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Preparation and Structure of Bis(bis(diphenylphosphino)methane)hexachlorodiniobium(III), $Nb_2Cl_6(dppm)_2$

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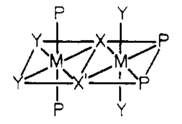
The reaction of $Nb_2Cl_6(SMe_2)_3$ with dppm gives $Nb_2Cl_6(dppm)_2$ in 68% yield. The molecular structure, determined by X-ray crystallography, is of the same type previously found for $Ta_2Cl_6(dmpe)_2$ and $Nb_2Cl_6(dppe)_2$ in which two octahedra are joined on a common edge with bridging Cl atoms and the diphosphine ligands are chelated in positions trans to the bridging positions. The virtual symmetry of the $M_2Cl_6P_4$ unit is thus D_{2h}. The $Nb_2Cl_6(dppm)_2$ molecule has some unusual dimensions, viz., a P–Nb–P angle of 67.36 (5)° and an $Nb{=}Nb$ distance of 2.696 (1) Å. The latter is the shortest $M{=}M$ distance known in molecules of this general class. The compound crystallizes in space group $P2_1/n$ with unit cell dimensions of $a = 10.614$ (1) Å, $b = 17.507$ (4) Å, $c = 14.126$ (2) Å, $\beta = 105.79$ (1)°, $V = 2526$ (1) Å^3, and $Z = 2$. There is a crystallographic inversion center at the midpoint of the $Nb{=}Nb$ bond.

Introduction

The phosphine complexes of Nb^{III} and Ta^{III} halides characteristically have binuclear structures in which there are edge-sharing bioctahedra. The M to M distances (ca. 2.7 Å) along with the diamagnetism of the molecules lead to the conclusion that $M{=}M$ double bonds are formed. This general result, however, may find expression in various possible detailed arrangements, several of which are shown as **1**–**4**. The first



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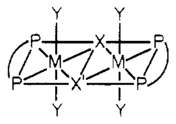

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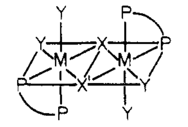

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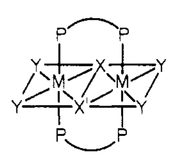

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$M_2Cl_6P_4$ type compound to be characterized crystallographically,[1] and still the only one in which the four phosphorus atoms belong to separate monophosphines, is $Ta_2Cl_6(PMe_3)_4$, which has the type of structure represented schematically as **1**. There are now two structurally characterized compounds with bidentate diphosphine ligands, $Ta_2Cl_6(dmpe)_2$[2] and $Nb_2Cl_6(dppe)_2$,[3] both having the type **2** structure (abbreviations used for diphosphine ligands: dmpe, $Me_2PCH_2CH_2PMe_2$; dppe, $Ph_2PCH_2CH_2PPh_2$; dppm, $Ph_2PCH_2PPh_2$.) As already noted,[2] provided the bidentate phosphine ligands are suited to forming unstrained chelate rings, as is the case with 1,2-diphosphinoethane ligands such as dmpe and dppe, structure **2** would appear to be preferred over **3** and **4** when nonbonded repulsive forces between ligands are considered. Nonetheless, in the case of $Ta_2OCl_4(SMe_2)(dmpe)_2$ a structure of type **3** was found,[4] with O and Me_2S occupying the bridging positions.

The work reported here was undertaken with the idea that a structure of type **4** would be favored if a ligand more suited to bridging than chelating were to be used. A structure of type **4** was desired as a starting point from which a triply bonded $M_2Cl_4(\mu\text{-PP})_2$ molecule might be obtained by reduction. The diphosphine ligand chosen was dppm, $Ph_2PCH_2PPh_2$. While dppm is known to form chelate rings[5] in many cases, it has also been shown to serve as a bridge in dinuclear molecules in which an enormous variety of other ligands and an enormous range of M to M distances (from ca. 2.1 to ca. 3.7 Å) are found.[6] We felt that in a $Nb_2Cl_6(dppm)_2$ molecule, structure **4** might be the stable one. Nature demurred.

Table I. Summary of X-ray Diffraction Analysis for $Nb_2Cl_6(dppm)_2$

formula	$Nb_2Cl_6P_4C_{50}H_{44}$
fw	1167.33
space group	$P2_1/n$
a, Å	10.614 (1)
b, Å	17.507 (4)
c, Å	14.126 (2)
α, deg	90.0
β, deg	105.79 (1)
γ, deg	90.0
V, Å^3	2526 (1)
Z	2
d_{calcd}, g/cm^3	1.535
cryst size, mm	0.3 × 0.3 × 0.2
μ(Mo Kα), cm^{-1}	9.127
data collecn instrument	Enraf-Nonius CAD-4
radiation	Mo Kα (λ_α = 0.710 73 Å)
scan method	ω–2θ
data collecn range	$2 < 2\theta < 50°$; $+h, +k, \pm l$
no. of unique data	3023
no. of data with $F_o^2 \geq 3\sigma(F_o^2)$	2241
no. of parameters refined	280
R^a	0.0431
$R_w{}^b$	0.0554
quality-of-fit indicator^c	1.358
largest shift/esd, final cycle	0.02

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c} Quality of fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$.

Experimental Section

Preparation. All manipulations were performed under an atmosphere of argon by using standard techniques. $Nb_2Cl_6(SMe_2)_3$ was

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[2] Cotton, F. A.; Falvello, L. R.; Najjar, R. C. *Inorg. Chem.* **1983**, *22*, 375.

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[6] (a) McKeer, I. R.; Cowie, M. *Inorg. Chim. Acta* **1982**, *65*, L107 (Rh–Rh = 3.46 Å). (b) Grossel, M. C.; Moulding, R. P.; Seddon, K. R. *Ibid.* **1982**, *64*, L275. (c) Turney, T. W. *Ibid.* **1982**, *64*, L141. (d) Hanson, B. E.; Fanwick, P. E.; Mancini, J. S. *Inorg. Chem.* **1982**, *21*, 3811 (Co–Co = 2.64 Å). (e) Prest, D. W.; Mays, M. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1982**, 737. (f) Abbott, E. H.; Bose, K. S.; Cotton, F. A.; Hall, W. T.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 3240 (Mo–Mo = 2.14 Å). (g) Chakravarty, A. R.; Cotton, F. A.; Schwotzer, W. *Inorg. Chem.*, in press (Os–Os = 3.67 Å).

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Table II. Positional and Isotropic Equivalent Thermal Parameters for $Nb_2Cl_6(dppm)_2$[a]

atom	x	y	z	B, Å^2
Nb	0.02284 (6)	0.00435 (4)	0.41085 (4)	2.28 (1)
Cl(1)	−0.1968 (2)	−0.0105 (1)	0.4343 (1)	3.08 (4)
Cl(2)	0.0051 (2)	0.1403 (1)	0.3891 (1)	3.62 (5)
Cl(3)	0.4487 (2)	0.3707 (1)	0.1151 (1)	3.36 (4)
P(1)	−0.0810 (2)	0.0064 (1)	0.2166 (1)	2.70 (4)
P(2)	0.2029 (2)	0.0154 (1)	0.3123 (1)	2.73 (4)
C(1)	0.0812 (7)	0.0091 (5)	0.1903 (5)	3.8 (2)
C(2)	−0.1726 (8)	0.0888 (5)	0.1531 (6)	3.7 (2)
C(3)	−0.276 (1)	0.1143 (6)	0.1845 (7)	6.0 (3)
C(4)	−0.352 (1)	0.1744 (7)	0.1371 (9)	7.8 (3)
C(5)	−0.325 (1)	0.2119 (7)	0.0628 (8)	7.2 (3)
C(6)	−0.224 (1)	0.1867 (6)	0.0262 (7)	6.0 (3)
C(7)	−0.141 (1)	0.1261 (5)	0.0756 (7)	5.2 (2)
C(8)	−0.1656 (8)	−0.0742 (5)	0.1424 (6)	3.5 (2)
C(9)	−0.2210 (7)	−0.1314 (5)	0.1898 (7)	4.2 (2)
C(10)	−0.2850 (8)	−0.1934 (5)	0.1330 (7)	4.8 (2)
C(11)	−0.2924 (9)	−0.1972 (6)	0.0334 (7)	5.7 (3)
C(12)	−0.237 (1)	−0.1431 (7)	−0.0093 (9)	8.7 (4)
C(13)	−0.174 (1)	−0.0801 (6)	0.0467 (7)	7.9 (3)
C(14)	0.3214 (7)	−0.0604 (4)	0.3087 (6)	3.2 (2)
C(15)	0.3762 (8)	−0.1013 (5)	0.3922 (7)	4.1 (2)
C(16)	0.4724 (9)	−0.1569 (6)	0.3923 (7)	5.5 (2)
C(17)	0.5099 (9)	−0.1696 (7)	0.3065 (8)	6.3 (3)
C(18)	0.4524 (9)	−0.1286 (6)	0.2222 (7)	5.7 (3)
C(19)	0.3591 (8)	−0.0721 (5)	0.2229 (6)	4.5 (2)
C(20)	0.2986 (8)	0.1011 (4)	0.3083 (6)	3.3 (2)
C(21)	0.2385 (8)	0.1691 (5)	0.2701 (6)	4.2 (2)
C(22)	0.3152 (9)	0.2356 (5)	0.2700 (7)	5.2 (2)
C(23)	0.4476 (9)	0.2343 (6)	0.3092 (7)	5.5 (3)
C(24)	0.5093 (9)	0.1659 (6)	0.3489 (7)	5.9 (3)
C(25)	0.4371 (8)	0.0980 (5)	0.3489 (7)	4.6 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

prepared according to the literature method.[7] The ligand dppm was purchased from Strem Chemicals, Inc.

$Nb_2Cl_6(SMe_2)_3$ (0.3 g, 0.5 mmol) and dppm (0.4 g, 1.0 mmol) were placed in a flask and dissolved in 25 mL of toluene. The mixture was stirred for 2 days, and 0.4 g of purple solid (0.34 mmol; 68% yield of $Nb_2Cl_6(dppm)_2$) was obtained after filtration, washing with toluene, and vacuum drying of the precipitate. The compound was soluble in CH_2Cl_2 and THF but with decomposition. Crystalline material was obtained in the following manner: 0.3 g of Nb_2Cl_6(tetrahydrothiophene)$_3$ was dissolved in 10 mL of toluene, and the solution was filtered into a Schlenk tube. A 20-mL portion of a 1:2 hexane–toluene mixture was then layered on top of this solution, followed by 10 mL of a 1:1 hexane–toluene solution containing 0.3 g of dppm. Upon mixing of the reactants due to slow diffusion, crystals of $Nb_2Cl_6(dppm)_2$ were obtained. They had very irregular shapes, but examination on a diffractometer showed that they were single and were of good quality.

X-ray Crystallographic Procedures. The structure of a single crystal of $Nb_2Cl_6(dppm)_2$ was determined by application of general procedures that have already been fully described elsewhere.[8] The crystal parameters and basic information on data collection and structure refinement are summarized in Table I. Polarization and Lorentz corrections were applied to the intensity data.

The position of the Nb atom was obtained from a three-dimensional Patterson function. Three cycles of isotropic least-squares refinement gave values of $R = 0.442$ and $R_w = 0.516$. Subsequent series of Fourier syntheses and isotropic least-squares refinements revealed the positions of all non-hydrogen atoms. The final values of R and R_w obtained after the refinement with anisotropic thermal parameters were equal to 0.043 and 0.055, respectively, while the largest residual peak in the last difference Fourier map had an intensity of ca. 0.5 e/Å^3. A complete list of structure factors and a table of anisotropic thermal parameters are available as supplementary material.

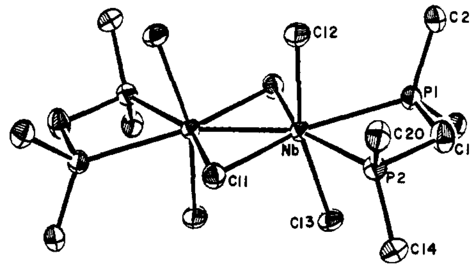

Figure 1. ORTEP drawing of the $Nb_2Cl_6(dppm)_2$ molecule, showing the atom-labeling scheme. There is a crystallographic inversion center relating the halves of the molecule. Each atom is represented by its ellipsoid of thermal vibration at the 40% probability level.

Table III. Bond Distances (Å) for $Nb_2Cl_6(dppm)_2$[a]

Nb–Nb′	2.696 (1)	C(8)–C(9)	1.417 (10)
Cl(1)	2.456 (2)	C(13)	1.334 (12)
Cl(1)′	2.451 (2)	C(9)–C(10)	1.410 (11)
Cl(2)	2.400 (2)	C(10)–C(11)	1.389 (13)
Cl(3)	2.400 (2)	C(11)–C(12)	1.341 (13)
P(1)	2.664 (2)	C(12)–C(13)	1.416 (13)
P(2)	2.660 (2)	C(14)–C(15)	1.367 (10)
P(1)–C(1)	1.859 (7)	C(19)	1.391 (10)
C(2)	1.833 (8)	C(15)–C(16)	1.411 (11)
C(8)	1.840 (8)	C(16)–C(17)	1.393 (12)
P(2)–C(1)	1.855 (7)	C(17)–C(18)	1.382 (13)
C(14)	1.838 (7)	C(18)–C(19)	1.402 (11)
C(20)	1.822 (7)	C(20)–C(21)	1.388 (10)
C(2)–C(3)	1.362 (11)	C(25)	1.426 (11)
C(7)	1.392 (11)	C(21)–C(22)	1.422 (11)
C(3)–C(4)	1.384 (12)	C(22)–C(23)	1.363 (12)
C(4)–C(5)	1.334 (14)	C(23)–C(24)	1.406 (13)
C(5)–C(6)	1.383 (13)	C(24)–C(25)	1.415 (11)
C(6)–C(7)	1.435 (12)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Selected Bond Angles (deg) for $Nb_2Cl_6(dppm)_2$[a]

Nb′–Nb–Cl(1)	56.58 (4)	Cl(2)–Nb–Cl(3)	162.87 (7)
Cl(1)′	56.77 (4)	P(1)	81.88 (6)
Cl(2)	98.52 (6)	P(2)	84.46 (6)
Cl(3)	98.61 (6)	Cl(3)–Nb–P(1)	83.67 (6)
P(1)	146.48 (5)	P(2)	81.53 (6)
P(2)	146.16 (5)	P(1)–Nb–P(2)	67.36 (5)
Cl(1)–Nb–Cl(1)′	113.35 (5)	Nb–Cl(1)–Nb′	66.65 (5)
Cl(2)	94.47 (7)	Nb–P(1)–C(1)	93.5 (2)
Cl(3)	94.64 (6)	C(2)	122.1 (3)
P(1)	89.91 (5)	C(8)	125.3 (3)
P(2)	157.19 (6)	Nb–P(2)–C(1)	93.7 (2)
Cl(1)–Nb–Cl(2)	94.86 (7)	C(14)	123.8 (2)
Cl(3)	94.79 (7)	C(20)	124.2 (2)
P(1)	156.73 (6)	P(1)–C(1)–P(2)	105.3 (3)
P(2)	89.42 (6)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Results and Discussion

Qualitative examination of the reactions of $Nb_2Cl_6(SMe_2)_3$ with diphosphines of the type $Ph_2P(CH_2)_nPPh_2$, where n = 1–6, has given very similar results in each case, independent of n. Upon stirring of a mixture of the Nb complex and excess diphosphine in toluene at room temperature, an abundant purple precipitate was obtained within 1–2 days. The products all dissolved in dichloromethane and tetrahydrofuran but underwent rapid decomposition into insoluble brown and blue species, for CH_2Cl_2 and THF, respectively. Analogous tantalum systems behave in essentially the same manner. Apparently in each case a complex of the type $M_2Cl_6(LL)_2$, where LL denotes a diphosphine, is formed. Structural properties of appropriate niobium[3] and tantalum[2] complexes and the trend observed in the mode of coordination of diphosphines[5] suggest that, for $2 \leq n \leq 6$, complexes with chelated LL were

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(8) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.

Table V. Important Bond Lengths in $M_2X_6P_4$ Molecules[a,b]

bond	$Ta_2Cl_6(PMe_3)_4$ (1)	$Ta_2Cl_6dmpe_2$ (2)	$Ta_2O(Me_2S)Cl_4dmpe_2$ (3)	$Nb_2Cl_6dppe_2$ (4)	$Nb_2Cl_6dppm_2$ (5)
M-M	2.721 (1)	2.710 (1)	2.726 (1)	2.729 [9]	2.696 (1)
M-Cl_b	2.452 [14][c]	2.460 [1]	*b*	2.450 [6]	2.454 [3]
M-Cl_t	2.399 [1]	2.415 [7]	2.407 [4]	2.394 [4]	2.400 [0]
M-P	2.656 [10][d]	2.603 [2]	2.629 [3]	2.678 [11]	2.662 [2]

[a] Numbers in brackets are variances, obtained from the expression $[(\Sigma\Delta_i^2)/n(n-1)]^{1/2}$, where Δ_i is the deviation of the *i*th value from the arithmetic mean and *n* is the total number of values averaged. [b] All have two μ-Cl atoms except 3 in which the bridging groups are O and Me_2S. [c] Nonequivalent values have been averaged. [d] Values for the two phosphorus atoms trans to each other were omitted from the average.

obtained. We had hoped, however, that for $n = 1$, that is with dppm, a bridging mode of coordination might be found. However, the $Nb_2Cl_6(dppm)_2$ molecule is also structurally of type **2**, as may be seen from the ORTEP drawing in Figure 1.

The atomic positional parameters and equivalent isotropic thermal parameters are listed in Table II, while Tables III and IV give bond distances and bond angles, respectively.

With the molecule of $Nb_2Cl_6(dppm)_2$ located on an inversion center there are two formula units per unit cell. The coordination sphere has the edge-sharing bioctahedron geometry with virtual D_{2h} symmetry. The $Nb_2P_4(Cl_b)_2$ moiety (Cl_b denotes the bridging chlorine atom) is essentially planar with the methylene carbon C(1) located approximately 0.11 Å away from the plane. The P(1)–Nb–P(2) angle of 67.36 (5)° is significantly more acute than in the related Ta–dmpe[2] and Nb–dppe[3] complexes (79.09 (5) and 77.7 [7]°, respectively). The presence of a formally double Nb–Nb bond is in accord with the oxidation state of the metal (+3) and the highly obtuse Cl(1)–Nb–Cl(1)′ and very acute Nb–Cl(1)–Nb′ angles, as well as the short metal–metal distance. The latter, equal to 2.696 (1) Å, is, in fact, considerably smaller than those in the similar, structurally characterized, complexes of Nb and Ta with tertiary phosphines. The shortest metal–metal separation previously observed in such complexes was found in $Ta_2Cl_6(dmpe)_2$, and it is equal to 2.710 (1) Å.

A comparison of some key distance in the five structures that have been determined is presented in Table V. It is first of all notable how little difference it makes whether the metal atoms are niobium or tantalum. The effect of the lanthanide contraction is very clearly seen in these molecules. The virtual constancy of the M═M bond distance in the first four compounds strongly suggests that the shorter distance in $Nb_2Cl_6(dppm)_2$ is of significance. We think it is connected with the fact that in this compound the P–M–P angle, 67.36 (5)°, is so much smaller than those, ca. 78°, found in compounds **2**–**4**. Whether this is an electronic or steric effect is uncertain. A purely steric effect is a possibility since the closing of the P–M–P angle would enable the Cl_b–M–Cl_b angles to open more easily as the M═M distance decreases.

The main question raised by this structure is why it is preferred to one of type **4**. It is possible that we have obtained a kinetically rather than thermodynamically preferred product, but in the absence of any evidence to support this, we shall assume that the structure found is truly more stable than one of type **4**. It may also be noted that we have recently obtained a compound,[9] $Mo_2Cl_6(dppm)_2$, that does have a structure of type **4**; thus, we know that there is no unsuspected inherent reason why such a structure is ruled out.

While several pertinent considerations can be mentioned, we have found no decisive argument favoring structure **2** over **4** in this case. Our speculations will therefore, in accord with the well-known First Law of Well-Regulated Discourse,[10] be brief. In the actual structure the apparent strain in the 4-membered chelate rings could be offset by enhanced Nb═Nb bond energy. At the same time, a structure of type **4** might be disfavored because phosphorus atoms, which usually manifest a greater trans weakening effect than chlorine atoms, are placed entirely trans to each other. This second point, however, is not very convincing since in $Ta_2Cl_6(PMe_3)_4$ there are two PMe_3 ligands trans to each other and in the aforementioned $Mo_2Cl_6(dppm)_2$ as well as in other molecules pairs of dppm ligands are known to adopt the type of trans–trans arrangement shown in **4**. In short, we have no good explanation for the present result.

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Registry No. **5**, 87352-18-9; $Nb_2Cl_6(SMe_2)_3$, 61069-51-0; Nb_2Cl_6(tetrahydrothiophene)$_3$, 38531-73-6; Nb, 7440-03-1.

Supplementary Material Available: Tables of additional bond angles, anisotropic thermal parameters, and observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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(9) Diane Beck Lewis and Willi Schwotzer, unpublished work.

(10) (a) Cotton, F. A.; Hunter, D. L. *J. Am. Chem. Soc.* **1976**, *98*, 1413 (especially ref 33 therein). (b) See also: Baral, S.; Cotton, F. A.; Ilsley, W. H. *Inorg. Chem.* **1981**, *20*, 2696.