Structural Characterization of a Doubly-bonded Diniobium Compound, Bis-(1,2-bis-diphenylphosphinoethane)hexachlorodiniobium(III)

F. ALBERT COTTON* and WIESLAW J. ROTH

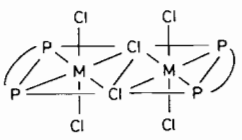
Department of Chemistry, Texas A&M University, College Station, Texas 77843, U.S.A.

Received September 15, 1982

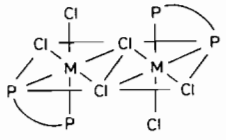
The compound $Nb_2Cl_6(Ph_2PCH_2CH_2PPh_2)_2$ has been prepared by a literature method and obtained in the form of crystals suitable for X-ray crystallography. These crystals, which also contain toluene and CH_2Cl_2 molecules, are triclinic (space group $P\bar{1}$) with the following unit cell dimensions: a = 15.733(3) Å, b = 19.489(4) Å; c = 11.683(3) Å, α = 100.21(2)°; β = 110.25(2)°; γ = 95.99(2)°; V = 3253(3) Å^3, Z = 2. The dinuclear molecules have a structure very similar to that previously found for $Ta_2Cl_6(Me_2PCH_2CH_2PMe_2)_2$, in which two octahedral $TaCl_4$(dmpe) units are united by two bridging Cl atoms with all P atoms trans *to these bridges. The $Nb_2Cl_6P_4$ set of atoms thus has approximate D_{2h} symmetry. The following bond lengths and angles were found: Nb–Nb: 2.721(2) Å, 2.738(3) Å. Nb–Cl_t(av): 2.397[3] Å. Nb–Cl_b(av): 2.450[6] Å. Nb–P(av): 2.678[11] Å. Nb–Cl_b–Nb(av): 67.7[1]°. Cl_b–Nb–Cl_b(av): 112.3[1]°. There are two crystallographically independent molecules, each residing on an inversion center.*

Introduction

As part of a program of studies of the chemistry of the group V elements in their lower oxidation states, we recently prepared and characterized the ditantalum(III) compound [1], $Ta_2Cl_6(dmpe)_2$, showing it to have a structure of type *1*. This compound was chemically rather intractable, being



1



2

unreactive and generally insoluble. We are now examining related complexes with modified diphosphine ligands and in the course of doing so, the previously reported [2] niobium compound, $[NbCl_3(dppe)]_2$, dppe = $Ph_2PCH_2CH_2PPh_2$, has been reexamined. The previous authors proposed that the molecule is dinuclear on the basis of its diamagnetism and a molecular weight measurement made on a related diarsine complex. They found the compound to be "too insoluble in toluene to permit recrystallization". They apparently made no further effort to characterize it structurally or chemically, but postulated, on the basis of NMR evidence, a structure of type *1*, rather than type *2*, which is also a reasonable one.

We have found that the compound is soluble in both methylene chloride and THF, although the solutions decompose rapidly at room temperature. Crystals can be obtained from a cold (*ca.* −15 °C) solution in CH_2Cl_2, despite the slow decomposition that is observed. Using crystals so obtained, we have determined the structure, which is, indeed, a dinuclear one of type *1*.

Experimental

Preparation

All manipulations were performed under an atmosphere of argon using standard techniques. $Nb_2Cl_6(SMe_2)_3$ was prepared according to the literature method [2]. The ligand dppe was purchased from Strem Chemicals.

$Nb_2Cl_6(SMe_2)_3$ (0.5 g, 0.84 mmol) and excess dppe (0.8 g, 2.0 mmol) were dissolved in 30 ml of toluene and the mixture stirred overnight. A large amount of precipitate was obtained, separated from the solution and then stirred for a few minutes with 10 ml of CH_2Cl_2. The resulting suspension was filtered and the purple solution, separated from the undissolved portion of the complex, was stored in a refrigerator at −15 °C. A few milligrams of dark red, plate-shaped crystals was obtained after several days.

X-Ray Crystallography

A crystal of approximate dimensions 0.2 × 0.2 × 0.05 mm was mounted in a glass capillary with the

*Author to whom correspondence should be addressed.

0020-1693/83/0000-0000/$03.00

TABLE I. Crystallographic Parameters.

FORMULA	$Nb_2Cl_{10}P_4C_{61}H_{60}$
Formula weight	1457.40
Space group	$P\bar{1}$
a, Å	15.733(3)
b, Å	19.489(4)
c, Å	11.683(3)
α, degrees	110.21(2)
β, degrees	100.25(2)
γ, degrees	95.99(2)
V, Å^3	3253(3)
Z	2
d_{calc}, g/cm^3	1.487
Crystal size, mm	0.2 × 0.2 × 0.05
μ(MoKα), cm^{-1}	8.848
Data collection instrument	Enraf-Nonius CAD-4
Radiation	Mo Kα ($\lambda\alpha$ = 0.71073 Å)
Scan method	ω-2θ
Data collection range	$0 \leq 2\theta \leq 50$; +h, ±k, ±l
No. unique data	6975
$F_o^2 \geq 3\sigma(F_o^2)$	3738
Number of parameters refined	648
R[a]	0.074
R_w[b]	0.092
Quality-of-fit indicator[c]	2.093
Largest shift/esd, final cycle	0.60

[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 = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

TABLE II. Positional Parameters and Their Estimated Standard Deviations[a].

Atom	x	y	z	B(Å^2)
NB(1)	−0.0414(1)	0.05692(9)	0.0201(2)	2.39(4)
Cl(1)	0.0353(3)	−0.0039(3)	0.1839(4)	3.1(1)
Cl(2)	0.0879(3)	0.1494(3)	0.0754(4)	3.4(1)
Cl(3)	−0.1915(3)	−0.0095(3)	−0.0284(5)	3.9(1)
P(1)	−0.1318(4)	0.1517(3)	−0.0944(5)	3.1(1)
P(2)	−0.0879(3)	0.1310(3)	0.1978(5)	2.9(1)
C(1)	−0.154(1)	0.215(1)	0.028(2)	4.7(6)
C(2)	−0.190(1)	0.167(1)	0.107(2)	3.6(5)
C(11)	−0.074(1)	0.2166(9)	−0.155(2)	3.9(6)
C(12)	−0.094(1)	0.201(1)	−0.288(2)	4.4(6)
C(13)	−0.047(1)	0.250(1)	−0.334(2)	5.5(7)
C(14)	0.010(1)	0.308(1)	−0.257(2)	4.9(7)
C(15)	0.031(2)	0.323(1)	−0.127(2)	5.5(7)
C(16)	−0.010(1)	0.275(1)	−0.076(2)	4.0(6)
C(21)	−0.246(1)	0.124(1)	−0.223(2)	3.7(5)
C(22)	−0.273(2)	0.054(1)	−0.294(2)	5.4(7)
C(23)	−0.358(2)	0.034(1)	−0.391(3)	7.4(9)
C(24)	−0.411(2)	0.083(1)	−0.427(3)	8.2(9)
C(25)	−0.389(2)	0.151(1)	−0.367(3)	7.5(8)
C(26)	−0.301(2)	0.176(1)	−0.255(2)	5.8(7)
C(31)	−0.005(1)	0.209(1)	0.313(2)	3.1(5)
C(32)	0.086(1)	0.205(1)	0.359(2)	3.7(5)
C(33)	0.147(1)	0.265(1)	0.448(2)	4.5(6)
C(34)	0.118(2)	0.324(1)	0.486(2)	4.8(6)
C(35)	0.019(1)	0.326(1)	0.438(2)	4.5(6)
C(36)	−0.042(1)	0.270(1)	0.353(2)	3.5(5)
C(41)	−0.129(1)	0.0827(9)	0.297(2)	3.1(5)
C(42)	−0.064(2)	0.082(1)	0.415(2)	5.0(6)
C(43)	−0.094(2)	0.044(1)	0.492(2)	5.4(6)
C(44)	−0.192(2)	0.014(1)	0.450(2)	7.8(8)
C(45)	−0.249(1)	0.016(1)	0.337(2)	5.4(6)
C(46)	−0.224(1)	0.050(1)	0.258(2)	4.8(6)
Nb(1A)	0.4524(1)	0.43947(9)	0.4129(2)	1.93(4)
Cl(1A)	0.4250(3)	0.5573(2)	0.3866(4)	2.8(1)
Cl(2A)	0.5493(3)	0.4310(3)	0.2924(4)	3.1(1)
Cl(3A)	0.3322(3)	0.4160(3)	0.4895(4)	3.0(1)
P(1A)	0.4452(3)	0.2993(3)	0.3647(4)	2.6(1)
P(2A)	0.3095(3)	0.3973(3)	0.1961(4)	2.6(1)
C(1A)	0.367(1)	0.2687(9)	0.199(2)	2.8(5)
C(2A)	0.276(1)	0.3017(9)	0.186(2)	3.1(5)
C(11A)	0.548(1)	0.2620(9)	0.368(2)	3.0(5)
C(12A)	0.543(2)	0.201(2)	0.302(3)	9.1(9)
C(13A)	0.626(2)	0.169(2)	0.314(3)	9.1(9)
C(14A)	0.706(2)	0.207(2)	0.398(2)	9.9(9)
C(15A)	0.712(2)	0.268(2)	0.479(3)	11(1)
C(16A)	0.630(2)	0.293(1)	0.458(3)	7.4(9)
C(21A)	0.397(1)	0.2453(9)	0.446(2)	2.9(5)
C(22A)	0.424(1)	0.269(1)	0.575(2)	4.0(6)
C(23A)	0.394(1)	0.227(1)	0.645(2)	5.0(6)
C(24A)	0.334(2)	0.162(1)	0.589(2)	6.3(7)
C(25A)	0.302(1)	0.139(1)	0.456(2)	6.6(7)
C(26A)	0.334(1)	0.181(1)	0.383(2)	3.9(5)
C(31A)	0.207(1)	0.435(1)	0.187(2)	3.0(5)
C(32A)	0.139(1)	0.400(1)	0.221(2)	4.4(6)
C(33A)	0.061(1)	0.429(1)	0.217(2)	5.4(7)
C(34A)	0.051(2)	0.494(1)	0.174(3)	7.3(9)
C(35A)	0.120(2)	0.530(2)	0.143(3)	9(1)
C(36A)	0.199(1)	0.498(1)	0.147(2)	4.8(6)
C(41A)	0.321(1)	0.4035(9)	0.049(1)	2.4(5)
C(42A)	0.280(2)	0.349(1)	−0.060(2)	4.9(6)
C(43A)	0.287(2)	0.352(1)	−0.179(2)	6.4(8)
C(44A)	0.342(2)	0.414(1)	−0.180(2)	5.7(7)
C(45A)	0.382(1)	0.463(1)	−0.075(2)	5.4(7)
C(46A)	0.376(1)	0.464(1)	0.047(2)	4.1(5)*
C(50)	0.825(2)	0.873(2)	0.171(3)	7.9(9)
Cl(51)	0.7002(7)	0.8483(4)	0.1024(7)	10.0(3)
Cl(52)	0.8607(6)	0.8372(5)	0.3006(9)	10.8(3)
C(60)	0.467(3)	0.681(2)	0.011(4)	11.(1)*
Cl(61)	0.384(1)	0.6566(9)	0.092(2)	16.1(6)*
Cl(62)	0.437(1)	0.759(1)	−0.009(2)	18.5(7)*
C(70)	0.500	0.000	0.000	12(3)*
Cl(71)	0.471(3)	0.938(3)	0.103(5)	15(2)*
Cl(72)	0.449(4)	1.000(3)	0.079(6)	20(2)*
C(80)	0.221(3)	0.626(2)	−0.263(4)	17(2)*
C(81)	0.137(2)	0.508(1)	−0.308(2)	6.9(7)*
C(82)	0.118(2)	0.516(2)	−0.427(3)	12(1)*
C(83)	0.149(2)	0.548(2)	−0.498(3)	9.1(9)*
C(84)	0.207(3)	0.542(2)	−0.364(4)	13(1)*
C(85)	0.177(3)	0.600(2)	−0.473(4)	15(2)*
C(86)	0.811(3)	0.420(2)	0.219(4)	14(1)*

[a]Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: B = 1/3 trace **B**.

TABLE III. Bond Distances (Å) for the $Nb_2Cl_6(dppe)_2$ Molecules.

	Molecule 1	Molecule 2
Nb(1)–Nb(1)′	2.738(3)	2.721(2)
Nb(1)–Cl(1)	2.455(4)	2.433(4)
Nb(1)–Cl(1)′	2.462(4)	2.451(4)
Nb(1)–Cl(2)	2.391(4)	2.405(4)
Nb(1)–Cl(3)	2.398(4)	2.393(4)
Nb(1)–P(1)	2.709(4)	2.671(4)
Nb(1)–P(2)	2.672(4)	2.661(4)
P(1)–C(1)	1.87(2)	1.85(1)
P(1)–C(11)	1.86(2)	1.83(2)
P(1)–C(21)	1.85(2)	1.81(2)
P(2)–C(2)	1.87(2)	1.85(2)
P(2)–C(31)	1.86(2)	1.82(2)
P(2)–C(41)	1.86(2)	1.82(2)
C(1)–C(2)	1.61(2)	1.60(2)
C(11)–C(12)	1.44(2)	1.27(2)
C(11)–C(16)	1.38(2)	1.34(2)
C(12)–C(13)	1.44(2)	1.48(3)
C(13)–C(14)	1.33(2)	1.33(2)
C(14)–C(15)	1.40(3)	1.36(4)
C(15)–C(16)	1.41(2)	1.40(3)
C(21)–C(22)	1.39(2)	1.39(2)
C(21)–C(26)	1.42(2)	1.41(2)
C(22)–C(23)	1.38(2)	1.42(2)
C(23)–C(24)	1.36(3)	1.38(3)
C(24)–C(25)	1.32(3)	1.42(3)
C(25)–C(26)	1.50(3)	1.45(2)
C(31)–C(32)	1.37(2)	1.41(2)
C(31)–C(36)	1.45(2)	1.40(2)
C(32)–C(33)	1.42(2)	1.40(2)
C(33)–C(34)	1.36(2)	1.44(3)
C(34)–C(35)	1.46(2)	1.42(3)
C(35)–C(36)	1.36(2)	1.44(3)
C(41)–C(42)	1.40(2)	1.40(2)
C(41)–C(46)	1.43(2)	1.40(2)
C(42)–C(43)	1.43(2)	1.45(2)
C(43)–C(44)	1.46(3)	1.42(3)
C(44)–C(45)	1.32(3)	1.32(2)
C(45)–C(46)	1.37(2)	1.45(2)

TABLE IV. Bond Angles (deg.) for the $Nb_2Cl_6(dppe)_2$ Molecules.

	Molecule 1	Molecule 2
NB(1)′–NB(1)–Cl(1)	56.29(9)	56.46(9)
NB(1)′–NB(1)–Cl(1)′	56.03(9)	55.83(9)
NB(1)′–NB(1)–Cl(2)	98.6(1)	99.0(1)
NB(1)′–NB(1)–Cl(3)	96.7(1)	97.9(1)
NB(1)′–NB(1)–P(1)	142.8(1)	141.8(1)
NB(1)′–NB(1)–P(2)	140.1(1)	139.8(1)
Cl(1)–NB(1)–Cl(1)′	112.3(1)	112.3(1)
Cl(1)–NB(1)–Cl(2)	95.0(1)	94.6(1)
Cl(1)–NB(1)–Cl(3)	94.0(1)	95.3(1)
Cl(1)–NB(1)–P(1)	160.9(1)	161.5(1)
Cl(1)–NB(1)–P(2)	84.1(1)	83.5(1)
Cl(1)′–NB(1)–Cl(2)	94.6(1)	95.4(1)
Cl(1)′–NB(1)–Cl(3)	93.5(1)	93.5(1)
Cl(1)′–NB(1)–P(1)	86.8(1)	86.1(1)
Cl(1)′–NB(1)–P(2)	162.8(1)	163.7(1)
Cl(2)–NB(1)–Cl(3)	164.6(1)	163.1(1)
Cl(2)–NB(1)–P(1)	81.8(1)	80.6(1)
Cl(2)–NB(1)–P(2)	88.6(1)	87.1(1)
Cl(3)–NB(1)–P(1)	85.6(1)	85.8(1)
Cl(3)–NB(1)–P(2)	79.9(1)	80.5(1)
P(1)–NB(1)–P(2)	77.0(1)	78.4(1)
NB(1)–Cl(1)–NB(1)′	67.7(1)	67.7(1)
NB(1)–P(1)–C(1)	106.8(5)	104.0(5)
NB(1)–P(1)–C(11)	121.1(5)	120.6(5)
NB(1)–P(1)–C(21)	121.4(6)	120.3(5)
C(1)–P(1)–C(11)	99.2(8)	103.2(7)
C(1)–P(1)–C(21)	103.5(8)	104.3(7)
C(11)–P(1)–C(21)	101.4(7)	102.1(7)
NB(1)–P(2)–C(2)	103.7(5)	103.2(5)
NB(1)–P(2)–C(31)	119.7(5)	116.5(5)
NB(1)–P(2)–C(41)	118.5(4)	121.3(5)
C(2)–P(2)–C(31)	105.8(7)	105.2(7)
C(2)–P(2)–C(41)	104.5(7)	106.2(7)
C(31)–P(2)–C(41)	103.1(7)	103.1(7)
P(1)–C(1)–C(2)	106(1)	106.6(9)
P(2)–C(2)–C(1)	106(1)	105.8(9)
P(1)–C(11)–C(12)	117(1)	122(2)
P(1)–C(11)–C(16)	122(1)	119(1)
C(12)–C(11)–C(16)	121(2)	118(2)
C(11)–C(12)–C(13)	117(2)	121(2)
C(12)–C(13)–C(14)	120(2)	117(2)
C(13)–C(14)–C(15)	123(2)	123(2)
C(14)–C(15)–C(16)	119(2)	115(2)
C(11)–C(16)–C(15)	119(2)	125(2)
P(1)–C(21)–C(22)	120(1)	117(1)
P(1)–C(21)–C(26)	118(1)	122(1)
C(22)–C(21)–C(26)	121(2)	121(1)
C(21)–C(22)–C(23)	120(2)	120(2)
C(22)–C(23)–C(24)	120(2)	122(2)
C(23)–C(24)–C(25)	124(2)	118(2)
C(24)–C(25)–C(26)	119(2)	121(2)
C(21)–C(26)–C(25)	116(2)	118(2)
P(2)–C(31)–C(32)	119(1)	120(1)
P(2)–C(31)–C(36)	118(1)	118(1)
C(32)–C(31)–C(36)	123(1)	122(1)
C(31)–C(32)–C(33)	118(2)	121(2)
C(32)–C(33)–C(34)	122(2)	118(2)
C(33)–C(34)–C(35)	119(2)	122(2)
C(34)–C(35)–C(36)	121(2)	118(2)
C(31)–C(36)–C(35)	117(1)	119(2)
P(2)–C(41)–C(42)	117(1)	122(1)
P(2)–C(41)–C(46)	122(1)	118(1)
C(42)–C(41)–C(46)	121(1)	120(1)
C(41)–C(42)–C(43)	118(2)	124(2)
C(42)–C(43)–C(44)	118(2)	116(2)
C(43)–C(44)–C(45)	120(2)	118(2)
C(44)–C(45)–C(46)	124(2)	129(2)
C(41)–C(46)–C(45)	118(2)	113(1)

use of epoxy cement. Triclinic unit cell parameters and intensity data were obtained on an Enraf-Nonius CAD-4 diffractometer using standard procedures. The summary of crystallographic data is presented in Table I. Polarization and Lorentz corrections were applied to the intensity data.

Structure Solution and Refinement

Positions of Nb atoms belonging to two crystallographically independent molecules, each located around an inversion center were obtained from a three-dimensional Patterson function. Three cycles of isotropic least squares refinement gave values of $R_1 = 0.42$ and $R_2 = 0.52$. Subsequent series of Fourier syntheses and isotropic least squares refinements revealed the positions of 64 non-hydrogen atoms plus a molecule of methylene chloride. A number of peaks, having intensity around 1–4 e/Å^3, which still remained in the difference Fourier map were assigned to poorly defined toluene and dichloromethane molecules. The latter was disordered over two positions with one of the carbon atoms, having occupancy 1/4, located on an inversion center. In the following least squares refinement only 66 atoms were assigned anisotropic thermal parameters since one carbon atom in one of the phosphine phenyl rings gave a non-positive definite temperature factor. The final values of R_1 and R_2 were equal to 0.074 and 0.092, respectively, while the largest peak in the last difference Fourier map had an intensity of *ca.* 0.9 e/Å^3.

The final positional parameters and isotropic thermal parameters equivalent to the anisotropic ones (available as a separate table from FAC) are listed in Table II. A table of the observed and calculated structure factors is also available, on request, from FAC.

Results and Discussion

The crystalline material we have obtained appears from the crystallographic examination to have the composition $Nb_2Cl_6(dppe)_2 \cdot C_6H_5CH_3 \cdot 2CH_2Cl_2$. However, there is some uncertainty about the exact degree of solvation since the toluene molecule and one of the dichloromethane molecules did not refine clearly.

The unit cell contains two crystallographically independent $Nb_2Cl_6(dppe)_2$ molecules, each residing on an inversion center and nearly identical in structure. The structure is of type *1* and closely resembles that found for $Ta_2Cl_6(dmpe)_2$ [1]. There appears to be a consistent preference for this structure rather than *2* and thus, insofar as structural factors control reactivity, a similar, low reactivity, as found in $Ta_2Cl_6(dmpe)_2$, may be a general characteristic of all substances of this composition.

The structure of molecule 1 is shown in Fig. 1, along with the atom numbering. The structure of molecule 2 is nearly identical, and the atom numbering scheme is analogous except for addition of the letter A to each one (*Cf.* Table II). The bond lengths and angles are listed in Tables III and IV.

The analogous bond lengths and bond angles in $Nb_2Cl_6(dppe)_2$ and $Ta_2Cl_6(dmpe)_2$ match very closely, throughout. The only difference that seems worthy of note is that the Nb=Nb distances found here are each longer, by 0.028(3) Å and 0.011(2) Å, than the Ta=Ta distance in $Ta_2Cl_6(dmpe)_2$.

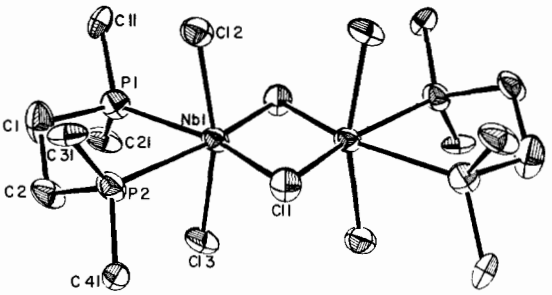


Fig. 1. ORTEP drawing of the $Nb_2Cl_6(dppe)_2$ molecule. Phenyl rings have been omitted for clarity. This is molecule 1. Molecule 2 is virtually identical and is similarly numbered (see text).

Acknowledgement

We are grateful to the National Science Foundation for support.

References

1 F. A. Cotton, L. R. Falvello and R. C. Najjar, *Inorg. Chem.*, *22*, 375 (1983).
2 A. D. Allen and S. Naito, *Can. J. Chem.*, *54*, 2948 (1976).