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Complexes of Facultative Hexadentate Ligands. Structure of 7,7′-(Ethylenediiminodiethylenedinitrilo)bis(7-methyl-*o*-cresolato-*O*,*N*,*N*′,*N*″,*N*‴,*O*′)cobalt(III) Hexafluorophosphate–Acetone (1/1)*

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Abstract. $[Co(C_{22}H_{28}N_4O_2)][PF_6].C_3H_6O$, $M_r = 642{\cdot}5$, monoclinic, $P2_1/n$, $a = 14{\cdot}082\,(2)$, $b = 13{\cdot}448\,(1)$, $c = 15{\cdot}016\,(1)$ Å, $\beta = 101{\cdot}81\,(1)°$, $V = 2783{\cdot}5$ Å^3, $Z = 4$, $D_x = 1{\cdot}533$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 7{\cdot}70$ cm^{-1}, $F(000) = 1328$, $T = 293$ K, $R = 0{\cdot}069$ for 3426 observed reflections. The coordination around Co is approximately octahedral with Co—N(amine) 1·953 (5) and 1·966 (5) Å, Co—N(imine) both 1·915 (5) Å, and Co—O 1·875 (4) and 1·869 (4) Å. No angle at Co differs by more than 7° from either 90 or 180°.

Introduction. Facultative hexadentate ligands capable of octahedral coordination to a transition-metal ion may encapsulate it in a 1:1 complex whose exterior exhibits the properties of an organic material. Such species are of interest in a variety of contexts, particularly in the production of metal-containing pharmaceuticals. The molecular structures of a nickel(II) (Cradwick, Cradwick, Dodson, Hall & Waters, 1972) and an iron(III) complex (Sinn, Sim, Dose, Tweedle & Wilson, 1978) with a hexadentate salicylaldehyde ligand have been determined, thereby confirming the ability of such a ligand to reach all octahedral sites on a transition-metal ion.

As part of an investigation into complexes of lipophilic ligands capable of encapsulating metal ions, the structure of the cobalt(III) complex with a similar hexadentate Schiff base ligand, 7,7′-(ethylenediiminodiethylenedinitrilo)bis(7-methyl-*o*-cresol) $[(Hmoc)_2trien]$, has been elucidated. The preparation of the complex is described by Rothin, Banbery, Berry, Hamor, Jones & McCleverty (1989).

Experimental. A crystal of $[Co\{(moc)_2trien\}]$-$PF_6.(CH_3)_2CO$ with dimensions 0·4 × 0·6 × 0·4 mm was used. Measurements were made on an Enraf–Nonius CAD-4 diffractometer. Lattice parameters were determined from the setting angles of 25 reflections (θ 18 to 24°). Intensity data were measured with ω–2θ scans in the range $2 < \theta < 24°$, index range h −16 to 16, k −16 to 16, l 0 to 17. Three standard reflections, measured every 2 h, showed no significant variation over the period of data collection. 9050 reflections were scanned, of which 4344 were unique ($R_{\rm int} = 0{\cdot}0192$) and 3426 were considered observed $[F > 5\sigma(F)]$ and were used in the analysis. No absorption correction was applied.

The structure was solved using Patterson and Fourier methods. H atoms were placed in calculated positions, riding on their bonded atoms. Coordinates for all non-H atoms were refined using full-matrix least squares on F values with weights $w = 1/[\sigma^2(F) + 0{\cdot}00035F^2]$. The heavier atoms were assigned anisotropic thermal parameters, and the H atoms of the cation and of the acetone molecule were each assigned one overall isotropic temperature factor which refined to 0·085 (5) and 0·250 (34) Å^2, respectively. The F atoms of the hexafluorophosphate anion were refined isotropically. The refinement was terminated when all shifts were less than half their respective e.s.d.'s, and $R = 0{\cdot}069$, $wR = 0{\cdot}096$, for the 3426 observed reflections. The residual electron density in a final difference synthesis was within +0·9 to −0·9 e Å^{-3}.

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974); computations were carried out with *SHELX*76 (Sheldrick, 1976) and *PLUTO*78 (Motherwell & Clegg, 1978).

Discussion. Atomic coordinates are listed in Table 1,† and bond lengths and angles in Table 2. Fig. 1 shows the atomic numbering for the complex. The asymmetric unit consists of a monomeric cobalt(III) cationic complex, a hexafluorophosphate anion and a molecule of acetone. The Schiff base ligand is bonded through all six donor atoms (ONNNNO) to

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† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52404 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional atomic coordinates* ($\times 10^4$) *with e.s.d.'s in parentheses and equivalent isotropic temperature factors* ($Å^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Co(1)	4267 (1)	568 (1)	2391 (1)	32
N(1)	5263 (3)	1558 (3)	2645 (3)	36
N(2)	5076 (4)	−149 (4)	3400 (3)	38
N(3)	4880 (4)	−256 (4)	1584 (4)	48
N(4)	3261 (4)	−414 (3)	2157 (3)	40
O(1)	3532 (3)	1260 (3)	1402 (3)	43
O(2)	3653 (3)	1308 (3)	3164 (3)	37
C(1)	3921 (4)	1881 (4)	897 (4)	37
C(2)	3387 (5)	2063 (5)	7 (4)	48
C(3)	3733 (6)	2708 (5)	−569 (4)	53
C(4)	4604 (5)	3179 (5)	−292 (5)	55
C(5)	5126 (5)	3030 (5)	568 (5)	51
C(6)	4809 (4)	2393 (4)	1202 (4)	38
C(7)	5388 (4)	2292 (4)	2120 (4)	38
C(8)	6142 (6)	3085 (5)	2475 (5)	64
C(9)	5874 (5)	1457 (5)	3565 (4)	48
C(10)	5510 (5)	619 (5)	4075 (4)	42
C(11)	5840 (5)	−718 (5)	3064 (5)	56
C(12)	5415 (6)	−1094 (5)	2134 (5)	63
C(13)	4075 (6)	−641 (5)	871 (5)	59
C(14)	3249 (6)	−958 (5)	1287 (5)	56
C(15)	2600 (5)	−566 (4)	2634 (4)	41
C(16)	1802 (6)	−1305 (6)	2317 (6)	70
C(17)	2595 (4)	−5 (4)	3466 (4)	37
C(18)	2021 (5)	−333 (5)	4085 (5)	51
C(19)	1911 (5)	217 (6)	4822 (5)	57
C(20)	2362 (5)	1133 (5)	4983 (5)	49
C(21)	2947 (4)	1469 (4)	4418 (4)	39
C(22)	3084 (4)	915 (4)	3654 (4)	30
P(1)	7992 (1)	882 (1)	1603 (1)	54
O(1*A*)	581 (5)	2954 (4)	872 (5)	96
C(1*A*)	714 (5)	2063 (6)	950 (6)	64
C(2*A*)	1202 (8)	1620 (9)	1838 (8)	116
C(3*A*)	394 (10)	1396 (8)	160 (8)	120
F(1)*	9051 (7)	408 (8)	1880 (7)	‡103 (3)
F(2)*	6848 (7)	1018 (8)	1303 (7)	‡109 (3)
F(3)*	7930 (7)	413 (8)	2554 (7)	‡109 (3)
F(4)*	8088 (9)	1945 (9)	2083 (9)	‡138 (5)
F(5)*	7851 (8)	−125 (8)	1097 (8)	‡119 (3)
F(6)*	8125 (8)	1413 (8)	706 (7)	‡123 (3)
F(11)†	9052 (18)	1024 (22)	2048 (18)	‡139 (8)
F(12)†	7112 (13)	1467 (14)	983 (13)	‡101 (5)
F(13)†	7603 (15)	1113 (17)	2516 (14)	‡121 (6)
F(14)†	8607 (15)	1870 (15)	1773 (13)	‡106 (6)
F(15)†	7449 (14)	−187 (14)	1609 (14)	‡111 (6)
F(16)†	8180 (17)	491 (18)	647 (16)	‡136 (7)

* Site occupancy 0·65 (1).
† Site occupancy 0·34 (1).
‡ U_{iso}.

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

Co(1)—N(1)	1·915 (5)	C(3)—C(4)	1·367 (10)
Co(1)—N(2)	1·953 (5)	C(4)—C(5)	1·365 (10)
Co(1)—N(3)	1·966 (5)	C(5)—C(6)	1·418 (8)
Co(1)—N(4)	1·915 (5)	C(6)—C(7)	1·457 (9)
Co(1)—O(1)	1·875 (4)	C(7)—C(8)	1·523 (8)
Co(1)—O(2)	1·869 (4)	C(9)—C(10)	1·510 (9)
N(1)—C(7)	1·298 (7)	C(11)—C(12)	1·490 (10)
N(1)—C(9)	1·476 (8)	C(13)—C(14)	1·491 (10)
N(2)—C(10)	1·489 (7)	C(15)—C(16)	1·503 (9)
N(2)—C(11)	1·489 (8)	C(15)—C(17)	1·460 (8)
N(3)—C(12)	1·506 (9)	C(17)—C(18)	1·422 (9)
N(3)—C(13)	1·484 (9)	C(17)—C(22)	1·417 (8)
N(4)—C(14)	1·494 (8)	C(18)—C(19)	1·366 (10)
N(4)—C(15)	1·302 (8)	C(19)—C(20)	1·384 (10)
O(1)—C(1)	1·320 (7)	C(20)—C(21)	1·375 (9)
O(2)—C(22)	1·306 (6)	C(21)—C(22)	1·414 (8)
C(1)—C(2)	1·414 (8)	O(1*A*)—C(1*A*)	1·215 (9)
C(1)—C(6)	1·419 (8)	C(1*A*)—C(2*A*)	1·494 (13)
C(2)—C(3)	1·382 (9)	C(1*A*)—C(3*A*)	1·482 (13)

Range of P—F bond lengths
Major orientation 1·547 (11) to 1·596 (10)
Minor orientation 1·517 (25) to 1·630 (20)

N(1)—Co(1)—N(2)	84·4 (2)	C(2)—C(3)—C(4)	120·7 (6)
N(1)—Co(1)—N(3)	96·8 (2)	C(3)—C(4)—C(5)	119·7 (6)
N(2)—Co(1)—N(3)	86·5 (2)	C(4)—C(5)—C(6)	122·8 (6)
N(1)—Co(1)—N(4)	178·9 (2)	C(1)—C(6)—C(5)	117·0 (6)
N(2)—Co(1)—N(4)	95·4 (2)	C(1)—C(6)—C(7)	123·0 (5)
N(3)—Co(1)—N(4)	84·3 (2)	C(5)—C(6)—C(7)	120·0 (6)
N(1)—Co(1)—O(1)	94·3 (2)	N(1)—C(7)—C(6)	121·8 (5)
N(2)—Co(1)—O(1)	177·8 (2)	N(1)—C(7)—C(8)	119·4 (6)
N(3)—Co(1)—O(1)	91·8 (2)	C(6)—C(7)—C(8)	118·8 (5)
N(4)—Co(1)—O(1)	85·9 (2)	N(1)—C(9)—C(10)	110·5 (5)
N(1)—Co(1)—O(2)	85·4 (2)	N(2)—C(10)—C(9)	107·9 (5)
N(2)—Co(1)—O(2)	93·0 (2)	N(2)—C(11)—C(12)	108·2 (6)
N(3)—Co(1)—O(2)	177·7 (2)	N(3)—C(12)—C(11)	108·6 (5)
N(4)—Co(1)—O(2)	93·6 (2)	N(3)—C(13)—C(14)	110·1 (5)
O(1)—Co(1)—O(2)	88·7 (2)	N(4)—C(14)—C(13)	110·8 (5)
Co(1)—N(1)—C(7)	126·3 (4)	N(4)—C(15)—C(16)	120·2 (6)
Co(1)—N(1)—C(9)	112·7 (4)	N(4)—C(15)—C(17)	121·2 (5)
C(7)—N(1)—C(9)	120·9 (5)	C(16)—C(15)—C(17)	118·5 (6)
Co(1)—N(2)—C(10)	106·1 (3)	C(15)—C(17)—C(18)	120·2 (5)
Co(1)—N(2)—C(11)	109·8 (4)	C(15)—C(17)—C(22)	122·3 (5)
C(10)—N(2)—C(11)	111·3 (5)	C(18)—C(17)—C(22)	117·3 (6)
Co(1)—N(3)—C(12)	108·5 (4)	C(17)—C(18)—C(19)	122·4 (6)
Co(1)—N(3)—C(13)	105·9 (4)	C(18)—C(19)—C(20)	120·0 (6)
C(12)—N(3)—C(13)	110·9 (5)	C(19)—C(20)—C(21)	119·7 (6)
Co(1)—N(4)—C(14)	112·0 (4)	C(20)—C(21)—C(22)	121·7 (6)
Co(1)—N(4)—C(15)	126·3 (4)	O(2)—C(22)—C(17)	124·7 (5)
C(14)—N(4)—C(15)	121·5 (5)	O(2)—C(22)—C(21)	116·5 (5)
Co(1)—O(1)—C(1)	122·8 (4)	C(17)—C(22)—C(21)	118·8 (5)
Co(1)—O(2)—C(22)	123·3 (3)	O(1*A*)—C(1*A*)—C(2*A*)	120·9 (9)
O(1)—C(1)—C(2)	116·7 (5)	O(1*A*)—C(1*A*)—C(3*A*)	120·3 (9)
O(1)—C(1)—C(6)	124·3 (5)	C(2*A*)—C(1*A*)—C(3*A*)	118·8 (9)
C(2)—C(1)—C(6)	118·9 (6)		
C(1)—C(2)—C(3)	120·8 (7)		

the metal, which exhibits a slightly distorted octahedral geometry. Both O atoms are *trans* to amine N atoms, while the two imine N atoms, N(1) and N(4), are mutually *trans*.

The coordination of all six donor atoms results in encapsulation of the metal atom by the ligand, producing three five-membered and two six-membered chelate rings.

The maximum angular distortions from ideal octahedral geometry involve the angles subtended at the metal atom by adjacent amine and imine N atoms, which differ from 90° by 6·8 (2)° for N(1)—Co—N(3), and by 5·7 (2)° for N(3)—Co—N(4). There are two sets of Co—N bond lengths, corresponding to the two types of N atom present in the complex. The Co—N(amine) bonds are the longest, with values of 1·953 (5) and 1·966 (5) Å for N(2) and N(3), respectively. The Co—N(imine) bond lengths are both 1·915 (5) Å. The Co—O bond lengths are 1·875 (4) and 1·869 (4) Å.

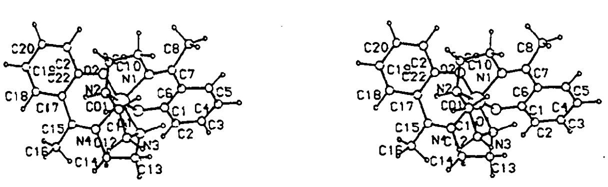

Fig. 1. Stereoscopic view of the cationic complex showing the atom numbering.

The structure may be compared to the structures of Fe^{III} and Ni^{II} complexes containing the corresponding $H(sal)_2trien$ ligand (sal = salicylidene): $[Fe(sal)_2trien]NO_3.H_2O$, $[Fe(sal)_2trien]Cl.H_2O$ (Sinn *et al.*, 1978) and [Ni(sal)$_2$trien].6H$_2$O (Cradwick *et al.*, 1972). All the complexes have the same configuration of the hexadentate ligand, with the terminal O atoms mutually *cis*. The deviation from perfect octahedral geometry for the CoN$_4$O$_2$ unit, maximum angular distortion 6·8°, is comparable to that of the related iron complexes, which show maximum deviations of 6·5 and 6·2°. The NiN$_4$O$_2$ unit exhibits a much greater deviation, 15·6°. The metal–ligand distances for the Co^{III} complex are somewhat shorter than those of the Fe^{III} compounds, where Fe is in the low-spin state; mean Fe—O 1·883, Fe—N(imine) 1·931 and Fe—N(amine) 2·003 Å. However, the metal–ligand distances in the Ni^{II} complex are much longer: Ni—O 2·058, Ni—N(imine) 2·029, Ni—N(amine) 2·159 Å.

The C—N bond lengths and the bond angles around the N atoms can be divided into two distinct groups. Angles at N(1) and N(4) add up to 359·9 and 359·8°, respectively, close to 360°, as expected for trigonal planar, while those at N(2) and N(3) are typical for tetrahedral bonding, mean 109·1° for N(2) and 108·4° for N(3). Both imine N atoms exhibit large distortions from ideal values in the angles Co(1)—N(1)—C(9) and Co(1)—N(4)—C(14) which are 112·7 (4) and 112·0 (4)°, respectively. This can be attributed to the electronic repulsion of the C═N double bond and to the participation of these atoms in the five-membered chelate rings. The angles Co(1)—N(1)—C(7) and Co(1)—N(4)—C(15) are concomitantly large at 126·3 (4)°.

The F atoms of the hexafluorophosphate counterion are disordered between two sets of atomic positions. The site occupancies refined to 0·65 (1) and 0·34 (1), and were then fixed at these values during the final cycle of refinement. The P—F lengths of the major orientation average 1·580 Å, some 0·03 Å larger than has generally been found previously (Banbery & Hamor, 1988).

The acetone molecule forms a weak hydrogen bond with one of the amine N atoms: N(2)···O(1*A*) = 2·995 (8), H(2N)···O(1*A*) = 2·05 Å.

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References

BANBERY, H. J. & HAMOR, T. A. (1988). *Acta Cryst.* **C44**, 1683–1684.

CRADWICK, P. D., CRADWICK, M. E., DODSON, G. G., HALL, D. & WATERS, T. N. (1972). *Acta Cryst.* **B28**, 45–49.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO78*. Program for plotting molecular and crystal structures. Report *Cambridge Crystallographic Files* (1981), Manchester Computing Centre, Manchester, England.

ROTHIN, A. S., BANBERY, H. J., BERRY, F. J., HAMOR, T. A., JONES, C. J. & MCCLEVERTY, J. A. (1989). *Polyhedron*, **8**, 491–504.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

SINN, E., SIM, G., DOSE, E. V., TWEEDLE, M. F. & WILSON, L. J. (1978). *J. Am. Chem. Soc.* **100**, 3375–3390.

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Structures of the Antiferrodistortive Layer Perovskites Bis(phenethylammonium) Tetrahalocuprate(II), Halo = Cl$^-$, Br$^-$

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Abstract. Bis(phenethylammonium) tetrachlorocuprate(II), $2C_8H_{12}N^+.CuCl_4^{2-}$, $M_r = 449{\cdot}8$, orthorhombic, *Pcab*, $a = 7{\cdot}328\,(1)$, $b = 7{\cdot}295\,(1)$, $c = 38{\cdot}618\,(5)$ Å, $V = 2064{\cdot}7\,(6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}47$ g cm^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}54178$ Å, $\mu = 63{\cdot}6$ cm^{-1}, $F(000) = 924$, $T = 295$ K, final $R = 0{\cdot}068$ for 1198 observed unique reflections. Bis(phenethylammonium) tetrabromocuprate(II), $2C_8H_{12}N^+.CuBr_4^{2-}$, $M_r = 627{\cdot}5$, orthorhombic, *Pcab*, $a = 7{\cdot}654\,(4)$, $b = 7{\cdot}756\,(4)$, $c = 38{\cdot}042\,(18)$ Å, $V = 2258\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}85$ g cm^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}54178$ Å, $\mu = 97{\cdot}5$ cm^{-1}, $F(000) = 1212$, $T = 295$ K, final $R = 0{\cdot}067$ for 1207 observed unique reflections. Both salts contain layers of corner-shared tetragonally elongated octahedra sandwiched between layers of the organic cations. Each copper(II) ion forms four short Cu—X (X = Cl$^-$, Br$^-$) bonds in a planar arrangement. Two longer, semi-coordinate Cu—X bonds

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