Notes

Crystal Structure of Tetrachlorobis[*o*-phenylenebis(dimethylarsine)]-niobium(IV)

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The crystal structure of the title compound, $[NbCl_4\{C_6H_4(AsMe_2)_2\}_2]$, has been determined by single-crystal *X*-ray diffraction at 295 K and refined by full-matrix least squares to a residual of 0.044 for 789 independent 'observed' reflections. Crystals are tetragonal, space group $I\bar{4}2m$, with a = 9.288(2), c = 16.361(3) Å, and Z = 2. The co-ordination about the niobium is dodecahedral: Nb–As 2.732 7(8); Nb–Cl 2.515(1) Å.

THE first eight-co-ordinate compound of the first transition series to be structurally characterised was $[TiCl_4(pdma)_2]$ [pdma = *o*-$C_6H_4(AsMe_2)_2$].[1,2] A number of other metal tetrahalides have been found to form bis adducts with this ligand and assumed to have the same structure on the basis of similar *X*-ray powder patterns. The properties of the d^1 niobium(IV) complexes have been studied in detail,[3-5] and the absorption bands in the visible region of their electronic spectra assigned assuming a closely similar structure to the titanium complex. Because of the expected sensitivity of *d*-orbital energies to small changes in stereochemistry, however, a structure determination of the niobium(IV) derivative has been undertaken to secure this point. The relative sizes of titanium(IV) and niobium(IV) in such complexes is also of interest as niobium(IV) has been found to form eight-co-ordinate complexes more readily than titanium(IV); *e.g.* titanium tetrachloride only forms eight-co-ordinate complexes with the first three ditertiary arsines of the following list, whereas niobium tetrachloride forms similar bis adducts with all but the last ligand:[6,7] *o*-phenylenebis(dimethylarsine); 1,2-bis(dimethylarsino)-4-methylbenzene; 1,8-bis(dimethylarsino)naphthalene; *o*-phenylenebis(diethylarsine); 1,2-bis(dimethylarsino)-3-fluorobenzene; 1,2-bis(dimethylarsino)-4-fluorobenzene; 1,2-bis(dimethylarsino)-3,3,4,4,5,5-hexafluorocyclopentane; and 1,2-bis(dimethylarsino)-3,3,4,4-tetrafluorocyclobutene.

EXPERIMENTAL

The compound was prepared as described previously[3] and recrystallised from pyridine, the specimen selected for the crystallographic work being an equilateral triangular plate, edge 0.47 mm and thickness 0.26 mm.

Crystal Data.—$C_{20}H_{32}As_4Cl_4Nb$, M = 807, Tetragonal, space group $I\bar{4}2m$ (D_{2d}^{11}, no. 121), a = 9.288(2), c = 16.361(3) Å, U = 1 411(1) Å^3, D_m = 1.91(1), Z = 2, D_c = 1.90 g cm^{-3}, $F(000)$ = 786, monochromatic Mo-K_α radiation (λ = 0.710 69 Å), μ = 53.1 cm^{-1}.

Structure Determination.—A Syntex $P\bar{1}$ four-circle diffractometer was used in the 2θ—θ mode, $\{hkl\}$ and $\{\bar{h}\bar{k}l\}$ data being gathered within the limit $2\theta < 80°$ and averaged to yield 1 300 reflections. A total of 789 reflections with $I < 3\sigma(I)$ were considered 'observed' and used in the structure solution and refinement after correction for absorption (prior to averaging). The structure was solved by vector methods and refined by full-matrix least squares; hydrogen-atom positions were estimated [r(C–H) = 0.96 Å] and constrained, U_H being set at 0.06 Å^2. Non-hydrogen atoms were refined with anisotropic thermal parameters. Refinement converged at R = 0.044, R' = 0.056, S = 1.54, reflection weights being $[\sigma^2(F_o) + 0.000\,5(F_o)^2]^{-1}$, and the Larson extinction parameter 12.0(4) × 10^{-4}. Neutral-atom scattering factors were used throughout, those for Nb, As, and Cl being corrected for anomalous dispersion (f', f'').[8-10] Calculations were carried out with the 'X-RAY '76' program system[11] implemented on a CYBER 73 computer. Final co-ordinates are given in Table 1, bond lengths and angles in Table 2. Tables of structure-factor am-

TABLE 1

Atom co-ordinates

Atom	10^4x	10^4y	10^4z
Nb	0 000(–)	*a*	5 000(–)
As	1 241.6(7)	*a*	6 340.2(5)
Cl	1 827(2)	*a*	4 540(1)
C(1)	548(9)	*a*	8 860(5)
H(1) [b]	915(–)	*a*	9 367(–)
C(2)	1 057(8)	*a*	8 130(5)
H(2) [b]	1 788(–)	*a*	8 125(–)
C(3)	495(7)	*a*	7 362(5)
C(4)	3 307(8)	1 015(11)	6 467(5)
H(4α) [b]	3 657(–)	1 562(–)	6 924(–)
H(4β) [b]	3 562(–)	20(–)	6 539(–)
H(4γ) [b]	3 678(–)	1 385(–)	5 962(–)

[a] $y = x$. [b] Parameter constrained.

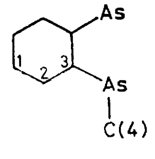

TABLE 2

Non-hydrogen molecular geometry (independent values only). Transformations of the asymmetric unit are: i ($\bar{x},\bar{y},z$); ii (y,x,z); iii ($x,y,1-z$)

(*a*) Distances (Å)

Nb–As	2 732 7(8)	C(3)–C(3^{i})	1.300(7)
Nb–Cl	2.515(1)	C(3)–C(2)	1.456(11)
As · · · As^{i}	3.261 8(8)	C(2)–C(1)	1.369(11)
As–C(4)	1.941(8)	C(1)–C(1^{i})	1.440(8)
As–C(3)	1.939(7)		

(*b*) Angles (°)

(*i*) intraligand

C(1′)–C(1)–C(2)	119.2(7)	C(3)–As–C(4)	102.9(3)
C(1)–C(2)–C(3)	120.4(5)	C(4)–As–C(4^{ii})	101.7(4)
C(2)–C(3)–C(3′)	120.4(7)	C(3)–As–Nb	113.0(2)
C(2)–C(3)–As	119.2(4)	C(4)–As–Nb	117.2(3)
C(3′)–C(3)–As	120.4(6)		

(*ii*) niobium core

As–Nb–Cl	70.76(5)	As–Nb–Cl^{iii}	76.12(5)
As–Nb–As^{i}	73.28(2)	Cl–Nb–Cl^{i}	145.20(7)
As–Nb–Cl^{i}	144.04(5)	Cl–Nb–Cl^{iii}	95.13(4)
As–Nb–As^{iii}	130.08(2)		

plitudes and thermal parameters are available as Supplementary Publication No. SUP 22912 (8 pp.).*

Atom labelling within the diarsine ligand is as above, hydrogen atoms being labelled according to the parent carbon, suffixed α, β, γ where necessary for distinguishing purposes.

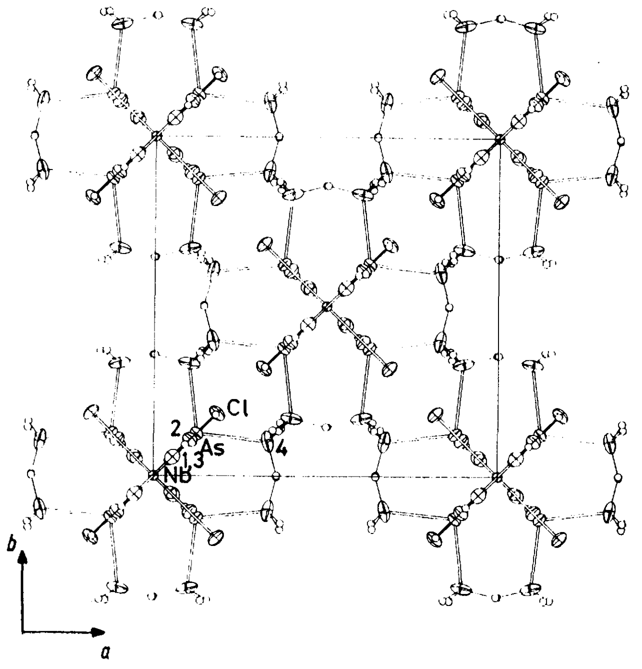

FIGURE 1 Unit-cell contents projected down the unique axis. Non-hydrogen atoms are shown with 50% probability thermal ellipsoids, hydrogen atoms with a radius of 0.1 Å

DISCUSSION

The structure comprises discrete molecules of the title complex, the niobium atom being located on a special crystallographic position of $\bar{4}2m$ symmetry, while the arsine ligands have crystallographically imposed $2m$ symmetry. The niobium environment is thus a dodecahedron with the arsenic atoms occupying the A sites and the chlorine atoms the B sites. The angular parameters of the dodecahedron [12] (Table 3) are very similar to those reported in related complexes, $\phi_{A,B}$ being the angles made by the metal–ligand bonds with the $\bar{4}$ axis. The Nb^{IV}–As distance is only 0.02 Å larger than the Ti^{IV}–As, while the Nb^{IV}–Cl distance is 0.05 Å larger than the

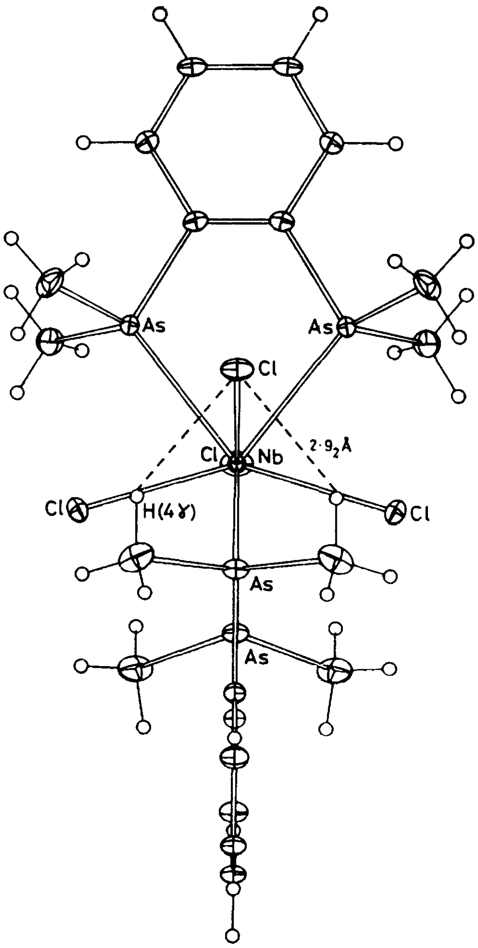

FIGURE 2 Projection of a single molecule down one of the niobium–chlorine bonds, showing the methyl-hydrogen-atom disposition relative to the chlorine. ' Contacts ' with Cl · · · H < 4.3 Å are shown

TABLE 3

Structural parameters of $[MCl_4(pdma)_2]^{x+}$

Compound	Angle/°		Distance/Å	
	ϕ_A	ϕ_B	M–Cl	M–As
$[Nb^{IV}Cl_4(pdma)_2]$ [a]	36.6	107.4	2.515	2.733
$[Ti^{IV}Cl_4(pdma)_2]$ [b]	36.4	107.5	2.46	2.71
$[Nb^{V}Cl_4(pdma)_2]_2[Nb^{V}O_2Cl_3]$ [c]	36.3	107.0	2.43_5	2.74
$[Nb^{V}Cl_4(pdma)_2][Nb^{V}OCl_4]$ [c]	36.5	107.0	2.42_6	2.74_3
$[Ta^{V}Cl_4(pdma)_2][Ta^{V}Cl_5(OEt)]$ [c]	36.3	107.1	2.40	2.76
$[Mo^{V}Cl_4(pdma)_2][I_3]$ [d]	37.8	107.3	2.45	2.65

[a] This work. [b] Ref. 1. [c] J. C. Dewan, D. L. Kepert, C. L. Raston, and A. H. White, *J.C.S. Dalton*, 1975, 2031. [d] M. G. B. Drew, G. M. Egginton, and J. D. Wilkins, *Acta Cryst.*, 1974, **B30**, 1895.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

Ti^{IV}–Cl. Comparison of the bond lengths with those in $[Nb^{V}Cl_4(pdma)_2]^+$ shows that the Nb^{IV}–As distance is equal to, or shorter than, the Nb^{V}–As, whereas the Nb^{IV}–Cl distance is 0.09 Å longer than the Nb^{V}–Cl. This can be attributed to the single *d* electron in the d_{xy} orbital repelling the four chlorine atoms which lie almost in the same plane, even though the orbital lobes are directed between these atoms. (This d_{xy} orbital cannot participate in π bonding with the arsenic atom.) This interaction may also be present in the d^1 molybdenum(V), complex, but the comparison is less clear because of the smaller metal atom.

Within the ligand the following features may be noted. (*i*) The three C–As–C angles are all very nearly 102°. (*ii*) The angle C(3)–As–Nb is less than C(4)–As–Nb, presumably a consequence of chelation, whereas (*iii*) C(3′)–C(3)–As is 120°, as are all skeletal angles of the benzene ring. However, (*iv*) the bond lengths within the benzene ring display a distinct preference for one of the two possible Kekulé forms. (*v*) Unlike many related diarsine metal complexes in which the metal atom deviates substantially from the ligand plane,[13] the metal atom, the arsenic atoms, and the aromatic ring atoms are rigorously coplanar (because of symmetry considerations) together with two of the chlorine atoms (Figure 2). Deviations of H(4α,β,γ) from the plane are 1.5_0, 1.3_8, and 2.3_3 Å respectively.

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[13] See, for example, B. W. Skelton and A. H. White, *J.C.S. Dalton*, 1980, 1556 and references therein.