Structural Studies of the 1 : 1 Addition Complexes of Niobium and Tantalum Pentachlorides with *o*-Phenylenebis(dimethylarsine)

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The addition of *o*-phenylenebis(dimethylarsine), ' diars,' in equimolar ratio to the pentachlorides of tantalum and niobium has yielded addition complexes shown by *X*-ray crystallographic structure determination to have the probable stoicheiometries $[TaCl_4(diars)_2]^+[TaCl_5(OEt)]^-$ (I), $[NbCl_4(diars)_2]^+{}_2[NbCl_3O_2]^{2-}$ (II), and $[NbCl_4(diars)_2]^+[NbOCl_4]^-$ (III). Crystals of (I) are triclinic, space group $P\bar{1}$, $a = 12.983(4)$, $b = 14.484(6)$, $c = 12.359(6)$ Å, $\alpha = 108.04(3)$, $\beta = 102.17(5)$, $\gamma = 110.35(5)°$, $Z = 2$, 2 448 observed reflections being refined to R 0.09. Crystals of (II) are monoclinic, space group $C2/c$ or Cc, $a = 20.877(4)$, $b = 16.086(3)$, $c = 19.458(2)$ Å, $\beta = 106.25(1)°$, $Z = 4$, 1 183 observed reflections refined to R 0.08. Crystals of (III) are triclinic, space group $P\bar{1}$, $a = 14.815(3)$, $b = 12.273(2)$, $c = 10.397(2)$ Å, $\alpha = 92.03(1)$, $\beta = 103.56(2)$, $\gamma = 110.80(2)°$, $Z = 2$, 2 473 observed reflections refined to R 0.06. In all three, an eight-co-ordinate dodecahedral cation is found; mean distances: Ta–As 2.76_1, Ta–Cl 2.40, Nb–As 2.74_3, and Nb–Cl 2.42_6 Å. The structures were determined from diffractometer data [(I) and (III) by the heavy-atom method, (II) by direct methods].

ADDITION of *o*-phenylenebis(dimethylarsine), ' diars,' to niobium and tantalum pentachlorides dissolved in dry carbon tetrachloride immediately precipitates the red $[NbCl_5(diars)]$ and yellow $[TaCl_5(diars)]$ respectively. These compounds are diamagnetic and isomorphous and, although significant conductivities in acetonitrile were observed, were reported as seven-co-ordinate complexes.[1] In view of our current interest in the detailed stereochemistry of complexes of high co-ordination number, particularly those containing bidentate chelate groups, a crystal-structure determination was initiated on these compounds. Previous attempts to recrystallize $[NbCl_5(diars)]$ from dry, redistilled but otherwise unpurified, nitromethane with the aid of prolonged heating yielded red, diamagnetic, chlorine-deficient compounds which were formulated as $[Nb_2OCl_8(diars)_2]$ and $[NbOCl_3(diars)]$.

Since it is generally observed that niobium oxy-compounds are much more readily formed than tantalum oxy-compounds,[2] initial attempts at recrystallization for this work were with the tantalum derivative. A sample of $[TaCl_5(diars)]$ prepared as previously described [1] was recrystallized slowly from hot acetonitrile, which had been dried over calcium hydride and fractionally distilled, yielding *ca.* 1 g of a well crystallized yellow solid (I). The results of this study indicated that a typical crystal selected for *X*-ray structure determination was not the expected $[TaCl_5(diars)]$, but instead almost certainly $[TaCl_4(diars)_2]^+[TaCl_5(OEt)]^-$. The tantalum ethoxide formation presumably arises from traces of ethanol in the solvent, too small to be detected by n.m.r. spectroscopy, but found qualitatively by gas-phase chromatography, and apparently formed by reduction of

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[1] R. J. H. Clark, D. L. Kepert, and R. S. Nyholm, *J. Chem. Soc.*, 1965, 2877.

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

the acetic acid impurities [3] in the solvent by the drying agent. Tantalum pentachloride is known to react vigorously with excess of ethanol under very mild conditions to form $[TaCl_2(OEt)_3]$, while complete replacement of chlorine to form $[Ta(OEt)_5]$ or complex anions such as $[Ta(OEt)_6]^-$ is readily achieved by removal of the liberated hydrogen chloride.[2] Analysis of the bulk sample of (I) was intermediate between that required for $[TaCl_5(diars)]$ and for $[Ta_2Cl_9(OEt)(diars)_2]$.

The finding of this eight- and six-co-ordinated ionic compound cast doubt upon some of the conclusions arising out of the earlier work, so the preparation of crystals of $[NbCl_5(diars)]$ was attempted. From the first preparation attempted a very small quantity of tiny red crystals (II) was obtained, accompanied by an appreciable quantity of a white decomposition product. A further preparation yielded a much greater quantity of red crystals (III); neither (II) nor (III) were isomorphous with the triclinic (I), (II) being monoclinic $C2/c$ or Cc, and (III) triclinic. For (II) and (III) the volumes of the asymmetric units were different, and, in addition, different from that of (I).

We now describe the determination of the structures of (I), (II), and (III) by *X*-ray diffraction methods. (In previous preparations, analytical determinations of stoicheiometry have varied widely. Accordingly they are of little corroborative value and are not reported here.)

EXPERIMENTAL

Cell dimensions were obtained in each case by a least-squares fit of the angular parameters of 15 reflections centred in the counter aperture of a Syntex $P\bar{1}$ four-circle diffractometer. For (I), data were collected by a rapid but otherwise conventional ω-scan (to avoid any problems due to possible crystal decomposition) for the range h0—8, k—10—10, l—8—8 by use of Nb-filtered Mo-$K_{\bar{\alpha}}$ radiation ($\lambda = 0.710\ 69$ Å) yielding 3 550 independent reflections of which 2 448 having $I > 3\sigma(I)$ were used in the subsequent solution and refinement with unit weights after correction for absorption (crystal size 0.35 × 0.21 × 0.24 mm).

For (II), a unique data set in the range $2\theta > 100°$ was collected by a conventional 2θ—θ scan with Ni-filtered Cu-K_α radiation ($\lambda = 1.5418$ Å) yielding 2 093 reflections of which 1 183 with $I > 2\sigma(I)$ were used in the subsequent solution and refinement with unit weights; crystal dimensions 0.10 × 0.15 × 0.11 mm.

For (III), a small crystal fragment, approximated to a sphere 0.07 mm diameter for absorption correction purposes, was used. A unique data set in the range $2\theta < 100°$ was collected by use of Cu-K_α radiation, but terminated during the $h = 8$ sequence because of a prolonged machine malfunction. 2 814 Reflections were obtained, of which 2 473 having $I > \sigma(I)$ were considered 'observed' and included in the structure solution and refinement after correction for absorption.

Crystal Data.—(I), Assuming $[TaCl_4(diars)_2]^+[TaCl_5(OEt)]^-$. $C_{22}H_{37}As_4Cl_9OTa_2$, $M = 1\ 298$, Triclinic, $a = 12.983(4)$, $b = 14.484(6)$, $c = 12.359(6)$ Å, $\alpha = 108.04(3)$, $\beta = 102.17(5)$, $\gamma = 110.35(5)°$, $U = 1\ 935(1)$ Å^3, $D_m = 2.27(2)$, $Z = 2$, $D_c = 2.23$ g cm^{-3}, $F(000) = 1216$. μ(Mo-$K_{\bar{\alpha}}$) = 101.8 cm^{-1}. Space group $P\bar{1}$, (No. 2, C_i^1).

(II), Assuming $[NbCl_4(diars)_2]^+{}_2[NbO_2Cl_3]^{2-}$. $C_{40}H_{64}As_8Cl_{11}Nb_3O_2$, $M = 1\ 845$, Monoclinic, $a = 20.877(4)$, $b = 16.086(3)$, $c = 19.458(2)$ Å, $\beta = 106.25(1)°$, $U = 6\ 273(2)$ Å^3, $D_m = 2.02(1)$, $Z = 4$, $D_c = 1.95$ g cm^{-3}, $F(000) = 3\ 376$. μ(Cu-K_α) = 144.4 cm^{-1}. Space group $C2/c$ or Cc (Nos. 15, C_{2h}^6 or 9, C_s^4).

(III), Assuming $[NbCl_4(diars)_2]^+[NbOCl_4]^-$. $C_{20}H_{32}As_4Cl_8Nb_2O$, $M = 1\ 057.6$, Triclinic, $a = 14.815(3)$, $b = 12.273(2)$, $c = 10.397(2)$ Å, $\alpha = 92.03(1)$, $\beta = 103.56(2)$, $\gamma = 110.80(2)°$, $U = 1\ 717(1)$ Å^3, $D_c = 2.05$ g cm^{-3}, $Z = 2$, $F(000) = 1\ 020$. μ(Cu-K_α) = 161.2 cm^{-1}. Space group $P\bar{1}$ (No. 2, C_i^1).

The structure of (I) was solved by the heavy-atom method and refined by 9 × 9 block-diagonal least-squares, the parameters of the TaCl As_4 core being refined as a single matrix in the latter stages. Anisotropic thermal parameters of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ were employed for the metal, chlorine, arsenic, and oxygen atoms, the remainder being isotropic. In the cationic species, aromatic hydrogen positions were fixed assuming C–H 0.95 Å, and included as invariants in the refinement. The final R was 0.091, R' $[= (\Sigma w||F_o| - |F_c||^2/\Sigma|wF_o|^2)^{\frac{1}{2}}$ being 0.110. In the final least-squares cycle, no parameter shift exceeded 0.3σ. There is some doubt about the anion stoicheiometry; given the empirical formula $TaCl_5(diars)$ and the clearly defined $[TaCl_4(diars)_2]^+$ species arising from the solution, the anion ought to be $[TaCl_6]^-$. Location of five of the chlorine atoms was unequivocal but difference maps showed the sixth to be absent with much weaker observed peaks in the vicinity suggesting the presence of co-ordinated acetonitrile or the geometrically more reasonable ethoxide group. An i.r. spectrum of the bulk sample of (I) in Nujol mull showed a band at 1 044 cm^{-1} typical of the ethoxide ν(C–O); [4] the bands at 2 300 cm^{-1} characteristic of acetonitrile co-ordinated to tantalum [5] were absent. Co-ordinated ethoxide is also more reasonable on valence considerations in the light of the diamagnetism of the complex, suggesting the presence of Ta^V throughout. Refinement of the group as ethoxide was straightforward, although the final geometry of the relatively feebly scattering carbon and oxygen atoms is somewhat erratic.

The structure of (II) was solved by direct methods in space group $C2/c$ and similarly refined to R 0.076, R' 0.083. In this structure also, the cation was well defined but difficulties arose again with the anion, somewhat exacerbated in this case by the limited data set. Whereas the cation occupies a general disposition in the crystal lattice, the niobium Nb(2) of the anion is located on a special position on the two-fold crystallographic axis at $(0, y, \frac{1}{4})$. The distribution of peaks in a difference map about Nb(2) was not centrosymmetric and clearly not $[NbCl_6]^-$ or any similar entity, a possibility which was moreover unreasonable from considerations of valence and stoicheiometry (unless Nb^{IV} is present). Peaks above and below the Nb(2), related by the two-fold axis and *ca.* 2.4 Å away, clearly suggested chlorine atoms and were successfully refined as such, whereas the remaining peaks were disposed as three dumb-bells of separation 0.5—0.1 Å each aligned normal to the two-fold axis and bisected by a plane through it and through Nb(2). Clearly, either

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[3] D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, 'Purification of Laboratory Chemicals,' Oxford, 1966.

[4] D. M. Adams, 'Metal–Ligand and Related Vibrations,' Edward Arnold, London, 1967, p. 241 and refs. therein.

[5] D. L. Kepert and R. S. Nyholm, *J. Chem. Soc.*, 1965, 2871.

TABLE 1

Final non-hydrogen atomic fractional cell parameters (*x*, *y*, *z*) and thermal parameters ($\times 10^2$ Å^2), with least-squares estimated standard deviations in parentheses

(*a*) (I) *x*, *y*, *z*: Ta, As $\times 10^4$ others $\times 10^3$

(i) The cation

	x	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ta(1)	3 853(2)	1 396(2)	2 465(2)	6.5(2)	6.6(2)	3.4(1)	3.6(1)	1.8(1)	0.4(1)
As(11)	2 096(5)	−0 437(4)	0 502(4)	7.7(4)	6.5(3)	4.5(3)	3.4(3)	1.9(3)	0.3(2)
As(12)	3 417(5)	1 933(4)	0 512(4)	7.7(4)	7.1(4)	3.7(3)	3.1(3)	1.4(2)	0.7(2)
As(21)	3 939(5)	2 353(4)	4 812(4)	7.5(4)	7.2(4)	3.7(3)	4.1(3)	2.4(2)	0.7(2)
As(22)	5 908(5)	1 657(5)	4 010(4)	7.8(4)	9.0(4)	4.3(3)	5.0(3)	2.0(3)	0.7(3)
Cl(11)	326(1)	−008(1)	306(1)	6.4(10)	8.5(9)	5.2(8)	5.0(7)	1.6(6)	−0.1(6)
Cl(12)	515(1)	327(1)	309(1)	8.6(10)	7.3(8)	4.1(8)	3.0(7)	2.8(6)	0.8(6)
Cl(21)	212(1)	169(1)	240(1)	6.8(10)	10.1(10)	5.3(9)	5.6(8)	2.1(6)	1.3(7)
Cl(22)	488(1)	071(1)	128(1)	9.2(11)	10.3(11)	4.2(8)	5.5(8)	2.6(7)	−0.1(7)

	x	*y*	*z*	*U*/Å^2		*x*	*y*	*z*	*U*/Å^2
C(111)	242(5)	−172(5)	002(5)	10(2)	C(13)	187(4)	097(4)	−202(4)	7(1)
C(112)	055(4)	−108(4)	068(5)	8(2)	C(14)	103(5)	004(4)	−311(5)	9(2)
C(121)	466(5)	241(4)	−007(5)	8(2)	C(15)	054(5)	−091(4)	−309(5)	8(2)
C(122)	300(5)	315(5)	075(5)	9(2)	C(16)	084(4)	−110(4)	−207(4)	7(2)
C(211)	263(4)	156(4)	522(4)	7(2)	C(21)	529(4)	260(4)	608(4)	6(1)
C(212)	401(4)	380(4)	527(4)	7(1)	C(22)	611(4)	231(4)	581(4)	7(2)
C(221)	604(5)	031(5)	387(5)	10(2)	C(23)	726(4)	249(4)	662(4)	7(1)
C(222)	739(5)	253(4)	388(5)	9(2)	C(24)	741(5)	298(5)	784(5)	10(2)
C(11)	173(4)	−021(3)	−094(4)	5(1)	C(25)	648(5)	327(5)	820(5)	9(2)
C(12)	213(4)	071(3)	−102(4)	6(1)	C(26)	554(5)	310(4)	732(5)	8(2)

(ii) The anion

	x	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ta(2)	8 939(2)	6 034(2)	2 579(2)	7.4(2)	7.3(1)	4.0(1)	3.6(1)	1.5(1)	0.3(1)
Cl(1)	871(2)	615(1)	447(1)	14(2)	15(1)	4(1)	5(1)	3.6(9)	2.4(9)
Cl(2)	915(2)	603(1)	071(1)	14(2)	15(1)	4(1)	6(1)	4.4(9)	1.6(9)
Cl(3)	012(1) *	794(1)	345(1)	12(1)	7(1)	9(1)	3.5(9)	4.2(9)	0.8(8)
Cl(4)	768(1)	415(1)	171(1)	9(1)	7(1)	10(1)	2.6(8)	2.3(9)	−0.3(8)
Cl(5)	716(1)	623(1)	201(1)	9(1)	14(1)	6(1)	7(1)	2.9(8)	2.5(8)
O(1)	018(3) *	564(3)	296(3)	4(2)	15(3)	7(3)	3(2)	1(2)	−1(2)

	x	*y*	*z*	*U*/Å^2		*x*	*y*	*z*	*U*/Å^2
C(1)	080(8) *	474(7)	299(8)	18(3)	C(2)	194(6) *	468(6)	314(7)	14(3)

(*b*) (II) *x*, *y*, *z*: Nb, As, Cl $\times 10^4$; others $\times 10^3$

(i) The cation

	x	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nb(1)	8 242(2)	0 130(3)	5 478(2)	4.4(3)	11.5(4)	3.0(3)	2.4(2)	1.1(2)	1.6(2)
As(11)	8 351(2)	0 770(3)	4 208(2)	5.3(3)	8.1(4)	3.3(3)	01.3(3)	1.9(2)	−0.4(3)
As(12)	8 994(2)	1 547(4)	5 785(2)	6.6(4)	10.8(5)	5.0(3)	3.9(4)	−0.2(3)	−3.3(3)
As(21)	7 129(2)	−0 308(4)	5 880(2)	4.3(3)	16.5(6)	4.4(3)	2.9(4)	1.7(3)	2.9(3)
As(22)	8 458(2)	−1 444(4)	6 045(3)	4.2(3)	13.6(6)	6.2(4)	3.0(4)	1.5(3)	3.4(8)
Cl(11)	7 639(5)	−0 746(7)	4 512(5)	5.0(7)	9.5(10)	4.6(7)	1.2(7)	0.9(6)	0.6(7)
Cl(12)	8 576(5)	0 353(9)	6 779(5)	8.0(9)	19.2(15)	4.1(7)	6.7(10)	1.7(6)	1.7(8)
Cl(21)	7 422(5)	1 252(9)	5 203(5)	6.6(8)	15.7(13)	5.7(8)	5.4(8)	2.2(6)	4.0(8)
Cl(22)	9 342(4)	−0 336(7)	5 449(5)	4.3(7)	9.8(10)	5.4(7)	1.9(7)	1.8(5)	0.7(7)

	x	*y*	*z*	*U*/Å^2		*x*	*y*	*z*	*U*/Å^2
C(111)	879(2)	003(2)	368(2)	4(1)	C(13)	953(2)	288(3)	503(3)	12(2)
C(112)	752(2)	099(2)	348(2)	5(1)	C(14)	961(2)	319(3)	448(2)	11(2)
C(121)	989(2)	141(3)	642(3)	11(2)	C(15)	933(2)	298(3)	380(2)	10(2)
C(122)	862(3)	239(3)	625(3)	13(2)	C(16)	896(2)	221(3)	369(2)	10(2)
C(211)	629(2)	−029(3)	510(2)	9(2)	C(21)	718(2)	−142(2)	634(2)	6(1)
C(212)	690(2)	043(3)	660(2)	7(1)	C(22)	776(2)	−190(2)	642(2)	5(1)
C(221)	859(2)	−238(3)	538(2)	8(1)	C(23)	780(2)	−264(2)	672(2)	6(1)
C(222)	925(2)	−158(3)	688(2)	9(1)	C(24)	725(2)	−293(3)	696(2)	7(1)
C(11)	884(2)	179(2)	429(2)	6(1)	C(25)	669(2)	−246(3)	686(2)	6(1)
C(12)	912(2)	209(3)	498(2)	8(1)	C(26)	665(2)	−172(2)	659(2)	6(1)

(ii) The anion

	x	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nb(2)	5 000 †	0 187(4)	2 500 †	20.0(7)	4.8(4)	5.4(4)	0.0 †	4.0	0.0 †

	x	*y*	*z*	*U*/Å^2		*x*	*y*	*z*	*U*/Å^2
Cl(A)	490(1)	021(1)	369(1)	9.5(4)	Cl(C) ‡	531(1)	153(2)	270(1)	12(1)
Cl(B) ‡	444(1)	−121(2)	216(1)	9.4(8)	Cl(D) ‡	601(1)	−046(1)	290(1)	5.5(6)

TABLE 1 (*Continued*)

(*c*) (III) x, y, z: As, Nb, Cl, O $\times 10^4$; others $\times 10^3$

(i) The cation

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nb	1 594(1)	3 054(1)	2 593(1)	36(2)	22(1)	27(1)	12(1)	11(1)	2(1)
As(11)	2 384(2)	1 904(1)	4 497(2)	40(2)	27(1)	37(1)	14(1)	13(1)	7(1)
As(12)	2 844(2)	4 733(1)	4 703(2)	43(2)	25(1)	32(1)	12(1)	10(1)	0(1)
As(21)	−0 343(2)	2 669(1)	1 261(2)	36(2)	31(1)	37(1)	14(1)	13(1)	3(1)
As(22)	1 493(2)	2 984(1)	−0 072(2)	43(2)	34(1)	33(1)	17(1)	14(1)	3(1)
Cl(11)	0 875(4)	0 946(3)	1 805(4)	49(5)	22(2)	51(3)	9(2)	9(2)	−2(2)
Cl(12)	1 636(4)	4 987(3)	2 093(4)	59(5)	27(2)	46(2)	20(2)	10(2)	5(2)
Cl(21)	0 597(4)	2 873(4)	4 182(4)	52(5)	52(3)	36(2)	22(3)	20(2)	7(2)
Cl(22)	3 224(4)	3 373(3)	2 298(4)	35(5)	38(2)	45(2)	15(2)	10(2)	6(2)

	x	y	z	U/Å^2		x	y	z	U/Å^2
C(11)	332(1)	291(1)	606(1)	37(4)	C(21)	−060(1)	254(1)	−066(1)	36(4)
C(12)	351(2)	413(1)	616(1)	35(4)	C(22)	020(1)	272(1)	−122(1)	36(4)
C(13)	420(1)	490(1)	729(2)	42(5)	C(23)	003(1)	261(1)	−259(2)	46(5)
C(14)	472(2)	444(2)	828(2)	57(5)	C(24)	−098(1)	234(1)	−340(2)	40(5)
C(15)	455(2)	324(2)	821(2)	62(6)	C(25)	−179(1)	214(1)	−287(2)	52(5)
C(16)	380(1)	244(1)	707(2)	53(5)	C(26)	−160(1)	225(1)	−146(1)	38(4)
C(111)	144(1)	073(1)	522(2)	49(5)	C(211)	−139(2)	127(2)	155(2)	57(6)
C(112)	317(1)	106(1)	392(2)	47(5)	C(212)	−082(2)	391(1)	171(2)	55(5)
C(121)	221(1)	558(1)	561(2)	51(5)	C(221)	185(1)	174(1)	−085(2)	50(5)
C(122)	394(1)	600(1)	431(2)	44(5)	C(222)	239(1)	438(1)	−062(2)	44(5)

(ii) The anion

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nb	5 400(1)	1 052(1)	1 885(1)	38(2)	30(1)	40(1)	12(1)	12(1)	0(1)
O	5 088(10)	2 020(10)	2 727(12)	77(13)	53(8)	68(8)	36(8)	42(8)	0(6)
Cl(1)	4 080(4)	0 558(3)	−0 193(4)	38(5)	38(2)	56(3)	14(2)	3(2)	0(2)
Cl(2)	6 439(4)	2 477(3)	0 822(4)	45(5)	38(2)	58(3)	8(2)	9(3)	9(2)
Cl(3)	4 488(4)	−0 720(4)	2 577(5)	69(5)	50(3)	66(3)	16(3)	28(3)	15(2)
Cl(4)	6 866(4)	1 115(4)	3 481(4)	57(5)	57(3)	45(3)	17(3)	−2(3)	6(2)

* Add unit translation in x. † Parameter fixed by symmetry. ‡ Population 0.5.

the species is disordered, or the space group is *Cc* rather than *C*2/*c*, the deviation from the latter comprising only the Nb(2) environment and constituting only a small perturbation on the basically centrosymmetric structure. Consideration of intensity statistics suggested that this might be so, but attempts to formulate and refine a meaningful disposition of stoicheiometrically plausible combinations of chlorine and oxygen atoms about Nb(2) in space group *Cc* failed. The entity was finally refined by disposing half-chlorine atoms at the ends of each dumb-bell and refinement of the whole structure eventually was terminated with all parameter shifts $<0.15\sigma$; clearly the stoicheiometry $[NbCl_4(diars)_2]^+$-$[NbCl_2Cl_{6/2}]$ is unrealistic if the pentavalence of all niobium

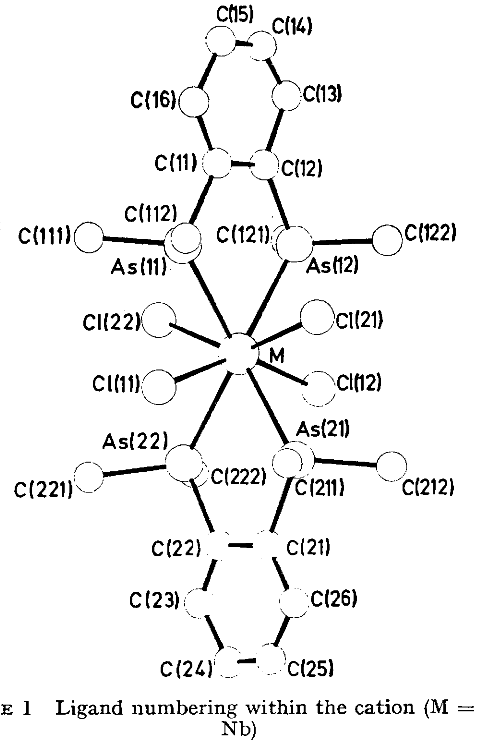

FIGURE 1 Ligand numbering within the cation (M = Ta or Nb)

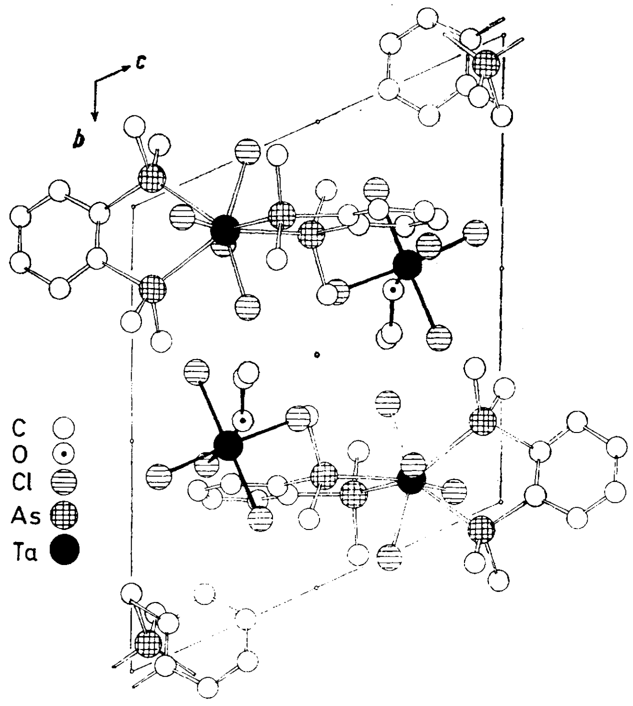

FIGURE 2 Unit-cell contents of (I) projected down *a**

atoms is to be preserved, and possibilities such as $[NbCl_3O_2]^{2-}$ with disorder present among the atomic sites normal to the two-fold axis are more reasonable.

The structure of (III) was solved by an attritional variant of the heavy-atom method and refined by 9 × 9 block-diagonal least-squares; in the final stages the parameters of the $NbOCl_4$ anion and the $NbAs_4Cl_4$ cationic core were refined as single matrices. Anisotropic thermal parameters were employed for niobium, arsenic, chlorine, and oxygen atoms, carbon atoms being refined isotropically. In the final least-squares cycle no parameter shift exceeded 0.05σ, R being 0.063 and R' 0.077. Hydrogen atoms were not located. In this structure the weighting scheme used was of the form $w = (\sigma^2|F_o| + 10^{-4}n|F_o|^2)^{-1}$, a value of $n = 4$ being found appropriate.

Neutral-atom scattering factors were employed throughout,[6] those for tantalum, niobium, arsenic, and chlorine being corrected for the effects of anomalous dispersion ($\Delta f'$,

TABLE 2

Interatomic distances (Å) and angles, with least-squares estimated standard deviations in parentheses

(*a*) The cations

(i) Metal-atom geometries; values are in the order (I), (II), (III)

M–Cl(11)	2.39(2), 2.41(1), 2.446(4)
M–Cl(12)	2.40(1), 2.46(1), 2.430(4)
M–Cl(21)	2.42(2), 2.44(1), 2.427(6)
M–Cl(22)	2.40(2), 2.43(1), 2.401(6)
Mean	2.40, 2.43$_5$, 2.42$_6$
As(11)–M–Cl(21)	76.8(3), 75.8(3), 76.7(1)
As(11)–M–Cl(22)	75.9(3), 77.2(3), 75.7(1)
As(21)–M–Cl(11)	76.1(3), 76.9(3), 76.5(1)
As(21)–M–Cl(12)	77.3(3), 76.3(3), 75.8(1)
As(12)–M–Cl(21)	75.7(4), 75.9(3), 76.2(1)
As(12)–M–Cl(22)	76.3(4), 76.9(3), 77.2(1)
As(22)–M–Cl(11)	75.1(3), 76.4(3), 77.0(1)
As(22)–M–Cl(12)	77.4(4), 75.7(4), 76.0(1)
Mean	76.3, 76.4, 76.4
As(11)–M–Cl(11)	70.6(3), 70.9(3), 71.1(1)
As(12)–M–Cl(12)	71.0(3), 70.9(4), 69.8(1)
As(21)–M–Cl(21)	70.6(3), 69.8(3), 70.4(1)
As(22)–M–Cl(22)	70.8(3), 71.0(3), 75.7(1)
Mean	70.8, 70.7, 71.8

As(11)–M–As(21)	130.0(2), 130.0(2), 131.6(1)
As(11)–M–As(22)	129.3(2), 131.3(2), 130.5(1)
As(12)–M–As(21)	131.0(2), 129.2(2), 128.6(1)
As(12)–M–As(22)	131.6(2), 131.3(2), 130.4(7)
Mean	130.5, 130.5, 130.3
Cl(11)–M–Cl(21)	95.8(5), 94.6(4), 93.6(2)
Cl(11)–M–Cl(22)	94.5(6), 95.3(4), 95.3(4)
Cl(12)–M–Cl(21)	94.7(5), 95.6(4), 95.6(2)
Cl(12)–M–Cl(22)	94.8(5), 94.1(4), 94.7(2)
Mean	95.0, 94.9, 94.8
As(11)–M–Cl(12)	143.2(4), 143.3(4), 143.0(1)
As(12)–M–Cl(11)	142.8(3), 143.3(3), 144.3(1)
As(21)–M–Cl(22)	143.8(4), 143.3(9), 143.6(1)
As(22)–M–Cl(21)	143.6(3), 142.7(3), 143.0(1)
Mean	143.4, 143.3, 143.5
Cl(11)–M–Cl(12)	146.2(4), 145.8(5), 145.9(1)
Cl(21)–M–Cl(22)	145.6(4), 146.2(4), 146.0(2)
Mean	145.9, 146.0, 146.0

(ii) The ligands: values for ligand (2) follow those for ligand (1) for each compound

	(I)	(II)	(III)	Mean
Me–As(1)	2.758(4), 2.759(6)	2.745(6), 2.742(6)	2.749(3), 2.740(3)	2.761 (Ta)
M–As(2)	2.766(7), 2.760(7)	2.737(7), 2.749(7)	2.748(2), 2.736(2)	2.743 (Nb)
As(1)–M–As(2)	72.2(2), 73.0(2)	72.4(2), 72.9(2)	73.38(6), 72.67(7)	72.8
As(1)–C(11)	1.99(7), 1.95(6)	1.97(4), 1.97(4)	1.94(2), 1.95(2)	
As(1)–C(12)	1.99(6), 1.96(6)	1.94(3), 1.99(4)	1.98(2), 1.98(2)	1.96
As(2)–C(21)	1.91(6), 1.98(6)	1.94(4), 2.04(6)	1.97(2), 1.97(2)	
As(2)–C(22)	1.98(8), 1.97(6)	1.92(6), 1.97(4)	1.94(2), 1.96(2)	
As(1)–C(1)	1.90(5), 1.92(5)	1.92(4), 1.99(4)	1.92(1), 1.93(1)	1.94
As(2)–C(2)	2.00(3), 2.04(5)	1.87(5), 1.94(4)	1.93(2), 1.91(2)	
C(1)–C(2)	1.30(7), 1.34(9)	1.40(5), 1.41(5)	1.42(2), 1.39(3)	
C(2)–C(3)	1.40(8), 1.49(8)	1.52(7), 1.32(5)	1.40(2), 1.38(2)	
C(3)–C(4)	1.42(5), 1.39(8)	1.23(8), 1.44(6)	1.40(3), 1.44(3)	1.39
C(4)–C(5)	1.31(9), 1.50(11)	1.34(6), 1.35(6)	1.40(3), 1.39(3)	
C(5)–C(6)	1.36(9), 1.33(8)	1.45(7), 1.29(6)	1.46(2), 1.42(2)	
C(6)–C(1)	1.45(5), 1.39(7)	1.42(7), 1.41(6)	1.38(3), 1.43(2)	
As(1) · · · As(2)	3.256(8), 3.283(10)	3.237(6), 3.262(7)	3.280(3), 3.244(4)	3.26$_0$
M–As(1)–C(11)	116(1), 116(1)	114(1), 115(1)	116.5(6), 117.3(6)	
M–As(1)–C(12)	117(1), 114(2)	117(1), 116(1)	115.0(5), 114.7(5)	116.0
M–As(2)–C(21)	118(2), 116(1)	116(2), 117(1)	116.3(5), 116.3(5)	
M–As(2)–C(22)	117(2), 117(2)	114(2), 116(1)	116.1(5), 116.3(4)	
M–As(1)–C(1)	113(1), 115(2)	115(1), 115(1)	114.5(5), 114.5(6)	114.5
M–As(2)–C(2)	114(2), 113(2)	114(1), 116(1)	114.4(4), 115.1(6)	
C(11)–As(1)–C(12)	101(3), 104(2)	100(1), 101(2)	103.8(8), 101.1(9)	102.1
C(21)–As(2)–C(22)	99(3), 103(3)	103(2), 102(2)	102.8(8), 100.4(8)	
C(11)–As(1)–C(1)	105(2), 103(2)	104(2), 107(2)	103.0(7), 103.4(7)	
C(12)–As(1)–C(1)	104(2), 103(2)	105(2), 102(2)	102.3(8), 104.0(8)	103.4
C(21)–As(2)–C(2)	102(2), 100(3)	105(2), 102(3)	102.1(8), 102.4(7)	
C(22)–As(2)–C(2)	105(2), 106(2)	104(2), 101(2)	103.1(8), 104.3(7)	
As(1)–C(1)–C(2)	121(4), 121(4)	123(3), 118(3)	119(1), 119(1)	
As(1)–C(1)–C(6)	121(4), 125(4)	123(3), 121(3)	120(1), 119(1)	119.7
As(2)–C(2)–C(1)	114(3), 117(4)	122(3), 118(3)	119(1), 119(1)	
As(2)–C(2)–C(3)	115(3), 121(4)	123(3), 123(3)	120(1), 121(1)	
C(1)–C(2)–C(3)	130(3), 130(3)	115(4), 119(4)	121(2), 120(2)	
C(2)–C(3)–C(4)	113(5), 111(5)	120(5), 119(3)	118(2), 119(2)	
C(3)–C(4)–C(5)	121(6), 120(5)	129(5), 121(4)	122(1), 123(2)	120.0
C(4)–C(5)–C(6)	123(4), 119(6)	115(5), 121(4)	119(2), 118(2)	
C(5)–C(6)–C(1)	120(5), 125(6)	120(4), 120(4)	118(2), 119(2)	
C(6)–C(1)–C(2)	113(5), 113(5)	121(4), 121(3)	121(1), 122(1)	

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

TABLE 2 (*Continued*)

(*b*) The anions

(i) (I)

Ta(2)–Cl(1)	2.38(2)	Cl(1)–Ta(2)–O(1)	90(1)
Ta(2)–Cl(2)	2.38(2)	Cl(2)–Ta(2)–Cl(3)	86.8(6)
Ta(2)–Cl(3)	2.38(1)	Cl(2)–Ta(2)–Cl(4)	94.0(6)
Ta(2)–Cl(4)	2.38(1)	Cl(2)–Ta(2)–Cl(5)	89.1(7)
Ta(2)–Cl(5)	2.41(2)	Cl(2)–Ta(2)–O(1)	93(1)
Ta(2)–O(1)	1.90(5)	Cl(3)–Ta(2)–Cl(4)	177.2(7)
O(1)–C(1)	1.77(13)	Cl(3)–Ta(2)–Cl(5)	91.8(6)
C(1)–C(2)	1.49(14)	Cl(3)–Ta(2)–O(1)	97(1)
		Cl(4)–Ta(2)–Cl(5)	85.5(6)
Cl(1)–Ta(2)–Cl(2)	175.8(8)	Cl(4)–Ta(2)–O(1)	85(1)
Cl(1)–Ta(2)–Cl(3)	90.0(6)	Cl(5)–Ta(2)–O(1)	171(1)
Cl(1)–Ta(2)–Cl(4)	89.1(6)	Ta(2)–O(1)–C(1)	155(3)
Cl(1)–Ta(2)–Cl(5)	88.3(7)	O(1)–C(1)–C(2)	140(7)

(ii) (II) Primed atoms are generated by the transformation: $1 - x, y, \frac{1}{2} - z$

Nb(2)–Cl(A)	2.39(1)	Nb(2)–Cl(C)	2.25(3)
Nb(2)–Cl(B)	2.54(3)	Nb(2)–Cl(D)	2.29(2)
Cl(A)–Nb(2)–Cl(B)	96.1(7)	Cl(C)–Nb(2)–Cl(A′)	93.1(8)
Cl(A)–Nb(2)–Cl(C)	85.0(8)	Cl(C)–Nb(2)–Cl(B′)	135.4(7)
Cl(A)–Nb(2)–Cl(D)	89.9(6)	Cl(C)–Nb(2)–Cl(C′)	34.0(8)
Cl(A)–Nb(2)–Cl(A′)	178.0(5)	Cl(C)–Nb(2)–Cl(D′)	133.4(8)
Cl(A)–Nb(2)–Cl(B′)	85.6(7)	Cl(D)–Nb(2)–Cl(A′)	91.0(6)
Cl(A)–Nb(2)–Cl(C′)	93.1(8)	Cl(D)–Nb(2)–Cl(B′)	36.1(7)
Cl(A)–Nb(2)–Cl(D′)	91.0(6)	Cl(D)–Nb(2)–Cl(C′)	133.4(8)
Cl(B)–Nb(2)–Cl(C)	169.3(8)	Cl(D)–Nb(2)–Cl(D′)	126.0(7)
Cl(B)–Nb(2)–Cl(D)	90.2(7)	Cl(A′)–Nb(2)–Cl(B′)	96.1(7)
Cl(B)–Nb(2)–Cl(A′)	85.6(7)	Cl(A′)–Nb(2)–Cl(C′)	85.0(8)
Cl(B)–Nb(2)–Cl(B′)	55.2(7)	Cl(A′)–Nb(2)–Cl(D′)	90.0(6)
Cl(B)–Nb(2)–Cl(C′)	135.4(7)	Cl(B′)–Nb(2)–Cl(C′)	169.3(8)
Cl(B)–Nb(2)–Cl(D′)	36.1(7)	Cl(B′)–Nb(2)–Cl(D′)	90.2(7)
Cl(C)–Nb(2)–Cl(D)	100.4(8)	Cl(C′)–Nb(2)–Cl(D′)	100.4(8)

(iii) (III) A prime denotes the centrosymmetrically related atom

Nb–O	1.70(2)	Cl(1)–Nb–Cl(2)	87.6(2)
Nb–Cl(1)	2.438(4)	Cl(1)–Nb–Cl(3)	89.0(2)
Nb–Cl(2)	2.382(5)	Cl(1)–Nb–Cl(4)	160.2(2)
Nb–Cl(3)	2.356(5)	Cl(1)–Nb–Cl(1′)	76.8(2)
Nb–Cl(4)	2.378(5)	Cl(2)–Nb–Cl(3)	163.8(2)
Nb–Cl(1′)	3.011(6)	Cl(2)–Nb–Cl(4)	88.8(2)
O–Nb–Cl(1)	99.8(4)	Cl(2)–Nb–Cl(1′)	80.8(2)
O–Nb–Cl(2)	95.7(4)	Cl(3)–Nb–Cl(4)	89.1(2)
O–Nb–Cl(3)	100.4(4)	Cl(3)–Nb–Cl(1′)	83.0(2)
O–Nb–Cl(4)	100.0(4)	Cl(4)–Nb–Cl(1′)	83.4(2)
O–Nb–Cl(1′)	175.2(4)		

TABLE 3

Equations of least-squares planes through the ligands [defined by C(1)—(6),As_2] in the form $pX + qY + rZ = s$; the estimated standard deviation of the defining atoms, σ, and the atomic deviations, Δ, are in Å. X (orthogonal, Å) is parallel to *a*; Z (orthogonal, Å) lies in the *ac* plane (towards *c*). χ^2 is given for 7 degrees of freedom

	(I)		(II)		(III)	
Ligand *i*	(1)	(2)	(1)	(2)	(1)	(2)
10^4p	9 587	1 759	8 385	1 696	8 833	−1 747
10^4q	−2 187	9 034	−5 396	4 132	1 225	9 819
10^4r	0 182	−3 910	0 752	8 947	−4 525	−0 730
s	2.703	1.322	12.590	11.606	−0.2253	3.197
σ	0.04	0.03	0.03	0.02	0.05	0.04
χ^2	4.9	1.8	3.2	2.9	122	109
ΔC(1)	0.03	−0.03	−0.02	0.01	−0.03	0.03
ΔC(2)	−0.03	−0.05	−0.01	0.02	−0.05	0.07
ΔC(3)	−0.05	0.01	0.01	0.01	−0.05	0.02
ΔC(4)	0.00	0.02	0.05	−0.03	0.04	−0.02
ΔC(5)	0.01	−0.01	−0.04	−0.04	0.08	−0.07
ΔC(6)	0.03	0.02	0.00	0.02	0.01	−0.03
ΔAs(1)	0.05	0.02	0.03	0.00	−0.02	0.07
ΔAs(2)	0.05	0.02	−0.02	−0.03	−0.06	0.01
ΔCl(*i*1)	−0.03	0.02	0.00	0.07	−0.01	−0.04
ΔCl(*i*2)	0.13	0.02	−0.03	0.08	0.07	−0.02
ΔM	0.03	0.02	−0.01	0.05	0.02	−0.01
Angle (1,2)°	87.6		89.2		89.9	

$\Delta f'')$.[7] Computation was carried out on the CDC 6200 machine at this University using a local adaptation of the '*X*-Ray '72' system.[8] Structure amplitude tables are deposited as a Supplementary Publication No. SUP 21384 (22 pp., 1 microfiche).*

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* For details, see Notice to Authors, No. 7, *J.C.S. Dalton*, Index issue, 1974.

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

[8] '*X*-Ray ' System of Programs, Technical Report, TR 192, Computer Science Centre, University of Maryland, June, 1972.

The cationic ligand numbering is given in Figure 1. Atoms are referred to as *e.g.* C(*ij*) where *i* is the ligand number (1 or 2) which is omitted where it is possible to do so unambiguously. Final atomic co-ordinates and thermal parameters are listed in Table 1, bond distances and angles in Table 2, and details of planes in Table 3. Figures 2—4 illustrate unit-cell contents for (I)—(III).

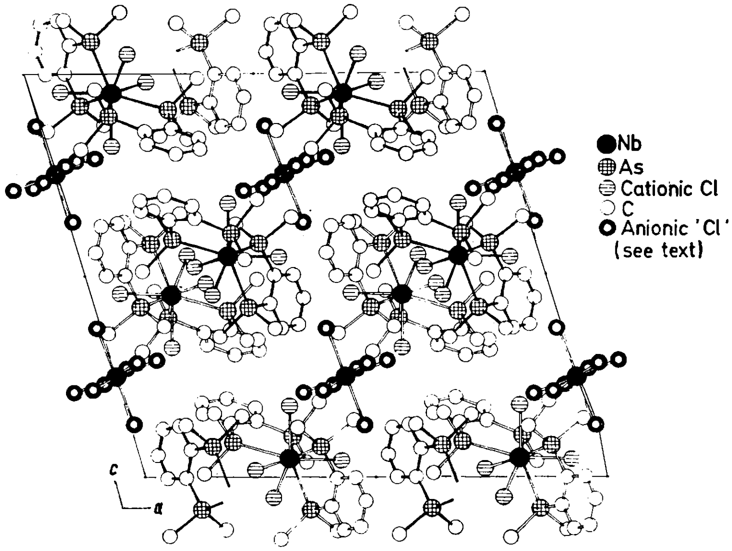

FIGURE 3 Unit-cell contents of (II) projected down *b*

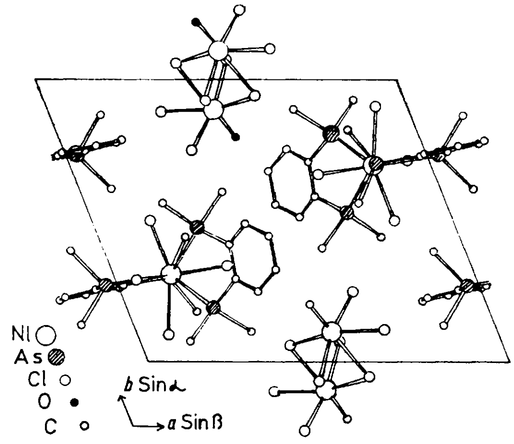

FIGURE 4 Unit-cell contents of (III) projected down *c*

DISCUSSION

Crystallographic evidence establishes clearly in all three above structures the presence of an eight-co-ordinate $[MCl_4(diars)_2]^{n+}$ cation; in (I) the cationic charge must almost certainly be 1+ and, in (II), although the value is dependent on the anion stoicheiometry, the red colour of the complex typical of the earlier reported Nb^V derivatives of this type {rather than, say, the green typical of $[Nb^{IV}Cl_4(diars)_2]$}[9] suggests that both cationic and anionic species contain Nb^V and that the cationic charge in (II) is probably also 1+. This is corroborated by (III) in which the anion stoicheiometry is much more clearly established. For niobium and tantalum in oxidation state V, these are novel examples of eight-co-ordinate stereochemistry of the type [M(bidentate)$_2$(unidentate)$_4$], although there are well established precedents with these ligands for titanium, zirconium, hafnium, vanadium, niobium, tantalum, and uranium in the IV state;[9] crystallographic data are available for $[TiCl_4(diars)_2]$,[10] the other M^{IV} derivatives (uranium excepted) being isomorphous.

The cation stereochemistry is the dodecahedron rather than the alternative square antiprism; this is established by the requirement of the latter that either ' planes ' (i) and (ii) [(i) is defined by As(12), As(22), Cl(12), Cl(22); (ii) by As(11), As(21), Cl(11), Cl(21)], or (iii) and (iv) [(iii) by As(12), As(21), Cl(12), Cl(21); (iv) by As(11), As(22), Cl(11), Cl(22)] be planar, which is not fulfilled; the mean deviations of the defining atoms in each case being As 0.25, Cl −0.25 Å. The metal atom is closely coplanar with the ligands and also with a pair of opposed chlorine atoms; these two planes interpenetrate at an angle very close to the expected 90°. Ligand–ligand repulsion calculations[11] predict that for a bidentate ligand bite of 1.19, as here, ψ_B will be 18.0° (for $n = 6$), compared with 17.1° (I), 17.0° (II), and 17.0° (III) observed. The only other compounds of stoicheiometry [M(bidentate)$_2$(unidentate)$_4$] are $[TiCl_4(diars)_2]$[10] [bite 1.19, ψ_B, found 17.5°, calc. ($n = 6$) 18.0°], and the similarly dodecahedral $[Cd(NO_3)_2(H_2O)_4]$[12] [bite 0.83, ψ_B, found 9.7°, calc. ($n = 6$) 9.9°], and $[W\{ON(Me)NO\}_2Me_4]$[13] and $[Ca(NO_3)_2(MeOH)_4]$[14] in which the two bidentate ligands are mutually *cis* rather than *trans*, and for which calculations have not yet been carried out.

The Ta–As and Nb–As distances are the only ones so far established crystallographically, although Nb–Cl distances are established.[15-21] The mean Nb–Cl(term) distance in (III) (2.42$_6$ Å) is consistent with the high co-ordination number of the metal; it is also longer than its counterpart (2.40 Å) in (I) (*cf.* mean Ta–Cl in gaseous $TaCl_5$, 2.30 Å);[17] this could be a consequence of the lanthanide contraction but, if so, it is interesting that the metal–arsenic distances follow a reversed trend (mean Nb–As 2.74$_3$, mean Ta–As 2.76$_1$). In (III), the more accurate geometry suggests that the arsenic–phenylene-carbon distances in the ligand (1.92 Å) may be slightly

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shorter than the arsenic–methyl-carbon distances (1.96 Å); this effect is probably an illusory consequence of the non-location of hydrogen atoms on the methyl groups. It is evident, however, that the co-ordination sphere of the arsenic atoms is considerably distorted about the metal atom, all C–As–C angles being *ca.* 103° while all Nb–As–C angles are *ca.* 115°, as is usual in complexes of this ligand.

The anions appear to be new species; in (I) the crystal structure strongly suggests the presence of [TaCl$_5$(OEt)]$^-$; the mean Ta–Cl distance (2.38 Å) is slightly shorter than that found in the cation, as expected. There appears to be no precedent for a Ta–O(alkoxide) distance. The anion in (II) remains an enigma. Clearly the atoms on the two-fold axis are chlorine, at 2.39 Å; the ' atoms ' in the plane through this axis are at significantly shorter distances and appear to consist of disordered oxygen and chlorine atoms superimposed, or alternatively this is a species of lower symmetry in the acentric space group *Cc* which we cannot resolve. We suggest that the species [NbCl$_3$O$_2$]$^{2-}$ may be present since it satisfies valence requirements and also the three-fold co-ordination in the plane through the two-fold axis, although it is less satisfactory with regard to sample density.

In (III), the anion is the first structurally established example of its type. It is basically square pyramidal in form with the apex of the pyramid occupied by an oxygen atom at 1.70(2) Å; this value may be slightly shorter than any previously determined values,[22-24] as a consequence of the lower co-ordination number, but the significance of such a deduction is very dubious. The Nb–Cl distances vary rather widely (Table 2); that Nb–Cl(1) [2.438(4) Å] is outstandingly long in comparison with the remainder is a consequence of the anion lying close to a centre of symmetry, so that Cl(1) bridges to the sixth co-ordination position about the niobium (opposite to the oxygen) with a very long contact of 3.011(6) Å. All O=Nb–Cl(*n*) angles are considerably greater than 90°. It is likely (but again at a somewhat indeterminate level of significance) that the remaining non-bridging Nb–Cl distances (mean *ca.* 2.37 Å) are considerably larger than the values found in other niobium(v) species containing several chlorine ligands such as NbOCl$_3$ (2.24 Å),[15] NbCl$_5$(POCl$_3$) (2.30 Å),[16] and NbCl$_5$ (2.28 Å).[19] However, this distance is considerably shorter than that found in the highly co-ordinated cation (2.42$_6$ Å) and other species with high co-ordination number and fewer chlorine ligands [NbCl(OMe)$_2$(CS$_2$·NEt$_2$)$_2$] 2.46,[21] [NbCl$_2$(OEt)O(bipy)] 2.45 Å.[20]

The interaction between the pair of anions is clearly very weak and it is not unlikely that in a compound of different lattice properties it could easily exist as a monomeric species, as it may well do also in solution. Salts of the [NbOCl$_4$]$^-$ anion with a variety of cations have been previously reported.[25-27]

We wished to establish the nature of the co-ordination stereochemistry in [MCl$_5$(diars)]. Although (I) appears homogeneous and beautifully crystalline, it is possible that it may be a mixture containing [TaCl$_4$(diars)$_2$]-[TaCl$_6$] as well which may very well be isomorphous with (I). From the crystallographic evidence for (II) and (III), it is clear from the symmetry and cell volume that there exist a variety of crystalline products, probably with similar cations but with anions exhibiting wide differences in the ratio of halogen-to-oxygen atoms and heavily dependent upon the relative care in solvent purification.

Nevertheless, these ionic compounds prepared from acetonitrile appear to be different to those prepared from carbon tetrachloride; the latter appear to be seven-co-ordinate monomers as originally formulated, although a crystalline product suitable for *X*-ray work has not yet been obtained. The clearest distinction between seven- and eight-co-ordinate metal atoms in the present case rests on the i.r. spectra in the region of the arsenic–methyl rocking and stretching vibrations, which are observed to shift to higher energies when the ligand is co-ordinated. The shift is greater by 5—10 cm^{-1} for six- and seven-co-ordination than it is for eight-co-ordination. The arsenic–methyl stretching vibrations at 568 and 576 cm^{-1} in the free ligand are at 590 and 609 cm^{-1} for (I) but at 611 and 622 cm^{-1} for [TaCl$_5$(diars)] precipitated from carbon tetrachloride. Similarly, the arsenic–methyl rocking vibrations at 846 and 885 cm^{-1} in the free ligand are at 872 and 909 cm^{-1} for (I) but at 872 and 913 cm^{-1} for a sample precipitated from carbon tetrachloride. This effect has also been observed for complexes of a large number of ditertiary arsines.[28]

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