Crystal Structure of Bis[hydroxo(triphenyl)arsonium(V)] Dodeca-μ-chloro-hexachloro-*octahedro*-hexaniobate(2−)

By **Ross Anthony Field, David Leslie Kepert, Bruce William Robinson,** and **Allan Henry White,***
Department of Inorganic Chemistry, University of Western Australia, Nedlands 6009, Western Australia

The crystal structure of the title compound has been determined by single-crystal photographic *X*-ray diffraction methods. The structure was solved from photographic data by the heavy-atom method and refined by block-diagonal least-squares to *R* 0·13 for 2326 reflections. Crystals are monoclinic, space group, $P2_1/n$, a = 15·76(2), b = 22·25(3), c = 8·62(1) Å, β = 91·6(3)°, Z = 2. The asymmetric unit is a $[Ph_3AsOH]^+$ cation and one half of a centrosymmetric $[(Nb_6Cl_{12})Cl_6]^{2-}$ anionic cluster unit. Bond lengths within the cation agree well with previously determined values for similar species (mean C–C 1·39, mean C–As 1·91 Å); As–O is 1·73(2) Å. The proximity of this bond to the special position ($\frac{1}{2}$,0,0), (0 $\frac{1}{2}$,$\frac{1}{2}$) and the O–O′ distance of 2·80 Å suggests that the cation oxygens are linked by a pair of hydrogen bonds. The point-symmetry of the cluster does not differ significantly from O_h, the octahedron of niobium atoms (mean Nb–Nb 3·01$_6$ Å) being surrounded by the usual two sets of axial (6) and edge (12) chlorine atoms, (mean Nb–Cl 2·48 and 2·24 Å). These distances differ significantly from those found in clusters of different oxidation state.

EXPERIMENTAL

THE title compound was prepared by dissolving $[(Nb_6Cl_{12})Cl_2(H_2O)_4],4H_2O$ [1] in warm dry ethanol, filtering to remove any insoluble residue and bubbling dry chlorine through the solution for *ca.* 3 min. The excess of chlorine was removed by flushing dry nitrogen through the solution for *ca.* 30 min; excess of anhydrous triphenylarsine oxide in ethanol was then added and the solution set aside in air. Precipitation of the crystalline solid commenced after 2—3 weeks and was allowed to continue until the solution was only faintly coloured. The product was filtered, washed with cold ethanol, and dried under vacuum (Found: C, 24·2; H, 2·5; As, 8·9; Cl, 32·8. $C_{36}H_{32}As_2Cl_{18}Nb_6O_2$ requires C, 23·5; H, 1·8; As, 8·1; Cl, 34·6%). The tantalum analogue was similarly prepared from a solution of anhydrous $(Ta_6Cl_{12})Cl_3$ dissolved in ethanol at 50 °C (Found: C, 19·2; H, 2·1; Cl, 26·4. $C_{36}H_{32}As_2Cl_{18}O_2Ta_6$ requires C, 18·2; H, 1·4; Cl, 26·9%). The Ta_6Cl_{15} was prepared from tantalum pentachloride and aluminium in a 400—200 °C temperature gradient in anhydrous aluminium chloride solvent (Found: Cl, 32·9. Ta_6Cl_{15} requires Cl, 32·9%). Salts of $[(Nb_6Cl_{12})Cl_6]^{2-}$, $[(Ta_6Cl_{12})Cl_6]^{2-}$, and $[(Ta_6Br_{12})Br_6]^{2-}$ with other protonated oxygen containing ligands were prepared similarly.[2]

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[1] R. A. Field, D. L. Kepert, and D. Taylor, *Inorg. Chim. Acta*, 1970, **4**, 113.

[2] R. A. Field, Ph.D. Thesis, University of Western Australia, 1972.

The conductivities of $(Ph_3AsOH)_2[(Nb_6Cl_{12})Cl_6]$ and the tantalum analogue in $PhNO_2$ are typical for 2 : 1 electrolytes (47, 50 cm^2 Ω^{-1} mol^{-1} at 4×10^{-4}M-respectively).

The i.r. spectrum of the niobium complex shows no As–O mode at 880 cm^{-1}, typical of triphenylarsine oxide. A band at 1033 cm^{-1} is tentatively assigned to a deformation hydroxy-mode. All other bands >400 cm^{-1} are typical of the organic cation. The spectrum in the region 245—400 cm^{-1} shows strong metal–chlorine absorptions at 353, 299, and 259 cm^{-1} typical of $[(Nb_6Cl_{12})Cl_6]^{2-}$ but not of $[(Nb_6Cl_{12})Cl_6]^{3-}$ (340, 290, and 250 cm^{-1}) or $[(Nb_6Cl_{12})Cl_6]^{4-}$ (330, 280, and 240 cm^{-1}).[3] Similarly, the tantalum compound shows strong absorption at 335, 292, and 257 cm^{-1} characteristic of $[(Ta_6Cl_{12})Cl_6]^{2-}$ but at frequencies significantly higher than for $[(Ta_6Cl_{12})Cl_6]^{3-}$ (330, 285, and 245 cm^{-1}) and $[(Ta_6Cl_{12})Cl_6]^{4-}$ (325 and 235 cm^{-1}).[3]

The absorption spectrum of the title compound in ethanol shows bands at 7·9 kK (ε *ca.* 0·30 l mol^{-1} cm^{-1} $\times 10^{-3}$), 10·35 (0·95), 17·0 (0·90), 21·15 (13·5), 33·8 (64), and 42·2 (8·9). For the tantalum analogue in $PhNO_2$ solution absorption bands are observed at 8·6, 9·05, 12·0, 18·8, 22·75, and 27·25 kK. The spectra are clearly diagnostic of $(M_6Cl_{12})^{x+}$ clusters in the +4 oxidation state.[4,5] The uncorrected gram susceptibilities of the title complex and the tantalum analogue are −0·174 and −0·284 c.g.s.u. respectively and are temperature-independent in the range 89—310 K. Application of diamagnetic corrections ($-10^6\chi_D$ c.g.s.u., 220 for Nb_6, 250 for Ta_6, 26 for Cl, and 204 for Ph_3AsOH) yields corrected molar susceptibilities of 780×10^{-6} and 450×10^{-6} respectively. These values and the difference between them are typical of the clusters in the +2 or +4 oxidation states.[6]

Analyses, electronic, and i.r. spectra, conductance and magnetic measurements were made as described previously.[1,7]

Crystal Structure Determination.—Crystals suitable for *X*-ray work were obtained by the slow evaporation of an ethanolic solution of the complex, as flattened rods, elongated along the *c* and flattened about the *b* axis. Sections suitable for data collection were cut from larger crystals as rectangular prisms of dimensions 0·05 × 0·04 × 0·06 mm. Multiple-film equi-inclination Weissenberg data were obtained for two crystal sections about *a* and *c*, because of progressive crystal deterioration (see later); unit-cell dimensions were obtained from zero-layer Weissenberg photographs about all axes, calibrated with aluminium powder [a_{298K}(Al) 4·0494 Å].[8]

Crystal Data.—$C_{36}H_{32}As_2Cl_{18}Nb_6O_2$, $M = 1842$, Monoclinic, (pseudo-orthorhombic), $a = 15{\cdot}76(2)$, $b = 22{\cdot}25(3)$, $c = 8{\cdot}62(1)$ Å, $\beta = 91{\cdot}6(3)°$, $U = 3021$ Å^3, D_m 2·00(2), $Z = 2$, $D_c = 2{\cdot}02$, $F(000) = 1764$, Ni-filtered Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å,[9] μ(Cu-K_α) = 184 cm^{-1}, transmission coefficient range 0·37—0·55. Data layers 0—4*kl*, *hk*0—5. 3898 Independent observed reflections. Space group $P2_1/n$ (C^5_{2h}, No. 14).[10] Temperature 298 K.

Data were corrected for absorption,[11] Lorentz and polarization factors, and scaled by internal correlation.[12]

The structure was solved by the heavy-atom method and refined (as described in ref. 13; Nb, As, and Cl atoms assigned anisotropic thermal parameters) by block-diagonal least squares to *R*, at convergence, 0·148; the significance of introducing anisotropic parameters was tested by a ratio test.[14] At this stage an agreement analysis revealed a significantly higher value of *R* for the outer layers of data 4*kl* and *hk*5, *R* being >0·16 for these, probably as a result of crystal deterioration. On removing the suspect data

TABLE 1

Final atomic parameters of the asymmetric unit

Atom	*x*	*y*	*z*	*B*/Å^2
Nb(1)	0·0986(1)	0·0393(1)	0·1413(2)	*
Nb(2)	0·9072(1)	0·0426(1)	0·1365(3)	*
Nb(3)	0·9982(1)	0·9236(1)	0·1486(3)	*
As(1)	0·4909(2)	0·8571(1)	0·9713(4)	*
Cl(1)	0·1089(5)	0·9583(3)	0·3253(8)	*
Cl(2)	0·8929(5)	0·9624(3)	0·3234(8)	*
Cl(3)	0·0053(4)	0·0922(3)	0·3104(7)	*
Cl(4)	0·1125(5)	0·1312(3)	0·9934(8)	*
Cl(5)	0·8981(4)	0·1350(3)	0·9881(8)	*
Cl(6)	0·2155(4)	0·9965(3)	0·0069(8)	*
Cl(7)	0·2138(5)	0·0851(3)	0·3036(9)	*
Cl(8)	0·7980(5)	0·0927(3)	0·2947(9)	*
Cl(9)	0·9967(5)	0·8344(3)	0·3209(8)	*
O(1)	0·489(1)	0·934(1)	0·975(2)	6·6(5)
C(1)	0·392(2)	0·828(1)	0·086(3)	4·1(5)
C(2)	0·349(2)	0·871(1)	0·160(4)	6·2(7)
C(3)	0·379(2)	0·770(1)	0·079(4)	6·3(7)
C(4)	0·281(3)	0·848(2)	0·235(5)	10·3(12)
C(5)	0·315(3)	0·748(2)	0·158(5)	9·7(11)
C(6)	0·261(2)	0·790(2)	0·245(4)	7·1(8)
C(7)	0·594(2)	0·832(1)	0·082(3)	4·5(5)
C(8)	0·639(2)	0·885(1)	0·145(4)	6·5(8)
C(9)	0·612(2)	0·775(1)	0·100(3)	5·0(6)
C(10)	0·720(2)	0·860(2)	0·231(4)	7·2(8)
C(11)	0·684(2)	0·754(1)	0·175(4)	6·2(7)
C(12)	0·737(2)	0·803(1)	0·247(3)	5·8(7)
C(13)	0·494(2)	0·830(1)	0·772(3)	4·7(6)
C(14)	0·413(2)	0·810(1)	0·697(3)	5·7(7)
C(15)	0·570(2)	0·828(1)	0·696(4)	5·9(7)
C(16)	0·418(2)	0·791(2)	0·551(4)	7·1(8)
C(17)	0·576(3)	0·808(2)	0·545(5)	9·5(11)
C(18)	0·506(2)	0·212(2)	0·513(4)	7·5(9)

* Final anisotropic thermal parameters ($\times 10^4$) of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Nb(1)	42(1)	15·8(4)	120(4)	−4(1)	−50(4)	−6(2)
Nb(2)	42(1)	16·7(5)	112(4)	1(1)	−39(4)	−4(2)
Nb(3)	45(1)	14·5(4)	122(4)	0(1)	−47(4)	2(2)
As(1)	55(2)	19·1(7)	205(7)	4(2)	−60(6)	−6(3)
Cl(1)	51(3)	23(1)	114(11)	4(3)	−67(13)	10(5)
Cl(2)	52(4)	22(1)	122(11)	−4(3)	8(12)	4(5)
Cl(3)	54(4)	19(1)	114(10)	0(3)	−37(11)	−22(5)
Cl(4)	56(4)	19(1)	135(11)	−10(4)	−57(12)	−3(6)
Cl(5)	58(4)	17(1)	109(9)	4(3)	−49(11)	−2(5)
Cl(6)	38(3)	27(2)	149(12)	2(3)	−56(12)	−15(7)
Cl(7)	57(4)	32(2)	149(13)	−13(4)	−121(13)	−25(8)
Cl(8)	49(3)	28(2)	174(13)	7(4)	−9(12)	−23(7)
Cl(9)	80(5)	19(1)	146(11)	6(4)	−57(13)	24(6)

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[4] B. Spreckelmeyer, *Z. anorg. Chem.*, 1969, **365**, 225.

[5] P. B. Fleming and R. E. McCarley, *Inorg. Chem.*, 1970, **9**, 1347.

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[7] R. L. Deutscher and D. L. Kepert, *Inorg. Chem.*, 1970, **9**, 2305.

[8] B. W. Delf, *J. Appl. Phys.*, 1963, **14**, 345.

[9] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, p. 59.

[10] Ref. 9, vol. I, 2nd edn., 1965.

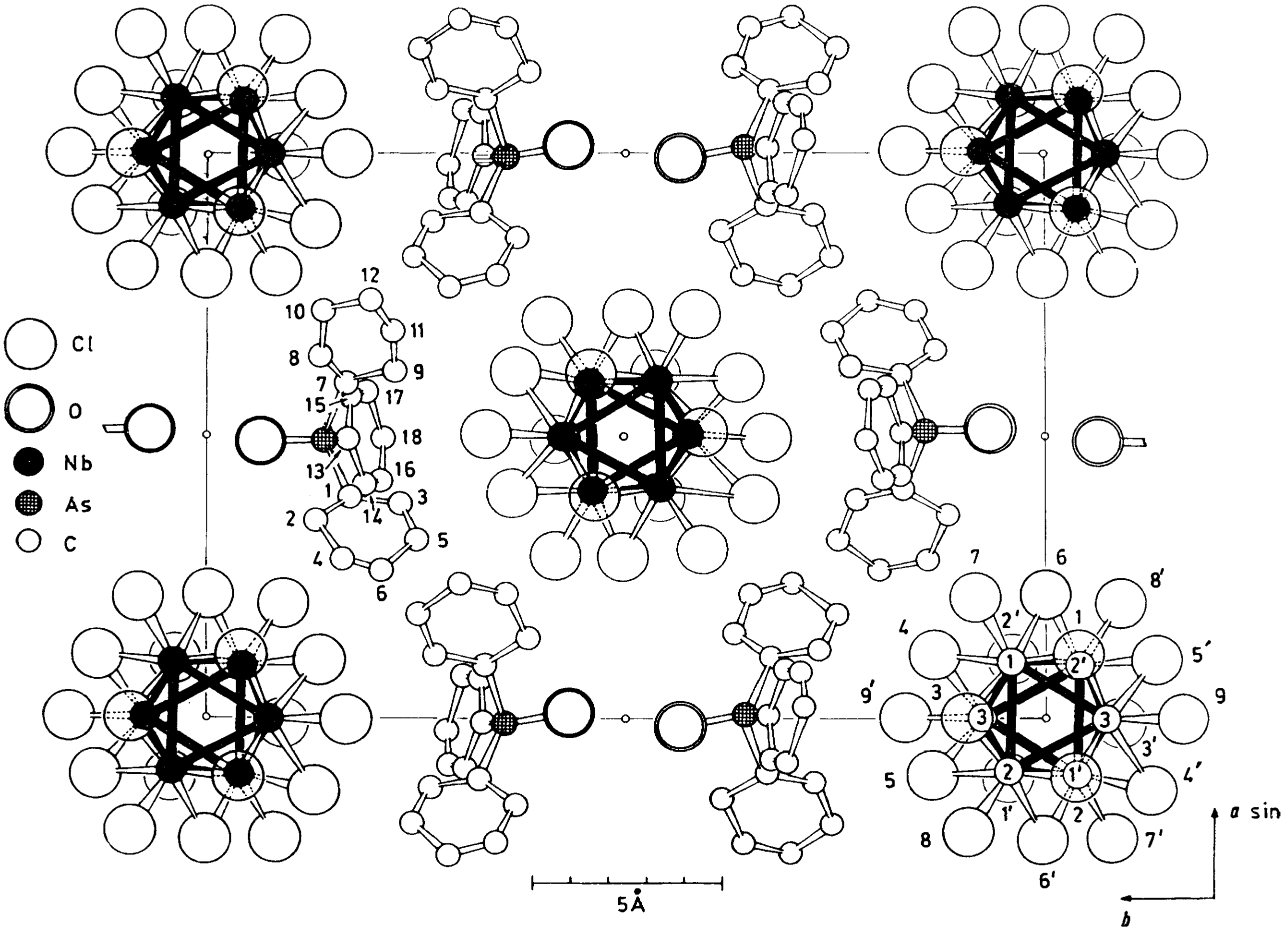
[11] N. W. Alcock, in 'Crystallographic Computing,' Munksgaard, Copenhagen, 1971, p. 271.

[12] W. C. Hamilton, J. S. Rollett, and R. A. Sparks, *Acta Cryst.*, 1965, **18**, 129.

[13] P. W. G. Newman and A. H. White, *J.C.S. Dalton*, 1972, 1460; J. M. Martin, P. W. G. Newman, B. W. Robinson, and A. H. White, *ibid.*, p. 2233.

[14] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

contributed by these two layers, R fell to 0·135 for 2326 reflections. Final weighting scheme parameters were: $a = 4{\cdot}55$, $b = 0{\cdot}055$ in a weighing scheme of the form $w = (a + |F_o| + b|F_o|^2)^{-1}$.[15] We attribute our inability to refine the structure further to non-uniformity of the data, owing to the use of two crystals and their decomposition; under these circumstances we consider the final R value of 0·135 satisfactory. During the final cycle of least-squares refinement, positional and thermal parameter shifts for the anisotropic atoms were 0·05σ and 0·1σ for the remainder. The final set of structure factors for R 0·135 is listed in Supplementary Publication No. SUP 20694 (4 pp., 1 microfiche).* No significant peaks were observed in a difference map computed after the final round of least squares. There was no evidence for disorder in the structure. Final atomic positional and thermal parameters, together with estimated standard deviations are given in Table 1. [Here, and in subsequent Tables and discussion, the estimated standard deviations in the final digit, given in parentheses, are derived by a block-diagonal process (3 × 3, 6 × 6) and are likely to be underestimates.] Unit-cell contents and atomic labelling are given in the Figure; interatomic distances and angles[16] are given in Table 2. Scattering factors for all atoms except niobium were for the neutral atoms,[17] those for arsenic and chlorine being corrected for anomalous dispersion ($\Delta f'$);[18] scattering factors for niobium were taken from refs. 19 and 20 and corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[21]



The contents of the unit cell viewed down the c axis, showing the atom labelling; primed atoms are inversely related to the reference atom

Computing was carried out on the DEC PDP10 computer at the University of Western Australia.

DISCUSSION

The crystal is composed of two distinct species based respectively on the triphenylarsine oxide and the $[(Nb_6Cl_{12})Cl_6]$ units.

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue (items less than 10 pp. are supplied as full size copies).

[15] D. W. Cruickshank, in 'Computing Methods in X-Ray Crystallography,' ed. J. S. Rollett, Pergamon Press, Oxford, 1965, p. 114.

[16] M. E. Pippy and F. R. Ahmed, Divn. Pure and Appl. Phys., NRC Ottawa, Canada, Program NRC 12.

[17] J. A. Ibers, ref. 9, p. 210.

[18] D. H. Templeton, ref. 9, p. 213.

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

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

[21] D. T. Cromer, *Acta Cryst.*, 1965, **19**, 224.

TABLE 2

Interatomic distances (Å) and angles (°). Primed atoms are related to the reference atoms by an inversion

(*a*) In the cation $[\mathrm{Ph_3AsOH}]^+$

(i) Distances

As–O	1·73(2)
As–C(1)	1·98(2)
As–C(7)	1·94(3)
As–C(13)	1·83(3)
C(1)–C(2)	1·34(4)
C(1)–C(3)	1·30(4)
C(2)–C(4)	1·37(4)
C(3)–C(5)	1·33(4)
C(4)–C(6)	1·33(3)
C(5)–C(6)	1·48(4)
C(7)–C(8)	1·47(4)
C(7)–C(9)	1·31(3)
C(8)–C(10)	1·56(5)
C(9)–C(11)	1·37(4)
C(10)–C(12)	1·30(3)
C(11)–C(12)	1·50(4)
C(13)–C(14)	1·48(4)
C(13)–C(15)	1·38(4)
C(14)–C(16)	1·33(4)
C(15)–C(17)	1·38(4)
C(16)–C(18)	1·33(5)
C(17)–C(18)	1·44(5)

(ii) Angles

O–As–C(1)	108(1)
O–As–C(7)	107(1)
O–As–C(13)	110(1)
C(1)–As–C(7)	109(1)
C(1)–As–C(13)	114(1)
C(7)–As–C(13)	109(1)
As–C(1)–C(2)	115(2)
As–C(1)–C(3)	115(2)
As–C(7)–C(8)	110(2)
As–C(7)–C(9)	121(2)
As–C(13)–C(14)	118(2)
As–C(13)–C(15)	120(2)
C(2)–C(1)–C(3)	130(3)
C(1)–C(2)–C(4)	112(3)
C(1)–C(3)–C(5)	117(3)
C(2)–C(4)–C(6)	126(3)
C(3)–C(5)–C(6)	119(3)
C(4)–C(6)–C(5)	116(3)
C(8)–C(7)–C(9)	129(3)
C(7)–C(8)–C(10)	107(3)
C(7)–C(9)–C(11)	124(3)
C(8)–C(10)–C(12)	124(3)
C(9)–C(11)–C(12)	113(3)
C(10)–C(12)–C(11)	124(3)
C(14)–C(13)–C(15)	122(2)
C(13)–C(14)–C(16)	116(2)
C(13)–C(15)–C(17)	123(3)
C(14)–C(16)–C(18)	119(3)
C(15)–C(17)–C(18)	110(4)
C(16)–C(18)–C(17)	130(4)

(iii) Some intra-ionic non-bonded distances (<4 Å)

As · · · C(2)	2·82(3)
As · · · C(3)	2·80(3)
As · · · C(8)	2·81(3)
As · · · C(9)	2·84(3)
As · · · C(14)	2·82(3)
As · · · C(15)	2·79(3)
O · · · C(1)	3·00(3)
O · · · C(7)	2·96(3)
O · · · C(13)	2·92(3)
O · · · C(2)	3·11(3)
O · · · C(8)	2·96(3)
C(1) · · · C(7)	3·19(4)
C(1) · · · C(13)	3·19(4)
C(7) · · · C(13)	3·07(4)
C(3) · · · C(9)	3·67(4)
C(3) · · · C(14)	3·47(4)
C(9) · · · C(15)	3·73(4)

(*b*) In the anion $[(\mathrm{Nb_6Cl_{12}})\mathrm{Cl_6}]^{2-}$

(i) Distances

Nb(1)–Nb(2)	3·016(3)
Nb(1)–Nb(2′)	3·012(3)
Nb(1)–Nb(3)	3·027(3)
Nb(1)–Nb(3′)	3·013(3)
Nb(2)–Nb(3)	3·016(3)
Nb(2)–Nb(3′)	3·011(3)
Nb(1)–Cl(1)	2·41(1)
Nb(1)–Cl(3)	2·41(1)
Nb(1)–Cl(4)	2·42(1)
Nb(1)–Cl(6)	2·40(1)
Nb(2)–Cl(2)	2·42(1)
Nb(2)–Cl(3)	2·40(1)
Nb(2)–Cl(6′)	2·43(1)
Nb(2)–Cl(5)	2·42(1)
Nb(3)–Cl(1)	2·41(1)
Nb(3)–Cl(2)	2·43(1)
Nb(3)–Cl(4′)	2·43(1)
Nb(3)–Cl(5′)	2·42(1)
Nb(1)–Cl(7)	2·48(1)
Nb(2)–Cl(8)	2·49(1)
Nb(3)–Cl(9)	2·48(1)

(ii) Angles

Nb(2)–Nb(1)–Nb(3)	59·9(1)
Nb(2)–Nb(1)–Nb(3′)	59·9(1)
Nb(3)–Nb(1)–Nb(3′)	90·0(1)
Nb(2)–Nb(1)–Nb(2′)	89·7(1)
Nb(1)–Nb(2)–Nb(3)	60·2(1)
Nb(1)–Nb(2)–Nb(3′)	60·0(1)
Nb(1)–Nb(2)–Nb(1′)	90·3(1)
Nb(3)–Nb(2)–Nb(3′)	90·2(1)
Nb(1)–Nb(3)–Nb(2)	59·9(1)
Nb(1)–Nb(3)–Nb(2′)	59·9(1)
Nb(1)–Nb(3)–Nb(1′)	90·0(1)
Nb(2)–Nb(3)–Nb(2′)	89·8(1)
Nb(1)–Cl(1)–Nb(3)	77·8(2)
Nb(2)–Cl(2)–Nb(3)	76·8(2)
Nb(1)–Cl(3)–Nb(2)	77·8(2)
Nb(1)–Cl(4)–Nb(3′)	76·7(2)
Nb(2)–Cl(5)–Nb(3′)	76·7(2)
Nb(1)–Cl(6)–Nb(2′)	77·1(3)
Cl(7)–Nb(1)–Cl(1)	84·2(2)
Cl(7)–Nb(1)–Cl(6)	82·9(3)
Cl(7)–Nb(1)–Cl(4)	82·9(3)
Cl(7)–Nb(1)–Cl(3)	84·7(3)
Cl(8)–Nb(2)–Cl(2)	83·4(3)
Cl(8)–Nb(2)–Cl(3)	83·9(3)
Cl(8)–Nb(2)–Cl(6′)	83·6(3)
Cl(8)–Nb(2)–Cl(5)	83·1(3)
Cl(9)–Nb(3)–Cl(1)	84·0(2)
Cl(9)–Nb(3)–Cl(5′)	83·2(2)
Cl(9)–Nb(3)–Cl(4′)	83·4(2)
Cl(9)–Nb(3)–Cl(2)	84·0(3)

TABLE 2 (*Continued*)

(iii) Some intra-ionic non-bonded distances and angles (<4 Å)

Nb(1) · · · Nb(1′)	4·273(3)
Nb(2) · · · Nb(2′)	2·253(3)
Nb(3) · · · Nb(3′)	4·269(3)
Cl(7)–Nb(1) · · · Nb(1′)	179·5(2)
Cl(8)–Nb(2) · · · Nb(2′)	179·6(2)
Cl(9)–Nb(3) · · · Nb(3′)	179·8(2)

(iv) Distances (Å) between nearest chlorine atoms

Cl(1) · · · Cl(2)	3·40
Cl(1) · · · Cl(3)	3·40
Cl(1) · · · Cl(5′)	3·41
Cl(1) · · · Cl(6)	3·37
Cl(1) · · · Cl(7)	3·28
Cl(1) · · · Cl(9)	3·28
Cl(2) · · · Cl(3)	3·39
Cl(2) · · · Cl(4′)	3·43
Cl(2) · · · Cl(6)	3·41
Cl(2) · · · Cl(8)	3·27
Cl(2) · · · Cl(9)	3·28
Cl(3) · · · Cl(4)	3·37
Cl(3) · · · Cl(5)	3·35
Cl(3) · · · Cl(7)	3·29
Cl(3) · · · Cl(8)	3·27
Cl(4) · · · Cl(5)	3·38
Cl(4) · · · Cl(6)	3·41
Cl(4) · · · Cl(7)	3·24
Cl(4) · · · Cl(9′)	3·26
Cl(5) · · · Cl(6′)	3·43
Cl(5) · · · Cl(8)	3·26
Cl(5) · · · Cl(9′)	3·25
Cl(6) · · · Cl(7)	3·23
Cl(6) · · · Cl(8′)	3·27

(*c*) Other interatomic distances (<3·9 Å)

Cl(1) · · · C(4)	3·76(5)	Cl(6) · · · C(2)	3·72(4)
Cl(2) · · · C(10)	3·62(4)	Cl(6) · · · C(8′)	3·76(3)
Cl(4) · · · C(10′)	3·32(4)	Cl(7) · · · C(5^{III})	3·67(4)
Cl(4) · · · C(12′)	3·52(3)	Cl(8) · · · C(11^{III})	3·61(3)
Cl(4) · · · C(18^{II})	3·88(4)	Cl(9) · · · C(13^{II})	3·68(3)
Cl(4) · · · C(16^{III})	3·61(3)	Cl(9) · · · C(14^{II})	3·62(3)
Cl(5) · · · C(4′)	3·39(5)	Cl(9) · · · C(16^{II})	3·82(3)
Cl(5) · · · C(6′)	3·58(3)	Cl(9) · · · C(3^{II})	3·75(3)
Cl(5) · · · C(18^{III})	3·81(4)	Cl(9) · · · C(9^{II})	3·85(3)
Cl(5) · · · C(17^{III})	3·88(4)		

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

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

Interionic distances <3·9 Å (Table 2) consist of chlorine–carbon contacts which are comparable with the C–H · · · Cl van der Waal's contact or the aromatic ring–chlorine contact of 3·50 Å.[22]

Cation Geometry.—The individual $\mathrm{Ph_3AsO}$ units have no intrinsic symmetry imposed by the requirements of the space group. Within the phenyl groups, the carbon–carbon distances vary between 1·30 and 1·50, mean 1·39 Å, which compares well with the distance in benzene (1·40 Å) and also in triphenylarsine oxide hydrate (1·38 Å).[23] The standard deviations are high, however (*ca.* 0·04 Å), and, in the context of block-diagonal least-squares estimates, poor data and dominance of the structure by the heavy atoms, it is unlikely that the differences are significant. Carbon–arsenic distances, to which the same factors apply, range from 1·83 to 1·98 Å, mean 1·92 Å, which agrees with that in triphenylarsine oxide hydrate [1·907(9) Å] and in $[\mathrm{Ph_3AsO(HgCl_2)}]_2$ [1·91(5) Å].[24] C–As–O angles are 107—114° and do not differ significantly from the tetrahedral angle. The arsenic–oxygen distance [1·73(2) Å] is of interest, despite the rather low accuracy. It is longer than the double-bond value of 1·644(7) found in $(\mathrm{Ph_3AsO}),\mathrm{H_2O}$ [23] and 1·66(2) Å in $[\mathrm{Ph_3AsO(HgCl_2)}]_2$ [24] and more in line with the 'single-bond' values 1·697(14), and 1·702(14) Å in

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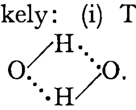
[22] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, New York, 1960, p. 260.

[23] G. Ferguson and E. W. Macaulay, *J. Chem. Soc.* (*A*), 1969, 1.

[24] C-I. Branden, *Arkiv Kemi*, 1964, **22**, 485.

$(Ph_3AsOH)Cl$,[25] 1·712(12) in $(Ph_3AsOH)Br$,[26] and 1·69 Å in *o*-phenylenediarsine oxide chloride.[5] The oxygen atom of this species is located close to the special position $(0,0,\frac{1}{2})$, $(\frac{1}{2},\frac{1}{2},0)$, of symmetry $\bar{1}$, and is thus at a distance of 2·80 Å from its inversion image. The proximity of the two oxygens at about the van der Waal's contact of 2·80 Å and a distance comparable with the $O \cdots H \cdots O$ distance in ice (2·75 Å),[22,27] suggests the presence of hydrogen bonds between pairs of cations. However, the presence of only four hydrogen bonds in such a large unit cell, coupled with the bulk of both cation and anion presumably prevents the usual infinite polymeric or large cyclic hydrogen bonded network. The symmetry requirements of the special position require a similarly centrosymmetric disposition of the protons. Three possibilities seem the most likely: (i) There are two hydrogen bonds of the type:  We are not aware of any comparable examples of this type of dual hydrogen bridge.

(ii) A proton is sited on the centre of symmetry, $O \cdots H \cdots O$. There is a precedent for this type in the recently reported[28] structure of $[(Ph_3AsO)_2H^+]_2(Hg_2Br_6)^{2-}$, in which the oxygen atoms are related in pairs to alternate pairs *via* a centre of symmetry; within each pair the oxygen–oxygen distance is short [2·40(3) Å]. The position of the hydrogen atom is supposed to be midway between these oxygen atoms. The $O \cdots O$ distance is rather shorter than ours (2·80 Å) and the As–O distance [1·68(2) Å] is similar to that [1·73(2) Å] in the present structure. (There are also comparable difficulties in formulating the cationic species.) If this were, in fact, the species present in the niobium structure, and if the anion is formulated as described, then a second proton must be accounted for. The substantial flatness of the difference Fourier makes it unlikely, even on a basis of partial occupancy, that a solvated proton exists in the lattice; moreover, this would require occupancy of a further special position by the solvated species which would be unlikely to be capable of satisfying the $\bar{1}$ symmetry requirements. There may also be the possibility that the space group $P2_1/n$ is only an approximation to one of lower symmetry; however, any unsymmetric distribution of the final proton would be likely to require an associated distortion of some of the other atoms. This seems unlikely and there is no evidence to suggest that the symmetry is in any way less than that of $P2_1/n$.

(iii) Some dynamic arrangement involving instantaneous asymmetric hydrogen bonding, but which becomes centrosymmetric on a time-averaged basis.

Anion Geometry.—The anion consists of an octahedron of niobium atoms surrounded by two types of chlorine atoms: ' bridging ', above each of the twelve edges of the niobium cluster and equidistant from the pair of niobium atoms in that edge, and ' terminal ', along the rectangular set of axes passing through the vertices of the octahedron. The $[(Nb_6Cl_{12})Cl_6]$ is centrosymmetric about the special position $(0,0,0)$, $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ which has symmetry $\bar{1}$, and in which it is central. Within the cluster, the niobium–niobium distances lie between **3·011** and **3·027** Å; as the block-diagonal refinement yields standard deviations of **0·003** Å and the accuracy of the unit-cell calibrations is no better than 0·1% in each dimension, it is unlikely that the differences are significant. The octahedron is therefore apparently regular with a mean niobium–niobium distance of **3·016** Å, the opposed cluster distances being substantially equal [4·26(1) Å]. Bridging chlorine atoms lie 2·42 Å from the niobium atoms, whereas the terminal chlorines are 2·48 ± 0·01 Å. Angles within the cluster are typically those expected for undistorted octahedra, means: Nb–Nb–Nb 60·0 and 90·1, Cl–Nb–Nb 179·6, Nb–Cl(br)–Nb 77·1, and Cl(term)–Nb–Cl(br) 83·6°.

Table 3 summarises structural data on $(M_6Cl_{12})^{x+}$ clusters, in which the ligands in all six terminal sites are equivalent, and hence the cluster is relatively undistorted.[1]

TABLE 3

Structural data (Å) available on $(M_6Cl_{12})^{x+}$ cluster compounds

	Electrons [a]	M–M	M–Cl(br)	M–Cl(term)
(Pt_6Cl_{12}) [b]	0 (or 48)	3·36	2·37	
$(pyH)_2[(Nb_6Cl_{12})Cl_6]$ [c]	14	3·02	2·43	2·48
$(Me_4N)_2[(Nb_6Cl_{12})Cl_6]$ [d]	14	3·02	2·42	2·46
$(Ph_3AsOH)_2[(Nb_6Cl_{12})Cl_6]$ [e]	14	3·02	2·42	2·48
$H_2[(Ta_6Cl_{12})Cl_6],6H_2O$ [f]	14	2·96	2·41	2·51
$(Ta_6Cl_{12})Cl_{6/2}$ [g]	15	2·92	2·43	2·56
$K_4[(Nb_6Cl_{12})Cl_6]$ [h]	16	2·91	2·49	2·60
$(W_6Cl_{12})Cl_6$ [i]	18	$2{\cdot}9_2$	$2{\cdot}3_0$	$2{\cdot}5_2$

[a] No. of electrons available for metal–metal bonding. [b] K. Brodersen, G. Thiele, and H. G. Schnering, *Z. anorg. Chem.*, 1965, **337**, 120. [c] B. Spreckelmeyer and H.-G. v. Schnering, *Z. anorg. Chem.*, 1971, **386**, 27. [d] F. W. Koknat and R. E. McCarley, *Inorg. Chem.*, 1972, **11**, 812. [e] This work. [f] C. B. Thaxton and R. A. Jacobson, *Inorg. Chem.*, 1971, **10**, 1460. [g] D. Bauer and H.-G. v. Schnering, *Z. anorg. Chem.*, 1968, **361**, 259. [h] A. Simon, H.-G. v. Schnering, and H. Schafer, *Z. anorg. Chem.*, 1968, **361**, 235. [i] R. Siepmann, H.-G. v. Schnering, and H. Schafer, *Angew. Chem. Internat. Edn.*, 1967, **6**, 637.

It can be seen that the anion geometry in $(Ph_3AsOH)_2[(Nb_6Cl_{12})Cl_6]$ is in good agreement with that found in the pyridinium and the tetramethylammonium salts. The analogous tantalum cluster $H_2[(Ta_6Cl_{12})Cl_6],6H_2O$ has significantly shorter metal–metal distances (2·96 compared with 3·02 Å), which is in line with the expected increase in metal–metal bonding for tantalum compared with niobium compounds.[29,30] Similarly the metal–

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[25] G. Ferguson and E. W. Macaulay, *Chem. Comm.*, 1968, 1288.

[26] W. R. Cullen and J. Trotter, *Canad. J. Chem.*, 1962, **40**, 1113.

[27] M. Blackman and N. D. Lisgarten, *Proc. Roy. Soc.*, 1957, *A*, **239**, 93.

[28] G. S. Harris, F. Inglis, J. McKechnie, K. K. Cheung, and G. Ferguson, *Chem. Comm.*, 1967, 442.

[29] D. L. Kepert and R. Mandyczewsky, *Inorg. Chem.*, 1968, **7**, 2091.

[30] D. L. Kepert, ' The Early Transition Metals,' Academic Press, London, 1972.

terminal-chlorine bonds are slightly longer in the tantalum compound (2·51 *vs.* 2·48 Å), and if significant reflect the decrease in metal–terminal-ligand bonding as the metal–metal bonding increases.[1]

Table 4 also shows that the metal–metal distances in $[(Nb_6Cl_{12})Cl_6]^{2-}$ are significantly longer (3·02 *vs.* 2·91 Å) and the metal–chlorine bonds significantly shorter (2·42 and 2·48 Å, *vs.* 2·49 and 2·60 Å) than in $[(Nb_6Cl_{12})Cl_6]^{4-}$, which has two more electrons available for metal–metal bonding. These changes are also reflected in the lower-energy metal–metal bonding to metal–metal antibonding electronic transitions in the visible spectra, and in the higher-energy niobium–chlorine vibrational frequencies, for the oxidised clusters (see Experimental section).

Clusters containing 24 electrons available for metal–metal bonding however have much shorter metal–metal distances (2·62 Å) and adopt a different geometry based on the $[(M_6Cl_8)Cl_6]^{2-}$ structure.[31,32]

R. A. F. acknowledges the financial assistance of a Commonwealth post-graduate award. We thank the Australian Research Grants Committee for financial support of part of this work, A. O'Connell, B. O'Connor, and G. B. Robertson for helpful advice, and B. N. Figgis and E. N. Maslen for making programs available.

[2/2771 *Received, 8th December,* 1972].

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[31] P. C. Healy, D. L. Kepert, D. Taylor, and A. H. White, *J.C.S. Dalton*, **1973**, 646.

[32] H.-G. v. Schnering, *Z. anorg. Chem.*, 1971, **385**, 75.