Inorganica Chimica Acta, 112 (1986) 147–152

A Dinuclear, Metal–Metal Bonded, Carboxylato-bridged Niobium(III) Complex

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Received May 25, 1985

Abstract

$Nb_2Cl_6(THT)_3$, THT = tetrahydrothiophene, reacts with excess tetramethylammonium acetate to give an ionic Nb(III) complex, $(NMe_4)[Nb_2Cl_2(THT)(CH_3CO_2)_5]\cdot CH_2Cl_2$. The compound has been characterized by NMR, IR, cyclic voltammetry and X-ray crystallography. It crystallizes in an orthorhombic space group $P2_12_12_1$ with $a = 11.326(3)$ Å, $b = 11.857(4)$ Å, $c = 24.343(6)$ Å, $V = 3269(3)$ Å^3 and $Z = 4$. The Nb–Nb distance is equal to 2.764(1) Å which together with the diamagnetism of the complex indicates a double metal–metal bond. The acetato ligands coordinate in three different modes: bridging bidentate, chelating and bridging unidentate.

Introduction

As part of our continuing effort to develop the chemistry of multiply metal–metal bonded complexes of Nb and Ta we have been exploring the preparation and properties of low-valent compounds of these two metals with carboxylate ligands. The RCO_2^- ligands play an important role in the area of complexes with multiple bonds between metal atoms for elements from Group 6 and higher [1, 2]. For the heavier Group 5 metals only a few examples of carboxylato compounds have been reported [3]. Our studies have concentrated upon examining the reactivity of complexes of the type $M_2Cl_6L_3$, M = Nb or Ta, L = $S(CH_3)_2$ or SC_4H_8 (THT), towards salts of carboxylic acids, specifically with R = t-C_4H_9 and C_6H_5. When the carboxylate/Nb ratio was greater than 2.0 trimeric bi-oxo-capped hexacarboxylates with Nb in average oxidation state $+3\frac{2}{3}$ were isolated [4]. A reaction of one equivalent of t-$C_4H_9CO_2Li$ with the Ta(III) dimer resulted in a substitution of one chloride by the pivalate ion which bridged the bimetallic unit [3]. In this paper we would like to report a compound obtained by reacting excess tetramethylammonium acetate with the Nb–THT starting material. The product, an ionic complex of the formula $(NMe_4)[Nb_2Cl_2(THT)(acetate)_5]\cdot CH_2Cl_2$, contains five acetato ligands coordinating in three different modes. Although it is only the second structurally characterized Nb or Ta complex in the oxidation state +3 with a carboxylate, a certain new pattern seems to be emerging for the doubly metal–metal bonded species of the two metals.

Experimental

All operations were performed under an atmosphere of argon, using standard Schlenk techniques and a double manifold vacuum line. $Nb_2Cl_6(THT)_3$ was prepared as previously [5]. Anhydrous $CH_3CO_2NMe_4$ was received from Aldrich Chemicals, Inc. Microanalyses were done by Galbraith Laboratories. NMR and IR spectra were recorded using a Varian EM-390 NMR spectrometer and a Perkin-Elmer 783 infrared spectrophotometer. Cyclic voltammetry experiments were done using a BAS-100 Electrochemical Analyzer (Bioanalytical Systems Inc.) on dichloromethane solutions containing 0.2 M n-Bu_4NPF_6 as supporting electrolyte with an Ag/AgCl reference electrode and a Pt disk as a working electrode.

Preparation

$Nb_2Cl_6(THT)_3$ (2.0 g, 3 mmol) was recrystallized by dissolution in benzene, filtration and removal of solvent, and redissolved in 100 ml of dichloromethane. $CH_3CO_2NMe_4$ (2.0 g, 15 mmol) was added and the mixture stirred for three days, affording a dark red solution containing some solid suspension. Upon filtration a slightly colored white precipitate was separated. After the solution was reduced in volume to about 20 ml, addition of hexane caused precipitation of a purple solid (1.6 g after drying). The supernatant liquid was brown–red and apparently contained some as yet unidentified secondary product. The crude material was recrystallized by dissolution in about 15 ml of dichloromethane and layering with hexane in a Schlenk tube. This procedure afforded a product in crystalline form (some crystals up to several millimeters in size) within a few days. The supernatant liquid was decanted and the solid washed three times with THF and dried. Yield

0020-1693/86/$3.50

1.3 g, 54%. *Anal.* Calc. for $Nb_2Cl_4SO_{10}NC_{19}H_{37}$: Cl, 17.74; S, 4.00; C, 28.55; H, 4.67. Found: Cl, 17.69; S, 4.26; C, 28.53; H, 4.40%.

^{1}H NMR ($CDCl_3$), δ in ppm: 2.15 and 2.18-η^2,μ_1- and η^2,μ_2-CH_3CO_2; 2.32-η^1,μ_2-CH_3CO_2; 2.40 and 2.87-SC_4H_8; 3.45-$N(CH_3)_4^+$; 5.30-CH_2Cl_2.

IR spectrum (KBr disk, cm^{-1}): 3440(m, br), 3012(m), 2943(m), 2908(m), 2841(w), 1723(s), 1620(w, br), 1523(s, br), 1472(vs), 1430(vs, br), 1377(m), 1349(m), 1300(w), 1252(m), 1180(s, br), 1120(sh), 1090(m), 1012(s, br), 951(s), 916(s), 870(w), 798(s), 722(sh), 686(vs), 672(vs), 613(s), 612(sh).

X-ray Crystallography

The unit cell determination and collection of intensity data were carried out by following routine procedures used in this laboratory that have been described elsewhere [6]. The structure was solved and refined by standard computational methods*. The intensity data were corrected for Lorentz and polarization effects. Azimuthal scans of reflections near $\chi = 90°$ showed less than 10% variation of intensities and therefore no correction for absorption was applied. Pertinent crystallographic data are summarized in Table I.

The positions of two independent niobium atoms were derived by direct methods (program MULTAN-81). The rest of the structure was developed by alternating series of least-squares refinements and difference Fourier calculations. The problem of disorder, found in the less important parts of the compound, was resolved by following the normal procedure. Appropriate atomic positions were determined from a difference Fourier map. Fractional occupancy factors were assigned by trial and error so as to give comparable values of B for corresponding atoms. For THT the disorder was conformational with the bottom edge of the envelope (second and third C atoms) positioned on both sides of the C–S–C plane with a multiplicity of 0.5 for each orientation. Two carbon atoms in the tetramethylammonium cation could be refined anisotropically and therefore only C(23) and C(24) were considered as being disordered. The final occupancy factors were 0.65 for the above mentioned atoms and 0.35 for C(23A) and C(24A). For the disordered molecule of dichloromethane four chlorine atoms were used, each with an occupancy of one half. Anisotropic displacement parameters were assigned to all nondisordered atoms except the carbon atom in CH_2Cl_2. The enantiomorphic structure was also refined to convergence but it gave higher values of R and R_w.

Tables of observed and calculated structure factors and anisotropic displacement parameters are available as supplementary material (see final section).

TABLE I. Crystallographic Data for $(NMe_4)[Nb_2Cl_2(THT)(CH_3CO_2)_5]\cdot CH_2Cl_2$

Formula	$Nb_2Cl_4SO_{10}NC_{19}H_{37}$
Formula weight	799.20
Space group	$P2_12_12_1$
Systematic absences	$h00, h \neq 2n; 0k0, k \neq 2n; 00l, l \neq 2n$
a (Å)	11.326(3)
b (Å)	11.857(4)
c (Å)	24.343(6)
α (deg)	90.0
β (deg)	90.0
γ (deg)	90.0
V (Å^3)	3269(3)
Z	4
D_c (g cm^{-3})	1.624
Crystal size (mm)	0.45 × 0.4 × 0.4
μ(Mo Kα) (cm^{-1})	11.057
Data collection instrument	Syntex P$\bar{1}$
Radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)
Orientation reflections, number, range (2θ)	15, $20.5 \leq 2\theta \leq 31.0$
Temperature (°C)	5
Scan method	$\omega - 2\theta$
Data collection range, 2θ (deg)	$4 \leq 2\theta \leq 50$
Number unique data, total with $F_o^2 > 3\sigma(F_o^2)$	3057, 2527
Number of parameters refined	323
R^a	0.0434
R_w^b	0.0571
Quality-of-fit indicator^c	1.270
Largest shift/e.s.d., final cycle	0.43
Largest peak (e/Å^3)	0.698

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

Results

Molecular Structure

The positional and isotropic-equivalent displacement parameters are given in Table II. Important bond distances and bond angles are presented in Tables III and IV, respectively. A complete listing of interatomic dimensions is included in the supplementary material.

The asymmetric unit contains the discrete dinuclear anion, the NMe_4^+ cation and a molecule of the solvent, CH_2Cl_2. The anionic dimer, represented by its ORTEP drawing in Fig. 1, consists of a Nb_2

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*Calculations were done on the VAX-11/780 computer at Department of Chemistry, Texas A&M University, College Station, Tex. with the VAX-SDP software package.

TABLE II. Positional and Isotropic-equivalent Displacement Parameters for $(NMe_4)[Nb_2Cl_2(THT)(CH_3CO_2)_5]\cdot CH_2Cl_2$ [a]

Atom	x	y	z	B(Å^2)
Nb(1)	0.17657(8)	0.12596(6)	−0.15659(3)	3.15(1)
Nb(2)	0.32099(7)	−0.01235(6)	−0.09467(3)	3.14(1)
Cl(1)	−0.0432(2)	0.1541(2)	−0.1586(1)	4.78(5)
Cl(2)	0.2818(3)	−0.1594(2)	−0.0231(1)	4.85(6)
S	0.3865(2)	0.1220(2)	−0.16023(9)	3.66(4)
O(1)	0.1391(5)	0.0087(5)	−0.0956(2)	3.3(1)
O(2)	0.0004(8)	−0.1235(7)	−0.1071(4)	6.9(2)
O(3)	0.1508(5)	−0.0239(5)	−0.2037(2)	3.5(1)
O(4)	0.2690(5)	−0.1371(5)	−0.1546(2)	3.5(1)
O(5)	0.1773(6)	0.2268(5)	−0.0827(2)	3.7(1)
O(6)	0.2936(5)	0.1145(5)	−0.0328(3)	3.9(1)
O(7)	0.1946(7)	0.3053(5)	−0.1834(3)	4.4(1)
O(8)	0.1862(7)	0.1772(6)	−0.2461(3)	4.4(1)
O(9)	0.4840(6)	−0.1082(6)	−0.1183(3)	4.6(1)
O(10)	0.4938(6)	0.0167(6)	−0.0538(2)	4.2(1)
C(1)	0.0434(9)	−0.0518(9)	−0.0797(4)	4.5(2)
C(2)	−0.007(1)	−0.012(2)	−0.0261(5)	9.2(5)
C(3)	0.1928(8)	−0.1197(8)	−0.1913(4)	3.7(2)
C(4)	0.147(1)	−0.2207(8)	−0.2221(4)	4.8(2)
C(5)	0.2292(9)	0.2010(8)	−0.0388(4)	3.9(2)
C(6)	0.215(1)	0.278(1)	0.0110(5)	6.8(3)
C(7)	0.1941(9)	0.2813(8)	−0.2336(4)	4.3(2)
C(8)	0.201(1)	0.370(1)	−0.2765(5)	6.6(3)
C(9)	0.5425(9)	−0.0615(9)	−0.0803(4)	4.4(2)
C(10)	0.672(1)	−0.096(1)	−0.0694(5)	6.6(3)
C(11)	0.479(1)	0.248(1)	−0.1423(6)	6.2(3)
C(12)	0.555(3)	0.270(3)	−0.202(1)	8.6(8)*
C(13)	0.537(3)	0.208(3)	−0.240(1)	8.4(8)*
C(14)	0.472(1)	0.081(1)	−0.2223(5)	6.5(3)
C(12A)	0.592(3)	0.237(2)	−0.177(1)	7.1(6)*
C(13A)	0.574(3)	0.152(3)	−0.228(1)	7.6(7)*
N	0.5590(8)	0.4845(7)	0.3800(3)	4.6(2)
C(21)	0.499(1)	0.499(1)	0.3254(4)	6.5(3)
C(22)	0.503(2)	0.555(2)	0.4231(6)	9.4(4)
C(23)	0.609(2)	0.364(2)	0.3845(8)	7.1(5)*
C(24)	0.681(2)	0.556(2)	0.3720(9)	7.9(5)*
C(23A)	0.527(3)	0.368(3)	0.401(1)	5.4(7)*
C(24A)	0.686(4)	0.506(4)	0.383(2)	8(1)*
C(30)	0.413(1)	0.641(1)	−0.1125(5)	6.2(3)*
Cl(3)	0.5605(7)	0.6208(6)	−0.1275(3)	7.0(1)*
Cl(4)	0.3256(6)	0.5278(5)	−0.1401(3)	6.2(1)*
Cl(3A)	0.5511(7)	0.5831(6)	−0.1178(3)	7.0(2)*
Cl(4A)	0.3141(8)	0.5248(7)	−0.1113(3)	8.3(2)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{4}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

unit coordinated by two bidentate bridging acetate ions, unidentate bridging THT and acetato ligands, two terminal chloride ions and two chelating acetate ions. It has a virtual mirror plane perpendicular to the Nb–Nb axis. Formally each metal atom is 7-coordinate, but if each chelating acetate ion is regarded as occupying a single coordination site, the molecule can be considered to have an edge-sharing-octahedra geometry. The plane defined by the niobium atoms and two monoatomic bridges incorporates both chloride ions and the carbon atoms of the chelating acetate ions. A table of selected least-squares planes is included in the supplementary material. Thus, the whole equatorial unit is essentially coplanar. Each bridging carboxylate ion is bent away from the direction perpendicular to that plane by 10°. The metal–metal separation of 2.764(1) Å is at the upper limit of the double Nb=Nb bond lengths. The metal–oxygen distances increase in the order: bridging monodentate, bridging bidentate and chelating acetate. The corresponding average values are: 2.076(1) Å, 2.151(6) Å, 2.240(9) Å, respectively. The Nb–

TABLE III. Important Bond Distances (Å) in the $[Nb_2Cl_2(THT)(CH_3CO_2)_5]^-$ Anion[a]

Nb(1)–Nb(2)	2.764(1)
Nb(1)–Cl(1)	2.512(3)
Nb(1)–S	2.379(3)
Nb(1)–O(1)	2.077(6)
Nb(1)–O(3)	2.135(6)
Nb(1)–O(5)	2.160(5)
Nb(1)–O(7)	2.233(6)
Nb(1)–O(8)	2.264(6)
Nb(2)–Cl(2)	2.505(3)
Nb(2)–S	2.373(2)
Nb(2)–O(1)	2.076(5)
Nb(2)–O(4)	2.160(6)
Nb(2)–O(6)	2.151(6)
Nb(2)–O(9)	2.244(6)
Nb(2)–O(10)	2.222(6)
O(1)–C(1)	1.356(12)
O(2)–C(1)	1.185(13)

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

TABLE IV. Important Bond Angles (deg) in the $[Nb_2Cl_2(THT)(CH_3CO_2)_5]^-$ Anion[a]

Nb(2)–Nb(1)–Cl(1)	132.54(7)
Nb(2)–Nb(1)–S	54.35(6)
Nb(2)–Nb(1)–O(1)	48.3(2)
Nb(2)–Nb(1)–O(3)	83.1(2)
Nb(2)–Nb(1)–O(5)	82.7(2)
Nb(2)–Nb(1)–O(7)	132.1(2)
Nb(2)–Nb(1)–O(8)	131.0(2)
Cl(1)–Nb(1)–S	172.73(9)
Cl(1)–Nb(1)–O(1)	84.3(2)
Cl(1)–Nb(1)–O(3)	88.0(2)
Cl(1)–Nb(1)–O(5)	86.9(2)
Cl(1)–Nb(1)–O(7)	87.6(2)
Cl(1)–Nb(1)–O(8)	89.6(2)
S–Nb(1)–O(1)	102.6(2)
S–Nb(1)–O(3)	95.7(2)
S–Nb(1)–O(5)	92.2(2)
S–Nb(1)–O(7)	85.2(2)
S–Nb(1)–O(8)	85.5(2)
O(1)–Nb(1)–O(3)	78.4(2)
O(1)–Nb(1)–O(5)	77.1(2)
O(1)–Nb(1)–O(7)	149.8(2)
O(1)–Nb(1)–O(8)	151.3(2)
O(3)–Nb(1)–O(5)	155.3(2)
O(3)–Nb(1)–O(7)	130.4(2)
O(3)–Nb(1)–O(8)	73.3(2)
O(5)–Nb(1)–O(7)	73.5(2)
O(5)–Nb(1)–O(8)	130.7(2)
O(7)–Nb(1)–O(8)	57.3(2)
Nb(1)–Nb(2)–Cl(2)	133.46(8)
Nb(1)–Nb(2)–S	54.55(6)
Nb(1)–Nb(2)–O(1)	48.3(2)
Nb(1)–Nb(2)–O(4)	82.9(2)
Nb(1)–Nb(2)–O(6)	83.2(2)
Nb(1)–Nb(2)–O(9)	130.4(2)
Nb(1)–Nb(2)–O(10)	132.3(2)
Cl(2)–Nb(2)–S	172.0(1)
Cl(2)–Nb(2)–O(1)	85.2(2)
Cl(2)–Nb(2)–O(4)	86.9(2)
Cl(2)–Nb(2)–O(6)	88.5(2)
Cl(2)–Nb(2)–O(9)	88.4(2)
Cl(2)–Nb(2)–O(10)	87.3(2)
S–Nb(2)–O(1)	102.8(2)
S–Nb(2)–O(4)	95.2(2)
S–Nb(2)–O(6)	92.7(2)
S–Nb(2)–O(9)	84.8(2)
S–Nb(2)–O(10)	85.5(2)
O(1)–Nb(2)–O(4)	78.7(2)
O(1)–Nb(2)–O(6)	77.3(2)
O(1)–Nb(2)–O(9)	151.0(2)
O(1)–Nb(2)–O(10)	149.4(2)
O(4)–Nb(2)–O(6)	155.9(2)
O(4)–Nb(2)–O(9)	72.8(2)
O(4)–Nb(2)–O(10)	130.5(2)
O(6)–Nb(2)–O(9)	130.8(2)
O(6)–Nb(2)–O(10)	72.9(2)
O(9)–Nb(2)–O(10)	57.9(2)
Nb(1)–S–Nb(2)	71.11(7)
Nb(1)–O(1)–Nb(2)	83.4(2)
Nb(1)–O(1)–C(1)	136.2(6)
Nb(2)–O(1)–C(1)	136.6(6)
Nb(1)–O(3)–C(3)	124.5(5)
Nb(2)–O(4)–C(3)	123.7(6)
Nb(1)–O(5)–C(5)	125.1(6)
Nb(2)–O(6)–C(5)	124.7(6)
Nb(1)–O(7)–C(7)	93.9(5)
Nb(1)–O(8)–C(7)	91.9(5)
Nb(2)–O(9)–C(9)	91.2(6)
Nb(2)–O(10)–C(9)	92.4(5)

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

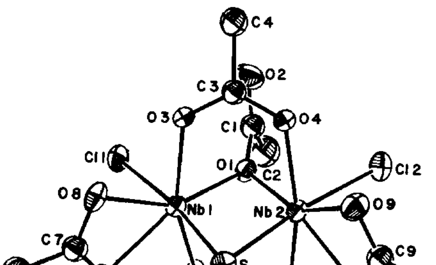

Fig. 1. ORTEP drawing of the $[Nb_2Cl_2(THT)(CH_3CO_2)_5]^-$ anion. Thermal ellipsoids enclose 30% of electron density. Carbon atoms in the bridging THT ligand have been omitted for the sake of clarity.

O–C bond angles decrease in the same order, *viz.* 136.4(4)°, 124.5(3)° and 92.4(6)°, respectively. The asymmetric character of the η^1,μ_2-acetate is expressed in a large difference between the C–O bond lengths, which are 1.356(12) Å and 1.185(13) Å for the coordinated and free oxygen atoms, respectively. The other C–O distances are all close to their average value of 1.263(3) Å.

Properties and Spectra

The compound has a deep purple color which is virtually indistinguishable from that of $Nb_2Cl_6L_3$. It dissolves readily in acetonitrile, dichloromethane and chloroform but is completely insoluble in THF and hydrocarbon solvents. In terms of stability it is one of the most robust Nb(III) species that we know but still it is an air-sensitive material. It undergoes an irreversible reduction at about −1.1 V (see Fig. 2).

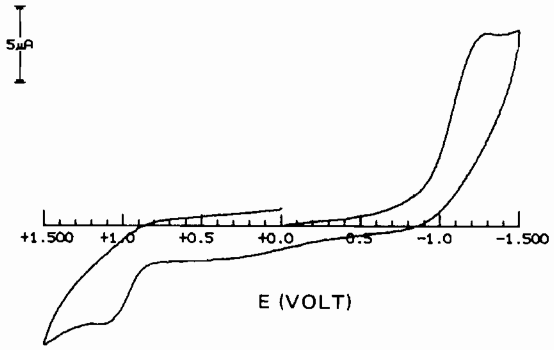

Fig. 2. Cyclic voltammogram for $(NMe_4)[Nb_2Cl_2(THT)(CH_3CO_2)_5]\cdot CH_2Cl_2$. The oxidation wave at *ca.* +1 V is due to chloride ion.

Normal proton NMR signals obtained for this $Nb(d^2)$ complex indicate that it is diamagnetic. The resonances for the two types of bidentate acetates appear at 2.15 and 2.18 ppm and it is not possible to assign them to a particular mode of coordination. The unidentate carboxylate is observed further downfield at 2.32 ppm. The THT ligand gives broad signals at 2.40 and 2.87 ppm. The chemical shifts for free THT are at 1.53 and 2.58 ppm in benzene [7], and 1.90 and 2.77 ppm in CCl_4*. The resonances due to bridging THT in $Nb_2Cl_6(THT)_3$ appear at 1.46 and 3.96 ppm [7]. In our case there is evidently a considerable downfield shift of the signal for protons on carbon atoms not bonded to sulfur. It may be due to steric crowding caused by the chelating acetates but other factors, for example solvent, can also contribute. The possibility that the complex is slightly paramagnetic, for instance due to excitation to a low-lying spin triplet state, has to be discounted since there is no comparable shift for the acetato protons, which would have been affected to approximately the same extent.

In the IR spectrum only the asymmetric CO_2, stretchings can be assigned unequivocally. For carboxylates they appear above 1500 cm^{-1} and no other distinct peaks are expected in this region [2, 8]. Thus, two prominent bands that we observe at 1523 (broad) and 1723 cm^{-1} are clearly due to both bidentate and the unidentate CO_2 groups, respectively. The relatively high frequency for the latter is associated with the fact that the second oxygen atom is essentially noncoordinated. The assignment of symmetric modes is complicated by the presence of THT, NMe_4^+ and CH_2Cl_2, which absorb in the pertinent region. Based on literature data [2, 8] we expect both bidentate modes to appear between 1400 and 1500 cm^{-1}. The unidentate acetate ion should have a band well below 1400 cm^{-1} in view of high energy of the asymmetric stretch. It seems impossible to make a convincing assignment.

Discussion

The compound reported here has several remarkable features. It contains acetate ligands coordinating in three different modes. One of them, the bridging unidentate mode, with one free oxygen atom, is apparently unprecedented in discrete molecules [2]. There are examples of complexes containing up to three differently bound types of carboxylates in one molecule [9] but no crystallographic proof for the unidentate bridge bonding mentioned above is available. The occurrence of two *trans* bridging bidentate carboxylate ions is also quite rare for low valent Nb and Ta complexes. Only recently has the first dimeric complex of either metal containing two bidentate bridging ligands of any kind been prepared [5]. This is $Nb_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-dmpm})_2$ in which the dmpm units bridge the metal atoms above and below the central $Cl_2Nb(\mu\text{-}Cl)_2NbCl_2$ plane. Bridging of this type has the potential of providing a dimer with stability against fragmentation. Thus, complexes of this type might be starting materials, which could be reduced to a lower oxidation state to afford products with a higher metal–metal bond order. One possible explanation of the irreversible reduction that we observe in the present case is that it is accompanied by a major structural change, such as migration of ligands. Such a process is expected to occur when the metal–metal bond order is changed.

The diamagnetism of the acetato compound, evidenced by its normal NMR spectrum, is consistent with the presence of a double bond between the Nb atoms. Almost all previously characterized dimers of Nb and Ta in the oxidation state +3 have a metal–metal distance around 2.7 Å [3]. In this case a significantly greater value is found but it is comparable with the Ta–Ta separation in $Ta_2Cl_5(\mu\text{-t-BuCO}_2)(\mu\text{-THT})(THF)_2$ [3]. These two examples suggest that possibly the elongation of the double M=M bond, M = Nb or Ta, is characteristic of the carboxylato complexes of these two metals in the +3 oxidation state. However, at this point it is only an emerging trend and we cannot rule out the possibility that steric crowding is the main factor responsible

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*Sadtler Standard NMR Spectra.

for this elongation. Another interesting feature is the retention of one THT ligand in the molecule. Usually ligand substitution in the confacial-bioctahedral $M_2Cl_6L_3$, M = Nb, Ta, gives an edge-sharing-bioctahedral molecule without the sulfur containing ligand. Even weakly coordinating alcohols can completely replace THT, producing $Nb_2Cl_5(OR)(ROH)_4$ [10]. In both of the known carboxylate complexes one original neutral ligand is retained.

Acknowledgements

We are grateful to the U.S. National Science Foundation for support. M.P.D. is a National Science Foundation Predoctoral Fellow and also holds a Texaco-IUCCP Fellowship from this department.

Supplementary Material

Tables of observed and calculated structure factors, anisotropic displacement parameters, complete listing of bond distances and angles, and selected least-squares planes (18 pages). These are available on request from F.A.C.

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