Co(1)–P(1)	96.8(2)	C(5)–C(6)–C(7)	121.7(6)
N(5)–Co(1)–P(1)	95.8(2)	C(5)–C(6)–N(2)	111.9(6)
N(7)–Co(1)–P(1)	94.9(2)	C(7)–C(6)–N(2)	126.1(6)
Co(1)–N(2)–C(6)	118.6(2)	Co(1)–N(2)–N(3)	118.2(4)
C(6)–N(2)–N(3)	121.5(5)	N(2)–N(3)–C(8)	121.8(6)
N(2)–N(3)–C(9)	112.9(5)	C(8)–N(3)–C(9)	121.2(6)
N(3)–C(9)–C(10)	124.1(6)	N(3)–C(9)–N(4)	114.4(6)
C(10)–C(9)–N(4)	121.4(6)	C(9)–C(10)–C(11)	120.4(7)
C(10)–C(11)–C(12)	120.6(7)	C(11)–C(12)–C(13)	115.6(6)
C(11)–C(12)–C(17)	127.4(7)	C(13)–C(12)–C(17)	117.0(6)
C(12)–C(13)–N(4)	124.6(6)	C(12)–C(13)–C(14)	120.6(6)
N(4)–C(13)–C(14)	114.9(6)	Co(1)–N(4)–C(9)	123.0(4)
Co(1)–N(4)–C(13)	118.4(4)	C(9)–N(4)–C(13)	117.4(5)
C(13)–C(14)–C(15)	121.2(6)	C(13)–C(14)–N(5)	113.9(6)
C(15)–C(14)–N(5)	124.9(6)	C(14)–C(15)–C(16)	117.4(6)
C(14)–C(15)–C(18)	115.6(6)	C(16)–C(15)–C(18)	127.0(6)
C(15)–C(16)–C(17)	122.1(7)	C(12)–C(17)–C(16)	121.8(7)
C(15)–C(18)–C(19)	121.7(7)	C(19)–C(20)–N(5)	123.0(6)
C(18)–C(19)–C(20)	118.1(7)	C(19)–C(20)–N(6)	122.3(6)
N(5)–C(20)–N(6)	114.7(6)	Co(1)–N(5)–C(14)	118.1(4)
Co(1)–N(5)–C(20)	124.0(4)	C(14)–N(5)–C(20)	116.5(5)
C(20)–N(6)–C(21)	118.4(6)	C(20)–N(6)–N(7)	111.8(5)
C(21)–N(6)–N(7)	119.4(6)	Co(1)–N(7)–N(6)	119.3(4)
Co(1)–N(7)–C(22)	118.4(5)	N(6)–N(7)–C(22)	120.4(6)
C(1)–C(22)–N(7)	112.1(6)	C(1)–C(22)–C(23)	120.9(6)
N(7)–C(22)–C(23)	127.0(7)	Co(1)–P(1)–O(1)	113.8(2)
Co(1)–P(1)–O(2)	120.8(3)	Co(1)–P(1)–O(3)	117.1(3)
O(1)–P(1)–O(2)	99.0(3)	O(1)–P(1)–O(3)	97.4(3)
O(2)–P(1)–O(3)	104.9(4)	P(1)–O(1)–C(24)	123.4(5)
P(1)–O(2)–C(25)	122.7(6)	P(1)–O(3)–C(26)	124.9(7)
F(1)–B(1)–F(2)	110.0(8)	F(1)–B(1)–F(3)	107.3(8)
F(1)–B(1)–F(4)	110.1(8)	F(2)–B(1)–F(3)	111.3(7)
F(2)–B(1)–F(4)	109.8(8)	F(3)–B(1)–F(4)	108.2(7)

(hydrazino) (2.236, 2.222), the Co–N(phen) (2.124, 2.149), and the Co–N(pyridine) (2.042 Å).

The angles subtended by adjacent nitrogen donor atoms occur in the range 68—74°, the N(phen)–Co–N (hydrazino) angles being less than 70°. The rigidity of the ligand accounts for these lower than expected bond

TABLE 8

Equations of least-squares planes * with selected atomic deviations (Å) shown in square brackets

Plane 1: N(1), N(2), N(4), N(5), N(7)

$7.31x + 3.76y - 16.65z = 5.53$

[Co(1) −0.357, P(1) −2.527, N(1) 0.182, N(2) −0.126, N(4) 0.025, N(5) 0.080, N(7) −0.160, C(7) 0.845, C(8) −0.686, C(21) −0.910, C(23) 0.657]

Plane 2: Pyridine ring

$7.38x + 2.64y - 17.65z = 5.34$

[Co(1) −0.334, N(1) −0.006, N(2) −0.258, N(7) −0.121, C(6) 0.022, C(7) 0.464, C(8) −0.832, C(21) −0.693, C(22) 0.126, C(23) 0.567]

Plane 3: Phenanthroline ring

$7.24x + 4.54y - 15.70z = 5.53$

[Co(1) −0.227, N(3) 0.037, N(4) 0.052, N(5) 0.048, N(6) −0.082, C(7) 1.243, C(8) −0.457, C(21) −0.392, C(23) 0.887]

Interplanar angles (°)	Plane	3	2
	1	4.7	6.5
	2	11.1	

The line joining Co(1) to P(1) has direction cosines of −0.641, −0.447, 0.623

Angles (°) between the line and normals to the planes

Plane	1	2	3
Angles	6.2	12.7	11.6

* x, y, and z are fractional atomic co-ordinates.

angles, and also for the long Co–N(hydrazino) bond distances. Strain in the macrocyclic ring system is observed in the deviation of the N(3)–C(9)–N(4) and N(5)–C(20)–N(6) bond angles from 120°, as would be expected for sp^2 hybridisation; the respective bond angles being 114.4 and 114.7°. Since this deviation from 120° has the result of pulling the ligand in, one would expect the interactions of the hydrogen atoms on adjacent methyl groups to be increased. This is offset by the doming of the ligand, and the methyl groups C(8) and C(21) are displaced towards the phosphorus, with C(7) and C(23) appearing on the other side of the N_5 donor plane.

The sum of the van der Waals radii for two hydrogen atoms is 2.4 Å and the twisting of the methyl groups minimises this interaction so that the shortest H · · · H non-bonding distance is 2.08 Å. The deviations of these methyl carbons from the N_5 donor plane are given in Table 7, along with other selected atomic deviations.

The sums of the bond angles at N(3) and N(6) are 355.9 and 349.6°, the deviations away from 360° for sp^2 hybridisation being due to the methyl interactions.

This is the first known example of a cobalt(I) macrocycle exhibiting a pentagonal pyramidal arrangement of ligands.

Comparing the six-co-ordinate cobalt(I) macrocycle with the seven-co-ordinate cobalt(II) macrocycle, we see that change in co-ordination number effects the planarity of the ligand and the position of the cobalt atom in relation to the N_5 donor plane. Hole size calculations, based on the radius of a circle centred at the middle of the triangle defined by N(1), N(4), and N(5), show no significant difference in radius (2.04 for Co^{I} compared with 2.10 Å for Co^{II}). It is useful to compare the structure of the six-co-ordinated macrocycle with the structures of $[Mn(L)(H_2O)][BF_4]_2 \cdot H_2O$,[22] $[Mn(L)Cl][BF_4]$,[1,2] $[Cu(L)(H_2O)][BF_4]_2 \cdot H_2O$,[22] and $[Zn(L)Cl][BF_4]$.[22] These all contain metal ions which are six-co-ordinate. However, the Cu^{II} species can be thought of as pseudo-five-co-ordinate (distorted square based pyramid) with the copper atom being displaced to one side of the macrocycle resulting in one much longer Cu–N(phen) bond. However, they show the general trends when the co-ordination geometry of the central metal atom changes from seven to six. These changes include a doming of the macrocyclic ligand with the metal atom consequently sitting out of the N_5 donor plane, and an increase in the M–N bond distances.

All the above mentioned macrocycles show skewing of the methyl groups, of which there are two distinct types: (*i*) the hydrazino-methyl groups are displaced to one side of the plane with the imine groups subsequently displaced on the opposite side; and (*ii*) the methyl groups are skewed in a tetrahedral manner. Both types of skewing are known and minimise van der Waals interactions.

EXPERIMENTAL

Infrared spectra were measured as Nujol mulls between KBr discs using Perkin-Elmer 257 and 457 spectrometers, over the range 400—4 000 cm^{-1}. Visible and u.v. spectra were measured in quartz cells using a Pye Unicam SP 8–100 spectrophotometer. Conductance measurements were made with a Wayne-Kerr Universal bridge. Magnetic moments were recorded on a Newport-Gouy balance and the reading corrected for ligand and inner-core diamagnetism by using Pascal's constants.[27] Microanalyses were performed by the University Chemical Laboratory Microanalytical Department. Proton n.m.r. spectra were measured on Bruker 400 MHz and Varian CFT–20 instruments.

Electrochemical measurements were performed on a Princeton Applied Research Electrochemistry System model 170. All readings were taken using a three-electrode potentiostatic system in acetonitrile with 0.1 mol dm^{-3} of $[NBu^n_4]^+[BF_4]^-$ present as supporting electrolyte. Cyclic voltammetric studies were carried out using platinum wires as auxiliary and working electrodes and a $Ag–AgNO_3$ reference electrode. Controlled potential electrolysis experiments were carried out using a platinum gauze as the working electrode, a salt bridge being incorporated to separate oxidised and reduced species. The e.s.r. spectra were measured as glasses in acetonitrile or as solid samples at 77 K. For the reduction products described, all solvents were distilled, dried, and degassed before use and the air-sensitive compounds were handled under a nitrogen or argon atmosphere using Schlenk tube techniques. The com-

pound 2,6-diacetylpyridine was used without further purification (Aldrich) and 2,9-di(1-methylhydrazino)-1,10-phenanthroline was prepared by the published procedure.[28]

Preparation of $[Co^{II}(L)(H_2O)_2][BF_4]_2$.[22]—Cobalt dichloride hexahydrate (0.10 g, 0.44 mmol) was dissolved in boiling water (50 cm^3), and solid 2,9-di(1-methyl hydrazino)-1,10-phenanthroline (0.11 g, 0.44 mmol) added with vigorous stirring. When all the solid had dissolved, solid 2,6-diacetylpyridine (0.07 g, 0.44 mmol) was added with a few drops of concentrated hydrochloric acid. The reaction mixture was refluxed under nitrogen for 2 h and allowed to cool to near 60 °C. Addition of excess of solid sodium tetrafluoroborate with stirring and further cooling gave the complex $[Co^{II}(L)(H_2O)_2][BF_4]_2$ as an orange crystalline product which was collected, washed copiously with diethyl ether, and dried *in vacuo* (yield, 75%).

The axially substituted cobalt(II) macrocyclic complexes were all prepared by the reaction of $[Co^{II}(L)(H_2O)_2][BF_4]_2$ with a ten-fold excess of the axial ligand in hot methanolic solution. Addition of counter ion yielded the corresponding axially substituted complex. The preparation of $[Co^{II}(L)(im)_2][PF_6]_2$ is typical.

Preparation of $[Co^{II}(L)(im)_2][PF_6]_2 \cdot 0.5H_2O$.—The compound $[Co^{II}(L)(H_2O)_2][BF_4]_2$ (0.1 g, 0.15 mmol) was dissolved in boiling methanol (40 cm^3) and a ten-fold excess of imidazole (0.1 g, 1.5 mmol) was added. The reaction mixture was refluxed for 5 min. Addition of a concentrated methanolic solution of ammonium hexafluorophosphate to the hot solution gave an orange precipitate of the pure product which was collected, washed copiously with diethyl ether, and dried *in vacuo* (yield, 90%).

TABLE 9

Atom co-ordinates ($\times 10^4$) for $[Co^{II}(L)(CH_3OH)_2][BF_4]_2$ with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
Co(1)	9 217(2)	1 911(1)	1 511(1)
O(1)	11 050(9)	1 469(6)	2 279(7)
O(2)	7 366(9)	2 293(6)	804(8)
N(1)	9 093(9)	1 962(7)	2 827(8)
C(1)	8 738(14)	2 105(9)	4 483(11)
C(2)	8 492(14)	1 414(10)	3 989(11)
C(3)	8 651(14)	1 357(9)	3 142(10)
C(4)	8 424(13)	641(9)	2 571(10)
C(5)	8 341(17)	−127(10)	3 005(13)
N(2)	8 442(10)	770(6)	1 731(8)
N(3)	8 249(11)	174(7)	1 063(9)
C(6)	7 317(15)	−403(9)	889(11)
C(7)	8 510(13)	430(9)	309(10)
C(8)	8 333(14)	−61(9)	−480(11)
C(9)	8 658(14)	231(10)	−1 160(12)
C(10)	9 182(14)	993(9)	−1 133(11)
C(11)	9 920(13)	1 406(9)	−316(10)
N(4)	8 993(10)	1 132(6)	390(8)
C(12)	9 517(15)	1 350(10)	−1 810(12)
C(13)	9 949(15)	2 057(10)	−1 702(12)
C(14)	9 760(13)	2 179(8)	−200(10)
C(15)	10 108(14)	2 514(9)	−882(11)
C(16)	10 534(14)	3 282(10)	−680(12)
C(17)	10 614(14)	3 648(9)	125(10)
N(5)	9 811(10)	2 539(6)	605(8)
N(6)	10 287(11)	3 600(6)	1 605(8)
C(18)	10 221(12)	3 267(8)	763(9)
C(19)	10 201(15)	4 441(9)	1 662(12)
N(7)	9 828(10)	3 117(7)	2 089(8)
C(20)	9 965(12)	3 228(8)	2 956(9)
C(21)	10 710(15)	3 861(9)	3 635(11)
C(22)	9 390(13)	2 644(8)	3 348(10)
C(23)	9 207(13)	2 720(9)	4 178(10)
C(24)	12 104(16)	1 829(12)	1 413(14)
C(25)	7 028(24)	3 093(18)	525(21)
B(1)	5 160(21)	1 265(14)	1 504(14)
F(1A)	5 846(10)	1 938(7)	1 695(9)
F(1B)	5 405(11)	900(7)	811(7)
F(1C)	5 601(14)	850(8)	2 309(8)
F(1D)	4 025(10)	1 454(9)	1 233(9)
B(2)	11 923(11)	115(7)	4 175(8)
F(2A)	12 692(16)	134(10)	5 091(8)
F(2A′)	11 821(33)	152(17)	5 023(14)
F(2B)	11 271(16)	−569(8)	4 025(12)
F(2B′)	11 994(30)	−646(9)	3 936(20)
F(2C)	11 154(14)	731(9)	3 987(14)
F(2C′)	12 966(17)	494(16)	4 247(25)
F(2D)	12 526(16)	137(11)	3 589(12)
F(2D′)	10 979(19)	467(16)	3 494(18)

TABLE 10

Hydrogen atom co-ordinates ($\times 10^4$) for for $[Co^{II}(L)(CH_3OH)_2][BF_4]_2$

Atom	*x/a*	*y/b*	*z/c*
H(1)	8 557	2 160	5 114
H(2)	8 178	919	4 259
H(5A)	8 875	−110	3 750
H(5B)	8 579	−634	2 701
H(5C)	7 405	−155	2 894
H(6A)	6 722	−337	1 257
H(6B)	7 772	−956	1 071
H(6C)	6 806	−381	141
H(8)	7 958	−637	−530
H(9)	8 517	−129	−1 768
H(12)	9 418	1 032	−2 440
H(13)	10 192	2 305	−2 247
H(16)	10 805	3 589	−1 178
H(17)	10 977	4 228	274
H(19A)	9 753	4 579	2 128
H(19B)	9 739	4 718	990
H(19C)	11 112	4 648	1 963
H(21A)	11 139	3 650	4 347
H(21B)	10 211	4 382	3 631
H(21C)	11 380	3 989	3 354
H(23)	9 432	3 254	4 576
H(24A)	12 946	1 552	2 815
H(24B)	12 133	2 429	2 626
H(24C)	11 944	1 802	1 674
H(25A)	7 491	2 546	598
H(25B)	7 355	3 497	143
H(25C)	7 185	3 327	1 213

Preparation of $[Co^{II}(L)(CH_3OH)_2][BF_4]_2$.—The compound $[Co^{II}(L)(H_2O)_2][BF_4]_2$ (0.1 g, 0.15 mmol) was dissolved in boiling methanol (40 cm^3) in a Schlenk tube under nitrogen. The solution was refluxed for 20 min and allowed to cool to 40 °C. Diethyl ether (*ca.* 10 cm^3) was slowly added and the solution cooled to −5 °C overnight. Air sensitive crystals of the dimethanol adduct separated out. The crystals were collected under nitrogen and excess solvent removed *in vacuo*.

Preparation of $[Co^{I}(L)\{P(OCH_3)_3\}][BF_4]$.—The compound $[Co^{II}(L)(H_2O)_2][BF_4]_2$ was dissolved in acetonitrile containing 0.1 mol dm^{-3} of $[NBu^n_4]^+[BF_4]^-$ as base electrolyte. One equivalent or an excess of $P(OCH_3)_3$ was added and the solution reduced by controlled potential electrolysis at −1.2 V under a constant stream of argon gas. The reaction mixture slowly changed from orange to dark green and, on completion of reduction, was transferred by syringe to a Schlenk tube. The cobalt(I) species was isolated as a dark green product by the addition of dry, oxygen-free diethyl ether.

Crystal Structure Determination of $[Co(C_{23}H_{21}N_7)(CH_3OH)_2][BF_4]_2$.—Red hexagonal plates were deposited from methanol. The crystals were slightly air sensitive and were mounted in 0.5 mm Lindemann tubes. 4 615 Intensities were recorded on a Stoe four-circle diffractometer using graphite monochromated Mo-K_α radiation, and a

crystal of dimensions *ca.* 0.473 × 0.365 × 0.221 mm. Unit-cell dimensions were determined from the angular measurements of 20 strong reflections ($15 < 2\theta < 25°$). Data were collected in the range $3.0 < 2\theta < 50.0°$, using a 140 step ω—θ scan procedure; the step width was 0.01° with a step time of 0.5 s, backgrounds being measured for 17.5 s at each end of the scan. Reflections for which the intensity was <6 counts s^{-1} in a preliminary 1 s prescan were not measured. Two check reflections were monitored periodically throughout data collection and showed no significant variation.

A semi-empirical absorption correction based on a pseudo-ellipsoid model and 407 azimuthal scan data from 25 independent reflections was applied. Transmission factors ranged from 0.838 to 0.798 for the full data set. Lorentz polarization corrections were also applied, and equivalent reflections averaged to give 1 754 unique observed intensities [$F > 5\sigma(F)$].

Crystal data. $C_{25}H_{29}B_2CoF_8N_7O_2$, $M = 692.1$, $a = 12.110(8)$, $b = 17.205(9)$, $c = 15.411(8)$ Å, $\beta = 112.62(3)°$, $U = 2\,963.9$ Å^3, $F(000) = 1\,412$, $D_c = 1.551$ g cm^{-3}, $Z = 4$, D_m = 1.54 g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 6.27 cm^{-1}. Space group $P2_1/n$ from systematic absences.

The Co atom position was determined from a Patterson synthesis. Subsequent Fourier difference maps revealed the locations of all the non-hydrogen atoms. One of the tetrafluoroborate anions was disordered. In the refinement it was treated as two interlocking tetrahedra of fluorine atoms surrounding the central boron atom. In each tetrahedron the B–F and F · · · F distances were fixed at 1.37(1) and 2.237(1) Å, respectively; the occupancies of the fluorines being refined as k and $(1 - k)$, k converged to 0.650(13). All the disordered fluorine atoms were assigned a common isotropic temperature factor. The methyl and aromatic-ring hydrogen atoms were constrained to ride 1.08 Å from the relevant carbon atom, and each type was assigned a common isotropic temperature factor. The Co, N, and O atoms of the cation and the B and F atoms of the ordered anion were assigned anisotropic thermal parameters. The structure was refined by blocked full-matrix least squares until convergence was achieved. In the final cycles of refinement a weighting scheme of the form $w = 1.8184/[\sigma^2(F) + 0.004|F|^2]$ was introduced since this minimised the dependence of $\omega\Delta^2$ on F and sin θ. The final residuals were $R = 0.088$ and $R' = \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}F_o = 0.094$. A final difference synthesis showed no significant regions of electron density. The final atomic fractional co-ordinates are presented in Table 9, and those of the hydrogen atoms in Table 10.

Crystal Structure Determination of [Co($C_{23}H_{21}N_7$){P(OCH$_3$)$_3$}][BF$_4$].—Air sensitive crystals, obtained as green-black hexagonal plates from acetonitrile and diethyl ether, were mounted in 0.5 mm Lindemann tubes under nitrogen. 3 869 Intensities were recorded on a Stoe four-circle diffractometer using a crystal with dimensions *ca.* 0.477 × 0.404 × 0.185 mm. Cell parameters were determined and data collected using the same parameters and conditions as for [Co(L)(CH$_3$OH)$_2$][BF$_4$]$_2$.

A semi-empirical absorption correction based on a pseudo-ellipsoid model and 353 azimuthal scan data from 30 independent reflections was applied. Transmission factors ranged from 1.00 to 0.942 for the full data set. Lorentz polarization corrections were also applied, and equivalent reflections averaged to give 2 519 unique observed intensities [$F > 3\sigma(F)$].

Crystal data. $C_{26}H_{30}BCoF_4N_7O_3P$, $M = 665.28$, $a = 10.745(4)$, $b = 10.721(5)$, $c = 24.722(8)$ Å, $\beta = 92.57(2)°$, $U = 2\,845.0$ Å^3, $F(000) = 1\,368$, $D_c = 1.553$ g cm^{-3}, $Z = 4$, D_m = not measured, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 6.87 cm^{-1}. Space group $P2_1/n$ from systematic absences.

TABLE 11

Atom co-ordinates (× 10^4) for [Co^I(L){P(OCH$_3$)$_3$}][BF$_4$] with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
Co(1)	8 729(1)	1 151(1)	984(1)
N(1)	9 405(5)	2 766(5)	1 322(2)
C(1)	10 354(7)	2 738(6)	1 708(3)
C(2)	10 703(8)	3 789(7)	2 015(3)
C(3)	10 069(9)	4 890(8)	1 916(4)
C(4)	9 125(8)	4 963(8)	1 528(3)
C(5)	8 797(7)	3 898(7)	1 234(3)
C(6)	7 835(7)	3 872(7)	815(3)
C(7)	7 362(8)	5 049(7)	543(3)
N(2)	7 528(5)	2 722(5)	674(2)
N(3)	6 672(5)	2 482(5)	251(2)
C(8)	5 468(8)	3 141(8)	201(3)
C(9)	6 828(7)	1 329(7)	22(3)
C(10)	6 093(8)	869(7)	−418(3)
C(11)	6 349(8)	−257(7)	−639(3)
C(12)	7 350(7)	−992(7)	−425(3)
C(13)	8 027(7)	−476(6)	17(3)
N(4)	7 796(5)	672(5)	238(2)
C(14)	9 028(6)	−1 148(6)	276(3)
C(15)	9 357(7)	−2 329(6)	100(3)
C(16)	8 665(7)	−2 832(7)	−355(3)
C(17)	7 710(8)	−2 221(7)	−597(3)
C(18)	10 320(7)	−2 917(7)	406(3)
C(19)	10 855(7)	−2 381(7)	850(3)
C(20)	10 445(7)	−1 158(6)	996(3)
N(5)	9 580(5)	−538(5)	713(2)
N(6)	10 957(5)	−524(5)	1 436(2)
C(21)	11 340(9)	−1 237(8)	1 922(3)
N(7)	10 414(5)	657(5)	1 494(2)
C(22)	11 024(7)	1 546(7)	1 742(3)
C(23)	12 309(7)	1 463(7)	2 017(3)
P(1)	7 365(2)	199(2)	1 534(1)
O(1)	6 791(6)	−1 047(5)	1 292(2)
C(24)	6 017(11)	−1 885(10)	1 595(4)
O(2)	6 110(6)	876(6)	1 689(3)
C(25)	6 068(11)	2 141(8)	1 836(4)
O(3)	7 926(7)	−370(7)	2 090(2)
C(26)	8 480(10)	313(11)	2 504(4)
B(1)	1 291(9)	336(8)	3 605(4)
F(1)	148(7)	389(7)	3 788(3)
F(2)	1 521(6)	1 354(6)	3 321(2)
F(3)	1 355(7)	−696(6)	3 298(3)
F(4)	2 131(8)	232(6)	4 020(3)

The Co atom position was derived from a Patterson synthesis and all the other non-hydrogen atoms were located from subsequent Fourier-difference syntheses. The structure was refined by blocked-cascade least squares with the Co, N, O, P, B, F, and phosphite C atoms assigned anisotropic thermal parameters. The hydrogen atoms of the macrocyclic ring and of the methyl groups were placed in geometrically idealised positions and constrained to ride 1.08 Å from the associated C atoms; each type of H atom was assigned a common isotropic temperature factor and the methyl groups were refined as rigid bodies. In the final cycles of refinement the weighting scheme $w = |\sigma^2(F) + 0.0008|F|^2|^{-1}$ was introduced. The converged residuals were $R = 0.069$ and $R' = \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}F_o = 0.070$. A final electron-density difference synthesis did not show any remaining regions of electron density. The final atomic fractional co-ordinates for the non-hydrogen are presented in Table 11 and those for the hydrogen atoms in Table 12.

Complex neutral-atom scattering factors [29] were employed throughout both structure refinements. Details of hydrogen bond angles, observed and calculated structure factors, and thermal parameters for both complexes may be found in Supplementary Publication No. SUP 23315 (33 pp.).*

TABLE 12

Hydrogen atom co-ordinates ($\times 10^4$) for $[Co^I(L)\{P(OCH_3)_3\}][BF_4]$

Atom	*x/a*	*y/b*	*z/c*
H(2)	11 448	3 738	2 323
H(3)	10 322	5 710	2 150
H(4)	8 643	5 834	1 450
H(7A)	8 049	5 742	664
H(7B)	6 470	5 310	693
H(7C)	7 290	4 990	107
H(8A)	5 360	3 750	543
H(8B)	4 743	2 441	192
H(8C)	5 401	3 680	−168
H(10)	5 318	1 414	−581
H(11)	5 786	−594	−981
H(16)	8 920	−3 734	−509
H(17)	7 193	−2 659	−930
H(18)	10 641	−3 822	280
H(19)	11 573	−2 858	1 090
H(21A)	11 546	−620	2 259
H(21B)	12 152	−1 793	1 846
H(21C)	10 577	−1 844	2 017
H(23A)	12 703	2 388	2 005
H(23B)	12 891	824	1 804
H(23C)	12 254	1 166	2 432
H(24A)	5 758	−2 661	1 335
H(24B)	5 187	−1 409	1 715
H(24C)	6 530	−2 224	1 951
H(25A)	5 152	2 448	1 892
H(25B)	6 499	2 746	1 550
H(25C)	6 592	2 174	2 219
H(26A)	8 829	−178	2 861
H(26B)	7 642	811	2 595
H(26C)	9 175	966	2 378

All computer calculations were performed on the University of Cambridge IBM 370/165 computer using programs written by Professor G. M. Sheldrick. The molecular plots were drawn by PLUTO, written by Dr. W. D. S. Motherwell.

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