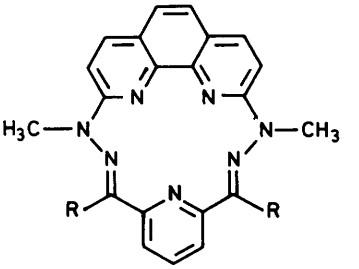
Synthesis and *X*-Ray Structure † of a Macrocyclic Pentagonal Bipyramidal Complex of Cobalt(II)

Christopher W. G. Ansell, Jack Lewis,* Paul R. Raithby, and John N. Ramsden
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

Condensation of 2,9-di(1-methylhydrazino)-1,10-phenanthroline with 2,6-pyridinedicarbaldehyde in the presence of Co^{II} ions leads to the isolation in high yield of the seven-co-ordinate complex $[Co(L^1)(H_2O)_2]^{2+}$. The *X*-ray structure of the hexafluorosilicate salt has been determined. The cobalt atom is coplanar with the five-co-ordinated nitrogens of the macrocycle and has two water molecules in axial sites. The complex crystallises in space group $C_{2/c}$ with a = 13.739(3), b = 19.262(4), c = 12.860(4) Å, β = 121.55(3)°, and Z = 4. The structure was solved by a combination of Patterson and Fourier-difference techniques and refined to R = 0.089 for 2 153 diffractometer data.

In this laboratory we are undertaking a systematic study of the synthesis, structure, and electrochemistry of the complexes of quinquedentate macrocyclic ligands which contain the 1,10-phenanthroline group. Our interest stems from the unusual geometries which may be imposed on the metal ion, and from possibility that the complexes may reflect some of the electrochemical features associated with the simpler complexes of phenanthroline. We have previously reported [1] the characterisation of a variety of complexes of the ligand L^2, prepared by the template condensation reaction of 2,9-di-(1-methylhydrazino)-1,10-phenanthroline with 2,6-diacetylpyridine in the presence of an appropriate metal ion. We report here the synthesis and *X*-ray structure of the Co^{II} complex of the related macrocycle L^1.



L^1, R = H L^2, R = CH_3

Results and Discussion

Condensation in an aqueous medium of 2,6-pyridinedicarbaldehyde with 2,9-di(1-methylhydrazino)-1,10-phenanthroline in the presence of Co^{II} ions, followed by precipitation with $NaBF_4$ solution, gives the macrocyclic complex $[Co(L^1)(H_2O)_2][BF_4]_2$ as orange crystals in greater than 60% yield. Metathesis in aqueous solution containing an excess of ammonium hexafluorosilicate gives large, well formed crystals of $[Co(L^1)(H_2O)_2][SiF_6]\cdot 6H_2O$. The conductivities of both species in nitromethane solution (Λ = 170 and 82 Ω^{-1} cm^2 mol^{-1} respectively) are consistent [2] with 2 : 1 and 1 : 1 electrolytic behaviour respectively in this solvent.

The *X*-ray structure determination of $[Co(L^1)(H_2O)_2][SiF_6]\cdot 6H_2O$ confirms the macrocyclic nature of the product and the seven-co-ordinate, pentagonal bipyramidal geometry of the metal ion, which is bound by five nitrogens of the macrocycle and has two water molecules in axial sites. The Figure is a diagram of the cation. The $Co-N_7$ unit is exactly planar, as are the phenanthroline and pyridine segments (maximum deviation ≤0.02 Å in each case). A crystallographic two-fold axis passes through atoms Co, N(1), and C(1) and bisects the C(11)–C(11′) and C(12)–C(12′) bonds. The angles between the phenanthroline and $Co-N_7$, and pyridine and $Co-N_7$, mean planes are instructive. For the system $[Co(L^2)(H_2O)_2]^{2+}$, the angles between these planes are 4.2 and 6.7° respectively,[3] and vary only slightly when M = Fe^{II} [1] or Ni^{II}.[4] The corresponding angles in the present structure are 1.2 and 1.4°. This greater overall planarity of the macrocycle may result from the easing of the effect of steric interaction between the peripheral substituents on going from L^2 (R = Me) to L^1 (R = H). Major distortions of the peripheral methyl groups from coplanarity due to van der Waals interactions are observed in the complexes of L^2.[1] The easing of such steric effects in the present structure is also apparent in other respects. Firstly, the sum of the angles around N(3) is 360.0°, and the atoms

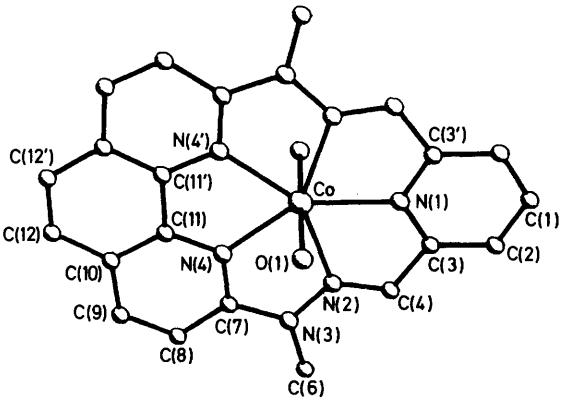


Figure. Molecular structure of the cation $[Co(L^1)(H_2O)_2]^{2+}$

† *Supplementary data available* (No. SUP 23373, 41 pp.): observed and calculated structure factors, thermal parameters, least-squares planes, full atomic co-ordinates. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Selected hydrogen-bonded contact distances (Å)

O(2)–O(1)	2.750(11)	O(3)–F(3)	2.896(12)
O(4)–O(1)	2.716(10)	O(3)–F(1′)	2.633(12)
O(2)–F(1)	2.711(13)	O(3)–O(4)	2.796(13)
O(2)–F(3′)	2.656(12)	F(1′)–O(4)	2.805(12)

N(2), N(3), C(6), C(7) are coplanar to within 0.01 Å. For $[Co(L^2)(H_2O)_2]^{2+}$, the analogous angle sum is 350.3°. In addition, the Co–axial water bond lengths become nominally shorter in the present structure as compared to $[Co(L^2)(H_2O)_2]^{2+}$ [2.150(5) *cf.* 2.184(6) and 2.177(5) Å]. Studies of related seven-co-ordinated systems [5] have led to the statement that the axial water to metal ion bond lengths appeared to be determined largely by non-bonded contacts involving the equatorial *N*-donors. For both the present structure and that of $[Co(L^2)(H_2O)_2]^{2+}$, the non-bonded contact distances between the *N*-donors and axial water ligands average to 3.0 Å, close to the sum of the van der Waals radii of both atoms, 2.9 Å.

The ' hole size ' of the present complex is 2.09 Å, as defined by the radius of the circle intersecting the two phenanthroline and the pyridine donor atoms. This is not significantly different from the value of 2.11 Å calculated for $[Co(L^2)(H_2O)_2]^{2+}$.

The six lattice water molecules were located and examination of interatomic distances between the co-ordinated and unco-ordinated waters and the counter ion points to the existence of extensive hydrogen bonding in the crystal lattice (Table 1).

Experimental

The substituted phenanthroline precursor was prepared as previously reported.[6]

(*a*) $[Co(L^1)(H_2O)_2][BF_4]_2$.—2,6-Pyridinedicarbaldehyde (0.13 g, 1 mmol) was added to an aqueous solution (50 cm³) of 2,9-di(1-methylhydrazino)-1,10-phenanthroline (0.30 g, 1 mmol) and $CoCl_2 \cdot 6H_2O$ (0.24 g, 1 mmol) which had been refluxed for 10 min. After 2 h of refluxing, concentrated aqueous $NaBF_4$ solution (10 cm³) was added and the orange microcrystalline precipitate of the product collected and dried. Yield 0.4 g, 63% (Found C, 39.6; H, 3.6; N, 15.4. Calc. for $C_{21}H_{17}B_2CoF_8N_7O_2$: C, 39.6; H, 3.5; N, 15.4%).

(*b*) $[Co(L^1)(H_2O)_2][SiF_6] \cdot 6H_2O$.—To $[Co(L^1)(H_2O)_2][BF_4]_2$ (0.2 g) in hot water (50 cm³) was added ammonium hexafluorosilicate (0.5 g, excess). On cooling/standing, analytically pure crystals of the hexafluorosilicate salt were deposited. Yield 70% (Found: C, 35.0; H, 4.1; N, 13.8. Calc. for $C_{21}H_{17}CoF_6N_7O_2Si \cdot 6H_2O$: C, 35.45; H, 4.6; N, 13.8%).

Crystal Structure Determination.—A suitable single crystal of dimensions 0.39 × 0.35 × 0.28 mm was mounted on a fibre and space group and cell dimensions determined *via* Weissenberg photography. The crystal was transferred to a Stöe four-circle diffractometer and 2 765 intensities were measured up to $2\theta_{max.}$ of 50° using graphite monochromated Mo-K_α radiation (λ = 0.710 69 Å), and a 140-step ω/θ scan technique. Lorentz, polarisation, and empirical absorption corrections were applied and the data were averaged to give 2 153 unique observed reflections [$F > 4\sigma(F)$].

Crystal data. $C_{21}H_{17}CoF_6N_7O_2Si \cdot 6H_2O$, M = 712, Monoclinic, space group $C_{2/c}$, a = 13.739(3), b = 19.262(4), c = 12.860(4) Å, β = 121.55(3)°, U = 2 900.0 Å³, Z = 4, D_c = 1.39 g cm⁻³, $F(000)$ = 1 395.95, μ(Mo-K_α) = 3.11 cm⁻¹.

The cobalt atom was located from a Patterson map and all remaining non-hydrogen atoms from subsequent difference maps. The structure was refined by full-matrix least-squares techniques. The Co, Si, O, C, and N atoms were assigned anisotropic temperature factors. The hydrogen atoms of the axial and lattice water molecules were not located. All other hydrogens were placed in geometrically idealised sites and constrained to ride 1.08 Å from the parent carbon atom. The methyl groups were refined as rigid bodies. The hexafluorosilicate counter ion was disordered and was refined as two interlocking octahedra of fluorines with Si–F and F ··· F distances fixed at 1.68 and 2.376 Å respectively. The occupan-

Table 2. Fractional atomic co-ordinates with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Co	0.000 00	0.919 58(6)	−0.250 00
O(1)	0.155 0(4)	0.920 2(2)	−0.253 0(5)
N(1)	0.000 00	1.028 60(38)	−0.250 00
N(2)	−0.098 7(5)	0.954 3(3)	−0.443 3(5)
N(3)	−0.144 4(5)	0.905 2(3)	−0.533 5(5)
N(4)	−0.058 4(5)	0.832 4(2)	−0.367 7(5)
C(1)	0.0000	0.171 8(5)	−0.2500
C(2)	0.056 9(7)	1.136 2(4)	−0.141 7(8)
C(3)	0.056 2(6)	1.063 4(3)	−0.144 0(6)
C(4)	−0.113 4(6)	1.020 1(4)	−0.465 3(6)
C(6)	−0.214 6(7)	0.922 8(5)	−0.661 8(7)
C(7)	−0.119 2(6)	0.837 5(3)	−0.489 2(7)
C(8)	−0.155 1(8)	0.777 6(4)	−0.564 3(8)
C(9)	−0.125 4(8)	0.713 4(4)	−0.509 1(9)
C(10)	−0.063 3(7)	0.707 0(3)	−0.379 9(8)
C(11)	−0.032 4(6)	0.769 3(3)	−0.316 9(7)
C(12)	−0.029 7(8)	0.642 8(4)	−0.312 4(9)
Si	0.500 00	1.085 85(13)	0.250 00
F(1)	0.464 7(5)	1.023 6(2)	0.316 1(5)
F(2)	0.461 1(5)	1.147 0(2)	0.314 4(5)
F(3)	0.366 5(2)	1.084 4(3)	0.127 6(3)
F(1′)	0.422 6(14)	1.155 8(6)	0.173 4(17)
F(2′)	0.391 8(11)	1.034 0(8)	0.153 2(15)
F(3′)	0.446 2(17)	1.089 6(10)	0.340 9(16)
O(2)	0.344 9(7)	0.987 3(4)	−0.071 2(7)
O(3)	0.156 8(8)	0.678 6(4)	−0.440 5(8)
O(4)	0.222 8(6)	0.809 3(3)	−0.330 1(6)

Table 3. Selected cation bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

Co–O(1)	2.150(5)	Co–N(1)	2.100(7)
Co–N(2)	2.223(5)	C(4)–N(2)	1.292(9)
Co–N(4)	2.118(5)	N(1)–C(3)	1.342(7)
N(2)–N(3)	1.367(8)	N(3)–C(7)	1.392(9)
N(3)–C(6)	1.451(10)	N(4)–C(7)	1.335(9)
C(11)–C(11′)	1.465(15)		
N(4)–C(11)	1.337(8)		
N(1)–Co–O(1)	89.7(1)	C(11)–N(4)–C(7)	118.9(6)
N(2)–Co–O(1)	90.5(2)	N(4)–Co–N(4′)	75.1(3)
N(2)–Co–N(1)	72.5(1)	C(2)–C(3)–N(1)	121.0(7)
N(4)–Co–O(1)	90.0(2)	C(3)–N(1)–C(3′)	120.1(8)
N(4)–Co–N(2)	70.0(2)	N(4)–C(7)–N(3)	114.7(5)
C(3)–N(1)–Co	119.9(4)	C(8)–C(7)–N(3)	124.1(7)
N(3)–N(2)–Co	118.7(4)	C(8)–C(7)–N(4)	121.2(7)
C(4)–N(2)–Co	118.3(5)	C(4)–N(2)–N(3)	122.9(6)
C(6)–N(3)–N(2)	122.6(6)	C(7)–N(3)–N(2)	113.3(5)
C(7)–N(3)–C(6)	124.0(6)	C(7)–N(4)–Co	123.8(4)
C(11)–N(4)–Co	117.8(5)		

cies of the fluorines were refined as k and $(1 - k)$; k refined to 0.216(3). The fluorines were assigned a common isotropic temperature factor. Complex neutral atom scattering factors [7] were used throughout, with the weighting scheme $w = 1/[\sigma^2(F) + 0.003F^2]$ introduced in the latter stages of refinement. Final $R = 0.089$, $R' = 0.098$. Atomic co-ordinates and bond lengths and angles are given in Tables 2 and 3. All crystallographic calculations were performed using SHELX.[8]

Acknowledgements

We thank the S.E.R.C. for financial support and ICI Ltd. for the award of a CASE studentship (to C. W. G. A.).

References

1 M. M. Bishop, J. Lewis, T. D. O'Donoghue, P. R. Raithby, and J. N. Ramsden, *J. Chem. Soc., Chem. Commun.*, 1978, 828; C. W. G. Ansell, J. Lewis, M. C. Liptrot, P. R. Raithby, and M. Schroder, *J. Chem. Soc., Dalton Trans.*, 1982, 1593; C. W. G. Ansell, J. Lewis, P. R. Raithby, J. N. Ramsden, and M. Schroder, *J. Chem. Soc., Chem. Commun.*, 1982, 546.
2 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
3 L. R. Hanton and P. R. Raithby, *Acta Crystallogr., Sect. B*, 1980, **36**, 1489.
4 J. N. Ramsden, Ph.D Thesis, University of Cambridge, 1980.
5 G. J. Wester and D. Palenik, *Inorg. Chem.*, 1976, **15**, 755; 1978, **17**, 864; 1979, **18**, 2445.
6 J. Lewis and T. D. O'Donoghue, *J. Chem. Soc., Dalton Trans.*, 1980, 743.
7 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
8 G. M. Sheldrick, SHELX-76 program system, University of Cambridge, 1976.

Received 19*th April* 1982; *Paper* 2/649