Synthesis, Crystal, and Molecular Structure of Paramagnetic Tri-t-butylphosphonium Tribromo(tri-t-butylphosphine)nickelate(II)

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Reaction of tri-t-butylphosphine with nickel(II) bromide in alcoholic solution yields green $[Bu^t{}_3PH][(Bu^t{}_3P)NiBr_3]$. Conductivity, magnetic-susceptibility, and electronic spectral measurements, and *X*-ray single-crystal analysis indicated the structure to be the same in solution as in the solid state. Crystals are monoclinic, space group *Cc*, with cell dimensions *a* = 24·069(3), *b* = 13·896(4), *c* = 18·739(2) Å, β = 148·91(1)°, *Z* = 4. The structure was solved by conventional heavy-atom methods and refined to *R* 0·088 for 1839 observed reflexions. Structural data for the paramagnetic anion, which has nearly C_{3v} symmetry (excluding the butyl groups), particularly reflect the bulkiness of the $Bu^t{}_3P$ ligand; mean dimensions: Br–Ni–Br 108·7°, P–C 2·02(10) and Ni–Br 2·38(2) Å, and a Ni–P bond length of 2·48(1) Å. The calculated $Ni–PBu^t{}_3$ cone angle is 180 ± 2°. The P(2)–H bond of the cation lies near the pseudo C_3 axis of the anion so that Ni ··· P(2) is 4·48 Å, with P(2) ··· Br 4·27—4·31 Å. These interion contacts indicate strong ion-pairing interaction in the solid-state structure.

EXTENSIVE investigations[1,2] on nickel(II) phosphine complexes of the type $[Ni(PR_3)_2X_2]$ have been principally concerned with the various factors which influence the adoption of a planar (diamagnetic) or a tetrahedral (paramagnetic) geometry. By contrast, few examples of pseudotetrahedral $[Ni(PR_3)X_3]^-$ complexes are known,[2,3] though a crystal-structure determination has confirmed the structure of the $[Ni(PPh_3)I_3]^-$ anion.[4] We report the *X*-ray structural determination of a paramagnetic nickel(II) complex of the latter type, and give

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[1] L. Sacconi, *Transition Metal Chem.*, 1968, **4**, 199, and refs. therein.

[2] K. K. Chow, W. Levason, and C. A. McAuliffe, in 'Transition-Metal Complexes of Phosphorus, Arsenic, and Antimony Ligands,' ed. C. A. McAuliffe, MacMillan, London, 1973, p. 33, and refs. therein.

[3] F. A. Cotton, O. D. Faut, and D. M. L. Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 344.

[4] R. P. Taylor, D. H. Templeton, A. Zalkin, and W. De. W. Horrocks, jun., *Inorg. Chem.*, 1968, **7**, 2629.

the first details of the stereochemistry of a tri-t-butylphosphine complex.[5]

The characterization of $[Ni(PR_3)_2X_2]$ complexes by various physical methods [1,2] allows the conclusion that, in general, aryldi- and tri-alkylphosphines exist as planar diamagnetic complexes both in the solid state and in solution, while triarylphosphines are paramagnetic and have tetrahedral structures. Confirmation of this prediction by *X*-ray analysis exists for several complexes.[6] With certain alkyldiarylphosphines, steric and electronic factors lead to a delicate balance as to which stereochemical arrangement is adopted. In the case of the green paramagnetic form of bis(benzyldiphenylphosphine)dibromonickel(II), the crystal structure [7] revealed both planar and tetrahedral configurations in the same unit cell. In allowing tri-t-butylphosphine to react with nickel(II) bromide, we expected to isolate square-planar or tetrahedral $[Ni(PBu^t_3)_2Br_2]$ by analogy with $[Ni\{P(C_6H_{11})_3\}_2X_2]$,[6d] since the bulkiness of both ligands is comparable.[8] Elemental analysis of the product suggested the possibility of air oxidation to $[Ni(PBu^t_3)_2Br_3]$ by comparison with $[Ni(PMe_2Ph)_2Br_3]$.[9] Isolation of the green paramagnetic compound which was shown by this *X*-ray analysis to be $[Bu^t_3PH][(Bu^t_3P)NiBr_3]$ was thus surprising, especially in view of the known synthetic routes to $[(Ph_3P)NiX_3]^-$ species.[3]

EXPERIMENTAL

Addition of Bu^t_3P (2 : 1 molar ratio) to $NiBr_2$ in ethanol or n-butanol under dry nitrogen gives a green solution from which a green solid was isolated. It was recrystallized from dichloromethane as dark green crystals [m.p. (decomp.) 195—196 °C], with analysis corresponding to $[Bu^t_3PH]$-$[(Bu^t_3P)NiBr_3]$ (I) (Found: C, 40·85; H, 7·70; Br, 34·45; $C_{24}H_{55}Br_3NiP_2$ requires C, 40·94; H, 7·87; Br, 34·05%). Although it is stable in air, solutions in dichloromethane and nitromethane decompose when set aside making physical measurements difficult. Solution (mmol) in dry acetonitrile had molar conductance 223 ohm^{-1} cm^{-2}; room-temperature solid-state magnetic moment 3·73 B.M. (Faraday method), solution measurement (Evans n.m.r. method) $\mu_{eff.}$ 3·87 B.M. Dichloromethane solution, electronic absorption bands (nm, molar extinction coefficients in parentheses): 382(3220), 540(13), 675(198), 720(194), 1040(45), 1140(55), and 1680(27b). Solid-state transmittance spectrum (Nujol mull): 388, 544, 690, 720, 1040, 1138, and 1670b nm.

Crystal Data.—$C_{24}H_{55}Br_3NiP_2$, $M = 704\cdot1$, Monoclinic, $a = 24\cdot069(3)$, $b = 13\cdot896(4)$, $c = 18\cdot739(2)$ Å, $\beta = 148\cdot91(1)°$, $U = 3236$ Å^3, $D_m = 1\cdot44(1)$, $Z = 4$, $D_c = 1\cdot44$, $F(000) = 1448$. Mo-K_α radiation, $\lambda = 0\cdot71069$ Å; $\mu(\text{Mo-}K_\alpha) = 46\cdot1$ cm^{-1}. Space group $C2/c$ or Cc (C_s^4, No. 9) from systematic absences: hkl for $h + k \neq 2n$, $h0l$ for h, $l \neq 2n$; shown to be Cc (see later).

Crystallographic Measurements.—Preliminary precession and Weissenberg photographs indicated monoclinic symmetry. The correct choice of space group (Cc) was eventually made after detailed analysis of the three-dimensional Patterson function (see later). Accurate unit-cell data were obtained from least-squares refinement of diffractometer setting angles of 12 reflexions. The crystal chosen for data collection was a cube *ca.* 0·33 × 0·35 × 0·37 mm. Intensity data were collected to $\theta_{max.}$ 25° on a Hilger and Watts Y 290 PDP 8I controlled diffractometer by use of graphite monochromatized Mo-K_α radiation. The θ—2θ scan technique was used with a symmetric scan of 0·8°, in steps of 0·01° s^{-1}. Stationary-crystal–stationary-counter background counts of 20 s were measured at each end of the integrated scan. The intensities of 3 standard reflexions, measured every 100 reflexions, showed a gradual decay (9·2%) at the end of data collection, indicating slow decomposition of the crystal. This was corrected for by scaling, making use of the standard-reflexion data and assuming decay to be linear between standards. Each intensity was corrected for background and the estimated standard deviation in intensity was obtained from $\sigma(I) = [S + 4(b_1 + b_2)]^{1/2}$, where S is the scan count and b_1 and b_2 are the two background counts. Of 2855 reflexions 1839 had $I > 3\sigma(I)$ and were considered observed and used in the solution and refinement of the structure. Data were corrected for Lorentz and polarization factors.

Structure Solution and Refinement.—An analysis of intensity distribution and E statistics gave a clear indication that the space group was the centrosymmetric $C2/c$ rather than the non-centrosymmetric Cc (Table 1). However, detailed analysis of the three-dimensional Patterson function in order to locate the heavy atoms, showed Cc to be correct because of the absence of vector peaks appropriate to $C2/c$. The first electron-density distribution, calculated [10] with phases obtained from structure-factor calculations on nickel and bromine atoms, clearly revealed all the carbon and phosphorus atom positions. The structure was refined by block-diagonal least-squares methods, initially with isotropic and finally with anisotropic thermal parameters. Absolute weights were used throughout and scattering factors for all atoms were obtained from ref. 11, with corrections for real and imaginary parts of the anomalous dispersion included for nickel and bromine.[12] The refinement converged when R was 0·088 and R' $\{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{\frac{1}{2}}\}$ was 0·101. On the last cycles of refinement the maximum shift in any positional parameter was $< 0\cdot35$ σ.

TABLE 1

$|E|$ Statistics and distribution

Mean	Found	Calc.	
		Centric	Acentric
$\lvert E \rvert$	0·800	0·798	0·886
$\lvert E^2 \rvert$	0·992	1·000	1·000
$\lvert E^2 - 1 \rvert$	0·963	0·968	0·736
$\lvert (E^2 - 1) \rvert^2$	1·793	2·000	1·000
$\lvert (E^2 - 1) \rvert^3$	7·411	8·000	2·000

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[5] M. Matsumoto, H. Yoshioka, K. Nakatsu, T. Yoshida, and S. Otsuka, *J. Amer. Chem. Soc.*, 1974, **96**, 3322.

[6] (*a*) G. Garton, D. E. Henn, H. M. Powell, and L. M. Venanzi, *J. Chem. Soc.*, 1963, 3625; (*b*) J. A. J. Jarvis, R. H. B. Mais, and P. G. Owston, *ibid.*, 1968, 1473; (*c*) G. Giacometti, V. Scatturin, and A. Turco, *Gazzetta*, 1958, **88**, 434; V. Scatturin and A. Turco, *J. Inorg. Nuclear Chem.*, 1958, **8**, 447; (*d*) P. L. Bellon, V. Albano, V. D. Bianco, F. Pompa, and V. Scatturin, *Ricerca Sci.*, 1963, **33**, 1213.

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

[8] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 2956.

[9] D. W. Meek, E. C. Alyea, J. K. Stalick, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1969, **91**, 4920.

[10] J. M. Stewart, '*X*-Ray '72,' Technical Report TR 192, 1972, University of Maryland Computer Science Center, College Park, Maryland.

[11] D. T. Cromer and J. Mann, *Acta Cryst.*, 1968, **A24**, 321.

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

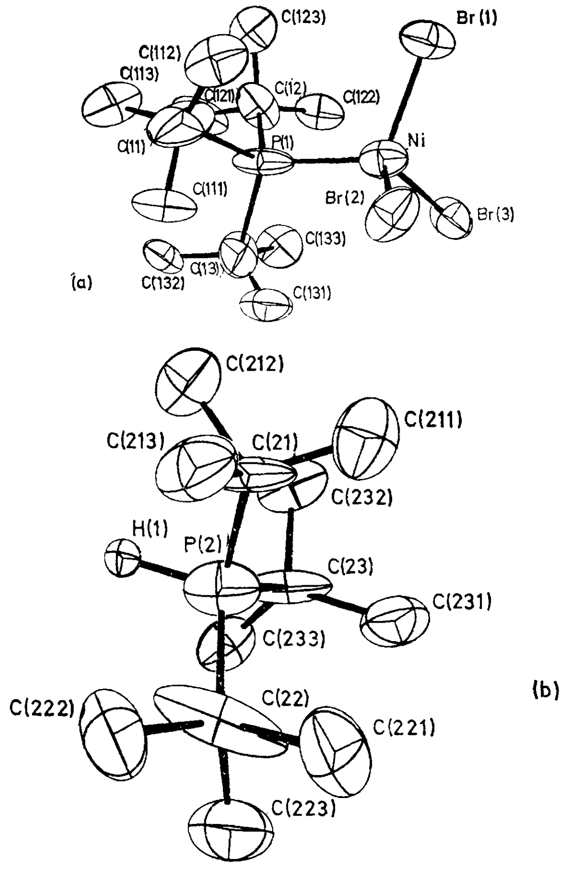

FIGURE 1 Views of (a) the $[(Bu^t_3P)NiBr_3]^-$ ion and (b) the $[Bu^t_3PH]^+$ ion; thermal ellipsoids are drawn at 50% probability level

TABLE 2

Final positional parameters

Atom	*x*	*y*	*z*
Ni	0·0603(5)	0·4998(4)	0·3342(6)
Br(1)	−0·0767(4)	0·5822(3)	0·2490(5)
Br(2)	0·0838(4)	0·5783(3)	0·2490(5)
Br(3)	0·0 *	0·3393(2)	0·2500 *
P(1)	0·2326(9)	0·5005(6)	0·5905(13)
C(11)	0·3033(40)	0·6309(38)	0.6689(46)
C(12)	0·2121(31)	0·4677(34)	0·6707(37)
C(13)	0·3368(29)	0·4015(33)	0·6641(38)
C(111)	0·3610(32)	0·6235(29)	0·6485(44)
C(112)	0·2133(36)	0·7014(20)	0·5697(48)
C(113)	0·3916(39)	0·6421(30)	0·8226(43)
C(121)	0·3158(34)	0·4446(32)	0·8292(47)
C(122)	0·1232(30)	0·3974(24)	0·5753(42)
C(123)	0·1608(33)	0·5740(30)	0·6436(46)
C(131)	0·3208(32)	0·4026(28)	0·5703(45)
C(132)	0·4534(28)	0·4117(34)	0·8281(43)
C(133)	0·2876(34)	0·3038(20)	0·6526(46)
P(2)	0·2529(9)	0·0006(7)	0·3711(11)
C(21)	0·1725(32)	0·0954(23)	0·3192(45)
C(22)	0·3000(41)	0·0229(23)	0·3355(63)
C(23)	0·1969(34)	−0·1206(20)	0·3247(45)
C(211)	0·0473(34)	0·0929(36)	0·1707(46)
C(212)	0·1940(36)	0·0899(31)	0·4306(47)
C(213)	0·2106(37)	0·2007(23)	0·3449(49)
C(221)	0·2024(37)	0·0592(34)	0·1725(49)
C(222)	0·3884(31)	0·1036(29)	0·4342(45)
C(223)	0·3423(36)	−0·0704(35)	0·3361(50)
C(231)	0·1017(36)	−0·1504(33)	0·1700(44)
C(232)	0·1451(36)	−0·1359(30)	0·3436(46)
C(233)	0·2946(35)	−0·1915(26)	0·4311(46)
H(1)	0·340	0·014	0·515

* Origin specification in space group *Cc*.

At the conclusion of the refinement, a difference map was calculated and contained a number of small peaks, one of the most significant being 0·9 $e\text{Å}^{-3}$ in a position corresponding to the phosphonium hydrogen atom (see Figure 1b). A number of other small peaks were close to the methyl carbons of the t-butyl groups but no logical ordered array of methyl hydrogen atoms could be discerned.

TABLE 3

Interatomic distances (Å) and angles (°)

(*a*) Anion

(i) Distances

Ni–Br(1)	2·39(1)	C(11)–C(112)	1·49(6)
Ni–Br(2)	2·37(2)	C(11)–C(113)	1·53(9)
Ni–Br(3)	2·38(1)	C(12)–C(121)	1·57(6)
Ni–P(1)	2·48(1)	C(12)–C(122)	1·48(6)
P(1)–C(11)	2·01(5)	C(12)–C(123)	1·70(8)
P(1)–C(12)	1·99(10)	C(13)–C(131)	1·44(14)
P(1)–C(13)	2·04(6)	C(13)–C(132)	1·60(5)
C(11)–C(111)	1·73(16)	C(13)–C(133)	1·70(9)

(ii) Angles

Br(1)–Ni–Br(2)	108·6(3)	C(111)–C(11)–P(1)	97·0(43)
Br(1)–Ni–Br(3)	107·3(4)	C(112)–C(11)–P(1)	105·3(30)
Br(2)–Ni–Br(3)	110·3(5)	C(113)–C(11)–P(1)	114·0(48)
Br(1)–Ni–P(1)	110·7(8)	C(121)–C(12)–C(122)	117·6(51)
Br(2)–Ni–P(1)	109·6(7)	C(121)–C(12)–C(123)	108·3(50)
Br(3)–Ni–P(1)	110·3(3)	C(122)–C(12)–C(123)	106·6(44)
Ni–P(1)–C(11)	112·6(16)	C(121)–C(12)–P(1)	117·1(56)
Ni–P(1)–C(12)	112·1(12)	C(122)–C(12)–P(1)	106·1(53)
Ni–P(1)–C(13)	110·8(18)	C(123)–C(12)–P(1)	99·3(46)
C(13)–P(1)–C(12)	106·9(28)	C(131)–C(13)–C(132)	122·5(64)
C(13)–P(1)–C(11)	109·3(29)	C(131)–C(13)–C(133)	115·3(46)
C(12)–P(1)–C(11)	104·8(38)	C(132)–C(13)–C(133)	101·6(45)
C(111)–C(11)–C(112)	110·3(73)	C(131)–C(13)–P(1)	106·2(29)
C(111)–C(11)–C(113)	109·7(59)	C(132)–C(13)–P(1)	110·9(45)
C(112)–C(11)–C(113)	118·2(72)		

(*b*) Cation

(i) Distances

P(2)–H(1)	1·42	C(22)–C(221)	1·68(10)
P(2)–C(21)	1·78(6)	C(22)–C(222)	1·57(6)
P(2)–C(22)	1·77(15)	C(22)–C(223)	1·64(12)
P(2)–C(23)	1·84(4)	C(23)–C(231)	1·56(7)
C(21)–C(211)	1·57(5)	C(23)–C(232)	1·57(16)
C(21)–C(212)	1·67(15)	C(23)–C(233)	1·56(6)
C(21)–C(213)	1·57(6)		

(ii) Angles

C(21)–P(2)–C(22)	114·2(33)	C(221)–C(22)–C(223)	98·3(73)
C(22)–P(2)–C(23)	115·4(39)	C(221)–C(22)–P(2)	112·9(59)
C(21)–P(2)–C(23)	113·8(33)	C(222)–C(22)–P(2)	109·9(76)
C(211)–C(21)–C(212)	106·5(72)	C(223)–C(22)–P(2)	116·9(52)
C(212)–C(21)–C(213)	110·7(55)	C(231)–C(23)–C(232)	101·3(54)
C(211)–C(21)–C(213)	107·2(31)	C(232)–C(23)–C(233)	104·1(61)
C(211)–C(21)–P(2)	119·2(41)	C(231)–C(23)–C(233)	114·3(53)
C(212)–C(21)–P(2)	104·7(31)	C(231)–C(23)–P(2)	115·7(48)
C(213)–C(21)–P(2)	116·4(59)	C(232)–C(23)–P(2)	114·6(47)
C(221)–C(22)–C(222)	107·6(54)	C(233)–C(23)–P(2)	106·3(34)
C(222)–C(22)–C(223)	110·5(67)		

(*c*) Interion contacts (with P < 4·5 and with C < 3·8 Å)

P(2) ··· Ni^{I}	4·48(1)	C(112) ··· C(232^{II})	3·72(11)
P(2) ··· Br(1^{I})	4·31(2)	C(131) ··· C(213)	3·68(8)
P(2) ··· Br(2^{I})	4·27(1)	C(223) ··· C(122^{III})	3·76(9)
P(2) ··· Br(3^{I})	4·29(1)		

Roman numeral superscripts refer to the following equivalent positions relative to the reference molecule at *x*, *y*, *z*:

I $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ III $\frac{1}{2} + x, y - \frac{1}{2}, z$
II $x, 1 + y, z$

Final positional parameters from the refinement and the co-ordinates of the phosphonium hydrogen atom are listed in Table 2, and bond lengths, angles, and intra- and inter-ion distances in Table 3. Structure-factor data, thermal parameters, and details of planes are listed in Supplementary Publication No. SUP 21305 (28 pp., 1 microfiche).*

RESULTS AND DISCUSSION

Anion Geometry.—The anion, cation, and the atom labelling scheme are illustrated in Figure 1. This *X*-ray analysis has established the pseudotetrahedral geometry around the nickel atom suggested by the comparison of the magnetic and spectral properties of the green product with those previously published [3] for the $[(Ph_3P)NiBr_3]^-$ anion. The similarity of the solution and solid-state magnetic and spectral data for $[(Bu^t_3P)NiBr_3]^-$ strongly infers that the same configuration is retained in solution as in the solid state.

The mean Ni–Br bond lengths [2·38(2) Å] are comparable to those in tetrahedral complexes of the type $[Ni(PR_3)_2Br_2]$ (2·35 Å) [6b,7] but longer than in square-planar complexes of the type $[Ni(PR_3)_2Br_2]$ (2·30 Å).[6c,d,7,9] A mean Ni–Br distance of 2·375 Å was reported for $[Ni(quinoline)Br_3]^-$,[13] the only other nickel anion having nearly C_{3v} symmetry for which Ni–Br bond lengths are known. A tetrahedral covalent radius for Ni^{II} of 1·27 Å has been calculated [4] using tetrahedral covalent radii for the halogens (Cl 0·99, Br 1·11, and I 1·28 Å) [14] and Ni–I 2·55 Å, the mean value in $[Ph_4As][(Ph_3P)NiI_3]$.[4] On this basis, one predicts Ni–Br 2·38 Å in pseudotetrahedral complexes of type $[LNiBr_3]^-$, and the values observed in $[(Bu^t_3P)NiBr_3]^-$ are in excellent agreement with this.

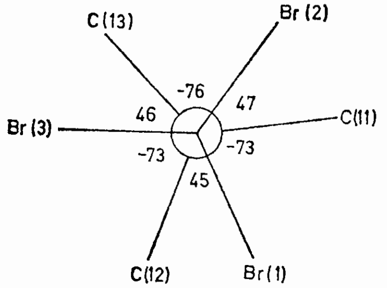

FIGURE 2 Torsion angles about the bond between Ni and P(1) in the $[(Bu^t_3P)NiBr_3]^-$ anion

The tribromo-groups of the anion are rotationally staggered with respect to the carbon atoms attached to the phosphorus of the Bu^t_3P group (Figure 2) giving the anion nearly C_{3v} symmetry (excluding the butyl groups). The P(1)–Ni bond is taken as the C_3 axis. The mean P–Ni–Br angle (110·2°) is only slightly greater than the tetrahedral angle (109·5°). The three Br–Ni–Br angles also vary slightly among themselves, the mean (108·7°) being slightly less than the tetrahedral angle. This contrasts significantly with mean angles in the $[(quinoline)NiBr_3]^-$ (N–Ni–Br 105·4, Br–Ni–Br 113·3°) [12] and $[(Ph_3P)NiI_3]^-$ (P–Ni–I 104·3, I–Ni–I 114·0°) [4] anions. Presumably there is greater steric repulsion of the halogens among themselves than with the co-ordinated ligand in the last two complexes. The greater steric interaction of the bromine atoms with the Bu^t_3P group does not permit the Br–Ni–Br angles to open up in the $[(Bu^t_3P)NiBr_3]^-$ anion. Rotational staggering of the tribromo-group relative to the Bu^t groups is doubtless also a manifestation of the bulkiness of the Bu^t_3P group since steric repulsion is thus minimized. Also, the higher $\mu_{eff.}$ for $[(Bu^t_3P)NiBr_3]^-$ is consistent with less distortion from true tetrahedral geometry than for $[(Ph_3P)NiI_3]^-$,[3,4] as might be inferred from the smaller Br–Ni–Br as compared to I–Ni–I angles.[3,4]

The Ni–P distance [2·48(1) Å] is considerably greater than that in $[(Ph_3P)NiI_3]^-$ (2·28 Å) [4] or in the tetrahedral form of $[Ni\{P(CH_2Ph)Ph_2\}Br_2]$ (2·31 Å).[6b] The Ni–P bond length is normally near 2·30 Å in tetrahedral and 2·25 Å in square-planar complexes of type $[Ni(R_3P)_2Br_2]$.[6,7,9] The elongated Ni–P bond length in the $[(Bu^t_3P)NiBr_3]^-$ anion is attributed to the inability of the bulky phosphine to approach within a normal bonding distance because of steric repulsion between the bromine atoms and the Bu^t groups. In a study of the positions of equilibria set up on addition of free phosphine ligands to solutions of $[NiL_4]$ (L = phosphine ligand), Tolman [8] concluded that the stability of the complexes are dominated by the steric interactions between ligands in the complexes and that electronic effects are relatively unimportant. He also showed that the binding energies correlated reasonably well with the apex angle formed at the centre of the nickel atom by the minimum cone containing the ligand, *i.e.* the apex angle of a cone, centred on the metal, which encloses the van der Waals radii of the outermost atoms of the ligand. In the case of Bu^t_3P, taking Ni–P as 2·28 Å, the cone angle was estimated [8] to be 182 ± 2°, considerably greater than that estimated for Ph_3P (145 ± 2°), the most widely used phosphorus ligand. Cone-angle calculations from the co-ordinates of Table 2 yield 180 ± 2° for the Bu^t_3PNi group in $[(Bu^t_3P)NiBr_3]^-$ in excellent agreement with the predicted value. The effect that t-butyl-substituted phosphines have on the co-ordination number and reactivity of metal complexes has been demonstrated by Shaw and co-workers in a number of studies.[15] An alternative explanation for the long Ni–P distance in the $[(Bu^t_3P)NiBr_3]^-$ anion in terms of weaker σ- or π-bonding ability of Bu^t_3P is untenable. Although the π-acceptor strength of the trialkylphosphine is very low relative to that of other phosphines,[8] the role of π-bonding in metal(II)–phosphorus bonds is now considered to be energetically insignificant.[16] The σ-bonding ability of Bu^t_3P should be comparable to that of Me_3P, whose high basicity enables it to form a range of complexes with Ni^{II} and other metal ions.[2]

Cation Geometry.—Juxtaposition of the cation and the neighbouring anions is shown in Figure 3. The t-butyl

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1974, Index issue.

[13] W. De W. Horrocks, jun., D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, 1968, **7**, 2303.

[14] L. Pauling, ' The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 246, Table 7–13.

[15] See *e.g.*, B. L. Shaw and R. E. Stainbank, *J.C.S. Dalton*, 1972, 223.

[16] A. Pidcock, ref. 2, p. 1.

groups are disposed in an approximate tetrahedral array about the phosphorus atom. The mean C–P–C angles are 114·5°, the greatest deviation from the tetrahedral angle being 5·9° for C(22)–P(2)–C(23). Opening up of the tetrahedral angle to relieve steric repulsion between the t-butyl groups is a consequence of the small stereochemical influence of the phosphonium hydrogen atom. By contrast, the greater bulk of the $NiBr_3$ moiety causes the C–P–C angles in the anion to be decreased to a mean of 107·0°. The mean C–C–P(2) and C–C–C angles in the cation are 112·9 and 105·6°, respectively, and the corresponding mean C–C–P(1) and C–C–C angles in the anion are 105·9 and 112·1°. This reversal in bond-angle values is apparently a consequence of the different environments of the two $Bu^t{}_3P$ groups.

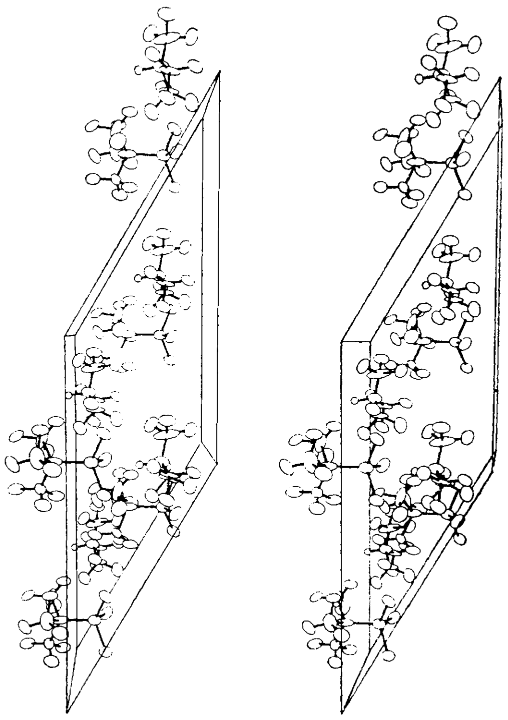

FIGURE 3 The ionic packing diagram

The mean P–C bond length [1·81(10) Å] is in excellent agreement with that reported recently for $[(PhCH_2)PPh_3]^+Cl^-$.[17] By contrast, the mean P–C bond length [2·02(10) Å] for the $Bu^t{}_3P$ group in the anion is significantly greater, although a slight increase in P–C distance is to be expected.[4,6]

The P(2)–H(1) bond distance was calculated to be 1·42 Å, using the hydrogen position found in the difference synthesis, and is in good agreement with the P–H distance (1·414 Å) determined for the tetrahedral PH_4^+ ion.[18]

Overall Geometry.—The crystal structure consists of discrete cations and anions. However, the packing diagram (Figure 3) shows that the P–H bond of the cation lies near the C_3 axis defined for the anion, on the side of the nickel atom opposite the co-ordinated $Bu^t{}_3P$ ligands. The bonding interaction implied by this orientation requires discussion as to whether the packing of the cation and anion in the solid-state structure is principally due to the minimization of the free-energy of the entire crystal lattice or to a specific ion-pairing interaction.

The two ions are oriented in the crystal so that the P(1)–Ni ··· H–P(2) system is essentially linear (178·7°) with the shortest calculated interion contacts [Table 3(*c*)] being between the cation-phosphorus and the three anion-bromine atoms [P(2) ··· Br 4·27—4·31 Å]. The Ni ··· P(2) distance (4·48 Å) represents one of the closest anion–cation approaches in the crystal. This interionic distance is significantly shorter than those (Ni ··· As 6·6—8·0 and Ni ··· N 6·0—6·9 Å) found for the complexes $[Ph_4As][Ni(Ph_3P)I_3]$ [4] and $[Bu_4N][Ni(quinoline)Br_3]$,[13] respectively. Horrocks and associates [4,13] suggested that the dominant mode of counterion approach in ion pairs in solution (along the 'C_3' axis) was not necessarily the same in the solid-state structure. Our results show that a strong interionic interaction does indeed exist along the C_3 axis of the anion in the crystal lattice of $[Bu^t{}_3PH][(Bu^t{}_3P)NiBr_3]$. Separate studies will be required to observe whether strong ion–ion interaction also occurs in solution.

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