calixarene conformation has been postulated to involve two circular H-bonding networks is, however, consistent with the behavior, so far as it is presently characterized, of both calix[6]arene and calix[8]arene as ditopic receptors.[17] Bimetallic systems are of interest for many reasons,[17-19] the nature of energy- and electron-transfer processes being especially important in lanthanide compounds.[20-22]

Acknowledgment. We gratefully acknowledge support of this work by The Australian Research Grant Scheme.

Registry No. $[Eu_2(LH_2)(DMF)_5]\cdot 4DMF$, 111004-80-9.

Supplementary Material Available: Thermal parameters (Table SUP-1), hydrogen parameters (Table SUP-2), ligand non-hydrogen geometries (Table SUP-3), and DMF geometries (Table SUP-4) (18 pages); a listing of structure factor amplitudes (62 pages). Ordering information is given on any current masthead page.

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Phosphorus Versus Nitrogen Donor Ligands in Edge-Sharing Bioctahedra of Niobium and Tantalum $M_2Cl_6(L\text{-}L)_2$ Complexes

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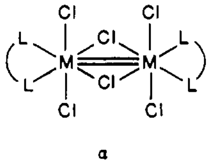
Received June 10, 1987

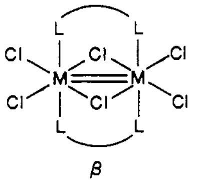
Three new edge-sharing bioctahedra, $Nb_2Cl_6(Et_2NCH_2CH_2NEt_2)_2$ (**1**), $Ta_2Cl_6(Et_2NCH_2CH_2NEt_2)_2$ (**2**), and $Nb_2Cl_6(Et_2PCH_2CH_2PEt_2)_2$ (**3**), have been prepared by a ligand displacement reaction on $M_2Cl_6(SMe_2)_3$ with $Et_2NCH_2CH_2NEt_2$ or $Et_2PCH_2CH_2PEt_2$. All three compounds have been structurally characterized in order to investigate the effect of different donor atoms on the metal–metal bond length. The following crystallographic parameters were found for the three compounds: $Nb_2Cl_6(Et_2NCH_2CH_2NEt_2)_2\cdot C_7H_8$, space group $P\bar{1}$, a = 10.335 (5) Å, b = 10.464 (3) Å, c = 9.482 (2) Å, α = 115.35 (2)°, β = 95.67 (3)°, γ = 94.07 (4)°, Z = 1, Nb=Nb = 2.764 (1) Å; $Ta_2Cl_6(Et_2NCH_2CH_2NEt_2)_2\cdot C_7H_8$, space group $P2_1/a$, a = 10.433 (1) Å, b = 16.680 (3) Å, c = 10.647 (3) Å, β = 99.72 (2)°, Z = 4, Ta=Ta = 2.7776 (6) Å; $Nb_2Cl_6(Et_2PCH_2CH_2PEt_2)_2$, space group $Pca2_1$, a = 14.857 (2) Å, b = 16.642 (3) Å, c = 13.605 (2) Å, Z = 4, Nb=Nb = 2.741 (3) Å.

Introduction

Ligand displacement reactions on niobium or tantalum $M_2Cl_6(SMe_2)_3$ or $M_2Cl_6(tht)_3$ (tht = tetrahydrothiophene) have been shown to give a variety of monomeric and dimeric products of differing geometries. Of particular interest to us is the formation of the edge-sharing bioctahedral dimers typically formed by use of bidentate ligands. These ligands may be arranged about the metal centers in one of two ways, chelating (α) or bridging (β):



α



β

The α-form is typically observed for ligands that form five-membered rings with the metal (e.g. 1,2-bis(diphenylphosphino)ethane (dppe),[1] 1,2-bis(dimethylphosphino)ethane (dmpe),[2] and 3,6-dithiaoctane (dto)[3], while ligands with a smaller bite size have been found in both chelating [e.g. bis(diphenylphosphino)methane (dppm)[4]] and bridging [e.g. bis(dimethylphosphino)methane (dmpm)[5]] modes.

The preparation of molecules of this type affords us the opportunity to study metal–metal interactions through a variety of ligand sets with different electronic and steric requirements.[6] To date, however, the majority of structurally characterized edge-sharing bioctahedra of niobium and tantalum of the types $M_2Cl_6L_4$ and $M_2Cl_6(L\text{-}L)_2$ contain phosphine donor ligands. We now report the synthesis and structural characterization of three new compounds, two of which contain nitrogen donor ligands. These compounds are $Nb_2Cl_6(dene)_2$ (**1**), $Ta_2Cl_6(dene)_2$ (**2**), and $Nb_2Cl_6(depe)_2$ (**3**) where dene is *N,N,N′,N′*-tetraethylethylenediamine and depe is 1,2-bis(diethylphosphino)ethane. This work was undertaken to see if the metal–metal bond length would be significantly affected by using a very basic, pure σ-donor ligand (dene) in place of a phosphine ligand (depe), which is less basic and can also participate in M→L π back-bonding.

Experimental Section

The air sensitivity of the reactants and products necessitated the use of standard Schlenk and vacuum-line techniques. The reaction products were prepared, filtered off, and washed under an atmosphere of argon with subsequent handling in an inert (N_2) atmosphere box. Solvents were freshly distilled from benzophenone ketyl and transferred to and from reaction vessels via stainless steel cannulae and/or syringes. The ligands, 1,2-bis(diethylphosphino)ethane (depe) and *N,N,N′,N′*-tetraethylethylenediamine (dene), were purchased from Organometallics, Inc., and Aldrich Chemical Co., respectively. Both compounds were deaerated prior to use. Infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer. Peaks coincident with those of Nujol are not reported.

Preparation and Crystallization of $Nb_2Cl_6(dene)_2$ (1). Into a Schlenk tube was filtered a solution of 0.12 g (0.21 mmol) of $Nb_2Cl_6(SMe_2)_3$ in

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12 mL of toluene. Tetraethylethylenediamine (0.25 mL, 1.2 mmol) in 10 mL of hexane was layered on top of this solution. Slow diffusion of reactants led to the formation of burgundy-colored crystals, recoverable in 51% yield upon filtration and washing with two 10-mL aliquots of hexane. X-ray crystallographic quality crystals were obtained from this reaction. IR (Nujol/CsI), cm^{-1}: 1762 (w), 1603 (w), 1496 (w), 1400 (w), 1335 (w), 1326 (w), 1305 (w), 1290 (w), 1260 (m), 1176 (w), 1170 (w), 1146 (w), 1130 (m), 1110 (s), 1080 (m), 1048 (s), 1028 (sh, m), 1020 (s), 1010 (s), 921 (m), 904 (w), 862 (w), 820 (m), 791 (m), 750 (s), 745 (s), 728 (s), 703 (s), 611 (m), 560 (m), 512 (w), 478 (m), 420 (w), 410 (w), 359 (s), 344 (s), 330 (s), 288 (s).

Preparation of $Ta_2Cl_6(dene)_2$ (2). Into a Schlenk tube was filtered a solution of 0.15 g (0.20 mmol) of $Ta_2Cl_6(SMe_2)_3$ in 12 mL of toluene. The diluted ligand, dene (0.25 mL, 1.2 mmol) in 10 mL of hexane, was layered on top of this. Slow diffusion produced a green-brown precipitate, $Ta_2Cl_6(dene)_2$, which could be recovered in 47% yield after filtration and washing with hexane. IR (Nujol/CsI), cm^{-1}: 1300 (w), 1285 (w), 1258 (w), 1170 (vw, br) 1155 (vw, br), 1138 (vw), 1106 (w), 1080 (vw), 1045 (w), 1030 (w), 1012 (m), 918 (vw), 840 (s, br), 790 (ms), 732 (vs, br), 698 (s), 610 (w), 660 (w), 510 (vw), 472 (w), 438 (w, br), 310 (vs, br), 280 (vs).

Crystallization of $Ta_2Cl_6(dene)_2$ (2). Crystals for X-ray diffraction were grown by dissolving 0.15 g (0.20 mmol) of $Ta_2Cl_6(SMe_2)_3$ in 12 mL of toluene and filtering the solution into a Schlenk tube. A second layer consisting of 8 mL of 50/50 hexane/toluene was placed on top of this, followed by a hexane solution (10 mL) containing 0.25 mL (1.2 mmol) of dene. Slow diffusion between layers produced green crystals of $Ta_2Cl_6(dene)_2$.

Preparation and Crystallization of $Nb_2Cl_6(depe)_2$ (3). The compound $Nb_2Cl_6(SMe_2)_3$ (0.13 g, 0.22 mmol) was dissolved in 12 mL of toluene, and the solution was filtered into a Schlenk tube. A 0.13-mL (0.57-mmol) solution of depe was layered on top of this. Diffusion of layers produced a purple crystalline solid, $Nb_2Cl_6(depe)_2$, which could be recovered in 53% yield after filtration and washing with hexane. X-ray crystallographic quality crystals were sometimes, but not always, produced by this procedure. IR (Nujol/CsI), cm^{-1}: 1497 (w), 1415 (w, br), 1350 (w, br), 1308 (w, br), 1256 (w), 1238 (w), 1168 (w), 1157 (w), 1140 (w), 1096 (w), 1075 (w), 1047 (s), 1036 (s), 985 (m), 937 (w), 899 (w), 878 (m), 868 (m), 830 (m), 770 (m), 762 (sh, m), 743 (sh, s), 733 (s), 727 (sh, s), 700 (m), 683 (w), 678 (w), 632 (w), 472 (w), 464 (w), 420 (w, br), 390 (w), 374 (w), 357 (w), 338 (sh, s), 329 (vs), 298 (w), 281 (s).

Crystallographic Study. Crystals of compounds **1**–**3**, grown as described above, were mounted in a protected environment by sealing the crystal in a glass capillary tube with epoxy resin. Single-crystal diffraction experiments were conducted with one of three automated four-circle X-ray diffractometers equipped with monochromated Mo Kα radiation. Routine unit cell identification and intensity data collection procedures were followed. These have been fully described elsewhere.[7] In order to ascertain crystal quality, and to verify lattice symmetry and dimensions, axial photographs were taken. Three check reflections were monitored for intensity fluctuation during data collection. Decay was noted for compounds **1** (−8%) and **2** (−9%), and corrections were applied. Empirical absorption corrections based on azimuthal scans of χ near 90° were applied to the data sets of compounds **1** and **2**. All three data sets were corrected for Lorentz and polarization effects. Standard computational procedures using the VAX-SDP software package on either a VAX-11/780 or MicroVAXII computer were used to solve and refine the structures.

Structure Solution and Refinement for $Nb_2Cl_6(dene)_2\cdot C_7H_8$ (1). The compound crystallizes in the triclinic space group $P\bar{1}$ with one dimer and one disordered solvent molecule per unit cell. The location of the unique niobium atom was determined from the Patterson map. The remaining non-hydrogen atoms were found from a series of alternating difference Fourier maps and least-squares refinement cycles. All atoms with the exception of those of the solvent molecule were refined anisotropically after performing a second empirical absorption correction.[8]

Structure Solution and Refinement for $Ta_2Cl_6(dene)_2\cdot C_7H_8$ (2). A monoclinic cell was determined from the unit cell dimensions and verified by axial photographs. The possibility of an orthorhombic *c*-centered cell was investigated and shown to be incorrect from the diagonal photograph taken. From systematic absences in the intensity data, the space group, $P2_1/a$, was uniquely determined. The Patterson map was used to obtain the coordinates for the unique tantalum atom. The remaining non-hydrogen atoms were found by a series of alternating difference Fourier maps and least-squares refinements. The solvent molecule, toluene, is located about an inversion center and is severely disordered, as seen in the model used to account for the electron density in this region. Prior to anisotropic refinement of the dimer, an additional empirical absorption correction was made.[8]

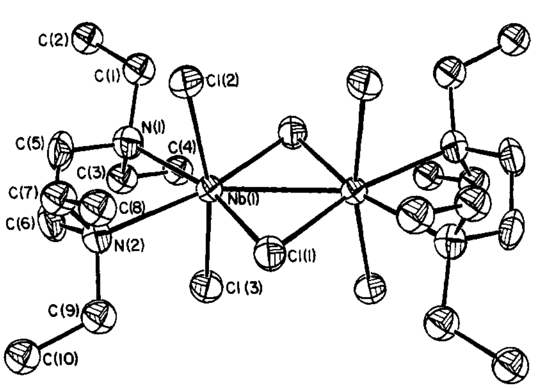

Figure 1. ORTEP view of $Nb_2Cl_6(dene)_2$ (**1**) with thermal ellipsoids drawn at the 50% probability level.

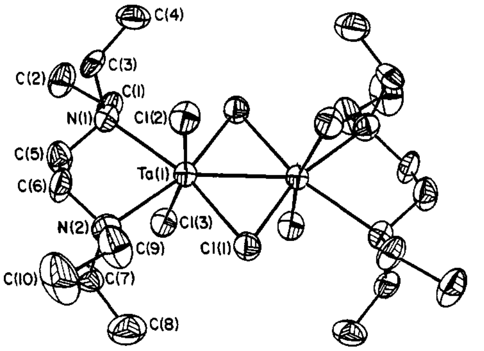

Figure 2. ORTEP view of $Ta_2Cl_6(dene)_2$ (**2**) with thermal ellipsoids drawn at the 50% probability level.

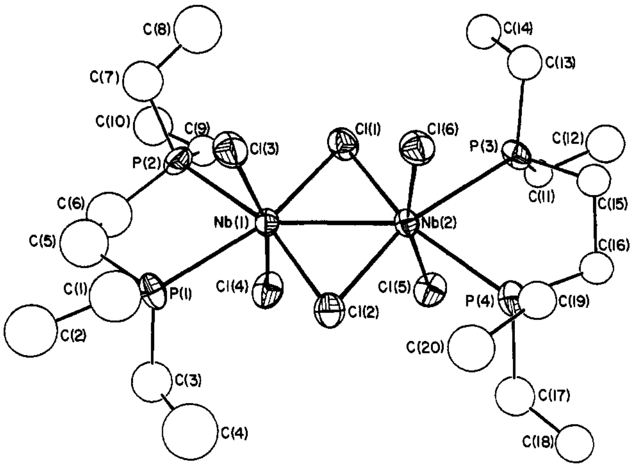

Figure 3. ORTEP drawing of $Nb_2Cl_6(depe)_2$ (**3**). Atoms are represented at the 50% level for thermal motion.

Structure Solution and Refinement for $Nb_2Cl_6(depe)_2$ (3). The unique niobium atom was located from the Patterson map. The systematic absences in the intensity data narrowed the choice of space group to $Pca2_1$ or *Pcam*. The centrosymmetric space group was chosen and found to be incorrect. The noncentrosymmetric space group and the first enantiomorph chosen gave the correct solution. All non-hydrogen atoms were located via a series of alternating difference Fourier maps and least-squares refinements. At this point, an empirical absorption correction based on the method of Walker and Stuart was made.[8] All non-hydrogen and non-carbon atoms were refined anisotropically. Because of the low data to parameter ratio, anisotropic refinement could not be conducted on the carbon atoms.

Pertinent crystallographic parameters for all three crystal structures are summarized in Table I. Final atomic positional and isotropic

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Table I. Crystal Data for $Nb_2Cl_6(dene)_2\cdot C_7H_8$ (**1**), $Ta_2Cl_6(dene)_2\cdot C_7H_8$ (**2**), and $Nb_2Cl_6(depe)_2$ (**3**)

compd	**1**	**2**	**3**
formula	$Nb_2Cl_6N_4C_{27}H_{56}$	$Ta_2Cl_6N_4C_{27}H_{56}$	$Nb_2Cl_6P_4C_{20}H_{48}$
fw	835.30	1011.39	811.03
space group	$P\bar{1}$	$P2_1/a$	$Pca2_1$
syst absences		$h0l$ ($h \neq 2n$) $0k0$ ($k \neq 2n$)	$h0l$ ($h \neq 2n$) $0kl$ ($l \neq 2n$)
a, Å	10.335 (5)	10.433 (1)	14.857 (2)
b, Å	10.464 (3)	16.680 (3)	16.642 (3)
c, Å	9.482 (2)	10.647 (3)	13.605 (2)
α, deg	115.35 (2)		
β, deg	95.67 (3)	99.72 (2)	
γ, deg	94.07 (4)		
V, Å^3	914.7 (6)	1826 (1)	3364 (1)
Z	1	2	4
d_{calcd}, g/cm^3	1.516	1.670	1.601
cryst size, mm	0.5 × 0.4 × 0.3	0.2 × 0.3 × 0.3	0.4 × 0.2 × 0.1
μ(Mo Kα), cm^{-1}	10.650	63.724	13.328
data col instrument	Enraf-Nonius CAD-4		Syntex P3
radiation (monochromated in incident beam)	Mo Kα (λ_α = 0.71073 Å)		Mo Kα (λ_α = 0.71073 Å)
orientation reflcns: no., range (2θ)	25, 12.2–41.5	25, 16.8–29.0	25, 20.2–29.4
temp, °C	22	22	22
scan method	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
data col range, 2θ, deg	4–50	4–45	4–45
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	3217, 2501	2517, 1919	1122, 1118
no. of params refined	161	161	188
trans factors: max, min	0.9995, 0.9456	0.9970, 0.6607	
R^a	0.04234	0.03338	0.05635
R_w^b	0.06106	0.05178	0.06466
quality-of-fit indicator^c	1.836	1.650	1.124
largest shift/esd, final cycle	0.01	0.05	0.02
largest peak, e/Å^3	1.118	1.080	0.662

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

Table II. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters and Their Estimated Standard Deviations for $Nb_2Cl_6(dene)_2\cdot C_7H_8$[a]

atom	x	y	z	B, Å^2
Nb(1)	0.41372 (5)	0.08170 (5)	0.09203 (5)	2.378 (9)
Cl(1)	0.4579 (1)	−0.1503 (1)	0.0724 (1)	3.16 (3)
Cl(2)	0.2250 (1)	−0.0141 (2)	−0.1093 (2)	3.47 (3)
Cl(3)	0.5712 (2)	0.2058 (2)	0.3272 (2)	3.76 (3)
N(1)	0.3309 (5)	0.3099 (5)	0.1595 (5)	3.5 (1)
N(2)	0.2636 (5)	0.0729 (5)	0.2725 (5)	3.2 (1)
C(1)	0.2849 (7)	0.3316 (6)	0.0159 (7)	4.3 (1)
C(2)	0.2170 (9)	0.4670 (7)	0.0491 (9)	6.7 (2)
C(3)	0.4165 (8)	0.4414 (6)	0.2835 (8)	5.0 (2)
C(4)	0.5357 (9)	0.4902 (7)	0.2288 (9)	5.8 (2)
C(5)	0.2126 (6)	0.2867 (6)	0.2304 (7)	4.1 (1)
C(6)	0.2437 (6)	0.2279 (6)	0.3485 (6)	4.0 (1)
C(7)	0.1307 (6)	−0.0119 (7)	0.2022 (8)	4.3 (2)
C(8)	0.1285 (8)	−0.1723 (7)	0.1246 (9)	5.4 (2)
C(9)	0.3256 (7)	0.0358 (7)	0.3988 (6)	4.4 (1)
C(10)	0.2494 (9)	0.0617 (8)	0.5382 (8)	6.1 (2)
C(11)	0.907 (1)	0.411 (1)	0.394 (1)	8.1 (3)*
C(12)	1.057 (1)	0.623 (1)	0.487 (1)	11.0 (4)*
C(13)	0.941 (2)	0.520 (1)	0.357 (2)	13.3 (5)*
C(14)	0.937 (3)	0.302 (2)	0.568 (3)	10.7 (7)*

[a] Starred values indicate atoms were refined isotropically. Anisotropically refined atoma are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. Estimated standard deviations in the least significant digits are given in parentheses.

Table III. Final Atomic Positional and Isotropic Equivalent Thermal Parameters for $Ta_2Cl_6(dene)_2\cdot C_7H_8$[a]

atom	x	y	z	B, Å^2
Ta(1)	0.09082 (3)	−0.00680 (2)	0.41913 (4)	2.412 (8)
Cl(1)	0.0425 (2)	−0.1086 (1)	0.5633 (3)	3.32 (5)
Cl(2)	−0.0517 (2)	−0.0626 (2)	0.2425 (3)	3.65 (6)
Cl(3)	0.2703 (2)	0.0474 (2)	0.5621 (3)	3.78 (6)
N(1)	0.1803 (7)	0.0699 (5)	0.2562 (8)	3.2 (2)
N(2)	0.2526 (7)	−0.1014 (4)	0.3581 (9)	3.6 (2)
C(1)	0.2183 (9)	0.1543 (5)	0.301 (1)	3.7 (2)
C(2)	0.290 (1)	0.2046 (6)	0.210 (1)	4.9 (3)
C(3)	0.1031 (9)	0.0734 (6)	0.1217 (9)	3.4 (2)
C(4)	0.018 (1)	−0.1255 (7)	0.891 (1)	4.6 (3)
C(5)	0.3046 (9)	0.0239 (6)	0.249 (1)	4.1 (2)
C(6)	0.2760 (9)	−0.0668 (6)	0.237 (1)	4.1 (2)
C(7)	0.3792 (9)	−0.1083 (7)	0.445 (1)	4.4 (3)
C(8)	0.376 (1)	−0.1510 (8)	0.572 (1)	6.3 (3)
C(9)	0.196 (1)	−0.1853 (6)	0.328 (1)	5.1 (3)
C(10)	0.284 (1)	−0.2453 (7)	0.275 (2)	7.8 (4)
C(11)	0.420 (1)	0.046 (1)	0.923 (2)	8.2 (4)*
C(12)	0.605 (2)	0.022 (1)	1.086 (2)	9.6 (5)*
C(13)	0.566 (2)	0.097 (2)	1.047 (3)	14.8 (8)*
C(14)	0.470 (3)	0.106 (2)	0.953 (3)	7.9 (8)*

[a] Starred values indicate atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. Estimated standard deviations in the least significant digits are given in parentheses.

equivalent thermal parameters for compounds **1**–**3** are listed in Tables II–IV, respectively. Selected bond distances and bond angles for **1** and **2** are found in Table V, while those values for **3** are tabulated in Table VI. ORTEP views of **1**–**3**, which also define the labeling scheme used in the tables, are shown in Figures 1–3, respectively.

Results and Discussion

Compounds **1** and **2** reside on positions of crystallographic inversion symmetry, located at the center of the metal–metal vector. The atoms M(1), Cl(1), N(1), and N(2) and their symmetry-related counterparts are roughly coplanar, with Cl(2) and Cl(3) located above and below the plane to form a slightly distorted edge-sharing bioctahedron. The effective symmetry of **1** and **2** is C_{2h}. Compound **3** does not possess any crystallographically imposed symmetry, but the overall core geometry is the same as for compounds **1** and **2**. This lack of symmetry allows for a different conformation of the chelating ligands in compound **3** compared to those found in compounds **1** and **2**, as illustrated in Figure 4. The molecule of compound **3** has effective D_2 symmetry. A notable feature typical of edge-sharing bioctahedra is the greater than 90° Cl_b–M–Cl_b bond angle, which correlates with metal–metal bond distance. The trend is for the compound with the shortest M–M bond to have the widest Cl_b–M–Cl_b angle [**1**, 2.764 (1) Å, 110.89 (3)°; **2**, 2.7776 (6) Å, 109.31 (9)°; **3**, 2.741 (3) Å, 112.0 [1]°]. Also typical is the distortion of the Cl_t–M–Cl_t bond angle from 180° [168.14 (4), 166.26 (9), and 164.0 [2]° for **1**,

Table IV. Final Atomic Positional and Isotropic Equivalent Thermal Parameters for $Nb_2Cl_6(depe)_2$[a]

atom	*x*	*y*	*z*	*B*, Å^2
Nb(1)	0.0872 (2)	0.2213 (2)	0.000	2.07 (4)
Nb(2)	−0.0501 (2)	0.2889 (2)	0.1063 (2)	2.04 (4)
Cl(1)	0.1034 (5)	0.3421 (5)	0.0987 (6)	3.2 (2)
Cl(2)	−0.0672 (4)	0.1658 (4)	0.0090 (6)	2.9 (2)
Cl(3)	0.0614 (6)	0.2895 (5)	−0.1525 (6)	3.6 (2)
Cl(4)	0.1431 (5)	0.1328 (5)	0.1256 (6)	3.7 (2)
Cl(5)	−0.0230 (5)	0.2181 (5)	0.2591 (6)	3.3 (2)
Cl(6)	−0.1109 (5)	0.3752 (5)	−0.0204 (6)	3.2 (2)
P(1)	0.1262 (6)	0.0969 (5)	−0.1119 (7)	3.1 (2)
P(2)	0.2594 (5)	0.2400 (5)	−0.0370 (7)	3.1 (2)
P(3)	−0.0858 (6)	0.4139 (5)	0.2213 (6)	2.5 (2)
P(4)	−0.2198 (5)	0.2619 (5)	0.1540 (6)	2.8 (2)
C(1)	0.068 (3)	0.092 (3)	−0.232 (3)	7 (1)*
C(2)	0.110 (3)	0.022 (3)	−0.302 (3)	7 (1)*
C(3)	0.111 (2)	−0.008 (2)	−0.057 (3)	5.2 (9)*
C(4)	0.013 (3)	−0.031 (3)	−0.053 (4)	9 (1)*
C(5)	0.243 (3)	0.110 (2)	−0.157 (3)	7 (1)*
C(6)	0.297 (3)	0.144 (3)	−0.084 (3)	7 (1)*
C(7)	0.297 (2)	0.314 (2)	−0.127 (3)	5.1 (9)*
C(8)	0.287 (3)	0.399 (3)	−0.078 (3)	8 (1)*
C(9)	0.330 (2)	0.258 (2)	0.073 (2)	3.6 (7)*
C(10)	0.435 (2)	0.257 (2)	0.054 (3)	6 (1)*
C(11)	−0.046 (2)	0.405 (2)	0.350 (2)	2.5 (6)*
C(12)	−0.084 (2)	0.474 (2)	0.418 (3)	4.9 (9)*
C(13)	−0.061 (2)	0.517 (2)	0.183 (2)	3.5 (7)*
C(14)	0.039 (2)	0.537 (2)	0.204 (2)	3.7 (7)*
C(15)	−0.214 (2)	0.421 (2)	0.220 (2)	3.0 (7)*
C(16)	−0.254 (2)	0.331 (2)	0.251 (2)	2.9 (6)*
C(17)	−0.247 (2)	0.160 (2)	0.215 (3)	4.2 (8)*
C(18)	−0.337 (2)	0.143 (2)	0.244 (2)	3.7 (7)*
C(19)	−0.309 (2)	0.279 (2)	0.064 (2)	3.5 (7)*
C(20)	−0.305 (2)	0.209 (2)	−0.017 (3)	5.0 (8)*

[a] Starred values indicate atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. Estimated standard deviations in the least significant digits are given in parentheses.

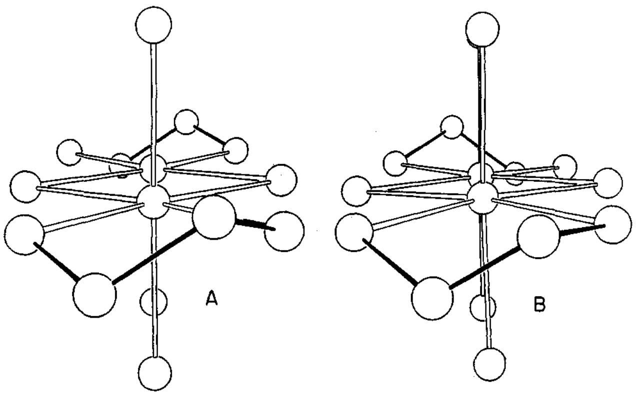

Figure 4. Partial ORTEP views of $Nb_2Cl_6(dene)_2$ (A), $Ta_2Cl_6(dene)_2$ (A), and $Nb_2Cl_6(depe)_2$ (B) illustrating the two different ligand conformations.

2, and 3, respectively]. Even though the chlorine bridge bonding is not in any of these compounds crystallographically required to be symmetrical, it is so within experimental error; this, of course, is to be expected on chemical grounds.

Comparison of Structures 1 and 2. The Nb–N distances are slightly shorter than the Ta–N distances by ca. 0.030 Å, and the Nb–Cl_t distances are slightly longer than the Ta–Cl_t distances by ca. 0.030 Å. These two observations may be related. When less electron density reaches the metal atoms from the nitrogen atoms, the metal atoms will retain a greater partial positive charge and thus attract the chloride ligands more strongly.

The fact that the Nb–Nb distance is shorter (by 0.014 Å) than the Ta–Ta distance is contrary to the trend seen in the only other exactly homologous pair of Nb/Ta compounds of the edge-sharing bioctahedral type, viz., the $M_2Cl_6(dmpm)_2$ compounds, where the Nb–Nb distance was longer than the Ta–Ta distance by 0.019 Å. In general, stronger bonds are formed by the heavier metal atoms, but when very basic ligands like dene are employed, they may donate more strongly to niobium, and this in turn may expand the metal d orbitals and allow better metal–metal overlap.

Table V. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $Nb_2Cl_6(dene)_2$ (**1**) and $Ta_2Cl_6(dene)_2$ (**2**)

atoms	dist (**1**)	dist (**2**)
M(1)–M(1)′	2.764 (1)	2.7776 (6)
M(1)–Cl(1)	2.433 (1)	2.401 (3)
M(1)–Cl(1)′	2.437 (1)	2.401 (2)
M(1)–Cl(2)	2.409 (1)	2.382 (2)
M(1)–Cl(3)	2.411 (1)	2.383 (2)
M(1)–N(1)	2.436 (4)	2.464 (8)
M(1)–N(2)	2.446 (3)	2.477 (8)
atoms	**angle (1)**	**angle (2)**
M(1)′–M(1)–Cl(1)	55.48 (3)	54.66 (6)
M(1)′–M(1)–Cl(1)′	55.36 (3)	54.65 (6)
M(1)′–M(1)–Cl(2)	95.94 (3)	97.00 (7)
M(1)′–M(1)–Cl(3)	95.91 (3)	96.74 (7)
M(1)′–M(1)–N(1)	139.74 (9)	140.7 (2)
M(1)′–M(1)–N(2)	139.71 (9)	141.4 (2)
Cl(1)–M(1)–Cl(1)′	110.84 (3)	109.31 (9)
Cl(1)–M(1)–Cl(2)	94.10 (4)	93.35 (8)
Cl(1)–M(1)–Cl(3)	92.28 (4)	94.96 (8)
Cl(1)–M(1)–N(1)	164.78 (9)	164.6 (2)
Cl(1)–M(1)–N(2)	84.23 (9)	86.8 (2)
Cl(1)′–M(1)–Cl(2)	92.64 (4)	94.74 (8)
Cl(1)′–M(1)–Cl(3)	94.41 (4)	92.82 (8)
Cl(1)′–M(1)–N(1)	84.39 (9)	86.1 (2)
Cl(1)′–M(1)–N(2)	164.93 (9)	163.9 (2)
Cl(2)–M(1)–Cl(3)	168.14 (4)	166.26 (9)
Cl(2)–M(1)–N(1)	85.0 (1)	84.6 (2)
Cl(2)–M(1)–N(2)	85.86 (9)	84.6 (2)
Cl(3)–M(1)–N(1)	86.24 (9)	84.4 (2)
Cl(3)–M(1)–N(2)	84.85 (9)	85.0 (2)
N(1)–M(1)–N(2)	80.5 (1)	77.9 (3)
M(1)–Cl(1)–M(1)′	69.16 (3)	70.69 (6)

Table VI. Selected Bond Distances (Å) and Bond Angles (deg) for $Nb_2Cl_6(depe)_2$ (**3**)

atoms	dist (**3**)	atoms	dist (**3**)
Nb(1)–Nb(2)	2.741 (3)	Nb(2)–Cl(1)	2.449 (7)
Nb(1)–Cl(1)	2.429 (8)	Nb(2)–Cl(2)	2.452 (8)
Nb(1)–Cl(2)	2.475 (7)	Nb(2)–Cl(5)	2.423 (8)
Nb(1)–Cl(3)	2.396 (8)	Nb(2)–Cl(6)	2.419 (8)
Nb(1)–Cl(4)	2.404 (8)	Nb(2)–P(3)	2.657 (8)
Nb(1)–P(1)	2.635 (9)	Nb(2)–P(4)	2.642 (8)
Nb(1)–P(2)	2.626 (8)		
atoms	**angle (3)**	**atoms**	**angle (3)**
Nb(2)–Nb(1)–Cl(1)	56.2 (2)	Nb(1)–Nb(2)–Cl(2)	56.6 (2)
Nb(2)–Nb(1)–Cl(2)	55.8 (2)	Nb(1)–Nb(2)–Cl(5)	97.5 (2)
Nb(2)–Nb(1)–Cl(3)	98.3 (2)	Nb(1)–Nb(2)–Cl(6)	98.4 (2)
Nb(2)–Nb(1)–Cl(4)	97.7 (2)	Nb(1)–Nb(2)–P(3)	141.3 (2)
Nb(2)–Nb(1)–P(1)	142.3 (2)	Nb(1)–Nb(2)–P(4)	140.3 (2)
Nb(2)–Nb(1)–P(2)	141.0 (2)	Cl(1)–Nb(2)–Cl(2)	112.1 (3)
Cl(1)–Nb(1)–Cl(2)	111.9 (3)	Cl(1)–Nb(2)–Cl(5)	93.3 (3)
Cl(1)–Nb(1)–Cl(3)	95.9 (3)	Cl(1)–Nb(2)–Cl(6)	95.9 (3)
Cl(1)–Nb(1)–Cl(4)	94.6 (3)	Cl(1)–Nb(2)–P(3)	85.9 (3)
Cl(1)–Nb(1)–P(1)	161.4 (3)	Cl(1)–Nb(2)–P(4)	163.9 (3)
Cl(1)–Nb(1)–P(2)	84.9 (3)	Cl(2)–Nb(2)–Cl(5)	94.3 (3)
Cl(2)–Nb(1)–Cl(3)	94.1 (3)	Cl(2)–Nb(2)–Cl(6)	94.2 (3)
Cl(2)–Nb(1)–Cl(4)	93.2 (3)	Cl(2)–Nb(2)–P(3)	162.1 (3)
Cl(2)–Nb(1)–P(1)	86.5 (3)	Cl(2)–Nb(2)–P(4)	83.8 (2)
Cl(2)–Nb(1)–P(2)	163.0 (3)	Cl(5)–Nb(2)–Cl(6)	164.2 (3)
Cl(3)–Nb(1)–Cl(4)	163.9 (3)	Cl(5)–Nb(2)–P(3)	84.8 (3)
Cl(3)–Nb(1)–P(1)	84.7 (3)	Cl(5)–Nb(2)–P(4)	82.3 (3)
Cl(3)–Nb(1)–P(2)	86.2 (3)	Cl(6)–Nb(2)–P(3)	83.1 (3)
Cl(4)–Nb(1)–P(1)	81.5 (3)	Cl(6)–Nb(2)–P(4)	85.4 (3)
Cl(4)–Nb(1)–P(2)	82.6 (3)	P(3)–Nb(2)–P(4)	78.4 (3)
P(1)–Nb(1)–P(2)	76.6 (3)	Nb(1)–Cl(1)–Nb(2)	68.4 (2)
Nb(1)–Nb(2)–Cl(1)	55.5 (2)	Nb(1)–Cl(2)–Nb(2)	67.6 (2)

Comparison of $Nb_2Cl_6(depe)_2$ and $Ta_2Cl_6(depe)_2$. The $Nb_2Cl_6(depe)_2$ molecule whose structure is reported here forms crystals that are strictly isomorphous with those of the same isomer of the tantalum analogue.[9] In both cases, the two chelate rings have the same (λ) conformation and the molecule is chiral. The two molecular structures have principal dimensions that do not differ significantly at the 3σ level. Thus, there are the following differences (esd's in parentheses): M–M, 0.004 (3) Å; M–P, 0.018 (8) Å; M–Cl_b, 0.009 (9) Å; M–Cl_t, 0.000 (10) Å. While corresponding Nb and Ta molecules of this class have previously been found to have similar dimensions, as in the comparison of **1** and **2** above, this is apparently the first case in which they have been so similar as to be identical within the 3σ criterion.

Comparison of 1 and 3. These two structures are surprisingly similar in view of the difference between dene and depe as ligands. The two Nb–Nb distances are different in a statistically significant sense, viz., 2.741 (3) Å in the depe compound (**3**) and 2.764 (1) Å in the dene compound (**1**), but in a chemical sense the difference is almost insignificant. The Nb–Cl distances do not differ from one compound to the other at the 3σ level. It must be concluded that the nature of the molecule, particularly its Nb–Nb bonding, is not sensitive to the change from depe to dene. Whether this would be true for comparable molecules with other metals, such as Mo or Re, remains to be seen, since there are no other dene/depe analogues available for comparison.

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Registry No. **1**, 111112-77-7; **2**, 111112-79-9; **3**, 111139-83-4; $Nb_2Cl_6(SMe_2)_3$, 61069-51-0; $Ta_2Cl_6(SMe_2)_3$, 77827-59-9; Nb, 7440-03-1; Ta, 7440-25-7.

Supplementary Material Available: For the crystal structures of $Nb_2Cl_6(dene)_2$, $Ta_2Cl_6(dene)_2$, and $Nb_2Cl_6(depe)_2$, full lists of bond distances, bond angles, and anisotropic displacement parameters (8 pages); tables of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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Crystal Structure of a Complex Basic Zirconium Sulfate

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A new complex basic zirconium sulfate, $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6}\cdot 33H_2O$, has been characterized by single-crystal X-ray techniques. The crystals are hexagonal, C_{6h}^2-$P6_3/m$, with $a = 33.779$ (4) Å, $c = 17.522$ (3) Å, $V = 17322$ (3) Å^3, and $R(F) = 0.083$ for 7218 observations [$I > 2\sigma(I)$] and 775 variables. The unit cell contains six complex molecules each consisting of a folded sheet of 18 zirconium atoms linked via oxygen bridges. Large channels between the complexes contain water molecules involved in linking the complexes via hydrogen bonding. The Zr atoms are found in both 7- and 8-fold coordination. This compound is much more basic than the previously characterized basic sulfates, and the structure is distinguished by the presence of triply bridging hydroxyl groups and quadruply bridging oxide ions and by the diminished importance of the sulfate groups in the Zr framework. Systematic rules for the formation of basic zirconium sulfates are discussed in light of these results.

Introduction

The complexity of systems containing zirconium and sulfate ions is well-known.[1–4] An astonishing array of compounds has been obtained from both neutral and acidic zirconium sulfate solutions.[3–5] Structural characterization of a number of neutral[6–11] (Zr:SO_4 ratio = 1:2) and basic[12,13] (Zr:SO_4 ratio greater than 1:2) zirconium sulfates has revealed a diversity of interesting bonding features. However, the number of known structures is small compared to the large number of possible known compounds. Therefore in 1964, Clearfield attempted to explain how such a diversity of compounds could form from sulfate solutions and to predict their structure and formation.[14] Determination of additional crystal structures would help to establish or modify the proposed theory. In particular, little is known about the more basic compounds, i.e., those in which the Zr:SO_4 ratio is large. As part of our interest in this aspect of zirconium chemistry, we have characterized a new basic zirconium sulfate whose composition and structure represent a significant departure from those previously reported. We present here the synthesis and crystal structure of the compound $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6}\cdot 33H_2O$ and discuss its relationship to the known zirconium sulfates.

Experimental Section

Synthesis. Single crystals of $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6}\cdot 33H_2O$ were supplied by Magnesium Elektron, Ltd. Their preparative procedure was as follows. To an aqueous solution of zirconyl chloride (0.64 M, 250 mL, 0.16 mol) were added 4.4 mL of 12 M HCl (0.053 mol) and 5 mL of 18.8 M H_2SO_4 (0.094 mol). The solution was allowed to stand in a stoppered flask at ambient temperature for about 10 days during which time clear, colorless crystals formed. The product was then collected and allowed to air dry.

Analysis. Zirconium was determined by EDTA titration using Xylenol orange as indicator. A 0.1-g sample was dissolved in 10 mL of 5 M sulfuric acid and diluted to 20 mL. The solution was then brought to a boil while being stirred magnetically, and after 15 min of boiling, the solution was diluted to 60 mL. A few drops of indicator were then added, and the solution was kept at 90 °C while being titrated to an orange color with 0.1 M EDTA. The mixture was then cooled and 10 mL of 7 M NH_4OH added so that it returned to its original mauve color. The flask was then returned to the hot plate and the titration completed. The color went from mauve to orange to yellow. Sulfate was determined gravimetrically as $BaSO_4$. A 0.2-g sample of the basic sulfate was boiled with 20 mL of 1 M NaOH. The slurry was then diluted by addition of 30 mL of water and filtered to remove hydrous zirconium dioxide, and sulfate was determined in the filtrate. A TGA weight loss curve was obtained

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