plays its usual role of counter-ion. Its geometry is normal (see supplementary material). This Co^I compound is isomorphous with [Ni(PMe$_3$)$_4$]BPh$_4$ (Gleizes, Dartiguenave, Dartiguenave, Galy & Klein, 1977), but the tetrahedral environment of the metal [P—Co—P = 101·1 (1)–125·4 (1)°, Table 2 and Fig. 1] is more distorted than in the Ni^{II} complex [P—Ni—P = 104·6(1)–119·9(1)°]. Similar distortions are also present in the related four-coordinate Co^I molecules CoCl(PMe$_3$)$_3$ [Cl—Co—P = 113·8 (2)°, P—Co—P = 104·8 (3)° (Jones, Stuart, Atwood & Hunter, 1983)] and CoI(PMe$_3$)$_3$ [I—Co—P = 119·26 (6)–109·77 (4)°, P—Co—P = 105·24 (4)–106·84 (7)° (Bandy, Green & Kirchner, 1985)], and they probably result from the phosphine methyl groups being interlocked to minimize steric hindrances about the metal. The bond lengths in the [Co(PMe$_3$)$_4$]$^+$ ion [av. 2·227 Å] remain roughly the same as in the iodo [av. 2·235 Å] and chloro [2·240 Å] compounds.

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Structure of a Nickel(II) Complex of 18-Crown-6 at 163 K

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Abstract. Tris(ethanol)(1,4,7,10,13,16-hexaoxacyclo-octadecane)nickel(II) bis(hexafluorophosphate), [Ni(C$_2$H$_6$O)$_3$(C$_{12}$H$_{24}$O$_6$)](PF$_6$)$_2$, $M_r = 751·16$, monoclinic, $P2_1/c$, $a = 8·976$ (2), $b = 16·533$ (4), $c = 22·230$ (6) Å, $\beta = 109·37$ (3)°, $V = 3112·2$ (14) Å^3, $Z = 4$, $D_x = 1·603$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0·71069$ Å, $\mu = 8·483$ cm^{-1}, $F(000) = 1552$, $R = 0·0404$ for 4161 reflections ($F \geq 6\sigma_F$). The Ni^{2+} ion is coordinated to three adjacent O atoms of the crown (O1, O4, O7) and to the O atoms of three ethanol solvate molecules, the O atoms forming a distorted octahedron. The range of Ni—O distances is 1·991 (2)–2·114 (3) Å. Two ethanol molecules are hydrogen bonded to crown O atoms and the third is hydrogen bonded to an F atom of one PF$_6^-$ ion. The crown has approximate mirror symmetry. The O1–O4–O7 and O10–O13–O16 planes have a dihedral angle of 106·2 (2)°. The average crown C—O bond lengths are 1·448 (2) Å for Ni-bound O atoms and 1·426 (4) Å for non-Ni-bound O atoms. The average C—O bond length in the ethanol molecules is 1·448 (7) Å. All C—C bonds have lengths in the range 1·489–1·505 Å.

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Experimental. The title compound was prepared by the reaction of 18-crown-6 with Ni(EtOH)$_6$(PF$_6$)$_2$ in ethanol and ethyl orthoformate (EOF). Ni(EtOH)$_6$(PF$_6$)$_2$ was prepared by the reaction of NiCl$_2$.6H$_2$O with AgPF$_6$ in ethanol and EOF. A pale-green crystal was mounted in a capillary tube with grease using a Schlenk apparatus to exclude moisture. The grease prevented an accurate measurement of crystal size; the maximum dimension was 0·5 mm. A summary of data collection and structural refinement is given in Table 1.
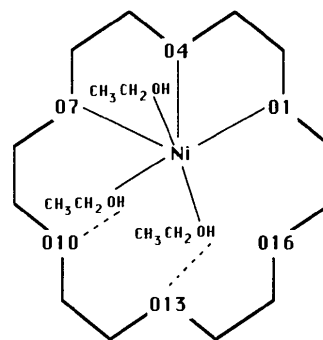
13 atoms obtained from *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) were

Table 1. *Summary of data collection and structure refinement*

(a) Data collection (163 K)[i,ii]

Mode	ω scan
Scan range	Symmetrically over 1.0° about $K\alpha_{1,2}$ max.
Background	Offset 1.0 and −1.0° in ω from $K\alpha_{1,2}$ max.
Scan rate (° min⁻¹)	3.0–6.0
Exposure time (h)	69.3
Stability analysis	
Computed s, t	−0.000119
	0.000003
Correction range on I	0.994–1.001
2θ range (°)	4.0–50.0
Range in hkl, min.	0, 0, −27
max.	11, 20, 25
Total reflections measured, unique	5477, 5477
Absorption correction	Not applied

(b) Structure refinement[iii]

Instability factor, p	0.04
Reflections used ($F \geq 6\sigma_F$)	4161
No. of variables	547
Goodness of fit, S	1.769
R, wR	0.0404, 0.0504
R for all data	0.0586
Max. shift/e.s.d.	< 0.02
Max., min. density in difference map (e Å⁻³)	1.04, −0.45

Notes: (i) Unit-cell parameters were obtained by least-squares refinement of the setting angles of 60 reflections with $25.4 < 2\theta < 30.4°$. (ii) Syntex $P2_1$ autodiffractometer with a graphite monochromator and a Syntex LT-1 inert-gas (N_2) low-temperature delivery system. Data reduction was carried out as described by Riley & Davis (1976). Crystal and instrument stability were monitored by remeasurement of four check reflections after every 96 reflections. As detailed by Henslee & Davis (1975), these data were analyzed to relate intensity to exposure time by the equation $y = 1.0 + sx + tx^2$, where x is exposure time (h), y is fractional intensity relative to $x = 0$ and s and t are coefficients determined by least-squares fit. (iii) Function minimized was $\Sigma w(F_o - F_c)^2$, where $w = \sigma_F^{-2}$. $\sigma_F = F\sigma_I/2I$; $\sigma_I = [N_{pk} + N_{bg1} + N_{bg2} + (pI)^2]^{1/2}$.

used initially. The model was improved with subsequent *ΔF* maps. All H atoms were located in a difference map at $R = 0.062$ (0.36–0.71 e Å⁻³). All atomic positional parameters, anisotropic thermal parameters for non-H atoms and isotropic for H atoms were refined by full-matrix least squares [*SHELX*76 (Sheldrick, 1976)]. The structure was refined in two blocks, one of which contained the Ni and all crown atoms and the other the Ni and all the remaining atoms. Scattering factors and anomalous-dispersion corrections for all non-H atoms taken from *International Tables for X-ray Crystallography* (1974); H scattering factors from Stewart, Davidson & Simpson (1965). Atomic parameters are listed in Table 2;* bond lengths and bond angles in

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* Tables of anisotropic thermal parameters, H-atom parameters, bond lengths and angles involving the H atoms, bond lengths and angles in the hexafluorophosphate ions and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51346 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Atomic positions and equivalent isotropic thermal parameters*

	x	y	z	U_{eq}†(Å²)
Ni	0.11850 (5)	0.27091 (2)	0.41225 (2)	0.01906 (14)
O(1)	0.1332 (3)	0.22757 (14)	0.50284 (10)	0.0241 (8)
C(2)	0.2763 (5)	0.2574 (2)	0.5501 (2)	0.0301 (13)
C(3)	0.2962 (5)	0.3436 (2)	0.5331 (2)	0.0284 (13)
O(4)	0.2950 (3)	0.34235 (13)	0.46798 (11)	0.0239 (8)
C(5)	0.2933 (5)	0.4208 (2)	0.4389 (2)	0.0300 (14)
C(6)	0.2813 (5)	0.4044 (2)	0.3709 (2)	0.0299 (14)
O(7)	0.1454 (3)	0.35287 (14)	0.34360 (11)	0.0254 (9)
C(8)	0.0949 (5)	0.3458 (2)	0.2750 (2)	0.0290 (13)
C(9)	0.1716 (5)	0.2780 (2)	0.2512 (2)	0.0289 (13)
O(10)	0.1083 (3)	0.20245 (15)	0.26211 (11)	0.0261 (9)
C(11)	0.1739 (5)	0.1343 (2)	0.2406 (2)	0.0278 (14)
C(12)	0.1136 (5)	0.0592 (2)	0.2619 (2)	0.0283 (13)
O(13)	0.1691 (3)	0.05775 (14)	0.32982 (11)	0.0266 (9)
C(14)	0.1226 (4)	−0.0136 (2)	0.3556 (2)	0.0295 (14)
C(15)	0.1800 (4)	−0.0060 (2)	0.4266 (2)	0.0276 (13)
O(16)	0.1007 (3)	0.06007 (15)	0.44351 (11)	0.0266 (9)
C(17)	0.1591 (5)	0.0782 (2)	0.5101 (2)	0.0287 (13)
C(18)	0.0770 (5)	0.1525 (2)	0.5215 (2)	0.0283 (14)
O(19)	−0.0474 (3)	0.3470 (2)	0.42566 (13)	0.0294 (10)
C(20)	−0.1836 (5)	0.3810 (3)	0.3765 (2)	0.035 (2)
C(21)	−0.2219 (5)	0.4635 (3)	0.3941 (2)	0.045 (2)
O(22)	−0.0480 (3)	0.2117 (2)	0.34454 (13)	0.0259 (9)
C(23)	−0.1906 (4)	0.1687 (3)	0.3408 (2)	0.0309 (14)
C(24)	−0.3099 (6)	0.1763 (3)	0.2756 (2)	0.047 (2)
O(25)	0.2833 (3)	0.1904 (2)	0.40639 (12)	0.0242 (9)
C(26)	0.4482 (4)	0.1997 (2)	0.4128 (2)	0.0278 (13)
C(27)	0.5430 (5)	0.1288 (3)	0.4456 (2)	0.037 (2)
P(1)	0.20679 (11)	0.83042 (6)	−0.06854 (5)	0.0310 (4)
F(1P1)	0.0721 (3)	0.7710 (2)	−0.10864 (13)	0.0631 (11)
F(2P1)	0.2151 (3)	0.78240 (15)	−0.00421 (11)	0.0431 (9)
F(3P1)	0.3404 (3)	0.89061 (15)	−0.02636 (13)	0.0517 (10)
F(4P1)	0.3389 (3)	0.7732 (2)	−0.07688 (13)	0.0564 (11)
F(5P1)	0.0754 (3)	0.8883 (2)	−0.05659 (13)	0.0580 (11)
F(6P1)	0.1962 (3)	0.8806 (2)	−0.13064 (13)	0.0648 (12)
P(2)	0.46911 (13)	0.42024 (7)	0.19846 (5)	0.0393 (4)
F(1P2)	0.4571 (3)	0.4046 (2)	0.26671 (13)	0.0747 (13)
F(2P2)	0.6515 (3)	0.3948 (2)	0.22551 (12)	0.0515 (10)
F(3P2)	0.4893 (3)	0.4274 (2)	0.12935 (13)	0.0767 (14)
F(4P2)	0.2888 (3)	0.4414 (2)	0.1695 (2)	0.096 (2)
F(5P2)	0.5206 (4)	0.5099 (2)	0.2150 (2)	0.096 (2)
F(6P2)	0.4223 (4)	0.3272 (2)	0.18259 (14)	0.0718 (13)

† $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* A_{ij}$, where A_{ij} is the dot product of the *i*th and *j*th direct-space unit-cell vectors.

Table 3. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°) *in the crown and solvate molecules*

1	2	3	4	1–2	1–2–3	1–2–3–4
O(1)	C(2)	C(3)	O(4)	1.450 (4)	107.0 (3)	−55.4 (4)
C(2)	C(3)	O(4)	C(5)	1.500 (6)	106.0 (3)	172.8 (3)
C(3)	O(4)	C(5)	C(6)	1.445 (5)	115.5 (3)	−176.3 (3)
O(4)	C(5)	C(6)	O(7)	1.447 (4)	105.9 (3)	54.0 (4)
C(5)	C(6)	O(7)	C(8)	1.505 (6)	107.3 (3)	166.7 (3)
C(6)	O(7)	C(8)	C(9)	1.446 (4)	114.6 (3)	89.6 (4)
O(7)	C(8)	C(9)	O(10)	1.446 (4)	114.4 (3)	73.3 (4)
C(8)	C(9)	O(10)	C(11)	1.500 (6)	109.8 (4)	179.7 (3)
C(9)	O(10)	C(11)	C(12)	1.427 (5)	113.8 (3)	173.1 (3)
O(10)	C(11)	C(12)	O(13)	1.425 (5)	108.6 (4)	−63.3 (4)
C(11)	C(12)	O(13)	C(14)	1.492 (6)	108.3 (3)	−177.9 (3)
C(12)	O(13)	C(14)	C(15)	1.425 (4)	113.1 (3)	−177.1 (3)
O(13)	C(14)	C(15)	O(16)	1.432 (5)	108.1 (3)	64.6 (4)
C(14)	C(15)	O(16)	C(17)	1.494 (5)	108.4 (3)	−173.7 (3)
C(15)	O(16)	C(17)	C(18)	1.420 (5)	113.0 (3)	175.3 (3)
O(16)	C(17)	C(18)	O(1)	1.429 (4)	108.4 (3)	−76.2 (4)
C(17)	C(18)	O(1)	C(2)	1.496 (6)	114.6 (4)	−81.2 (4)
C(18)	O(1)	C(2)	C(3)	1.451 (5)	113.1 (2)	−165.5 (3)
O(19)	C(20)	C(21)		1.455 (5)	111.4 (3)	
C(20)	C(21)			1.490 (7)		
O(22)	C(23)	C(24)		1.442 (5)	110.7 (4)	
C(23)	C(24)			1.494 (6)		
O(25)	C(26)	C(27)		1.447 (5)	111.4 (3)	
C(26)	C(27)			1.489 (6)		

Tables 3 and 4. Atom labeling is given in Fig. 1. Molecular packing is shown in Fig. 2. Principal computer programs are cited by Gadol & Davis (1982).

Table 4. *Distances* (Å) *and angles* (°) *in the* Ni²⁺ *coordination sphere and hydrogen bonding*

1	2	3	1–2	1–2–3
O(1)	Ni	O(4)	2·100 (2)	79·95 (10)
O(1)	Ni	O(7)		157·69 (9)
O(1)	Ni	O(19)		83·54 (11)
O(1)	Ni	O(22)		110·48 (11)
O(4)	Ni	O(7)	2·034 (2)	79·34 (9)
O(4)	Ni	O(19)		90·66 (10)
O(4)	Ni	O(22)		169·57 (11)
O(4)	Ni	O(25)		89·02 (10)
O(7)	Ni	O(19)	2·114 (3)	88·50 (11)
O(7)	Ni	O(22)		90·36 (10)
O(7)	Ni	O(25)		96·54 (11)
O(19)	Ni	O(22)	2·046 (3)	90·73 (11)
O(19)	Ni	O(25)		174·80 (12)
O(22)	Ni	O(25)	1·991 (2)	90·53 (11)
O(25)	Ni	O(1)	2·026 (3)	91·29 (11)
O(19)	H(19)	F(2P1)*	0·65 (6)	161· (5)
O(19)	F(2P1)*		2·863 (4)	
H(19)	F(2P1)*		2·24 (5)	
O(22)	H(22)	O(10)	0·69 (4)	162· (4)
O(22)	O(10)		2·656 (4)	
H(22)	O(10)		2·03 (4)	
O(25)	H(25)	O(13)	0·73 (4)	176· (4)
O(25)	O(13)		2·757 (3)	
H(25)	O(13)		1·99 (4)	

* Related to coordinates in Table 2 by $-x, y-\frac{1}{2}, \frac{1}{2}-z$.

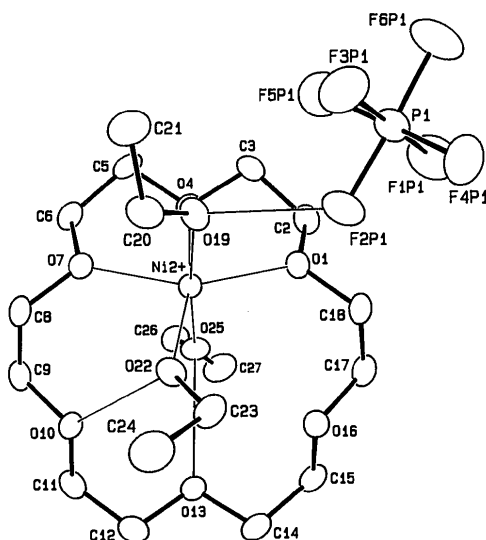Fig. 2. Perspective view of the molecular packing as viewed down the *a* axis.

Fig. 1. Perspective drawing indicating atom labeling, Ni²⁺ coordination and hydrogen bonding. The dihedral angles between the O19–O22–O25 plane and the planes O1–O4–O7 and O10–O13–O16 are 85·13 (9) and 68·48 (13)°, respectively. Thermal ellipsoids are drawn at the 50% probability level.

Related literature. No all-oxygen six-coordinate Ni complexes have been reported previously (Cambridge Structural Database, 1987). Mixed-donor crown-6 structures have been reported. These include mixed N and P (Ciampolini, Nardi, Zanobini, Cini & Orioli, 1983; Mealli, Sabat, Zanobini, Ciampolini & Nardi, 1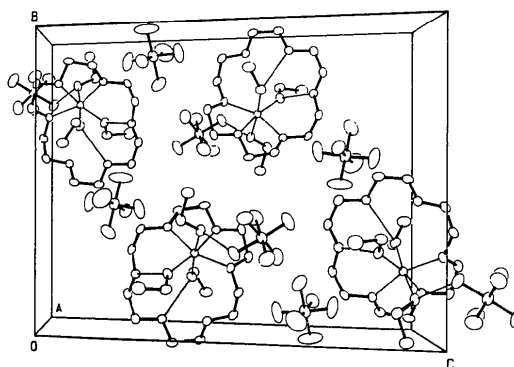985), mixed O and P (Dapporto, Ciampolini, Nardi & Zanobini, 1983), and mixed S and P (Ciampolini, Nardi, Dapporto & Zanobini, 1984; Ciampolini, Nardi, Dapporto, Innocenti & Zanobini, 1984; Ciampolini, Dapporto, Nardi & Zanobini, 1980).

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