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Tetraphenylarsonium Tribromo(triphenylphosphine)nickelate(II)

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Abstract. $C_{24}H_{20}As^+$. $C_{18}H_{15}Br_3NiP^-$, $[As(C_6H_5)_4][Ni(C_6H_5)_3PBr_3]$, monoclinic, $P2_1/c$, $a = 15{\cdot}798$ (2), $b = 9{\cdot}975$ (1), $c = 25{\cdot}142$ (4) Å, $\beta = 93{\cdot}46$ (2)°, $U = 3954{\cdot}8$ Å^3, $Z = 4$, $D_c = 1{\cdot}585$ Mg m^{-3}, μ(Cu $K\alpha$) = 5·53 mm^{-1}. Final $R = 0{\cdot}038$ for 5064 independent reflections. The pseudo-tetrahedral anion has approximate C_3 symmetry and in the tetraphenylarsonium-ion coordination round the As atom is virtually tetrahedral. The structure consists of these discrete anions and cations with a Ni···As distance of 7·18 Å.

Introduction. This study was undertaken as a continuation of our current interest in the detailed electronic and magnetic properties of trigonally distorted tetrahedral complexes (Gerloch & Hanton, 1980) and their interpretation within the bonding-orientated angular-overlap model which provides a unique probe for the relative roles of σ and π bonding in transition-metal complexes. In addition, recent studies (Davies, Gerloch & Phillips, 1979; Falvello & Gerloch, 1980) of metal–phosphine complexes with the angular-overlap model have demonstrated a significant π acidity for phosphine ligands, so that this compound provides a further opportunity to extend our investigations of the π-acceptor role of phosphine ligands in such first-row transition-metal complexes.

The anion was originally prepared as the tetraethylammonium salt (Cotton, Faut & Goodgame, 1961). However, Weissenberg photographs indicated that the crystals were cubic ($a = 17{\cdot}92$ Å), hence unsuitable for magnetic-anisotropy studies. The tetraphenylarsonium salt was then prepared in an analogous manner. Suitable green crystals were obtained by cooling the reaction mixture. These crystals have two different morphologies and it is the structure of the diamond-shaped monoclinic form that is reported. {The other square plate-like form was determined to be orthorhombic ($a = 18{\cdot}57$, $b = 9{\cdot}98$, $c = 21{\cdot}41$ Å) from Weissenberg photographs. The cell volume and experimental density [1·53 (5) Mg m^{-3}] imply $Z = 4$, and, since it is unlikely that the molecule would occupy a special position in the lattice, the

Table 1. *Atom coordinates* (×10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^3)

	x	y	z	U_{eq}
Ni(1)	2389 (1)	1636 (1)	3818 (1)	49 (1)
Br(1)	1607 (1)	3143 (1)	4324 (1)	64 (1)
Br(2)	2479 (1)	2290 (1)	2912 (1)	54 (1)
Br(3)	3736 (1)	972 (1)	4191 (1)	85 (5)
P(1)	1597 (1)	−327 (1)	3774 (1)	40 (1)
C(1)	1259 (3)	−863 (4)	4417 (2)	48 (3)
C(2)	489 (4)	−1456 (5)	4483 (2)	71 (4)
C(3)	245 (5)	−1844 (6)	4981 (3)	98 (5)
C(4)	780 (5)	−1653 (6)	5414 (3)	101 (7)
C(5)	1542 (5)	−1027 (8)	5359 (3)	112 (6)
C(6)	1783 (4)	−635 (6)	4857 (2)	83 (5)
C(7)	616 (2)	−243 (4)	3352 (2)	44 (2)
C(8)	246 (3)	−1404 (4)	3127 (2)	55 (3)
C(9)	−515 (3)	−1331 (5)	2823 (2)	41 (4)
C(10)	−901 (3)	−101 (6)	2742 (2)	68 (4)
C(11)	−542 (3)	1044 (5)	2961 (2)	65 (4)
C(12)	217 (3)	977 (4)	3267 (2)	53 (3)
C(13)	2014 (3)	−3075 (4)	3669 (2)	51 (3)
C(14)	2149 (2)	−1756 (4)	3507 (2)	41 (2)
C(15)	2695 (3)	−1529 (4)	3109 (2)	59 (3)
C(16)	3085 (3)	−2597 (5)	2867 (2)	72 (4)
C(17)	2930 (3)	−3890 (4)	3026 (2)	62 (4)
C(18)	2398 (3)	−4124 (4)	3426 (2)	56 (3)
C(19)	4006 (3)	−123 (4)	1607 (2)	54 (3)
C(20)	4025 (3)	396 (5)	2116 (2)	58 (3)
C(21)	4606 (3)	−76 (5)	2506 (2)	65 (3)
C(22)	5178 (3)	−1045 (5)	2382 (2)	65 (4)
C(23)	5171 (3)	−1558 (5)	1873 (2)	68 (4)
C(24)	4585 (3)	−1106 (5)	1478 (2)	61 (3)
C(25)	3466 (3)	−104 (6)	395 (2)	70 (4)
C(26)	3427 (5)	−1483 (7)	334 (3)	98 (5)
C(27)	3639 (5)	−2026 (8)	−159 (3)	119 (6)
C(28)	3874 (4)	−1189 (11)	−553 (3)	118 (9)
C(29)	3875 (4)	154 (10)	−486 (3)	111 (8)
C(30)	3684 (3)	722 (7)	−13 (2)	81 (5)
C(31)	2067 (3)	189 (4)	1206 (2)	52 (3)
C(32)	1467 (3)	270 (6)	785 (2)	74 (4)
C(33)	619 (3)	91 (6)	883 (3)	82 (4)
C(34)	379 (3)	−136 (5)	1393 (3)	75 (5)
C(35)	975 (3)	−198 (5)	1805 (2)	75 (4)
C(36)	1841 (3)	−47 (5)	1715 (2)	69 (3)
C(37)	3342 (3)	2499 (5)	1131 (2)	64 (4)
C(38)	2752 (4)	3236 (5)	1384 (2)	78 (4)
C(39)	2873 (4)	4592 (6)	1491 (3)	91 (5)
C(40)	3590 (5)	5204 (7)	1340 (3)	106 (6)
C(41)	4173 (5)	4504 (7)	1087 (4)	117 (8)
C(42)	4071 (4)	3115 (6)	987 (3)	97 (6)
As(1)	3216 (1)	600 (1)	1073 (1)	56 (3)

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Table 2. *Bond lengths* (Å)

Br(1)–Ni(1)	2·365 (1)	Br(2)–Ni(1)	2·383 (1)
Br(3)–Ni(1)	2·368 (1)	P(1)–Ni(1)	2·323 (1)
C(1)–P(1)	1·814 (4)	C(7)–P(1)	1·825 (4)
C(14)–P(1)	1·821 (4)	C(2)–C(1)	1·371 (7)
C(6)–C(1)	1·359 (7)	C(3)–C(2)	1·387 (9)
C(4)–C(3)	1·351 (10)	C(5)–C(4)	1·370 (12)
C(6)–C(5)	1·397 (9)	C(8)–C(7)	1·402 (6)
C(12)–C(7)	1·382 (6)	C(9)–C(8)	1·387 (6)
C(10)–C(9)	1·380 (7)	C(11)–C(10)	1·377 (7)
C(12)–C(11)	1·386 (6)	C(14)–C(13)	1·397 (5)
C(18)–C(13)	1·370 (6)	C(15)–C(14)	1·380 (6)
C(16)–C(15)	1·389 (7)	C(17)–C(16)	1·375 (6)
C(18)–C(17)	1·370 (7)	C(20)–C(19)	1·379 (7)
C(24)–C(19)	1·393 (6)	As(1)–C(19)	1·917 (4)
C(21)–C(20)	1·385 (7)	C(22)–C(21)	1·372 (7)
C(23)–C(22)	1·377 (8)	C(24)–C(23)	1·390 (7)
C(26)–C(25)	1·385 (9)	C(30)–C(25)	1·376 (8)
As(1)–C(25)	1·907 (5)	C(27)–C(26)	1·411 (11)
C(28)–C(27)	1·364 (12)	C(29)–C(28)	1·350 (14)
C(30)–C(29)	1·367 (10)	C(32)–C(31)	1·379 (7)
C(36)–C(31)	1·371 (7)	As(1)–C(31)	1·910 (4)
C(33)–C(32)	1·388 (8)	C(34)–C(33)	1·379 (9)
C(35)–C(34)	1·358 (8)	C(36)–C(35)	1·407 (8)
C(38)–C(37)	1·374 (7)	C(42)–C(37)	1·372 (8)
As(1)–C(37)	1·910 (5)	C(39)–C(38)	1·390 (8)
C(40)–C(39)	1·360 (10)	C(41)–C(40)	1·346 (11)
C(42)–C(41)	1·416 (10)		

Table 3. *Bond angles* (°)

Br(2)–Ni(1)–Br(1)	113·8 (1)	Br(3)–Ni(1)–Br(1)	116·8 (1)
Br(3)–Ni(1)–Br(2)	110·6 (1)	P(1)–Ni(1)–Br(1)	105·3 (1)
P(1)–Ni(1)–Br(2)	104·4 (1)	P(1)–Ni(1)–Br(3)	104·6 (1)
C(1)–P(1)–Ni(1)	113·1 (1)	C(7)–P(1)–Ni(1)	115·2 (1)
C(7)–P(1)–C(1)	104·2 (2)	C(14)–P(1)–Ni(1)	114·1 (1)
C(14)–P(1)–C(1)	105·7 (2)	C(14)–P(1)–C(7)	103·3 (2)
C(2)–C(1)–P(1)	123·0 (3)	C(6)–C(1)–P(1)	118·5 (4)
C(6)–C(1)–C(2)	118·4 (5)	C(3)–C(2)–C(1)	121·7 (5)
C(4)–C(3)–C(2)	119·6 (6)	C(5)–C(4)–C(3)	119·6 (6)
C(6)–C(5)–C(4)	120·5 (6)	C(5)–C(6)–C(1)	120·1 (6)
C(8)–C(7)–P(1)	121·1 (3)	C(12)–C(7)–P(1)	119·6 (3)
C(12)–C(7)–C(8)	119·3 (4)	C(9)–C(8)–C(7)	120·4 (4)
C(10)–C(9)–C(8)	119·3 (4)	C(12)–C(11)–C(10)	120·3 (4)
C(11)–C(10)–C(9)	120·7 (4)	C(18)–C(13)–C(14)	120·6 (4)
C(11)–C(12)–C(7)	120·0 (4)	C(15)–C(14)–P(1)	118·2 (3)
C(13)–C(14)–P(1)	123·0 (3)	C(16)–C(15)–C(14)	120·3 (4)
C(15)–C(14)–C(13)	118·6 (4)	C(18)–C(17)–C(16)	120·0 (4)
C(17)–C(16)–C(15)	120·1 (5)	C(24)–C(19)–C(20)	120·1 (4)
C(17)–C(18)–C(13)	120·3 (4)	As(1)–C(19)–C(24)	120·7 (4)
As(1)–C(19)–C(20)	119·0 (3)	C(22)–C(21)–C(20)	119·8 (5)
C(21)–C(20)–C(19)	120·4 (4)	C(24)–C(23)–C(22)	120·7 (5)
C(23)–C(22)–C(21)	120·2 (5)	C(30)–C(25)–C(26)	121·6 (5)
C(23)–C(24)–C(19)	118·7 (5)	As(1)–C(25)–C(30)	121·4 (5)
As(1)–C(25)–C(26)	117·0 (4)	C(28)–C(27)–C(26)	119·5 (8)
C(27)–C(26)–C(25)	117·9 (6)	C(30)–C(29)–C(28)	121·4 (7)
C(29)–C(28)–C(27)	121·0 (7)	C(36)–C(31)–C(32)	121·3 (4)
C(29)–C(30)–C(25)	118·6 (7)	As(1)–C(31)–C(36)	120·3 (3)
As(1)–C(31)–C(32)	118·1 (4)	C(34)–C(33)–C(32)	120·6 (5)
C(33)–C(32)–C(31)	118·9 (5)	C(36)–C(35)–C(34)	120·6 (5)
C(35)–C(34)–C(33)	119·9 (5)	C(42)–C(37)–C(38)	119·1 (5)
C(35)–C(36)–C(31)	118·6 (5)	As(1)–C(37)–C(42)	120·6 (4)
As(1)–C(37)–C(38)	119·7 (4)	C(40)–C(39)–C(38)	119·4 (6)
C(39)–C(38)–C(37)	121·3 (5)	C(42)–C(41)–C(40)	121·2 (7)
C(41)–C(40)–C(39)	120·3 (7)	C(25)–As(1)–C(19)	109·1 (2)
C(41)–C(42)–C(37)	118·7 (6)	C(31)–As(1)–C(25)	109·1 (2)
C(31)–As(1)–C(19)	112·5 (2)	C(37)–As(1)–C(25)	114·0 (2)
C(37)–As(1)–C(19)	105·0 (2)		
C(37)–As(1)–C(31)	107·2 (2)		

systematic absences determine the space group to be $Pca2_1$.}

For the monoclinic form 5813 reflections were recorded for $3·0 < 2\theta \leq 125·0°$ on a Syntex $P2_1$ four-circle diffractometer with graphite-monochromated Cu $K\alpha$ radiation, a 96-step $\omega/2\theta$ scan technique and a crystal 0·43 × 0·39 × 0·19 mm. Lp corrections and a semi-empirical absorption correction based on a pseudo-ellipsoid model with 426 azimuthal scans from 17 independent reflections were made; transmission factors ranged from 1·000 to 0·391. The data were averaged to give 5064 unique observed intensities $[F > 3\sigma(F)]$. Cell dimensions were derived from the angular measurements of 15 strong reflections in the range $50 < 2\theta < 60°$.

The As, Ni, P, and the three Br atoms were located by multisolution Σ_2 sign expansion, and the remaining non-hydrogen atoms from a difference synthesis. The structure was refined by blocked full-matrix least squares with all atoms anisotropic. The phenyl H atoms were constrained to ride 1·08 Å from the relevant C atom and were assigned a common isotropic temperature factor. Complex neutral-atom scattering factors (*International Tables for X-ray Crystallography*, 1974) were employed, with the weighting scheme $w = 2·4502/\sigma^2(F)$ for the final stages. The final $R = 0·038$ and $R' = \sum w^{1/2}\Delta/\sum w^{1/2}|F_o| = 0·041$. Atomic coordinates and equivalent isotropic temperature factors are given in Table 1, bond lengths and angles in Tables 2 and 3.*

Discussion. The anion, cation and atom labelling are illustrated in Fig. 1. The pseudo-tetrahedral structure expected on the basis of spectral and bulk magnetic studies (Cotton *et al.*, 1961; Bertini, Gatteschi & Mani, 1972) is confirmed. Although the Ni–Br lengths vary slightly, their mean [2·372 (1) Å] is in agreement with that found for other trigonally distorted pseudo-tetrahedral complexes (Horrocks, Templeton & Zalkin, 1968; Alyea, Costin, Ferguson, Fey, Goel & Restivo, 1975) and with the prediction (2·38 Å) based on the respective tetrahedral covalent radii (Alyea *et al.*, 1975). The Ni–P distance is comparable with that found in $[Ni(PPh_3)I_3]^-$ (2·28 Å) (Taylor, Templeton, Zalkin & Horrocks, 1968) or in pseudo-tetrahedral complexes of the type $[Ni(PR_3)_2Br_2]$ (Jarvis, Mais & Owston, 1968; Kilbourn & Powell, 1970) but considerably shorter than that in $[Ni(Bu^t_3P)Br_3]^-$, as discussed by those authors. The Br atoms are rotationally staggered with respect to the phenyl groups

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* Lists of structure factors, anisotropic thermal parameters, and parameters associated with the hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35391 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

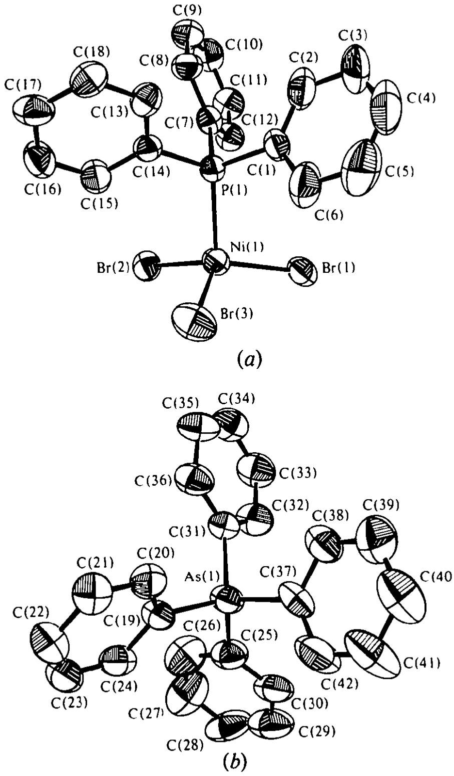

Fig. 1. An *ORTEP* plot (Johnson, 1965) of (*a*) the $[Ni(PPh_3)Br_3]^-$ anion and (*b*) the $[AsPh_4]^+$ cation; thermal ellipsoids are drawn at the 50% probability level.

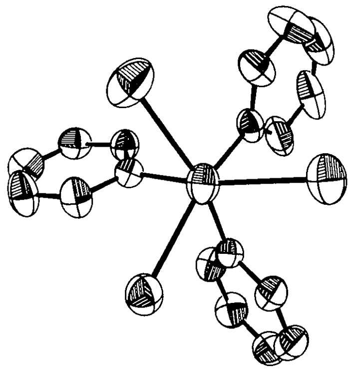

Fig. 2. The anion viewed down the Ni–P bond.

(Fig. 2) giving the anion approximate C_3 symmetry about the Ni–P bond. The phenyl rings are planar, with a maximum atomic deviation of 0·02 (1) Å from the least-squares plane. These rings are pitched as described for the analogous $[Ni(PPh_3)I_3]^-$ (Taylor *et al.*, 1968); the angles of pitch being 35·2 (2) {ring[C(1)–C(6)]}, 25·3 (2) {ring[C(7)–C(12)]}, 34·1 (2)° {ring[C(13)–C(18)]}. The three Br–Ni–Br angles show a small deviation from their mean, 113·7 (1)°, but are all greater than the tetrahedral angle, whereas the mean P–Ni–Br angle, 104·8 (1)°, is slightly less than the tetrahedral angle. This trend, implying that Br–Br steric repulsion is greater than Br–P, has been observed in similar complexes (Horrocks *et al.*, 1968; Taylor *et al.*, 1968), $[Ni(Bu^t_3P)Br_3]^-$ (Alyea *et al.*, 1975) being the exception.

In the cation the phenyl groups are arranged tetrahedrally about the As atom. The mean C–As–C angle is 109·5 (3)°, both the greatest deviations from this tetrahedral angle being 4·5 (3)°. The mean As–C length [1·911 (6) Å] is in excellent agreement with previous values (Taylor *et al.*, 1968).

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