References

BANDY, J. A., KENNARD, C. H. L., PARSONS, D. G. & TRUTER, M. R. (1984). *J. Chem. Soc. Perkin Trans.* 2, pp. 309–315.

BENETOLLO, F., BOMBIERI, G., DE PAOLI, G., HUGHES, D. L., PARSONS, D. G. & TRUTER, M. R. (1984). *J. Chem. Soc. Chem. Commun.* pp. 425–426.

BURDETT, J. K., HOFFMANN, R. & FAY, R. C. (1978). *Inorg. Chem.* **17**, 2553–2568.

FRENCH, S. & WILSON, K. (1978). *Acta Cryst.* A**34**, 517–525.

HABENSCHUSS, A. & SPEDDING, F. H. (1979). *Cryst. Struct. Commun.* **8**, 511–516.

HANSON, I. R., PARSONS, D. G. & TRUTER, M. R. (1979). *J. Chem. Soc. Chem. Commun.* pp. 486–488.

HANSON, I. R. & TRUTER, M. R. (1982). *Bioscience Rep.* **2**, 521–526.

HART, F. A., HURSTHOUSE, M. B., MALIK, K. M. A. & MOORHOUSE, S. (1978). *J. Chem. Soc. Chem. Commun.* pp. 549–550.

HURSTHOUSE, M. B. (1976). CAD-4 program for processing diffractometer data. Queen Mary College, London.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99 and 149. Birmingham: Kynoch Press.

JOHNSON, C. K. (1971). *ORTEP*II. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.

MITCHELL, J. JR & SMITH, D. M. (1980). *Aquametry*, 2nd ed. New York: John Wiley.

OWEN, J. D. (1981*a*). *J. Chem. Soc. Perkin Trans.* 2, pp. 12–18.

OWEN, J. D. (1981*b*). *GEOM*. Suite of crystallographic programs for the Prime computer. Rothamsted Experimental Station, Harpenden, Herts., England.

OWEN, J. D. (1983). *BAYES*. Application of Bayesian statistics to diffraction intensity measurements. Rothamsted Experimental Station, Harpenden, Herts., England.

PARSONS, D. G. (1978). *J. Chem. Soc. Perkin Trans.* 1, pp. 451–455.

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

SHELDRICK, G. M. (1978). *EMPABS*. Semi-empirical absorption corrections. Univ. of Cambridge, England.

Acta Cryst. (1985). C**41**, 38–40

Structure of Dichlorobis[*P,P,P′,P′*-tetramethyl-*o*-phenylenebis(phosphine)]nickel(III) Hexafluorophosphate Dihydrate, $[NiCl_2\{P_2(CH_3)_4(C_6H_4)\}_2]PF_6.2H_2O$

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Abstract. $M_r = 706{\cdot}9$, monoclinic, $C2/m$, $a = 12{\cdot}467\,(6)$, $b = 10{\cdot}497\,(4)$, $c = 11{\cdot}241\,(7)$ Å, $\beta = 100{\cdot}79\,(4)^\circ$, $V = 1445$ Å^3, $Z = 2$, $D_x = 1{\cdot}625$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}108$ mm^{-1}, $F(000) = 726$, room temperature, final $R = 0{\cdot}087$ for 1365 unique reflections. The Ni atom has a tetragonally distorted octahedral configuration with chlorine atoms in the axial positions and the anionic P atom has a regular octahedral configuration. The Ni—Cl and Ni—P bond lengths are 2·424 (4) and 2·255 (3) Å. The anion and cation are held together by van der Waals forces.

Introduction. Phosphines act as π-bond acceptors and σ-bond donors. The vacant $3d$ orbitals of the P atoms are capable of interaction with filled non-bonding d orbitals of a transition metal. Chelating diphosphine ligands are commonly used in the stabilization of a large number of oxidation states for many transition metals. With the lower oxidation states of the metals, the reducing properties of the ligands are an advantage, but in higher oxidation states any tendency towards dissociation will result in decomposition, since such complexes contain both an oxidizing and a reducing agent.

Ni^{III} complexes of Group V*b* donors offer a wealth of data over VI*b* donors that is of considerable importance in the elucidation of their electronic structures. EPR studies of dihalo complexes reveal a highly delocalized molecular wave function for the unpaired electron as evidenced by the very well resolved superhyperfine structure from all the immediately bonded nuclei of the ligands (Manoharan & Rogers, 1970; Bernstein & Gray, 1972). Sethulakshmi, Subramanian, Bennett & Manoharan (1979) have carried out EPR investigations on $[Ni(dp)_2Cl_2]ClO_4$ and $[Ni(dp)_2Br_2]PF_6$ without complete X-ray crystal structure data.

In the present compound, both dipolar interaction and hyperfine local field contribute to the broadening of the EPR peak (Ramakrishna, 1982). But the estimation of their relative contributions leading to the simulation of the line width can be made only with the availability of the detailed crystal structure. This prompted us to carry out the present work.

We report here the structure of the title compound, hereafter represented as $[Ni(dp)_2Cl_2]^+.[PF_6]^-.2H_2O$.

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Experimental. Title compound kindly supplied by Dr M. A. Bennet, Research School of Chemistry, The Australian National University. Unit-cell parameters by least-squares refinement of θ values of 25 high-angle reflections. Crystal 0·625 × 0·5 × 0·1 mm, Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\omega/2\theta$ scan. Standard reflections ($\bar{4}0\bar{6}$ and $\bar{5}3\bar{4}$) showed no significant change. All (3528) reflections (h: −17 to 17, k: 0 to 14, l: 0 to 15) in range $2 < 2\theta < 60°$ measured. Max. counting time for each reflection 60 s. 1365 unique reflections with $I > 3\sigma(I)$ considered observed. $R_{\rm int}$ from merging 81 equivalent reflections 0·023. No correction for absorption. hkl reflections with $h+k$ odd systematically absent, space group either $C2$ or $C2/m$; noncentrosymmetric $C2$, which gave strong correlations amongst atom parameters during refinement, abandoned in favour of $C2/m$. No extra systematic absences observed. Ni atoms assigned special positions 0, $\frac{1}{2}$, $\frac{1}{2}$ and $\frac{1}{2}$, 0, $\frac{1}{2}$ and anionic P atoms special positions 0, 0, 0 and $\frac{1}{2}$, $\frac{1}{2}$, 0 (point symmetry $2/m$). Similarly, Cl atoms and anionic axial F atoms assigned special positions x, 0, z; $\bar{x}$, 0, $\bar{z}$; $\frac{1}{2}+x$, $\frac{1}{2}$, z; $\frac{1}{2}-x$, $\frac{1}{2}$, $\bar{z}$ (point symmetry m). Structure solved by Fourier methods and refined by full-matrix least squares with *SHELX*76 (Sheldrick, 1976). Refinement of coordinates, anisotropic thermal parameters and scale factor (84 parameters) led to high thermal parameters for F atoms. $\sum w|\Delta F|^2$ minimized; max. and av. Δ/σ 0·111 and 0·023. Atomic scattering factors for Ni^{3+} from Cromer & Waber (1965) and for other non-hydrogen atoms from Cromer & Mann (1968); anomalous-dispersion correction factors from Cromer & Liberman (1970); H-atom scattering factors from Stewart, Davidson & Simpson (1965). Difference Fourier map contained peak of height 2·11 e Å^{-3} at special position and was treated as belonging to oxygen atom (O*W*). It refined with a large thermal factor [$U_{\rm iso} = 0{\cdot}214\ (6)$ Å^2]. Final difference Fourier maps revealed seven H atoms, their positions refined once. H atom bonded to C(5) and water molecule H atoms could not be located satisfactorily and were omitted from subsequent calculations. Final difference Fourier map showed two peaks with heights < 1·8 e Å^{-3} close to Ni (< 1·12 Å from Ni). Final $R = 0{\cdot}087$, $R_w = 0{\cdot}092$, $w = 1{\cdot}00/[\sigma^2(F_o)+0{\cdot}0294|F_o|^2]$.

Discussion. Fractional atomic coordinates of the non-hydrogen atoms are listed in Table 1.* Table 2 contains the interatomic distances and bond angles. An *ORTEP* (Johnson, 1965) plot of the cation with atom numbering scheme is presented in Fig. 1. The packing arrangement (with $\mathrm{NiCl_2P_4}$ and $\mathrm{PF_6}$ only for clarity) is shown in Fig. 2.

Table 1. *Fractional atomic coordinates* (×10⁴) *and equivalent isotropic thermal parameters* (×10³) *of the non-hydrogen atoms with e.s.d.'s in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i U_{ii}.$$

	x	y	z	$U_{\rm eq}$(Å^2)
Ni	5000	0	5000	41 (1)
Cl	3027 (3)	0	4763 (4)	53 (1)
P(1)	5046 (2)	1444 (3)	3525 (2)	48 (1)
C(1)	5627 (7)	661 (11)	2374 (9)	52 (3)
C(2)	6065 (9)	1304 (14)	1497 (10)	68 (5)
C(3)	6501 (10)	659 (15)	659 (11)	83 (6)
C(4)	3724 (9)	2044 (13)	2739 (12)	68 (4)
C(5)	5869 (10)	2859 (12)	3852 (13)	74 (5)
P(2)	5000	5000	0	71 (3)
F(1)	4327 (11)	3988 (11)	454 (14)	188 (7)
F(2)	5748 (21)	5000	1179 (18)	200 (13)
O*W*	3713 (16)	5000	3548 (18)	214 (6)*

* Isotropic thermal parameter.

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

Ni–Cl	2·424 (4)	Ni–P(1)	2·255 (3)
P(1)–C(1)	1·80 (1)	P(1)–C(4)	1·83 (1)
P(1)–C(5)	1·80 (1)	C(1)–C(1$^{\rm ii}$)	1·39 (2)
C(1)–C(2)	1·39 (2)	C(2)–C(3)	1·35 (2)
C(3)–C(3$^{\rm ii}$)	1·38 (3)	P(2)–F(1)	1·50 (1)
P(2)–F(2)	1·47 (2)		
P(1)···P(1$^{\rm i}$)	3·340 (4)	P(1)···P(1$^{\rm ii}$)	3·031 (5)
P(1)···Cl	3·447 (5)	P(1)···Cl$^{\rm i}$	3·168 (4)
F(1)···F(1$^{\rm iv}$)	2·12 (2)	F(1)···F(1$^{\rm v}$)	2·12 (2)
F(1)···F(2)	2·10 (2)	F(1)···F(2$^{\rm iv}$)	2·11 (2)
Cl–Ni–P(1)	94·8 (2)	Cl$^{\rm i}$–Ni–P(1)	85·2 (2)
P(1)–Ni–P(1$^{\rm i}$)	95·5 (2)	P(1)–Ni–P(1$^{\rm ii}$)	84·5 (2)
Ni–P(1)–C(1)	106·9 (4)	Ni–P(1)–C(4)	116·2 (5)
Ni–P(1)–C(5)	119·7 (5)	C(1)–P(1)–C(4)	104·9 (5)
C(1)–P(1)–C(5)	103·5 (6)	C(4)–P(1)–C(5)	104·0 (6)
P(1)–C(1)–C(2)	124 (1)	C(1)–C(2)–C(3)	121 (1)
		C(2)–C(3)–C(3$^{\rm ii}$)	120 (1)
F(1)–P(2)–F(2)	89·7 (9)	F(1)–P(2)–F(1$^{\rm iv}$)	90

Symmetry code: (i) $1-x, y, 1-z$; (ii) $x, -y, z$; (iii) $1-x, -y, 1-z$; (iv) $1-x, y, -z$; (v) $x, 1-y, z$.

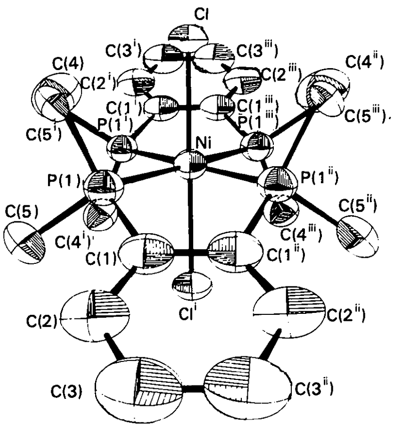

Fig. 1. Perspective view of the cation.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39745 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The metal atoms of the cations and the P atoms of the anions lie on planes that are parallel to each other as well as to the *ab* plane.

The low-spin Ni^{III} atom of the cation has the expected axially elongated octahedral configuration. The NiP_4Cl_2 chromophore exhibits C_{2h} ($2/m$) symmetry. The P atoms occupy the equatorial positions and the Cl atoms occupy the most electronegative axial positions. Distortions from the ideal D_{2h} (mmm) symmetry are reflected in small displacements of the Cl atoms from the axial positions and in the puckering of the five-membered ring [Ni–P(1)–C(1)–C(1^{ii})–P(1^{ii})]. (See Table 2 for the symmetry code.)

There are two different P···Cl distances, 3·447 (5) [P(1)···Cl] and 3·168 (4) Å [P(1)···Cl^{i}] with a difference (0·279 Å) that is significant. The two different P···Cl distances and two different Cl–Ni–P angles [Cl–Ni–P(1^{i}) = Cl–Ni–P(1^{iii}) = 85·2 (2)° and Cl–Ni–P(1) = Cl–Ni–P(1^{ii}) = 94·8 (2)°] create an asymmetric environment for the Cl atom, which is responsible for it shifting slightly away from the exact octahedral position. The Cl–Ni–Cl^{i} orientation is perpendicular to **b** and approximately along **a** (see Fig. 2).

The Ni–P distance is 2·255 (3) Å, which is less than the covalent distance, 2·29 Å. Stephenson (1964) suggests that double bonding (dative σ bond + dative π bond), which can only arise in transition-metal complexes, is responsible for the appreciable shortening of the Ni–As bond length from the normal covalent single-bond distance found in $NiBr_2$ triarsine and $Ni(diarsine)_2I_2$ compounds. The shortening of the metal–phosphorus bond in the present structure as well as in $[Ni(vpp)_2Br]^{+}$.$[BPh_4]^{-}$ (Parthasarathy, Noordik & Manoharan, 1982)* (Ni–P = 2·25 Å) can be explained in a similar way.

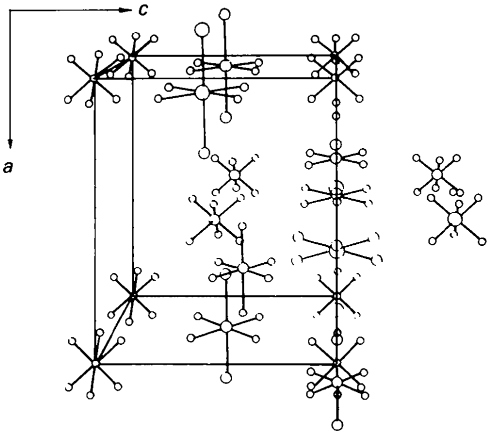

Fig. 2. Packing diagram (only $NiCl_2P_4$ and PF_6 shown) viewed along **b**.

The observed Ni–Cl distance in the present structure [2·424 (4) Å] coincides with that observed by Bernstein, Rodley, Marsh & Gray (1972) in dichlorobis(diarsine)Ni^{III} monochloride [2·425 (3) Å]. To explain these axial Ni–Cl bonds (longer than the normal covalent bond, 2·2 Å) the term semi-coordination may be used as has been introduced to explain the longer Cu–Cl axial bonds in Cu^{2+} hexacoordinate complexes.

The Cl^{-} ion approaches the Ni–P plane from a position of least electrostatic potential energy. Probably because of methyl–methyl repulsion between the two diphosphine groups, the angles Ni–P(1)–C(4) [116·2 (5)°] and Ni–P(1)–C(5) [119·7 (5)°] deviate significantly from the tetrahedral angle, whilst the other angles at P are less than tetrahedral.

The four cationic P atoms are not coplanar with the C atoms of the *o*-phenylene rings owing to the tetrahedral configuration of the P atoms.

The coordination of F atoms around the anionic P atom is a regular octahedron (see F–P–F angles in Table 2). The P–F distances are 1·50 (1) Å (equatorial) and 1·47 (1) Å (axial), the difference being statistically insignificant. The average P–F distance [1·49 (1) Å] is significantly less than the covalent distance, 1·73 Å (sum of covalent radii). The short P–F bond distance may be due to the very high thermal parameters of the fluorine atoms.

The anion and cation are held together by van der Waals forces. The shortest Ni···Ni, Ni···P(2) and P(2)···P(2) contacts are 8·149 (3), 7·572 (4) and 8·149 (3) Å, respectively.

References

BERNSTEIN, P. K. & GRAY, H. B. (1972). *Inorg. Chem.* **11**, 3035–3039.

BERNSTEIN, P. K., RODLEY, G. A., MARSH, R. & GRAY, H. B. (1972). *Inorg. Chem.* **11**, 3040–3043.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

JOHNSON, C. K. (1965). *ORTEP*II. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

MANOHARAN, P. T. & ROGERS, M. T. (1970). *J. Chem. Phys.* **53**, 1682–1685.

PARTHASARATHY, V., NOORDIK, J. H. & MANOHARAN, P. T. (1982). *J. Cryst. Mol. Struct.* **12**, 191–204.

RAMAKRISHNA, B. L. (1982). PhD thesis, Department of Chemistry, IIT, Madras 600 036, India.

SETHULAKSHMI, C. N., SUBRAMANIAN, S., BENNETT, M. A. & MANOHARAN, P. T. (1979). *Inorg. Chem.* **18**, 2520–2525.

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

STEPHENSON, N. C. (1964). *Acta Cryst.* **17**, 592–596.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

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* vpp is *P,P,P′,P′*-tetraphenylethylenebis(phosphine).