Preparation, Crystal and Molecular Structure of *trans*-Dibromobis[di(t-butyl)fluorophosphine]nickel(II)

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The title compound has been prepared by reaction of anhydrous nickel dibromide in benzene suspension with Bu^t_2PF. I.r., u.v., and magnetic measurements are reported. Crystals are monoclinic, space group $P2_1/n$, with a = 9·358(3), b = 14·530(5), c = 8·468(6) Å, β = 93·69(6)°, Z = 2. The molecule is *trans*-square planar and is centrosymmetric. The principal bond lengths and angles are: Ni–Br 2·288(1), Ni–P 2·232(3), P–C 1·86(1) and 1·88(1), and P–F 1·579(7) Å; C–P–F 97·3(5) and 97·9(5)°. The structure was solved by Patterson and Fourier methods and refined to R 0·088 for 1243 visually estimated unique reflections.

ALTHOUGH the chemistry of fluorophosphine complexes of transition metals is by now relatively well characterised,[1] it is only recently that any systematic structural studies of such compounds have been undertaken. Electron diffraction studies of the tetrahedrally co-ordinated complexes $Ni(PF_3)_4$,[2,3] $Pt(PF_3)_4$,[3] and $Rh(NO)(PF_3)_3$,[4] and the octahedrally co-ordinated $PF_3Mo(CO)_5$,[5] have displayed, with the notable exception of the platinum complex, a dramatic shortening of the metal–phosphorus bond length, in comparison with that found in other phosphine complexes of these metals. In the nickel complex, for instance, the bond-shortening is of the order 0·12—0·21, and in the molybdenum complex of the order 0·08—0·13 Å. A similar effect has also been observed in metal–phosphorus bond lengths obtained from the crystal-structure determinations of $HCo(PF_3)_4$ [6] and *cis*-$RhCl(PPh_3)(PF_2NEt_2)_2$.[7] From these values it may be inferred that π-acceptor properties of the phosphorus group as a ligand are greatly enhanced by the replacement of alkyl or aryl groups on phosphorus by fluorine. The effect of π bonding between the metal and phosphorus is most likely to be significant when the metal is in a low or zero oxidation state.

We have recently synthesised [8] a series of stable complexes of the type $NiX_2(PFBu^t_2)_2$ (X = Cl, Br, or I). The crystal structure of $NiBr_2(PFBu^t_2)_2$ has been investigated in order to ascertain the effect on molecular dimensions of the presence of divalent nickel and of Bu^t_2FP as ligand.

EXPERIMENTAL

Preparation.—Bis-(t-butyl)fluorophosphine [9] (3·28 g, 0·02 mol) was added to a benzene suspension (30 ml) of anhydrous $NiBr_2$ (4·76 g, 0·04 mol) under vigorous magnetic stirring. The reaction was complete after 24 h and the excess of $NiBr_2$ was filtered off under nitrogen. Solvent was removed *in vacuo* at room temperature and the brown-red crystals (5·0 g, 91%) obtained were recrystallised from either methylene chloride or acetone at −40 to −80 °C [Found: C, 34·9; H, 6·85; F, 7·0; P, 11·35%; M (cryoscopic, in benzene), 550. $C_{16}H_{36}Br_2F_2NiP_2$ requires C, 35·15; H, 6·65; F, 6·95; P, 11·35%; M, 546·9].

Solid $NiBr_2(PFBu^t_2)_2$ is relatively stable in air. Solutions in organic solvents, however, are very easily hydrolysed in contact with moisture.

U.v. and I.r. Spectra.—Methylene chloride solutions show 3 bands in the region 300—1000 nm: 315 (20 000), 407 (5 900), and 485 nm (1 200) (ε in parentheses). The positions of the absorption maxima are almost the same in the spectra obtained for Nujol mulls: 407, *ca.* 400, and 490 nm.

I.r. spectra obtained for Nujol mulls between caesium iodide windows show the bands of the free ligand,[10] which, except for ν(P–F) stretching vibration frequency, are not greatly influenced by complex formation. The P–F stretching frequency in the free ligand (754 cm^{-1}) is shifted 42 cm^{-1} (to 796 cm^{-1}) to higher wavenumbers on complex formation. In the far-i.r. region we could find only one ν(Ni–Br) (343 cm^{-1}) and one ν(Ni–P) (245 cm^{-1}) [band assignment was achieved by comparison of the i.r. spectra of compounds $NiX_2(PFBu^t_2)_2$ (X = Cl, Br, or I), and the free ligand Bu^t_2PF]. Number and position of ν(Ni–Br) and ν(Ni–P) indicate a *trans*-square planar arrangement of the ligands Br and Bu^t_2PF.[11]

N.m.r. and Magnetic Measurements.—^1H N.m.r. spectra of CH_2Cl_2 solutions of $NiBr_2(PFBu^t_2)_2$ show only one single band at δ_H 3·5 p.p.m. (relative to methylene chloride as internal standard), the ^{19}F n.m.r. spectrum a broad doublet at δ_F 175·0 p.p.m. (relative to CCl_3F as internal standard). Because of the low solubility in most inert organic solvents we could not obtain ^{31}P n.m.r. spectra. The ^1H as well as the ^{19}F n.m.r. spectra are temperature dependent.[8]

$NiBr_2(PFBu^t_2)_2$ is diamagnetic in CH_2Cl_2 solution, as well as in the solid state. Room-temperature magnetic measurements for solutions were carried out by the n.m.r. method of Evans,[12] with methylene chloride as solvent and toluene (5%) as standard. The calculation of exact diamagnetic susceptibilities is difficult because of partial decomposition of $NiBr_2(PFBu^t_2)_2$ in solution, yielding paramagnetic $NiBr_2$ in addition to Bu^t_2PF.

U.v. spectra were recorded on a Beckman Acta III spectrophotometer using quartz curvettes, i.r. spectra on

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[1] J. F. Nixon, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 363.

[2] A. Almenningen, B. Andersen, and E. E. Astrup, *Acta Chem. Scand.*, 1970, **24**, 1579.

[3] J. C. Marriott, J. A. Salthouse, and M. J. Ware, *Chem. Comm.*, 1970, 595.

[4] D. M. Bridges, D. W. H. Rankin, D. A. Clement, and J. F. Nixon, *Acta Cryst.*, 1972, **B28**, 1130.

[5] D. M. Bridges, G. C. Holywell, D. W. H. Rankin, and J. M. Freeman, *J. Organometallic Chem.*, 1971, **32**, 87.

[6] B. A. Frenz and J. A. Ibers, *Inorg. Chem.*, 1970, **9**, 2303.

[7] M. A. Bennett, G. B. Robertson, T. W. Turney, and P. O. Whimp, *Chem. Comm.*, 1971, 762.

[8] O. Stelzer and E. Unger, *J.C.S. Dalton*, in the press.

[9] M. Fild and R. Schmutzler, *J. Chem. Soc.* (*A*), 1970, 2359.

[10] M. Fild and O. Stelzer, unpublished results.

[11] K. Nakamoto, *Angew. Chem.*, 1972, **84**, 755; J. T. Wang, C. Udovich, K. Nakamoto, A. Quattrochi, and J. R. Ferraro, *Inorg. Chem.*, 1970, **9**, 2675; P. M. Boorman and A. J. Carty, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 101.

[12] D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

a Beckman IR 22 A and IR 11. N.m.r. spectra were recorded on a Varian HA 60A at 60 and 56·4 MHz for ^1H and ^{19}F respectively.

X-Ray Diffraction

A long prismatic crystal (0·028 × 0·028 × 0·06 cm) was sealed into a Lindemann glass capillary tube, and intensities were estimated visually from equi-inclination Weissenberg photographs (layers *hk*0—7 inclusive) taken with Ni-filtered Cu-K_α radiation. As it only proved possible to obtain good photographs for a crystal mounted about the *Z* [elongated] axis, it was necessary to make use of carefully timed exposures to estimate initial values for the inter-layer scale-factors. Lorentz, polarisation, and absorption corrections were applied. Accurate unit-cell dimensions were obtained from measurements of 37 *hk*0 and 18 *h*0*l* reflections on zero-layer Weissenberg photographs calibrated with tungsten ($a = 3·1653$ Å), using a least-squares routine which corrected for possible systematic eccentricity errors.

TABLE 1

Atom co-ordinates and isotropic vibrational amplitudes (Å × 10^4) with estimated standard deviations

Atom	x/a	y/b	z/c	U
C(3)	0·1358(17)	0·0329(11)	0·3897(19)	978(43)
C(4)	0·2963(21)	0·1743(14)	0·3808(23)	1236(58)
C(5)	0·3740(21)	0·0153(14)	0·2683(24)	1234(59)
C(6)	0·1477(16)	0·1815(12)	0·8012(19)	991(44)
C(7)	0·2644(18)	0·2819(12)	0·0132(21)	1072(49)
C(8)	0·3906(19)	0·1413(13)	0·9292(22)	1127(52)

TABLE 2

Atom co-ordinates and anisotropic vibrational amplitudes (Å × 10^4) † with estimated standard deviations

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br	0·7990(1)	0·0729(1)	0·0765(2)	569(8)	840(10)	1585(17)	−382(9)	217(8)	48(6)
Ni	0	0	0	500(13)	548(13)	625(17)	0	0	0
P	0·1419(3)	0·1124(2)	0·0985(4)	535(14)	571(15)	688(21)	−94(13)	135(13)	−18(12)
F	0·0499(7)	0·1932(5)	0·1644(9)	778(44)	703(41)	1125(58)	−394(40)	210(38)	−1(35)
C(1)	0·2465(14)	0·0844(9)	0·2870(15)	734(75)	882(85)	685(88)	−60(65)	45(62)	−74(62)
C(2)	0·2441(13)	0·1820(8)	0·9569(16)	705(70)	591(65)	945(96)	47(61)	110(63)	−73(54)

† The anisotropic temperature factor takes the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)]$.

Crystal Data.—$C_{16}H_{36}F_2P_2NiBr_2$, $M = 546·9$, Monoclinic, $a = 9·348(3)$, $b = 14·530(5)$, $c = 8·468(6)$ Å, $\beta = 93·69(6)°$, $U = 1149·0(9)$ Å^3, $D_m = 1·56$, $Z = 2$, $D_c = 1·58$. Cu-K_α radiation, $\lambda = 1·5418$ Å, μ (Cu-K_α) = 71·4 cm^{-1}. Centrosymmetric space group $P2_1/n$ (C^5_{2h}) uniquely determined from systematic absences: 0*k*0 with *k* odd, and *h*0*l* with $h + l$ odd. This is related to the standard space group $P2_1/c$ (No. 14) by the transformation matrix 0,0,$\bar{1}$ 0,1,0 1,0,1. In space group $P2_1/n$ the nickel atoms occupy two-fold special positions of the set (0,0,0; $\frac{1}{2},\frac{1}{2},\frac{1}{2}$) and all other atoms occupy four-fold general positions $\pm(x,y,z;\ \frac{1}{2}+x,\ \frac{1}{2}-y,\ \frac{1}{2}+z)$. The asymmetric unit consists of one half of one molecule.

Structure Solution and Refinement.—A three-dimensional Patterson synthesis was interpreted to give self-consistent sets of co-ordinates for the nickel, bromine, and phosphorus atoms. The remaining atoms, except for hydrogen, were located from difference electron-density syntheses. The structure was refined by full-matrix least squares, at first with isotropic temperature factors for all atoms. Interlayer scale factors were allowed to vary during the course of the initial refinement, but were then fixed on the introduction of anisotropic temperature factors. In the final cycles of refinement a total of 73 parameters were varied simultaneously, consisting of 33 positional parameters, 33 anisotropic temperature-factor components for the bromine, nickel, phosphorus, fluorine, and central butyl carbon atoms, 6 isotropic temperature factors for the other carbon atoms, and an overall scale factor. The introduction of anisotropic temperature factors for the non-central butyl carbon atoms did not produce a significant improvement in the generalised *R* index and, in addition, gave rise to several unrealistic values. An attempt to refine the Zachariasen secondary extinction coefficient [13] was likewise unsuccessful. Complex neutral-atom scattering factors [14,15] were employed for all atoms. The weighting scheme adopted was $w = (4·71 + |F_o| + 0·01276\ F_o^2)^{-1}$, which has been converted to an absolute scale of F_o.

The final weighted value $R'[=(\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}F_o)]$ was 0·098 for a total of 1243 unique observed reflections, with a corresponding unweighted index, *R*, of 0·088. A final difference-Fourier synthesis revealed some, but not all, of the hydrogen atom positions. No attempt was made to refine these. Otherwise, there were no unexpected features. The results from the final least-squares cycle are summarised in Tables 1 and 2; these results together with the full covariance matrix were used to calculate the bond lengths and angles, and their estimated standard deviations

TABLE 3

Interatomic distances (Å) and bond angles (°)

(*a*) Distances

Ni–Br	2·288(1)	Ni–P	2·232(3)
P–C(1)	1·86(1)	P–C(2)	1·88(1)
C(1)–C(3)	1·58(2)	C(2)–C(6)	1·55(2)
C(1)–C(4)	1·58(2)	C(2)–C(7)	1·54(2)
C(1)–C(5)	1·58(2)	C(2)–C(8)	1·53(2)
P–F	1·579(7)		

(*b*) Angles

P–Ni–Br	92·0(1)	F–P–Ni	110·6(3)
C(1)–P–Ni	115·3(4)	C(2)–P–Ni	118·1(4)
C(1)–P–F	97·3(5)	C(2)–P–F	97·9(5)
C(3)–C(1)–P	104·3(9)	C(6)–C(2)–P	104·4(9)
C(4)–C(1)–P	111·8(11)	C(7)–C(2)–P	111·6(10)
C(5)–C(1)–P	114·4(11)	C(8)–C(2)–P	112·9(10)
C(4)–C(1)–C(3)	107·8(12)	C(7)–C(2)–C(6)	108·8(12)
C(5)–C(1)–C(3)	106·3(12)	C(8)–C(2)–C(6)	110·3(12)
C(5)–C(1)–C(4)	112·1(13)	C(8)–C(2)–C(7)	108·6(12)
C(2)–P–C(1)	113·8(6)		

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[13] A. C. Larson, *Acta Cryst.*, 1967, **23**, 664.

[14] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[15] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

(Table 3). The shortest non-bonded distances are summarised in Table 4. Figure 1 shows the molecule in perspective, together with the numbering system, and Figure 2 the unit-cell contents shown in projection perpendicular to [001]. Final observed and calculated structure factors are noted in Supplementary Publication No. SUP 20652 (8 pp., 1 microfiche).*

TABLE 4

Selected non-bonded distances (Å), with transformations relating the co-ordinates of the second atom to those of the corresponding atom in the same asymmetric unit as the first atom

(*a*) Intramolecular, within the asymmetric unit (*x*, *y*, *z*)

Ni ··· F	3·155	Br ··· F	2·983
Ni ··· C(1)	3·47	Ni ··· C(2)	3·53
F ··· C(1)	2·59	F ··· C(2)	2·61
F ··· C(3)	3·08	F ··· C(6)	3·27
F ··· C(4)	2·87	F ··· C(7)	2·77
F ··· C(5)	4·04	F ··· C(8)	3·94

(*b*) Intramolecular, across the centre of symmetry (−*x*, −*y*, −*z*)

Br ··· C(1)	3·84	Br ··· C(2)	3·73
Br ··· C(3)	4·32	Br ··· C(6)	3·86
Br ··· C(5)	3·49	Br ··· C(8)	3·58
Br ··· P	3·139		

(*c*) Intermolecular (0·5 + *x*, 0·5 − *y*, 0·5 + *z*)

Br ··· C(4)	4·03	Br ··· C(7)	4·29
Br ··· C(6)	4·33	F ··· C(2)	4·30
F ··· C(4)	3·79	F ··· C(6)	4·40
F ··· C(7)	4·12	F ··· C(8)	3·67
C(4) ··· C(6)	3·99	C(4) ··· C(7)	4·50
C(6) ··· C(7)	4·24		

(*d*) Intermolecular (0·5 − *x*, 0·5 + *y*, 0·5 − *z*)

C(3) ··· C(7)	3·84	C(5) ··· C(7)	4·11

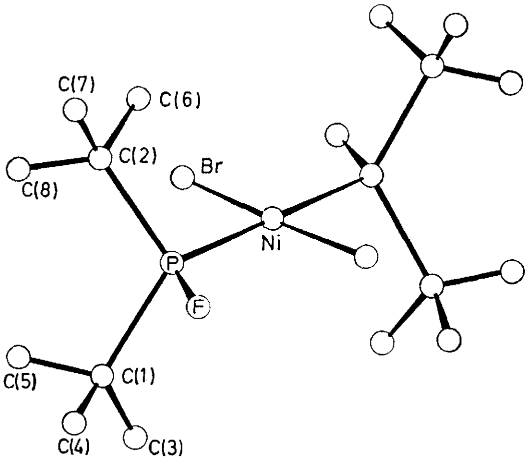

FIGURE 1 Molecular structure

DISCUSSION

The molecule $NiBr_2(PFBu^t_2)_2$ is *trans*-square planar and possesses a centre of symmetry. The weighted least-squares plane through the Br, Ni, P, and F atoms has the equation $0{\cdot}0382x - 0{\cdot}4557y + 0{\cdot}8851z = 0{\cdot}0124$. In this calculation the atoms were assigned weights equal to their atomic numbers. Deviations from this plane (Å) are: Br 0·006, Ni −0·012, P 0·032, and F −0·042. Thus the Ni,P,F plane makes a small dihedral angle of 3·8° with that of the Br, Ni, and P atoms.

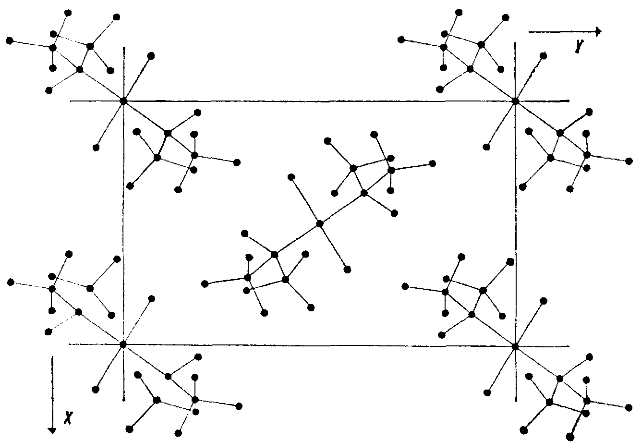

FIGURE 2 Projection of the crystal structure perpendicular to [001]

Results of previous structural studies [2,3,16–21] of complexes of the type $NiX_2(PR_3)_2$ (X = Cl or Br), and some other relevant compounds have been summarised in Table 5. It was concluded from a study [18] of $NiBr_2(PhCH_2PPh_2)_2$, in which both tetrahedral and *trans*-square planar molecules exist within the same unit cell, that the bond dimensions to be expected in *trans*-

TABLE 5

Bond lengths (Å) in $NiX_2(PR_3)_2$ (X = Cl or Br) and related complexes, with estimated standard deviations in parentheses

	Bond lengths		
Compound	Ni–X	Ni–P	Structure
$NiBr_2(PPh_3)_2$ [a]	2·346(3)	2·323(5)	Dist. tet.
$NiBr_2(PEt_3)_2$ [b]	2·30	2·26	*trans*-sq. pl.
$NiBr_2(PhCH_2PPh_2)_2$ [c]	2·305(3)	2·263(7)	*trans*-sq. pl.
	2·351(5)	2·316(7)	Tet.
	2·359(4)	2·314(8)	
$NiBr_2(PFBu^t_2)_2$ [d]	2·288(1)	2·232(3)	*trans*-sq. pl.
$NiCl_2(PPh_3)_2$ [e]	2·27	2·28	Dist. tet.
$NiCl_2Y_2$ [f]	2·212(2)	2·154(2)	*cis*-sq. pl.
$Ni(PF_3)_4$		2·099(3) [g]	Tet.
		2·116(10) [h]	Tet.
$Ni(Et_3P)_2(C{\equiv}CPh)_2$ [i]		2·174(5)	*trans*-sq. pl.

[a] Ref. 16. [b] Ref. 17. [c] Ref. 18. [d] This work. [e] Ref. 19. [f] Ref. 20; Y = 1-benzyl-Δ^3-phospholen. [g] Ref. 2. [h] Ref. 3. [i] Ref. 21. Dist. = Distorted, tet. = tetrahedral, sq. pl. = square planar.

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[16] J. A. Jarvis, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc.* (*A*), 1968, 1473.

[17] G. Giacometti, V. Scatturin, and A. Turco, *Gazzetta*, 1958, **88**, 434.

[18] B. T. Kilbourne and H. M. Powell, *J. Chem. Soc.* (*A*), 1970, 1688.

[19] G. Garton, D. H. Henn, H. M. Powell, and L. M. Venanzi, *J. Chem. Soc.*, 1963, 3625.

[20] A. T. McPhail, R. C. Komson, J. F. Engel, and L. D. Quin, *J.C.S. Dalton*, 1972, 874.

[21] G. R. Davies, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc.* (*A*), 1967, 1750.

square planar complexes are significantly shorter than those in tetrahedral complexes: for Ni–Br, 0·05, and for Ni–P, 0·05 Å. Therefore, in $NiBr_2(PFBu^t_2)_2$ the Ni–Br bond length of 2·288(1) Å is slightly shorter than the values observed previously in analogous molecules. A more pronounced shortening is observed in the case of the Ni–P bond length [2·232(3) Å]. However, the shortening of the Ni–P bond length of *ca.* 0·03 Å is very small when compared with that observed in tetrahedral $Ni(PF_3)_4$. It may be inferred that the role of π bonding in square planar complexes is not greatly enhanced by the replacement of alkyl- or aryl-phosphine ligands by the Bu^t_2FP ligand. It will require further structural work to elucidate the effects of bivalent nickel, of only one fluorine on the phosphorus, or of different hybridisation in square planar as opposed to tetrahedral complexes.

The P–F bond length [1·579(7) Å] does not differ significantly from that observed for PF_3.[22] The C–P–F angles [97·3(5) and 97·9(5)°] are also similar to the F–P–F angles [97·8(2)°] observed for that compound.

The P–C(1) and P–C(2) bond lengths [1·86(1) and 1·88(1) Å] agree closely with the value quoted [23] for the sum of the covalent radii (1·87 Å). The mean value [1·56(2) Å] for the C–C bond length agrees with accepted values,[24] but it is difficult to understand why a mean value of 1·58(2) Å is obtained for the C–C bonds within the C(1) butyl group, whereas a value of 1·54(2) Å is found for those within the C(2) butyl group.

The tertiary butyl groups are distorted from tetrahedral symmetry as evidenced by the small P–C(1)–C(3) and P–C(2)–C(6) angles of 104·3(9) and 104·4(9)°. It seems reasonable to attribute this effect to steric interactions, as demonstrated in particular by the short intramolecular F · · · C(4), F · · · C(7), Br · · · C(5), and Br · · · C(8) distances.

Calculations were carried out on the Braunschweig ICL 1907 computer. Data reduction, least-squares refinement, and Fourier operations were performed by use of programs written by Dr. G. M. Sheldrick. All other programs were written by W. S. S., who thanks the Alexander von Humboldt-Stiftung for the award of a research fellowship.

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[22] Y. Morino, K. Kuchitzu, and T. Moritani, *Inorg. Chem.*, 1969, **8**, 867.

[23] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960.

[24] *Chem. Soc. Special Publ.*, No. 11, 1958; No. 18, 1965.