

2.045. The solution ESR spectrum in chloroform at 213 K reveals a three-line pattern characteristic of the ^{14}N ligand hyperfine interaction with the unpaired electron and corresponds to $\langle A \rangle = 14.4$ G and $\langle g \rangle = 2.047$. The iron complex need not retain its linear Fe-N-O group, but there is also no known reason for this group to bend in solution. Although the solution g value agrees well with that in the solid, this does not establish a linear Fe-N-O group in both cases. The three components of g , and A , were determined from the spectrum of the iron compound in the diamagnetic $[\text{Co}(\text{NO})(i\text{-Prdtc})_2]$ host at 100 K. The method used was illustrated by Goodman et al.²⁵ The results are tabulated with the spectra in Figure 3c. The average g and A values calculated from these results are similar to those obtained in the other media (Figure 3a,b). This indicates either that the Fe-N-O group remains linear despite the nonlinearity of the cobalt host or, more likely, that the Fe-N-O group is bent but without great influence on the ESR parameters, especially the g value. The g values are similar to, but larger than, those for $[\text{Fe}(\text{NO})\{\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2\}_2]$,²⁵ which has 2.042, 2.038, 2.027 for g_x, g_y, g_z compared with 2.054, 2.050, 2.037 in the present complex. The A values are also generally slightly larger at 12.5, 13.0, 16.25 G for A_x, A_y, A_z in the present complex, compared with 12.8, 11.1, 14.5 G. Although the slightly larger values could be a manifestation of greater electron coupling in the linear Fe-N-O linkage, the difference is small enough to be explicable in terms of other causes.

The lower value of the $\nu_{\text{N-O}}$ energy in the bent Co-N-O linkage (1610 cm^{-1}) than in its linear Fe-N-O analogue (1695 cm^{-1}) is in keeping with the general trend that is apparent for linear and bent M-N-O groups (Table V). However, it should be noted that this is only a trend, with a number of exceptions, the most noteworthy of which is that the $\nu_{\text{N-O}}$ for the linear Fe-N-O in $[\text{Fe}(\text{NO})(i\text{-Prdtc})_2]$ falls well within the range of the bent linkages! Thus, while comparisons of very similar complexes can give some structural information, the individual values of $\nu_{\text{N-O}}$ bear no general relationship to structures. All other features in the region $4000\text{--}800\text{ cm}^{-1}$

are identical for the two compounds. In the far-infrared region, a strong absorption is observed for both compounds at 375 cm^{-1} , which is assigned as the M-S stretch. In the M-NO stretching region, the iron complex exhibits a single sharp peak at 280 cm^{-1} for the ordered linear Fe-NO group. By contrast, the bent Co-NO group manifests itself as three peaks in the region $275\text{--}305\text{ cm}^{-1}$, possibly reflecting the threefold Co-N-O disorder.

On the basis of the very low bending frequency for the $\{\text{Fe-N-O}\}^7$ group, we had previously suggested that minor changes in the molecular packing can have a substantial effect on the Fe-N-O angle. The dramatic difference in the structure of the M-N-O group in the otherwise extremely similar and crystallographically isomorphous $[\text{Fe}(\text{NO})(i\text{-Prdtc})_2]$ and $[\text{Co}(\text{NO})(i\text{-Prdtc})_2]$ complexes further supports this. The activation of the nitrosyl group in the catalytic reduction of CO is believed to require interconversion between linear and bent M-N-O configurations.⁴⁴ However, this interconversion has only been observed in two cases where an extra ligand is added to the coordination sphere.^{39,45} The present results provide an example in which the geometry is determined by very minor molecular changes, indicative of a very facile interconversion between the geometries.

Acknowledgment. Support received under NSF Grant No. CHE0770B72 and MBS Grant No. 5S06RR08016-11 NIH/DDR is gratefully acknowledged.

Registry No. $\text{Fe}(\text{NO})(i\text{-Prdtc})_2$, 72251-12-8; $[\text{Co}(\text{NO})(\text{en})_2](\text{ClO}_4)_2$, 15334-82-4; $\text{Co}(\text{NO})(i\text{-Prdtc})_2$, 83897-62-5.

Supplementary Material Available: Listings of thermal parameters, bond lengths and angles, least-squares planes, and structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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A Bis(diphosphine)hexachloroditantalum Complex with a Ta-Ta Double Bond: Hexachlorobis[bis(dimethylphosphino)ethane]ditantalum(III)

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The title compound has been prepared in good yield by reaction of bis(dimethylphosphino)ethane with $\text{Ta}_2\text{Cl}_6(\text{Me}_2\text{S})_3$. It has an edge-sharing bioctahedral structure with the metal atoms, two bridging chlorine atoms, and the phosphorus atoms forming a central plane and four chlorine atoms occupying axial positions to complete octahedra about each metal atom. The Ta atoms are drawn together with Ta-Cl-Ta and Cl-Ta-Cl angles in the central bridging unit of $66.88(4)$ and $113.12(4)^\circ$, respectively, and a Ta=Ta distance of $2.710(1)\text{ \AA}$. The molecule differs structurally from the previously reported $\text{Ta}_2\text{Cl}_6(\text{PMe}_2)_4$ in the location of all phosphorus atoms in equatorial positions and chemically in its lack of reaction with H_2 . The crystals belong to space group $P2_1/n$ with $a = 9.342(1)\text{ \AA}$, $b = 13.353(1)\text{ \AA}$, $c = 10.632(1)\text{ \AA}$, $\beta = 95.70(1)^\circ$, and $Z = 2$. Each molecule lies on a crystallographic inversion center. Refinement of a model omitting hydrogen atoms converged with $R_1 = 0.024$ and $R_2 = 0.037$, with use of 1958 data and 109 variables. Low solubility has thwarted effects to study the compound in solution.

Introduction

In continuation of our studies¹ of the chemistry of niobium and tantalum in their III oxidation state, we have been examining compounds containing halide ions and phosphine molecules as ligands. Both Ta^{III} and Nb^{III} have a marked tendency to form binuclear complexes in which there are

M=M double bonds, although there are mononuclear compounds as well. In the case of mixed halo-phosphine complexes both mono- and dinuclear complexes have been reported.²⁻⁴ Two compounds of the type $\text{Ta}_2\text{Cl}_6(\text{PR}_3)_4$ have

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(2) Sattelberger, A. P.; Wilson R. B., Jr.; Huffman, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7111.

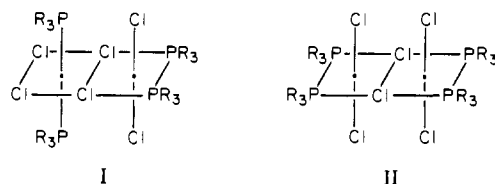
(3) Hubert-Pfalzgraf, L. G.; Tsunoda, M.; Riess, J. G. *Inorg. Chim. Acta* **1981**, *52*, 231.

Table I. Crystallographic Parameters for $Ta_2Cl_6(dmpe)_2$

space group	$P2_1/n$
a , Å	9.342 (1)
b , Å	13.353 (1)
c , Å	10.632 (1)
β , deg	95.70 (1)
V , Å ³	1320 (2)
d_{calcd} , g/cm ³	2.22
Z	2
fw	874.90
cryst size, mm	$0.10 \times 0.20 \times 0.30$
μ (Mo $K\alpha$), cm ⁻¹	90.439
range 2θ , deg	0-50
no. of unique data	2144
no. of data, $F_o^2 > 3\sigma(F_o^2)$	1958
no. of variables	109
R_1^a	0.024
R_2^b	0.037
esd	1.204
largest shift ^c	0.51
largest peak ^d	1.01

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. ^c Largest parameter shift in final least-squares cycle. ^d Largest scale in final difference Fourier map.

been described. The one with $PR_3 = PMe_3$ has been characterized structurally² and shown to have the ligand arrangement I. The structure of the compound with $PR_3 = PMe_2Ph$ is unknown.³



Arrangement I is probably preferred over arrangement II for steric reasons; it avoids having both pairs of PR_3 ligands, which are the bulkier ones, cis to each other. On the other hand, an arrangement with all PR_3 groups on axial sites, while it would entirely avoid cis PR_3 groups, would probably be even less acceptable because of axial-axial crowding.

We undertook the work reported here to see if a compound of type II could be obtained by using two chelating diphosphine ligands instead of four monophosphines. It had been reported² that in an attempt to prepare a dinuclear tantalum complex containing dmpe by reduction of $TaCl_5$ in the presence of the diphosphine only $TaCl_4(dmpe)_2$ and $TaCl_2(dmpe)_2$ were obtained. Both of these compounds had previously been described by Datta and Wreford.⁴

We have found, once again, that $Ta_2Cl_6(Me_2S)_3$ is an excellent reagent for preparing Ta^{III} compounds, and by using it we have obtained the desired product, $Ta_2Cl_6(dmpe)_2$, in excellent yield.

Experimental Section

All manipulations were carried out under anaerobic and anhydrous conditions with use of Schlenk, vacuum-line, or syringe techniques. Bis(dimethylphosphino)ethane, dmpe, was prepared by the literature method.⁵ Dichloromethane and hexane were distilled over P_2O_5 and potassium benzophenone ketal, respectively. Preparation of $Ta_2Cl_6(SMe_2)_3$ has been reported previously.⁶ The infrared spectrum was recorded on a Nujol mull with use of a Unicam SP1100 spectrophotometer.

Preparation. $Ta_2Cl_6(SMe_2)_3$ (0.2 g, 0.26 mmol) was dissolved in 20 mL of CH_2Cl_2 . Four equivalents of dmpe (0.2 mL, 1.2 mmol) was added dropwise via syringe to the stirred solution.⁷ After 4 h

Table II. Table of Positional Parameters and Their Estimated Standard Deviations for $Ta_2Cl_6(dmpe)_2^a$

atom	x	y	z
Ta(1)	0.04299 (2)	0.05360 (2)	0.10525 (2)
Cl(1)	0.0773 (2)	0.2133 (1)	0.0045 (1)
Cl(2)	0.0304 (2)	-0.0767 (1)	0.2603 (1)
Cl(3)	-0.2100 (2)	0.0372 (1)	0.0185 (1)
P(1)	-0.0643 (2)	0.1621 (1)	0.2765 (2)
P(2)	0.2761 (2)	0.1094 (1)	0.2413 (2)
C(1)	-0.1571 (9)	0.2792 (6)	0.2292 (8)
C(2)	-0.1887 (9)	0.1005 (7)	0.3729 (8)
C(3)	0.0833 (8)	0.1973 (7)	0.3942 (8)
C(4)	0.2226 (9)	0.2179 (7)	0.3373 (8)
C(5)	0.3680 (9)	0.0241 (7)	0.3538 (9)
C(6)	0.4220 (7)	0.1628 (6)	0.1615 (7)

^a Estimated standard deviations in the least significant digits are given in parentheses.

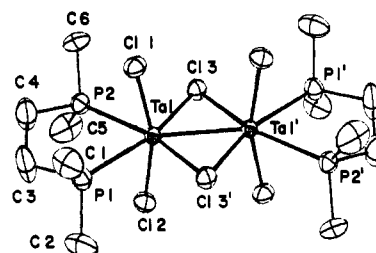


Figure 1. Molecular structure of $Ta_2Cl_6(dmpe)_2$. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 30% of its electron density. The labeling scheme is defined; unlabeled atoms are related to labeled ones by a center of inversion.



Figure 2. Stereo packing diagram showing the arrangement of molecules in the unit cell.

of stirring, the yellow-brown solution was filtered through a Celite pad. A portion of the filtrate was transferred to a Schlenk tube and layered with hexane. Red-brown crystals were obtained after two days in ca. 85% yield. Once formed, the mildly air-sensitive (decomposition in <10 h) crystals were insoluble in organic solvents. IR (mull): 1430 (sh), 1416 (br), 1304 (s), 1265 (m), 1141 (s), 1099 (br), 1021 (br), 998 (m), 982 (m), 901 (s), 865 (sh), 840 (sh), 742 (s), 650 (s), 569 (sh) cm^{-1} .

X-ray Crystallography. Collection and Refinement of Data. Crystals used for X-ray analysis were sealed in capillary tubes under nitrogen. Data were collected on an Enraf-Nonius CAD-4F diffractometer at $25 \pm 1^\circ C$. A graphite-crystal monochromator was used in the incident beam of Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data collection and refinement parameters are summarized in Table I. The standard CAD-4 centering, indexing, and data collection programs were used. Details concerning collection and reduction of data have been previously reported.⁸ Three intensity standards were measured every hour of X-ray exposure, and no intensity decay of the data was observed. Lorentz and polarization corrections were applied to the data as were empirical absorption corrections⁹ based on ψ scans near $\chi = 90^\circ$.

Solution and Refinement of the Structure.¹⁰ The crystals were found to be monoclinic with a unit cell volume corresponding to $Z = 2$. The

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(10) All corrections and refinement were done with the use of a PDP 11/60 computer at Bert Frenz and Associates, College Station, TX, equipped with the Enraf-Nonius structure determination package.

Table III. Table of Bond Distances (Angstroms) for Ta₂Cl₆(dmpe)₂^a

Ta(1)-Ta(1)'	2.710 (1)	P(1)-C(1)	1.834 (7)
-Cl(1)	2.422 (1)	-C(2)	1.821 (7)
-Cl(2)	2.408 (1)	-C(3)	1.829 (7)
-Cl(3)	2.460 (1)	P(2)-C(4)	1.868 (8)
-Cl(3)'	2.459 (1)	-C(5)	1.806 (8)
-P(1)	2.604 (1)	-C(6)	1.821 (7)
-P(2)	2.601 (1)	C(3)-C(4)	1.515 (11)

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

Table IV. Table of Bond Angles (Degrees) for Ta₂Cl₆(dmpe)₂^a

Ta(1)'-Ta(1)-Cl(1)	98.13 (4)	Cl(3)'-Ta(1)-P(1)	163.22 (5)
-Cl(2)	98.79 (4)	-P(2)	84.16 (5)
-Cl(3)	56.54 (3)	P(1)-Ta(1)-P(2)	79.09 (5)
-Cl(3)'	56.59 (3)	Ta(1)-Cl(3)-Ta(1)'	66.88 (4)
-P(1)	140.19 (4)	-C(1)	119.2 (3)
-P(2)	140.69 (4)	-C(2)	117.0 (3)
Cl(1)-Ta(1)-Cl(2)	163.08 (5)	-C(3)	107.8 (2)
-Cl(3)	94.42 (5)	C(1)-P(1)-C(2)	103.2 (4)
-Cl(3)'	94.52 (5)	-C(3)	105.8 (4)
-P(1)	84.03 (5)	C(2)-P(1)-C(3)	102.2 (4)
-P(2)	81.57 (5)	Ta(1)-P(2)-C(4)	105.8 (3)
Cl(2)-Ta(1)-Cl(3)	94.68 (5)	-C(5)	120.3 (3)
-Cl(3)'	94.99 (5)	-C(6)	118.5 (2)
-P(1)	82.83 (5)	C(4)-P(2)-C(5)	105.2 (5)
-P(2)	85.51 (5)	-C(6)	101.8 (4)
Cl(3)-Ta(1)-Cl(3)'	113.12 (4)	C(5)-P(2)-C(6)	103.1 (4)
-P(1)	83.65 (5)	P(1)-C(3)-C(4)	113.1 (6)
-P(2)	162.58 (5)	P(2)-C(4)-C(3)	111.4 (6)

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

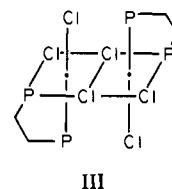
data contained systematic absences of $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$, which specified the space group as $P2_1/n$. A three-dimensional Patterson function provided the position for the Ta atom, which was refined by the full-matrix least-squares procedure. Alternating difference Fourier syntheses and least-squares calculations readily provided the positions of all non-hydrogen atoms. Residuals obtained after all non-hydrogen atoms were assigned anisotropic thermal parameters are listed in Table I. Positional parameters are listed in Table II. Tables of anisotropic thermal parameters and structure factors are available as supplementary material.

Results

The molecules, which are illustrated in Figure 1, reside on positions of crystallographic inversion symmetry, located at the midpoint of the Ta-Ta bond. The edge-sharing bioctahedral structure has Ta(1), P(1), P(2), and Cl(3) approximately coplanar with Cl(1) and Cl(2) above and below the plane. Bond lengths and angles are listed in Tables III and IV, respectively. The Cl(1)-Ta(1)-Cl(2) angle deviates from linearity by 16.92°; the Cl atoms are bent away from the center of the molecule. Other distortions from octahedral geometry about each Ta atom are observed for the planar portions of the molecule: the P(1)-Ta-P(2) angle is 79.09 (5)° while the Cl(3)-Ta-Cl(3)' bond angle is 113.12 (4)°. The torsional angle of the P(1)-C(3)-C(4)-P(2) moiety is 54.9°.

Discussion

On the assumption suggested in the Introduction that the relative stabilities of I and II (and any other geometrical isomers one might wish to consider) are heavily influenced by steric factors (not, however, to the complete exclusion of electronic ones), we reasoned that, with two chelating diphosphines instead of four monophosphines, a structure of type II should be obtainable. Clearly the use of chelating diphosphines conclusively rules out I, but there are other isomers of the bioctahedral structure in which chelate rings span cis positions such as III. While III is compatible with the che-



III

lating requirements of the diphosphine itself, it has two disadvantages relative to II. First, while II and III both provide each phosphorus atom with three cis chlorine ligands as nearest neighbors, III also provides an additional close contact for each axial phosphorus atom, namely, an axial chlorine atom of the other octahedron. These two additional repulsive contacts should have a significantly destabilizing effect on III relative to II. Second, the arrangement in II conforms neatly with inherent tendencies in the M₂X₁₀ skeleton when there is a drawing together of the metal atoms as a result of M=M bond formation. The close approach of the metal atoms opens the X-M-X angles in the central rhombus, and that in turn tends to close the opposite X-M-X angles. Since the M(diphos) chelate ring naturally subtends a P-M-P angle much less than 90°, there is an inherent compatibility of structure II with the presence of M=M bonding. In short, we believe that the structure found is the one that should reasonably have been expected.

The Ta=Ta distance, 2.710 (1) Å, is very similar to M=M (double) bond distances found in a number of other binuclear Ta^{III} and Nb^{III} compounds. It is not significantly (in a chemical sense) different from the distance of 2.721 (1) Å found² in Ta₂Cl₆(PMe₃)₄. It is, however, considerably longer than the W=W distances found in several bioctahedral W^{IV} complexes, namely, 2.482 (1) Å in W₂(OR)₄Cl₄(ROH)₂¹¹ and 2.530 (2) Å in W₂S₂(Et₂NCS₂)₄.¹²

Unfortunately, the compound Ta₂Cl₆(dmpe)₂ is rather insoluble and we have not been able to obtain NMR spectra or other data concerning its nature in solution. This lack of solubility also interferes with studies of its reactivity.

Undoubtedly, the most interesting reaction found for the Ta₂Cl₆(PR₃)₄ molecules^{2,3} is with hydrogen gas, under extremely mild conditions, to give 1:1 adducts. For the PMe₃ compound this adduct has been structurally characterized.² For our dmpe compound attempts to produce a reaction with H₂ under comparable conditions, as well as under more severe conditions, have been fruitless. While the fact that, because of the insolubility of Ta₂Cl₆(dmpe)₂, these attempts have all entailed heterogeneous conditions is doubtless an extrinsic inhibitory factor, it is possible that formation of an H₂ adduct is intrinsically inhibited by the structural nature of the Ta₂Cl₆(dmpe)₂ molecule. The bite of the dmpe ligands does not allow the adoption of the ligand arrangement characteristics of the hydrido products formed by the Ta₂Cl₆(PR₃)₄ compounds. We are currently investigating this situation with the goal of identifying the inhibitory factor and finding a way to eliminate it while still retaining the type II structure.

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Registry No. Ta₂Cl₆(dmpe)₂, 83731-89-9; Ta₂Cl₆(SMe₂)₃, 77827-59-9; Ta, 7440-25-7.

Supplementary Material Available: Listings of anisotropic thermal parameters and observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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