Table 3. *Bond distances (Å) and bond angles (°) for* $[TcCl_4(PMe_2Ph)_2]$

Numbers in parentheses are e.s.d.'s in the least-significant digits.

Tc—Cl(1)	2·325 (1)	C(1)—C(2)	1·395 (6)
Tc—Cl(2)	2·322 (1)	C(1)—C(6)	1·405 (6)
Tc—P	2·531 (1)	C(2)—C(3)	1·404 (6)
P—C(1)	1·815 (4)	C(3)—C(4)	1·402 (8)
P—C(7)	1·817 (5)	C(4)—C(5)	1·365 (8)
P—C(8)	1·827 (5)	C(5)—C(6)	1·389 (8)

Cl(1)—Tc—Cl(2)	89·91 (4)	P—C(1)—C(2)	117·5 (3)
Cl(1)—Tc—P	94·63 (4)	P—C(1)—C(6)	122·3 (4)
Cl(2)—Tc—P	89·69 (4)	C(2)—C(1)—C(6)	120·2 (4)
Tc—P—C(1)	115·0 (1)	C(1)—C(2)—C(3)	119·7 (5)
Tc—P—C(7)	112·3 (2)	C(2)—C(3)—C(4)	119·5 (5)
Tc—P—C(8)	112·4 (2)	C(3)—C(4)—C(5)	120·1 (5)
C(1)—P—C(7)	104·5 (2)	C(4)—C(5)—C(6)	121·6 (5)
C(1)—P—C(8)	106·7 (2)	C(1)—C(6)—C(5)	118·9 (5)
C(7)—P—C(8)	105·1 (3)		

Fig. 1. *ORTEP* (Johnson, 1965) drawing of $[TcCl_4(PMe_2Ph)_2]$. The ellipsoids are drawn at 40% probability level.

known in other compounds, such as corresponding pairs of Mo^{III} and W^{III} complexes, where the differences are *ca* 0·02 Å (Canich, Cotton, Daniels & Lewis, 1987). An explanation for this does not appear to have been presented. If it were a relativistic effect it might have been expected to shorten all metal–ligand distances. It may be that the heavier atom has *d* orbitals better suited for π bonding to the P atom.

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Structures of Two Niobium(IV) Complexes: [N(C2H5)4]2[NbCl6] and [P(CH3)2(C6H5)H][NbCl5{P(CH3)2(C6H5)}]

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Abstract. Bis(tetraethylammonium) hexachloroniobate(IV), $M_r = 566·13$, monoclinic, $C2/c$, $a = 14·006$ (2), $b = 14·366$ (4), $c = 13·206$ (3) Å, $\beta = 90·67$ (2)°, $V = 2657$ (2) Å^3, $Z = 4$, $D_x = 1·415$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0·7107$ Å, $\mu = 9·12$ cm^{-1}, $F(000) = 293$, $T = 295$ K, $R = 0·055$ for 1184 observed reflections. The independent Nb—Cl distances and the average value are 2·413 (2), 2·422 (2), 2·393 (2) and 2·409 (9) Å. The Cl—Nb—Cl angles average 90° by symmetry and range from 89·36 (8) to 90·78 (8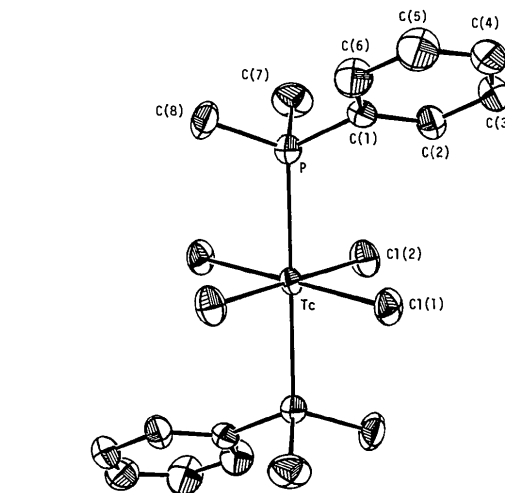)°. Dimethylphenylphosphonium penta-chloro(dimethylphenylphosphine)niobate(IV), $M_r = 547·48$, orthorhombic, $P2_12_12_1$, $a = 12·830$ (3), $b = 13·633$ (6), $c = 13·021$ (5) Å, $V = 2277$ (2) Å^3, $Z = 4$, $D_x = 1·597$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0·7107$ Å, $\mu = 12·33$ cm^{-1}, $F(000) = 275$, $T = 295$ K, $R = 0·0546$ for 1257 observed reflections. The quasi-octahedral anion has an Nb—P distance of 2·673 (5) Å, an Nb—Cl distance *trans* to P of 2·405 (5) Å and *cis* Nb—Cl distances of 2·366 (10), 2·362 (10), 2·360 (10) and 2·394 (10) Å, which give an average of 2·363 (2) Å, excluding the last one which is affected by hydrogen bonding. Thus, there is a *trans* influence from the phosphine ligand of 0·042 (5) Å.

Table 1. *Crystallographic data*

	$(NEt_4)_2NbCl_6$	$(PMe_2PhH)[NbCl_5(PMe_2Ph)]$
Systematic absences	$(hkl), h + k \neq 2n$	$(h00), h \neq 2n$
	$(h0l), l \neq 2n$	$(0k0), k \neq 2n$
		$(00l), l \neq 2n$
Crystal size (mm)	$0.40 \times 0.30 \times 0.10$	$0.40 \times 0.35 \times 0.20$
Orientation reflections, number, range 2θ (°)	25, 13–27	25, 20–30
Data-collection instrument	Enraf–Nonius CAD-4	Nicolet $P3/F$ equivalent
Scan method	ω–2θ	ω–2θ
Scan width	$\Delta\omega = (1.3 + 35\tan\omega)°$	$\Delta(2\theta) = (K\alpha_1 - 1.0) - (K\alpha_2 + 1.0)$
Background scans	First and last 1/6 of scan	Stationary, at terminus of peak scan
Scan speed in ω (° min^{-1})	1.93–8.24	2.0–29.3
Data-collection range, 2θ (°)	4–45	4–50
Index ranges	h: 0–14; k: 0–15; l: $\overline{14}$–13	h: $\overline{10}$–15; k: 0–16; l: 0–15
Number of unique data, total	1475	2477
with $F_o^2 > 3\sigma(F_o^2)$	1184	1257
R_{int}	0.044	0.041
Number of parameters refined	134	196
Transmission factors (relative) max., min.	–	1.00, 0.90
R	0.055	0.055
wR, $w = 1/\sigma^2(|F_o|)$	0.069	0.064
Quality-of-fit indicator	2.07	1.22
Largest shift/e.s.d., final cycle	0.01	0.12
Largest peak (e Å^{-3})	0.64	0.96

Introduction. The phosphine complexes of niobium-(IV) show great structural diversity and the chemistry by which they are obtained is often very complex (Cotton, Duraj & Roth, 1984). While some are six-coordinate (quasi-octahedral), higher coordination numbers (7, 8) are common. The quasi-octahedral complexes are of structural interest because they may be compared with similar complexes formed by the elements that follow, *viz* Mo, Tc, Ru, to see how atomic size and d-orbital populations affect bonding. We report here the structures of two species that are basic to any such comparative studies, the $NbCl_6^{2-}$ ion, and the monosubstituted $[NbCl_5(PMe_2Ph)]^-$ ion.

Experimental. All manipulations were performed under an atmosphere of argon. $(NEt_4)_2NbCl_6$ was prepared by a literature method (Fowles, Tidmarsh & Walton, 1969). $(PMe_2PhH)[NbCl_5(PMe_2Ph)]$ was prepared by reducing $NbCl_5$ (1.0 g, 3.7 mmol) in toluene with one equivalent of Na/Hg in the presence of PMe_2Ph (1 ml). The solution was filtered and evaporated to dryness. The residue was dissolved in 10 ml of CH_2Cl_2 and a layer of hexane placed over this solution. Crystals of the dinuclear compound $Nb_2Cl_8(PMe_2Ph)_4$ were produced (Cotton & Roth, 1984). The supernatant liquid was then transferred to another Schlenk tube, and a layer of hexane again allowed to diffuse in. This caused the deposition of orange crystals of $(PMe_2PhH)[NbCl_5(PMe_2Ph)]$ in about 5% yield based on $NbCl_5$.

The structure determinations of both compounds proceeded relatively smoothly. Pertinent information can be found in the *Abstract* and in Table 1. The systematic absences for $(NEt_4)_2NbCl_6$ indicated
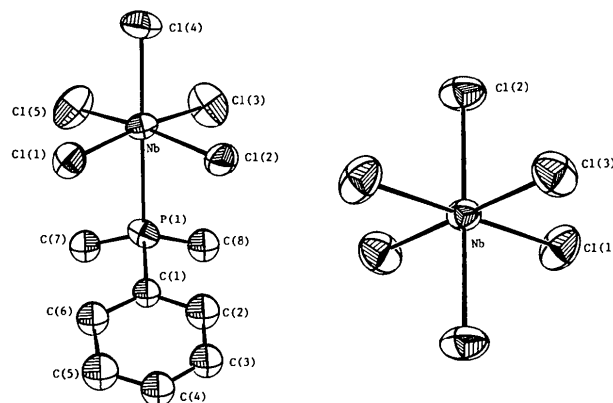

Fig. 1. Structure and atom-labeling schemes for the two niobium(IV) anions. Each atom is represented by its ellipsoid of thermal displacement drawn at the 40% probability level.

either Cc or $C2/c$. The solution and refinement of the structure (initially using Patterson functions) indicated unambiguously that the centrosymmetric space group is correct. The NEt_4^+ ions are located on twofold axes, but one of them had its α-C atoms disordered over two positions each, and thus four atoms with half occupancy, C(21)–C(24), were refined. The terminal C atoms of these ethyl groups were ordered. The $NbCl_6^{2-}$ ion resides on an inversion center.

Since the space group of the phosphine complex, $P2_12_12_1$, is chiral, non-equivalent (Friedel) pairs of reflections were collected and used in refinement. The enantiomer that gave the lower residuals is reported. The formula unit is the asymmetric unit. The phenyl groups were refined as rigid bodies (Sheldrick, 1976), geometrically idealized as hexagons with C—C =

Table 2. *Positional and equivalent isotropic displacement parameters for* (NEt₄)₂(NbCl₆)

$$B_{eq} = (1/3)\Sigma_i\Sigma_j B_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Nb	0·250	0·250	0·000	3·59 (2)
Cl(1)	0·0848 (1)	0·2194 (2)	0·0377 (2)	5·94 (5)
Cl(2)	0·2168 (2)	0·4154 (2)	0·0041 (2)	5·82 (5)
Cl(3)	0·2890 (2)	0·2510 (2)	0·1769 (2)	5·97 (5)
N(1)	0·500	0·0089 (6)	0·750	4·2 (2)
N(2)	0·500	0·4891 (7)	0·250	5·5 (2)
C(11)	0·5874 (6)	−0·0496 (7)	0·7187 (8)	7·1 (4)
C(13)	0·5612 (8)	−0·1226 (7)	0·6334 (7)	7·0 (3)
C(12)	0·4698 (6)	0·0659 (7)	0·6556 (8)	7·0 (3)
C(14)	0·3937 (6)	0·1404 (7)	0·6802 (8)	7·7 (3)
C(21)†	0·453 (1)	0·478 (1)	0·364 (1)	6·4 (5)
C(22)†	0·554 (1)	0·578 (1)	0·257 (2)	7·6 (5)
C(23)†	0·416 (1)	0·502 (2)	0·178 (1)	7·3 (5)
C(24)†	0·545 (1)	0·398 (1)	0·234 (1)	7·2 (5)
C(25)	0·3923 (8)	0·4021 (8)	0·3724 (9)	9·0 (3)
C(26)	0·6480 (7)	0·577 (1)	0·315 (1)	10·8 (4)

† Denotes atomic site with 50% occupancy.

Table 3. *Positional parameters and equivalent isotropic displacement parameters for* (PMe₂PhH)[NbCl₅(PMe₂Ph)]

$$B_{eq} = (1/3)\Sigma_i\Sigma_j B_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Nb	−0·1824 (1)	−0·1979 (1)	−0·2420 (3)	4·00 (4)
Cl(1)	−0·309 (1)	−0·1776 (8)	−0·3725 (5)	5·9 (2)
Cl(2)	−0·3075 (9)	−0·1725 (7)	−0·1117 (5)	5·6 (2)
Cl(3)	−0·0483 (8)	−0·199 (1)	−0·1141 (7)	8·9 (3)
Cl(4)	−0·1984 (5)	−0·3736 (3)	−0·2417 (9)	7·3 (2)
Cl(5)	−0·0489 (8)	−0·196 (1)	−0·3667 (7)	8·0 (3)
P(1)	−0·1713 (4)	−0·0021 (3)	−0·2413 (7)	4·2 (1)
P(2)	−0·3127 (8)	−0·6320 (8)	−0·4013 (6)	8·0 (3)
C(1)	−0·295 (2)	0·058 (1)	−0·247 (1)	4·8 (5)
C(2)	−0·347 (2)	0·081 (1)	−0·156 (1)	4·5 (8)
C(3)	−0·445 (2)	0·125 (1)	−0·160 (1)	9 (1)
C(4)	−0·490 (2)	0·147 (1)	−0·254 (1)	7·1 (7)
C(5)	−0·439 (2)	0·124 (1)	−0·345 (1)	7 (1)
C(6)	−0·341 (2)	0·079 (1)	−0·342 (1)	9 (1)
C(7)	−0·095 (2)	0·051 (3)	−0·345 (2)	8 (1)
C(8)	−0·108 (2)	0·043 (2)	−0·126 (2)	5·6 (8)
C(11)	−0·320 (1)	−0·631 (1)	−0·264 (2)	5·2 (5)
C(12)	−0·411 (1)	−0·610 (1)	−0·209 (2)	10 (1)
C(13)	−0·411 (1)	−0·615 (1)	−0·102 (2)	13 (2)
C(14)	−0·321 (1)	−0·641 (1)	−0·050 (2)	7·3 (9)
C(15)	−0·230 (1)	−0·661 (1)	−0·104 (2)	7·0 (9)
C(16)	−0·230 (1)	−0·657 (1)	−0·211 (2)	6·2 (8)
C(17)	−0·190 (2)	−0·594 (2)	−0·449 (2)	8·6 (8)
C(18)	−0·416 (2)	−0·573 (4)	−0·449 (2)	12 (1)

Table 4. *Bond distances* (Å) *and bond angles* (°) *for* (NEt₄)₂(NbCl₆) *with their e.s.d.'s in parentheses*

Nb—Cl(1)	2·413 (2)	N(2)—C(24)	1·46 (2)
Nb—Cl(2)	2·422 (2)	C(11)—C(13)	1·580 (14)
Nb—Cl(3)	2·393 (2)	C(12)—C(14)	1·547 (13)
N(1)—C(11)	1·545 (10)	C(21)—C(25)	1·39 (2)
N(1)—C(12)	1·547 (11)	C(22)—C(26)	1·51 (2)
N(2)—C(21)	1·66 (2)	C(23)—C(26)	1·41 (2)
N(2)—C(22)	1·49 (2)	C(24)—C(25)	1·67 (2)
N(2)—C(23)	1·52 (2)		

Cl(1)—Nb—Cl(2)	89·36 (8)	C(22)—N(2)—C(23)	109 (1)
Cl(1)—Nb—Cl(3)	90·46 (8)	C(22)—N(2)—C(24)	124 (1)
Cl(2)—Nb—Cl(3)	90·78 (8)	C(23)—N(2)—C(24)	110 (1)
C(11)—N(1)—C(11)	114·2 (7)	N(1)—C(11)—C(13)	111·9 (7)
C(11)—N(1)—C(12)	106·5 (5)	N(1)—C(12)—C(14)	112·3 (8)
C(11)—N(1)—C(12)	107·0 (5)	N(2)—C(21)—C(25)	113 (1)
C(12)—N(1)—C(12)	116·0 (7)	N(2)—C(22)—C(26)	118 (1)
C(21)—N(2)—C(22)	103 (1)	N(2)—C(23)—C(26)	122 (2)
C(21)—N(2)—C(23)	106 (1)	N(2)—C(24)—C(25)	109 (1)
C(21)—N(2)—C(24)	103 (1)		

Table 5. *Selected bond distances* (Å) *and bond angles* (°) *for* (PMe₂PhH)[NbCl₅(PMe₂Ph)] *with their e.s.d.'s in parentheses*

Nb—Cl(1)	2·366 (10)	Nb—Cl(4)	2·405 (5)
Nb—Cl(2)	2·362 (10)	Nb—Cl(5)	2·360 (10)
Nb—Cl(3)	2·394 (10)	Nb—P(1)	2·673 (5)

Cl(1)—Nb—Cl(2)	91·9 (3)	Cl(2)—Nb—P(1)	83·5 (3)
Cl(1)—Nb—Cl(3)	173·2 (5)	Cl(3)—Nb—Cl(4)	93·1 (5)
Cl(1)—Nb—Cl(4)	93·4 (4)	Cl(3)—Nb—Cl(5)	87·5 (3)
Cl(1)—Nb—Cl(5)	90·2 (4)	Cl(3)—Nb—P(1)	88·0 (4)
Cl(1)—Nb—P(1)	85·5 (3)	Cl(4)—Nb—Cl(5)	94·2 (4)
Cl(2)—Nb—Cl(3)	89·4 (4)	Cl(4)—Nb—P(1)	178·1 (2)
Cl(2)—Nb—Cl(4)	95·0 (3)	Cl(5)—Nb—P(1)	87·4 (4)
Cl(2)—Nb—Cl(5)	170·5 (4)		

Tables 2 and 3 list the positional parameters and Tables 4 and 5 list the principal bond distances and angles for the two compounds.* In both cases the cations have the expected dimensions and require no discussion. The two complex anions have essentially octahedral structures which will be compared below with those of several other quasi-octahedral complexes of niobium(IV).

There is a close approach of the cationic P atom to Cl(3), viz 4·00 Å, and the three Cl(3)···P—C angles are 72, 119 and 134°. This suggests that there is a hydrogen bond to Cl(3), and this, in turn, would explain why the Nb—Cl(3) distance, 2·394 (10) Å, is significantly longer than the average of the other three cis Nb—Cl distances, 2·363 (2) Å, by 0·031 (10) Å. [For an example of a similar situation, see Veal & Hodgson (1972).]

The isolation of the [NbCl₅(PMe₂Ph)]⁻ anion was unexpected. Previous work (Cotton, Duraj &

1·395 and C—H = 0·98 Å. However, each C atom was permitted to have a freely varying anisotropic displacement tensor. All phenyl H atoms were required to have the same isotropic thermal parameter. The methyl C atoms in the coordinated PMe₂Ph ligand were assigned H atoms at idealized positions. All were then refined using a riding model and with the same thermal parameter. Attempts to introduce H atoms for the methyl groups of the cation were fruitless.

Discussion. The structures and atom-numbering schemes of the two anions are shown in Fig. 1.

Table 6. *Bond distances* (Å) *in niobium*(IV) *chloro phosphine complexes*

	Nb—Cl (*trans* to Cl)	Nb—Cl (*trans* to P)	Nb—P
[NbCl₆]²⁻	2·409 [9]	–	–
[NbCl₅(PMe₂Ph)]⁻	2·363 [2]*	2·405 (5)	2·673 (5)
trans-NbCl₄(PEt₃)₂†	2·366 [9]	–	2·664 (3)
trans-NbCl₄(PEtPh₂)₂†	2·367 [34]	–	2·706 (1)

* Averaged over only three Nb—Cl distances as explained in text.

† Cotton, Duraj & Roth (1984).

Roth, 1984) had shown that in a solution of Nb₂Cl₈(PMe₂Ph)₄ there is a dissociation equilibrium,

$$Nb_2Cl_8(PMe_2Ph)_4 \rightleftarrows 2NbCl_4(PMe_2Ph)_2.$$
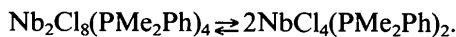
We had hoped to obtain crystals of the monomer by employing dilute solutions. However, as noted in *Experimental* we obtained instead the ionic compound (PMe₂PhH)[NbCl₅(PMe₂Ph)]. Presumably, over the time required for crystal growth some hydrolysis occurred, giving HCl, which reacted with NbCl₄(PMe₂Ph)₂ to give the ionic product.

The present results can be compared with those for a few other quasi-octahedral Nb^IV chloro complexes. Table 6 summarizes bond lengths for the present compounds and two other phosphine complexes (Cotton, Duraj & Roth, 1984). For *cis*-NbCl₄-(CH₃CN)₂, Nb—Cl distances in the range 2·328 (2) and 2·349 (4) Å have been found (Benton, Drew, Hobson & Rice, 1981).

The bond lengths in Table 6 are internally consistent. There are several small differences, but each one seems to have a straightforward explanation. The longest Nb—P distance is found for the least basic phosphine. There is a distinct *trans* effect from the phosphine in the [NbCl₅(PMe₂Ph)]⁻ ion, with the *trans* Nb—Cl bond being 0·042 (5) Å longer than the *cis* bonds, excluding from consideration the Nb—Cl(3) bond which appears to be lengthened by hydrogen bonding with the P—H bond of the cation. Finally, we note that in the NbCl₆²⁻ ion the Nb—Cl bonds are somewhat longer than those in the complexes with one or two neutral ligands, in keeping with the probable ionic character of these bonds, whereby the more of them there are to the same positive center, the weaker each one will become.

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Structures of Three Bis(3-ethoxy-*N-R*-salicylideneaminato)nickel(II) Complexes (*R* = H, Methyl, Ethyl)

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Abstract. (I): Bis(3-ethoxysalicylideneaminato)nickel-(II), [Ni(C₉H₁₀NO₂)₂], $M_r = 387·06$, triclinic, $P\bar{1}$, $a = 11·906$ (4), $b = 10·089$ (7), $c = 8·442$ (4) Å, $\alpha = 102·39$ (4), $\beta = 97·38$ (3), $\gamma = 111·18$ (4)°, $V = 899·54$ Å³, $Z = 2$, $D_m = 1·45$ (by flotation), $D_x = 1·43$ Mg m⁻³, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1·105$ mm⁻¹, $F(000) = 404$, room temperature, $R = 0·034$ for 3443 observed unique reflections. (II): Bis(3-ethoxy-*N*-methylsalicylideneaminato)nickel(II), [Ni(C₁₀H₁₂NO₂)₂], $M_r = 415·11$, monoclinic, $P2_1/c$, $a = 8·660$ (3), $b = 17·959$ (6), $c = 6·283$ (3) Å, $\beta = 97·13$ (2)°, $V = 969·64$ Å³, $Z = 2$, $D_m = 1·41$ (by flo-