energy is seen on oxidizing ZrBr to Zr_2Br_2C while scandium(III) in Sc_2Cl_2C differs from that in $ScCl_3$ by a remarkable 3.2 eV. Similar effects have been reported for $Sc_7Cl_{10}C_2$,[21] where the scandium oxidation state in the metal chain is +2.5, and for ZrH_2 and ZrClH relative to $ZrCl_2$.[16] These differences must arise from the greater covalency (lower polarity) of the metal–carbon bonds relative to the metal–halogen bonds. It could be argued that final-state relaxation effects are responsible for up to half of the difference seen with Zr_2Cl_2C, but this is clearly less plausible for the filled-band Sc_2Cl_2C.

Acknowledgment. The authors wish to express their appreciation to Prof. R. A. Jacobson for provision of the single-crystal X-ray diffraction facilities and to J. W. Anderegg for the XPS measurements. Samuel von Winbush was supported as a DOE Faculty Research Participant.

Registry No. Sc_2Cl_2C, 97005-30-6; Sc_2Cl_2N, 99654-89-4; Y_2Cl_2C, 99665-56-2; Zr_2Cl_2C, 99665-57-3; Zr_2Br_2C, 99665-58-4; Zr_2Cl_2N, 99654-90-7; $ScCl_3$, 10361-84-9; YCl_3, 10361-92-9; $ZrCl_4$, 10026-11-6; $ZrBr_4$, 13777-25-8; Sc, 7440-20-2; Y, 7440-65-5; Zr, 7440-67-7; N_2, 7727-37-9; NaN_3, 26628-22-8; ZrNCl, 13932-08-6; C, 7440-44-0; graphite, 7782-42-5.

Supplementary Material Available: Listings of observed and calculated structure factor data for Sc_2Cl_2Z, Z = C, N, and the Guinier powder patterns of 1T-Sc_2Cl_2C, -Sc_2Cl_2N, and -Y_2Cl_2C (4 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
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Oxidative Addition of Diphenyl Disulfide across a Ta═Ta Bond. Preparation and Characterization of $[TaCl_3(Me_2S)]_2(\mu\text{-}SPh)_2$

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Received August 30, 1985

The tantalum complex $(SMe_2)Cl_2Ta(\mu\text{-}Cl)_2(\mu\text{-}SMe_2)TaCl_2(SMe_2)$, possessing a $\sigma^2\pi^2$ Ta═Ta double bond, reacts readily with PhSSPh to give $(SMe_2)Cl_3Ta(\mu\text{-}SPh)_2TaCl_3(SMe_2)$. In this reaction, the starting material loses the bridging SMe_2 ligand and two chloride bridges are broken while only two new SPh bridges are formed in the final product. This oxidative-addition reaction of the S—S single bond to the Ta═Ta double bond converts the face-sharing bioctahedron structure of the starting compound to an edge-sharing bioctahedron structure in the final dimer, with concomitant change of the oxidation state of tantalum from III to IV. The product is the first example of a d^1–d^1 ditantalum thiolate-bridged dimer. Important structural data for $(SMe_2)Cl_3Ta(\mu\text{-}SPh)_2TaCl_3(SMe_2)$, which has an inversion center, are as follows: Ta–Ta distance, 3.165(1) Å; Ta–S(SMe_2), 2.707 (2) Å; Ta–S(μ-SPh), 2.372 (2) Å for sulfur trans to SMe_2 ligand; Ta–S(μ-SPh), 2.448 (2) Å for sulfur trans to Cl(2) atom; Ta–Cl(1) and Ta–Cl(3), 2.328 (2) and 2.331 (2) Å, respectively; Cl(1) and Cl(3) atoms located above and below the $Ta(\mu\text{-}SPh)_2Ta$ parallelogram plane. The new compound crystallizes in the monoclinic space group *C*2/*c* with $a = 17.934$ (5) Å, $b = 12.445$ (4) Å, $c = 11.705$ (4) Å, $\beta = 92.50$ (3)°, $V = 2610$ (2) Å^3, and $Z = 4$. Solid-state ^{13}C NMR spectroscopy with cross polarization and magic-angle spinning (CP/MAS) at 28 and −103 °C provides evidence that this compound is diamagnetic, which is in accord with the results of a Fenske–Hall calculation predicting a single bond for the tantalum–tantalum d^1–d^1 pair.

Introduction

Complexes possessing multiple metal–metal bonds, which may be viewed as units of unsaturation containing metal atoms in lower oxidation states, are usefully reactive. This can be illustrated by several previously reported oxidative-addition reactions that these complexes undergo. The following are representative:

$$Mo_2Cl_4(dppe)_2 + EtSSEt \rightarrow (dppe)Cl_2Mo(\mu\text{-}SEt)_2MoCl_2(dppe)^1$$

$$Mo_2(O\text{-}i\text{-}Pr)_6 + i\text{-}PrOO\text{-}i\text{-}Pr \rightarrow Mo_2(O\text{-}i\text{-}Pr)_8{}^2$$

$$Mo_2(O\text{-}i\text{-}Pr)_6 + 2Cl_2 \rightarrow Mo_2(O\text{-}i\text{-}Pr)_6Cl_4{}^2$$

$$Nb_2Cl_6(Me_2S)_3 + PhN{=}NPh \rightarrow Nb_2Cl_6(Me_2S)_2(NPh)_2{}^3$$

$$W_2(OCMe_3)_6 + PhNO \rightarrow [W(OCMe_3)_2(NPh)]_2(\mu\text{-}O)(\mu\text{-}OCMe_3)_2{}^4$$

We are currently conducting a broadly based systematic study of oxidative addition reactions involving double, triple, and quadruple bonds between metal atoms with the objective of providing generally useful, predictable synthetic chemistry. One class of starting materials that figure prominently in our program comprises the dinuclear, doubly metal–metal-bonded compounds of niobium and tantalum, of general formula $M_2X_6L_3$. Those most commonly used by us are the ones with X = Cl and L = Me_2S, Et_2S, or $(CH_2)_4S$. In this paper, we report the reaction of $Ta_2Cl_6(Me_2S)_3$ with PhSSPh, to give a dinuclear, Ta–Ta bonded product in which the PhSSPh reagent has reacted to give two μ-SPh groups. The product has been characterized by X-ray crystallography and solid-state ^{13}C NMR spectroscopy, and the electronic structure has been examined by means of a molecular orbital calculation.

Experimental Section

All manipulations were carried out under an atmosphere of argon. Standard Schlenk and vacuum-line techniques were used. Benzene and hexane were freshly distilled from benzophenone ketyl prior to use. Solutions and solvents were transferred via stainless-steel cannulae and/or syringes. Diphenyl disulfide was purchased from Eastman and was deaerated under vacuum at room temperature. $Ta_2Cl_6(Me_2S)_3$ was prepared according to a literature procedure.[5] The IR spectrum was recorded on a Perkin-Elmer 783 spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Inc.

Solid-state, 25.02-MHz ^{13}C CP/MAS (cross polarization and magic-angle spinning) NMR spectra of ca. 400 μL (ca 0.9 g.) of $[TaCl_3(Me_2S)]_2(\mu\text{-}SC_6H_5)_2$ were obtained in a Kel-F rotor on a Chemagnetics spectrometer. The matched spin-lock contact time was 1 ms, and 2000 scans were acquired per spectrum. All chemical shifts were measured relative to tetramethylsilane by using hexamethylbenzene as a secondary substitution reference. The sample rotor was packed in a Vacuum Atmospheres drybox and magic-angle spinning was performed with dry nitrogen in order to avoid contacting the sample with air or moisture.

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Table I. Crystal Data for $[TaCl_3(Me_2S)]_2(\mu\text{-}SPh)_2$

formula	$Ta_2Cl_6S_4C_{16}H_{22}$
fw	917.20
space group	*C*2/*c*
syst abs	hkl ($h + k \neq 2n$), $h0l$ ($l \neq 2n$)
a, Å	17.934 (5)
b, Å	12.445 (4)
c, Å	11.705 (4)
β, deg	92.50 (3)
V, Å^3	2610 (2)
Z	4
d_{calcd}, g/cm^3	2.335
cryst size, mm	0.25 × 0.40 × 0.50
μ(Mo Kα), cm^{-1}	97.51
data colln instrum	CAD-4
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)
orientation reflections: no. range (2θ), deg	25; $11.30 \leq 2\theta \leq 38.98$
temp, °C	22
scan method	ω–2θ
data colln range (2θ), deg	$4 \leq 2\theta \leq 48$
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	1775, 1583
no. of parameters refined	127
R^a	0.0316
$R_w{}^b$	0.0421
quality-of-fit indicator^c	1.28
largest shift/esd, final cycle	0.01
largest peak, e/Å^3	1.246

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

Preparation of $[TaCl_3(Me_2S)]_2(\mu\text{-}SPh)_2$. A solution of $Ta_2Cl_6(Me_2S)_3$ (2.17 g, 2.85 mmol) in 90 mL of benzene was prepared in a Schlenk tube. Diphenyl disulfide (1.05 g, 4.80 mmol) was added to this solution, and the reaction mixture was stirred for 72 h at 20–25 °C. The color of the reaction mixture changed gradually from yellow-brown to dark green, and at the same time a green, shiny, microcrystalline precipitate was formed. The solid was filtered off, washed several times with 20-mL aliquots of freshly distilled hexane, and dried under vacuum (yield: 42%, 1.1 g). The compound decomposes to a white solid immediately upon exposure to air. IR (Nujol), cm^{-1}: 1320 (s), 1300 (w), 1255 (m), 1180 (m), 1155 (w), 1090 (vw), 1065 (w), 1035 (s), 1020 (s), 995 (s), 980 (vs), 955 (vw), 920 (w), 830 (vw), 800 (w), 735 (vs), 695 (w), 680 (s).

Anal. Calcd for $C_{16}H_{22}Cl_6S_4Ta_2$: C, 20.95; H, 2.42; S, 13.98. Found: C, 18.72, 18.04; H, 2.32, 2.19; S, 10.13, 9.00.

Crystallographic Study. Crystallographic quality crystals were obtained by a modification of the above preparative procedure. The solution of $Ta_2Cl_6(Me_2S)_3$ in benzene (20 mL) was carefully covered with a layer of diphenyl disulfide dissolved in hexane (20 mL) in a Schlenk tube, and the reaction mixture was allowed to stand undisturbed for 2–3 weeks. Large, blocky, green crystals of $[TaCl_3(Me_2S)]_2(\mu\text{-}SPh)_2$ were formed upon slow diffusion of the two solutions (yield: 27%, 0.7 g). The IR spectrum of these crystals is identical with the IR spectrum obtained on the product prepared in bulk.

The crystal used for data collection was mounted in a capillary tube and sealed in place with epoxy cement. The general procedures used in determining the structure have already been described elsewhere.[6] The crystal parameters and basic information pertaining to data collection and structure refinement are given in Table I. Polarization, Lorentz, and absorption corrections were applied to the intensity data. The tantalum atoms were found by employing a three-dimensional Patterson function. The remaining non-hydrogen atoms were located by a series of alternating difference Fourier syntheses and least-squares refinements. The final difference Fourier map revealed several residual peaks, but only one peak, located in the vicinity of the tantalum atom, possessed electron density above 1 e/Å^3 (see Table I). All fourteen atoms were refined anisotropically.

Results and Discussion

Synthetic Reaction. The reaction between $Ta_2Cl_6(Me_2S)_3$ and diphenyl disulfide, PhSSPh, in benzene proceeds smoothly under rather mild conditions to give a green crystalline product $(Me_2S)Cl_3Ta(\mu\text{-}SPh)_2TaCl_3(Me_2S)$, which has been characterized by X-ray crystallography, IR spectroscopy elemental analyses and solid-state ^{13}C NMR spectroscopy. The new compound is highly air-sensitive and is either not soluble in common organic solvents or reacts with some of them, presumably by replacement of the terminal, labile dimethyl sulfide ligands.[7] These properties of the compound precluded the recording of good quality UV or NMR spectra in solution.

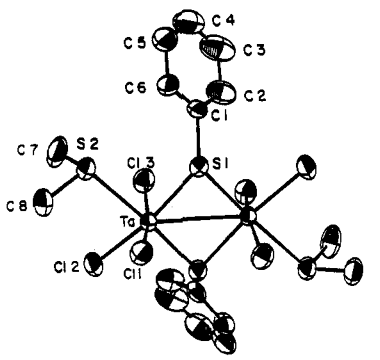
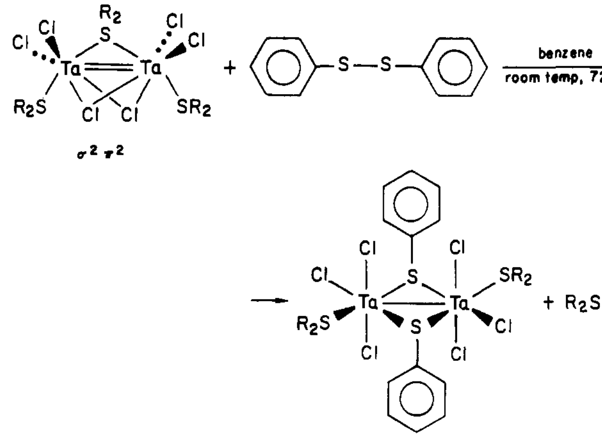


Figure 1. ORTEP drawing of the $[TaCl_3(Me_2S)]_2(\mu\text{-}SPh)_2$ complex, which also defines the labeling scheme. The thermal ellipsoids enclose 50% of the electron density.

The synthetic reaction reported here is essentially the oxidative addition of one molecule of PhSSPh to one of $(Me_2S)Cl_2Ta(\mu\text{-}Me_2S)(\mu\text{-}Cl)_2TaCl_2(Me_2S)$ with concomitant loss of one bridging dimethyl sulfide group and an increase in the oxidation number of tantalum from III to IV as shown in eq 1.



(1)

Structurally, the reaction is a process wherein a starting material containing two metal atoms in a face-sharing bioctahedral structure is smoothly converted to a product having an edge-sharing bioctahedral structure.

The bridging SPh moieties come from splitting of the single sulfur–sulfur bond. This type of reaction is superior to other conceivable reactions involving the use of thiols or alkali-metal thiolate salts as the source of the bridging groups since it avoids the well-known offensive odors of such reagents.

From the viewpoint of elemental analysis, this compound proved to be intractable. Under the standard conditions used, C, H, and S analyses were consistently low and it was only through X-ray crystallography that we were able definitively to identify the compound.

Molecular Structure. The identification of the product was accomplished unambigously by X-ray crystallography. Crystals of $[TaCl_3(Me_2S)]_2(\mu\text{-}SPh)_2$ are composed of an ordered array of discrete molecules that reside on centers of inversion. An ORTEP drawing of the entire molecule is shown in Figure 1, which also defines the numbering scheme. The final atomic positional and

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[6] See for example: Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.

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Table II. Positional and Isotropic Equivalent Thermal Parameters for $[TaCl_3(Me_2S)]_2(\mu\text{-}SPh)_2$

atom	x	y	z	B,[a] Å^2
Ta	0.05668 (2)	0.23028 (3)	0.15007 (3)	2.623 (7)
Cl(1)	0.0467 (2)	0.4155 (2)	0.1260 (2)	4.19 (6)
Cl(2)	0.1878 (1)	0.2418 (2)	0.1212 (2)	4.34 (6)
Cl(3)	0.0582 (2)	0.0446 (2)	0.1239 (2)	3.93 (5)
S(1)	−0.0798 (1)	0.2239 (2)	0.1489 (2)	3.26 (5)
S(2)	0.0413 (2)	0.2266 (2)	−0.0810 (2)	3.90 (5)
C(1)	−0.1416 (5)	0.3108 (8)	0.0683 (7)	3.4 (2)
C(2)	−0.1746 (7)	0.3963 (9)	0.117 (1)	5.2 (3)
C(3)	−0.2232 (8)	0.461 (1)	0.046 (1)	7.2 (4)
C(4)	−0.2361 (8)	0.435 (1)	−0.072 (1)	6.5 (3)
C(5)	−0.2044 (6)	0.347 (1)	−0.1163 (9)	6.0 (3)
C(6)	−0.1552 (6)	0.2805 (9)	−0.0470 (8)	4.5 (2)
C(7)	0.1094 (6)	0.1309 (9)	−0.1361 (8)	4.7 (2)
C(8)	0.0799 (7)	0.348 (1)	−0.1362 (8)	5.9 (3)

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table III. Bond Lengths (Å) for $[TaCl_3(Me_2S)]_2(\mu\text{-}SPh)_2$[a]

Ta–Ta′	3.165 (1)	S(1)–C(1)	1.790 (8)
Ta–Cl(1)	2.328 (2)	S(2)–C(7)	1.842 (10)
Ta–Cl(2)	2.395 (2)	S(2)–C(8)	1.795 (11)
Ta–Cl(3)	2.331 (2)	C(1)–C(2)	1.355 (13)
Ta–S(1)	2.448 (2)	C(1)–C(6)	1.411 (12)
Ta–S(1)′	2.372 (2)	C(2)–C(3)	1.427 (15)
Ta–S(2)	2.707 (2)	C(3)–C(4)	1.43 (2)
		C(4)–C(5)	1.34 (2)
		C(5)–C(6)	1.436 (14)

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

Table IV. Bond Angles (deg) for $[TaCl_3(Me_2S)]_2(\mu\text{-}SPh)_2$[a]

Ta′–Ta–Cl(1)	92.35 (5)	Cl(3)–Ta–S(2)	81.56 (7)
Ta′–Ta–Cl(2)	140.41 (6)	S(1)–Ta–S(1)′	97.79 (7)
Ta′–Ta–Cl(3)	96.23 (5)	S(1)–Ta–S(2)	86.30 (7)
Ta′–Ta–S(1)	47.93 (5)	S(1)′–Ta–S(2)	174.91 (7)
Ta′–Ta–S(1)′	49.98 (5)	Ta–S(1)–Ta′	82.08 (7)
Ta′–Ta–S(2)	134.23 (5)	Ta–S(1)–C(1)	125.5 (3)
Cl(1)–Ta–Cl(2)	89.67 (8)	Ta–S(1)′–C(1)′	125.5 (3)
Cl(1)–Ta–Cl(3)	165.17 (8)	Ta–S(2)–C(7)	108.7 (3)
Cl(1)–Ta–S(1)	87.69 (8)	Ta–S(2)–C(8)	108.7 (4)
Cl(1)–Ta–S(1)′	99.35 (8)	C(7)–S(2)–C(8)	98.4 (5)
Cl(1)–Ta–S(2)	83.78 (8)	S(1)–C(1)–C(2)	121.6 (7)
Cl(2)–Ta–Cl(3)	91.38 (8)	S(1)–C(1)–C(6)	114.8 (7)
Cl(2)–Ta–S(1)	171.42 (7)	C(2)–C(1)–C(6)	123.6 (9)
Cl(2)–Ta–S(1)′	90.70 (8)	C(1)–C(2)–C(3)	118 (1)
Cl(2)–Ta–S(2)	85.29 (8)	C(2)–C(3)–C(4)	120 (1)
Cl(3)–Ta–S(1)	89.11 (8)	C(3)–C(4)–C(5)	121 (1)
Cl(3)–Ta–S(1)′	95.43 (7)	C(4)–C(5)–C(6)	120 (1)
		C(1)–C(6)–C(5)	118 (1)

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

isotropic equivalent thermal parameters are presented in Table II, and the bond lengths and bond angles are given in Tables III and IV, respectively.

The structure of $[TaCl_3(Me_2S)]_2(\mu\text{-}SPh)_2$ is based on an edge-sharing bioctahedral configuration of the core atoms. There are, of course, various deviations from ideal octahedral angles and distances around each tantalum atom. The nonlinear Cl(1)–Ta–Cl(3) group (angle of 165° instead of 180°) is, as usual, due to repulsion between the Cl(1)/Cl(3)′ and Cl(1)′/Cl(3) pairs of atoms. The two Ta–S bridge bonds differ somewhat in length, with the shorter one, 2.372 (2) Å, being trans to the long Ta–S(2) bond, while the longer one, 2.448 (2) Å, is trans to the short Ta–Cl(2) bond.

Most significant are the deviations in the central Ta–S(1)–Ta′–S(1)′ core of the molecule. The angles at the S(1) atoms are 82.08 (7)° while those at the Ta atoms are 97.79 (7)°. We take this as an indirect indication that there is a bonding force between the metal atoms. The Ta–Ta distance, 3.165 (1) Å, is consistent with the presence of direct Ta–Ta bonding. We shall return to this question of Ta–Ta bonding in more detail below.

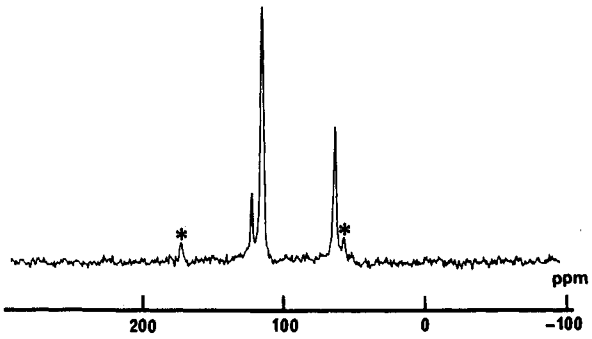

Figure 2. ^{13}C CP/MAS NMR spectrum of $[TaCl_3(Me_2S)]_2(\mu\text{-}SPh)_2$ complex at room temperature. Spinning sidebands are labeled with asterisks.

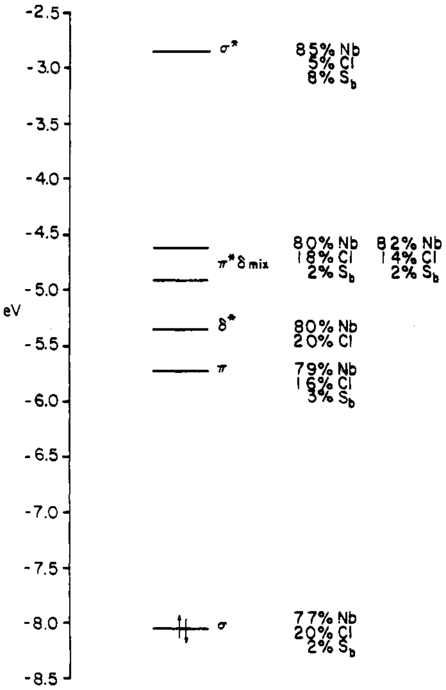

Figure 3. A diagram showing the energies and compositions of those MO's that are formed mainly from the metal d orbitals other than those used in metal–ligand σ bonds.

Solid-State ^{13}C NMR Spectroscopy. Because of the insolubility of the compound, it was necessary to obtain NMR data by employing the cross-polarization/magic angle spinning (CP/MAS) technique. The ^{13}C spectrum so obtained at 28 °C is shown in Figure 2. There are three genuine signals, at 59, 112, and 119 ppm, whose relative intensities are consistent with the following assignments. The signal at 59 ppm is attributed to the carbon atoms of the $(CH_3)_2S$ groups. The signals at 119 and 112 ppm are attributed to C(1) and to C(2)–C(6), respectively, of the C_6H_5S groups. The spectrum was also measured at −103 °C where the line widths and chemical shifts were essentially identical with those at 28 °C. We take this behavior as strong evidence that the substance is diamagnetic.[8]

Electronic Structure. The NMR evidence that the compound is diamagnetic does not require that a Ta–Ta single bond exist, since electrons on the two Ta^{IV} atoms could become spin-paired by interaction through the bridging sulfur atoms. Moreover, while there is structural evidence for a direct Ta–Ta bonding interaction,

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(8) Studies in this laboratory by J. F. Haw and G. D. Campbell have shown that while some paramagnetic complexes may have relatively sharp ^{13}C CP/MAS NMR spectra, these have temperature-dependent chemical shifts.

the Ta–Ta distance is not short enough to make this inference unambiguous. The most direct comparisons we can make to related compounds are somewhat imperfect, but for what they are worth, they are as follows. In a series of $Nb_2Cl_4L_4(\mu\text{-}S)_2$ molecules,[9,10] the Nb–Nb distances are 2.87 ± 0.01 Å. This is about 0.20 Å shorter than we find here. On the other hand in Nb_2Cl_{10}, where there cannot be a metal–metal bond, the distance is 3.951 (2) Å.[11] Although this is much longer, it must be noted that here the formal charge on the metal atoms is +5 rather than +4, and this should favor a longer distance.

To get some further insight into the likelihood that a metal–metal single bond might exist in $[TaCl_3(Me_2S)]_2(\mu\text{-}SPh)_2$, we have carried out a molecular orbital calculation on the idealized model system $[NbCl_3(H_2S)]_2(\mu\text{-}SH)_2$ by the Fenske–Hall method.[12] In Figure 3 we show a diagram dealing with only those MO's to which the metal atom d orbitals not primarily involved in metal–ligand σ bonding make their primary contributions. The center of gravity of this entire set of MO's is at ca. −5.5eV. The π and δ interactions are so small that the δ, δ^*, π, and π^* orbitals are spread over only a narrow range, ca. 1.1 eV. The σ interaction, on the other hand, is much greater, and the electrons occupying the σ-bonding orbital are stabilized by several electron volts. The σ-bonding orbital, which is the HOMO of the molecule, has mainly metal character (77%) and thus we conclude that it is reasonable to regard this molecule as containing an authentic metal–metal bond. This conclusion is consistent with all of the experimental data.

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Registry No. $[TaCl_3(Me_2S)]_2(\mu\text{-}SPh)_2$, 99687-25-9; $Ta_2Cl_6(Me_2S)_3$, 77827-59-9; diphenyl disulfide, 882-33-7; tantalum, 7440-25-7.

Supplementary Material Available: Tables of observed and calculated structure factors and anisotropic thermal parameters (9 pages). Ordering information is given on any current masthead page.

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Synthesis and Reactivity of Hydroxo-Bridged Binuclear Ethylenediamine Complexes of Iridium(III) and the X-ray Crystal Structure of [Aquabis(ethylenediamine)iridium(III)]-(μ-hydroxo)hydroxobis(ethylenediamine)iridium(III) Dithionate Perchlorate Hydrate

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The preparations of salts of the binuclear cations $\Delta,\Lambda\text{-}[(en)_2Ir(OH)_2Ir(en)_2]^{4+}$ (diol) and $\Delta,\Lambda\text{-}[(H_2O)(en)_2Ir(OH)Ir(en)_2(OH)]^{4+}$ (aqua hydroxo monool) are reported. One member of this series, $\Delta,\Lambda\text{-}[(H_2O)(en)_2Ir(OH)Ir(en)_2(OH)](S_2O_6)_{3/2}ClO_4 \cdot 2.75H_2O$, has been structurally characterized at 105 K by X-ray crystallography. The compound crystallizes in the space group $I2/a$ with a = 17.058 (5) Å, b = 18.140 (2) Å, c = 18.947 (3) Å, β = 93.68 (2)°, and Z = 8. On the basis of 4546 unique reflections, the structure has been refined to R = 0.034 and R_w = 0.042. The terminally coordinated hydroxo and aqua groups in the complex cation interact by a very short symmetrical hydrogen bond, 2.429 (9) Å, the existence of which was predicted from thermodynamic and kinetic data. The four independent Ir–O distances are similar in magnitude, $\langle \text{Ir–O} \rangle$ = 2.076 Å, and with the exception of one ethylenediamine ligand, the complex cation has almost mirror plane symmetry. The water of crystallization is distributed over six partially populated positions. The thermodynamics and kinetics for the equilibration reaction between diol and monool have been studied spectrophotometrically within the range $[H^+] = 10^{-5}$ to 1.0 M (I = 1.0 M; $(Na,H)ClO_4$). The first-order rate constants, k_{obsd}, for the reaction show a $[H^+]$ dependence, which was interpreted in terms of the equilibria shown in Scheme I. Rate constants and activation parameters (at 25 °C) are as follows: $k_1 = 1.48\ (11) \times 10^{-6}\ s^{-1}$ ($\Delta H^\ddagger$ = 113 (2) kJ mol^{-1}, $\Delta S^\ddagger$ = 22 (6) J mol^{-1} K^{-1}), $k_{-1} = 2.58\ (35) \times 10^{-7}\ s^{-1}$ ($\Delta H^\ddagger$ = 114 (4) kJ mol^{-1}, $\Delta S^\ddagger$ = 13 (4) J mol^{-1} K^{-1}), $k_{-2} = 5.1\ (8) \times 10^{-7}\ s^{-1}$ ($\Delta H^\ddagger$ = 81 (8) kJ mol^{-1}, $\Delta S^\ddagger$ = −94 (27) J mol^{-1} K^{-1}), $k_2/K_{a3} = 2.40\ (5) \times 10^{-4}\ s^{-1}\ M^{-1}$ ($\Delta H^\ddagger - \Delta H^\circ$ = 68.8 (17) kJ mol^{-1}, $\Delta S^\ddagger - \Delta S^\circ$ = −84 (6) J mol^{-1} K^{-1}). Independently of the kinetic data a spectrophotometric determination of K_{a1} and $K_1 = k_1/k_{-1}$ gave the following values (at 25 °C): K_{a1} = 0.0122 (7) (ΔH° = 10.8 (67) kJ mol^{-1}, ΔS° = −1 (22) J mol^{-1} K^{-1}), K_1 = 5.7 (8) (ΔH° = −1.5 (47) kJ mol^{-1}, ΔS° = 10 (15) J mol^{-1} K^{-1}). The acid dissociation constant for the aqua hydroxo monool has been determined potentiometrically as pK_{a2} = 9.04 (3) (ΔH° = 53.3 (50) kJ mol^{-1}, ΔS° = 6 (14) J mol^{-1} K^{-1}) at 25 °C.

Introduction

The mechanism of the cleavage and formation of the hydroxo bridge in binuclear M(III) complexes in acidic solution has been the subject of several investigations.[2-20] Tri-, di- and mono-hydroxo-bridged cobalt(III) complexes react essentially by an acid-catalyzed bridge cleavage (and formation), which presumably

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