Appendix II. Current-Potential Curve Parameters

The quantities of ΔE_p (peak-to-peak separation), E_c, and width used in the differential-pulse methods are defined in Figure 6.

In cyclic voltammetry (Figure 7), two quantities have been used. The width is given by $|E_p - E_{p/2}|$. The peak-to-peak separation is defined as

$$\Delta E_p = |E_p(\text{cathodic}) - E_p(\text{anodic})|$$

The absolute values are taken to allow application of the parameters to either initially cathodic (Figure 7) or initially anodic processes. $E_{p/2}$ is defined as the potential at which the current is half the peak current.

Registry No. $[((NH_3)_5Ru)_2(4,4'\text{-bpy})]^{4+}$, 36451-88-4; $[((NH_3)_5Ru)_2\text{pym}]^{4+}$, 76232-99-0; $[((NH_3)_5Ru)_2(1,2\text{-dicyanobenzene})]^{4+}$, 76233-00-6; $[((NH_3)_5Ru)_2(1,4\text{-dicyanobenzene})]^{4+}$, 76233-01-7; $[((NH_3)_5Ru)_2(1,5\text{-dicyanonaphthalene})]^{4+}$, 76233-02-8.

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Reactions of Niobium(III) and Tantalum(III) Compounds with Acetylenes. 3. Preparation and Structure of $[TaCl_2(SC_4H_8)(Me_3CC{\equiv}CMe)]_2(\mu\text{-}Cl)_2$

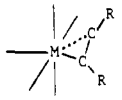
F. ALBERT COTTON* and WILLIAM T. HALL

Received April 11, 1980

The reaction of $Ta_2Cl_6(SC_4H_8)_3$ with $CH_3C{\equiv}CCMe_3$ gives rise to the binuclear compound $[(CH_3CCCMe_3)(SC_4H_8)Cl_2Ta]_2(\mu\text{-}Cl)_2$. We have isolated this compound and characterized it by X-ray crystallography. The crystals are monoclinic, and in space group $P2_1/n$ the unit cell parameters are a = 10.952 (9) Å, b = 11.716 (4) Å, c = 13.097 (6) Å, β = 107.45 (5)°, V = 1603 (3) Å^3, and Z = 2. Each molecule lies on a center of inversion and has a planar central $Ta(\mu\text{-}Cl)_2Ta$ rhombus with Ta—Cl = 2.496 (3) Å, Ta—Cl′ = 2.736 (4) Å, Cl—Ta—Cl = 75.3 (1)°, and Ta—Cl—Ta = 104.7 (1)°. The coordination sphere of each Ta atom is completed by two terminal Cl atoms (2.364 (3) Å), one sulfur atom (2.634 (3) Å), and the acetylene molecule, which is very strongly bonded, with Ta—C distances of 2.03 (1) Å, a C—C distance of 1.32 (2) Å, and C—C≡C angles of 138 (1) and 139 (2)°.

Introduction

In several earlier communications[1-3] we have reported some results of our studies of the interaction of acetylenes with the niobium and tantalum compounds of the type $M_2X_6(SC_4H_8)_3$. Complexes which we have already described in detail are of types **1**[1,2] and **2**,[3] each of which has features of unusual interest.



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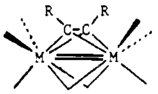

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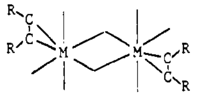

3

We have now succeeded in characterizing structurally another stable alkyne complex which has still a different, but also novel and interesting, structure. Again our M^{III} starting material has been McCarley's $Ta_2Cl_6(THT)_3$,[4] where THT is a code for tetrahydrothiophene. As will be shown in the sequel, the new compound is of structural type **3**.

Experimental Section

Synthesis and Crystal Preparation. Approximately 0.1 mL (~0.75 mmol) of *tert*-butylmethylacetylene (TMBA) was syringed into a flask containing 0.1 g (0.12 mmol) of $Ta_2Cl_6(THT)_3$ (THT = tetrahydrothiophene) dissolved in 25 mL of toluene. This mixture was allowed to stand overnight at room temperature; a small amount of precipitate developed, and the solution was filtered into a separate flask. After 3 days, orange plate-shaped crystals formed on the walls of the vessel. These crystals were suitable for X-ray study, and the product was shown to be $Ta_2Cl_6(THT)_2(TMBA)_2$. The yield, on the basis of Ta starting material, was about 50%.

The compound decomposed within minutes on contact with air. All manipulations were performed under a nitrogen atmosphere, and toluene was distilled from sodium/benzophenone ketyl.

Table I. Atomic Positional Parameters for $Ta_2Cl_6(CH_3CCCMe_3)_2(SC_4H_8)_2$

	x	y	z
Ta(1)	0.107 988	0.108 566	0.436 681
Cl(1)	0.019 998	0.070 695	0.608 406
Cl(2)	0.164 655	0.286 926	0.521 844
Cl(3)	0.285 795	0.000 575	0.537 463
S(1)	−0.118 905	0.202 665	0.355 170
C(1)	0.091 844	0.112 413	0.278 315
C(2)	0.207 875	0.146 821	0.332 964
C(11)	0.015 275	0.086 502	0.165 047
C(21)	0.325 252	0.190 889	0.309 943
C(22)	0.429 907	0.224 073	0.416 450
C(23)	0.374 057	0.097 644	0.249 319
C(24)	0.288 520	0.296 678	0.237 466
C(30)	−0.170 435	0.281 956	0.457 998
C(31)	−0.221 630	0.397 204	0.401 851
C(32)	−0.131 882	0.435 929	0.341 839
C(33)	−0.091 994	0.334 022	0.282 833

Data Collection and Structure Solution. A crystal was sealed in a capillary, in mineral oil, and mounted on a Syntex P$\bar{1}$ diffractometer. Preliminary photographic examination indicated that the crystals are monoclinic, and ω scans on several reflections showed the crystal selected to be of good quality. Systematic absences were consistent with space groups $P2_1/c$ or the equivalent alternate setting $P2_1/n$. The latter choice was made, and the following cell constants were obtained by centering on 15 intense reflections in the range 15° < 2θ < 28°: a = 10.952 (9) Å, b = 11.716 (4) Å, c = 13.097 (6) Å, β = 107.45 (5)°, V = 1603 (3) Å^3. For Z = 2 and a formula weight of 949.31, the calculated density is 1.966.

Data were collected at 20 ± 2 °C, with use of molybdenum Kα radiation. The θ–2θ scan technique was employed with use of a variable scan rate of 4.0–24.0°/min with a scan range of 0.9° below Kα_1 to 0.9° above Kα_2. A total of 2182 reflections were collected in the range 0° < 2θ ≤ 45°; 1942 of these had intensities greater than 3σ and were employed to solve and refine the structure. The intensities of three standard reflections, measured every 97 reflections, showed no change with time. Lorentz and polarization corrections were applied to the data, as was an empirical absorption correction based on ψ scans of four reflections near χ = 90°.

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Table III. Bond Lengths (Å) for $Ta_2Cl_6(CH_3CCCMe_3)_2(SC_4H_8)_2$

Ta(1)-Cl(1)	2.496 (3)	C(1)-C(2)	1.32 (2)	S(1)-C(30)	1.86 (2)
-Cl(2)	2.362 (3)	C(1)-C(11)	1.50 (3)	-C(33)	1.88 (2)
-Cl(3)	2.365 (3)	C(2)-C(21)	1.50 (2)	C(30)-C(31)	1.56 (3)
-C(1)	2.029 (13)	C(21)-C(22)	1.57 (2)	C(31)-C(32)	1.50 (3)
-C(2)	2.033 (16)	-C(23)	1.54 (2)	C(32)-C(33)	1.55 (3)
-S(1)	2.634 (3)	-C(24)	1.54 (2)	Ta-Ta'	4.144 (1)
-Cl(1)'	2.736 (4)				

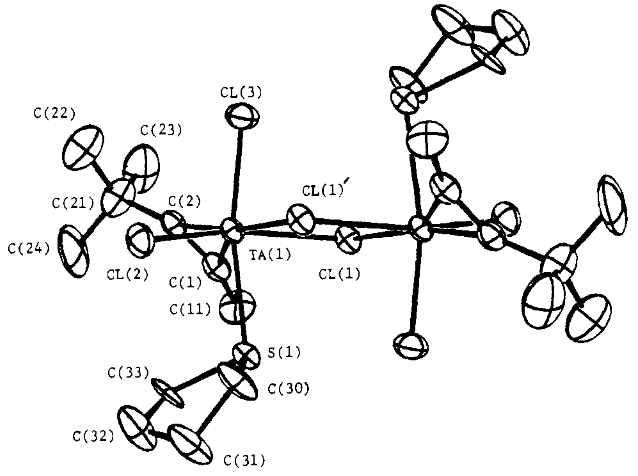


Figure 1. Molecular structue of $Ta_2Cl_6(CH_3CCCMe_3)_2(SC_4H_8)_2$. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 30% of its electron density. The atom numbering scheme used in all tables is defined.

The Ta position was determined from the three-dimensional Patterson function and refined by least-squares methods. The rest of the structure was revealed by subsequent difference maps. It was found in this way that the molecular formula is $Ta_2Cl_6(SC_4H_8)_2[(CH_3)_3CC{\equiv}CCH_3]_2$.

The structure was then refined by the full-matrix, least-squares method, with all atoms treated anisotropically. The final values of R_1 and R_2 were 0.040 and 0.058, respectively, and the error in an observation of unit weight was 1.340. Anomalous dispersion effects were included in the calculated structure factors for all atoms. A table of structure factors is available as supplementary material.

Computer programs used in the structure solution and refinement were those of the Enraf-Nonius structure determination package on a PDP 11/45 computer. All procedures, definitions, and sources of data required in the structure solution and refinement have been discussed and referenced elsewhere.[5]

Results and Discussion

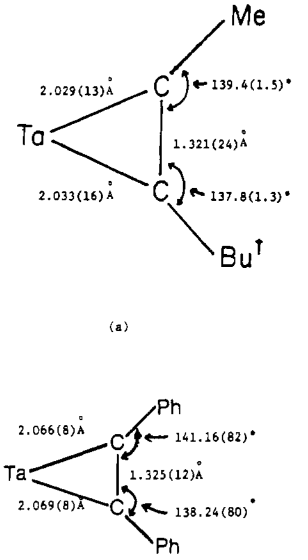
The positional parameters for all atoms are listed in Table I. The thermal parameters are listed in Table II, which is available as supplementary material. Figure 1 shows the overall structure and defines the numbering scheme. The bond distances and angles are listed in Tables III and IV, respectively.

The unit cell contains two molecules, which make normal van der Waals contacts with their neighbors. There is a center of inversion in each molecule midway between the Ta atoms which are thus coplanar with Cl(1) and Cl(1)'. This center related each half of the molecule. Each Ta atom is seven-coordinate if the acetylenic carbon atoms are counted separately. Chlorine atoms Cl(1), Cl(2), and Cl(3) and the THT sulfur atoms, S(1), form a meridional set; the acetylenic carbon atoms C(1) and C(2) and Cl(1)' complete the coordination. Similar coordination was found in the tantalum-tolane and di-*tert*-butylacetylene complexes.[2,3]

The strong binding of the TBMA is similar to the binding of tolane in **1**; the tantalum-acetylene bonding parameters are compared in Figure 2. The bond lengths and angles are essentially the same, and the same bonding description holds. The arrangement seems to be best described as a Ta^V metallocyclopropene, with additional interaction of the organic π system with the metal d orbitals.

Table IV. Selected Bond Angles (Deg) for $Ta_2Cl_6(CH_3CCCMe_3)_2(SC_4H_8)_2$

Cl(3)-Ta(1)-Cl(1)	89.5 (1)	S(1)-Ta(1)-C(1)	78.1 (5)
-Cl(1)'	83.6 (1)	-C(2)	105.6 (4)
-Cl(2)	98.9 (1)	C(1)-Ta(1)-C(2)	38.0 (7)
-C(1)	112.8 (5)	Ta(1)-Cl(1)-Ta(1)'	104.7 (1)
-C(2)	88.4 (4)	C(11)-C(1)-C(2)	139 (2)
-S(1)	165.7 (1)	C(1)-C(2)-C(21)	138 (1)
Cl(1)-Ta(1)-Cl(1)'	75.3 (1)	C(2)-C(21)-C(22)	111 (1)
-Cl(2)	154.9 (1)	-C(23)	108 (1)
-C(1)	84.6 (5)	-C(24)	109 (1)
-C(2)	113.8 (4)	C(22)-C(21)-C(23)	111 (1)
-S(1)	82.1 (1)	-C(24)	110 (1)
Cl(1)'-Ta(1)-Cl(2)	82.1 (1)	C(23)-C(21)-C(24)	109 (1)
-C(1)	154.2 (5)	C(30)-S(1)-C(33)	94.8 (9)
-C(2)	167.9 (4)	S(1)-C(30)-C(31)	104 (1)
-S(1)	83.1 (1)	C(30)-C(31)-C(32)	108 (2)
Cl(2)-Ta(1)-C(1)	113.2 (4)	C(31)-C(32)-C(33)	111 (2)
-C(2)	90.2 (4)	C(32)-C(33)-S(1)	106 (1)
-S(1)	165.7 (1)		



(a)

(b)

Figure 2. Comparison of tantalum-acetylene bonding parameters for (a) $Ta_2Cl_6(THT)_2(TBMA)_2$ and (b) $[TaCl_4(py)(tolane)]^-$.

Evidence of strong π interaction in the Ta-TBMA complex can be noted in the substantial asymmetry in the bond lengths of the bridging chlorine atoms, Cl(1) and Cl(1)'. The Ta-Cl(1)' bond, trans to the acetylene, is 0.24 Å longer than the Ta-Cl(1) bond in the meridional position. This is expected when there is significant π donation from the acetylene to the metal. We see no steric reason for the asymmetry in the bonding to the bridging chlorine atoms.

The Ta-Ta distance is this compound is 4.144 (1) Å, too long for any bonding interaction. The geometry of the compound is such that it could accommodate a Ta-Ta bond if the

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(5) Cotton, F. A.; Frenz, B. A.; Stultz, B. R.; Webb, T. R. *J. Am. Chem. Soc.* **1976**, *98*, 2768.

electronic environment at the metal were favorable, i.e., if the tantalum atom were still in the III state. The lack of direct metal–metal interaction suggests the two d electrons, formerly associated primarily with metal, are now localized in bonding with acetylene. This view is consistent with the formulation of the compound as a Ta^{V} metallacyclopropene.

When the structure of the tantalum–tolane compound was determined, there was some question as to whether the unusual bonding of the acetylene was somehow stabilized by the phenyl substituents. We can now see this is not the case. We might also have expected $Me_3CC{\equiv}CCMe_3$ to form a tantalacyclopropene complex, but perhaps the bulk of the two *tert*-butyl substituents is sufficient to prevent its formation.

Acknowledgment. We thank the National Science Foundation for financial support.

Registry No. $Ta_2Cl_6(THT)_2(TMBA)_2$, 76430-66-5; $Ta_2Cl_6(THT)_3$, 66758-43-8.

Supplementary Material Available: Table II, giving thermal vibration parameters, and a table of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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X-ray Molecular Structures of $Mn(CO)_5(O_2CCF_3)$ and $Mn(CO)_3(C_5H_5N)_2(O_2CCF_3)$

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The role of the effective charge of the metal atom in determining the bond lengths of the carboxyl group in a MOC(O)R group has been elucidated by preparing and structurally characterizing the compounds $Mn(CO)_5O_2CCF_3$ (**1**) and $Mn(CO)_3(C_5H_5N)_2O_2CCF_3$ (**2**). Their structures have been determined by three-dimensional, single-crystal X-ray diffraction methods. Crystal data are as follows. **1**: monoclinic space group, $P2_1/n$, a = 6.927 (2) Å, b = 13.454 (4) Å, c = 11.603 (3) Å, β = 92.11 (2)°, V = 1080.7 (8) Å^3, Z = 4. **2**: monoclinic space group, $P2_1/c$, a = 12.615 (2) Å, b = 8.512 (2) Å, c = 15.940 (2) Å, β = 96.761 (9)°, V = 1703 (1) Å^3, Z = 4. The structures were refined by conventional full-matrix least-squares techniques to final discrepancy indices of R_1 = 0.038 and R_2 = 0.048 for **1** (for 1195 observed data) and R_1 = 0.068 and R_2 = 0.072 for **2** (for 1216 observed data). The principal structural features of interest are a short trans M—C(O) bond distance and normal (M)O—C and C=O bond lengths for the O_2CCF_3 ligand in **1** and essentially equivalent (M)O—C and C=O bond lengths in **2**.

Introduction

Recent interest in transition-metal compounds containing carboxylate ligands has centered on the use of these ligands to stabilize unusual types of complexes. Two of the more studied species are dimers of the type $M_2(O_2CR)_4$ (M = Cr, Mo), which contain strong, multiple metal–metal bonds,[1] and trimers of the type $[M_3(O)_2(O_2CCH_3)_6(H_2O)_3]^{n+}$ (M = Mo, W), which contain a symmetrical triangular arrangement of metal atoms.[2-4] While conducting studies concerning the reaction pathways for the formation of these dimer and cluster species, we characterized, by X-ray crystallography, the complexes $PPN[M(CO)_5O_2CCF_3]$ (M = Cr, Mo) and $PPN[Mo(CO)_5O_2CCH_3]$.[5] We observed in these structures rather unusual configurations for the monodentate acetate and trifluoroacetate groups. The carbon–oxygen bond distance for the coordinated oxygen was found to be shorter than that of the free oxygen, i.e., D(MO—C(O)R) < D(R(O)C=O). In seeking the origin of this effect, we have undertaken an X-ray structural investigation of $Mn(CO)_5(O_2CCF_3)$ and its pyridine-substituted derivative, *fac*-$Mn(CO)_3(C_5H_5N)_2(O_2CCF_3)$. The results of this study and their interpretation are reported here.

Experimental Section

Materials. Silver trifluoroacetate was obtained from Eastman Kodak Co. Bromopentacarbonyl manganese was purchased from Pressure Chemicals. Dichloromethane and chloroform were dried over phosphorus pentoxide; hexane was dried over Na/K alloy. All reactions were carried out under an amosphere of dry nitrogen in standard Schlenk apparatus.

Preparations of $Mn(CO)_3(L)_2(O_2CCF_3)$ (L = CO, C_5H_5N). The pentacarbonyl, $Mn(CO)_5O_2CCF_3$ (**1**), was prepared according to the published procedure by the reaction of $BrMn(CO)_5$ with AgO_2CCF_3 in dichloromethane. Crystals suitable for X-ray study were grown by slow cooling of a CH_2Cl_2/hexane solution (1:2) from room temperature to −10 °C. ν_{CO} in CH_2Cl_2: 2149 ($A_1^{(2)}$), 2063 (E), 2012 cm^{-1} ($A_1^{(1)}$).

The bis(pyridine)adduct, $Mn(CO)_3(C_6H_5N)_2O_2CCF_3$ (**2**), was prepared according to the literature method[7] by the reaction of **1** with a slight excess of pyridine in refluxing chloroform. Crystals used in the diffraction study were obtained at −10 °C upon reducing the volume of the final reaction solution and adding hexane. ν_{CO} in CH_2Cl_2: 2038 (A_1), 1957 and 1920 cm^{-1} (E).

X-ray Diffraction Studies. Crystals suitable for X-ray work were attached to the ends of thin glass fibers with epoxy cement and mounted on a Syntex P$\bar{1}$ (**1**) or an Enraf-Nonius CAD-4 (**2**) automatic diffractometer. The unit cell constants were obtained from a least-squares fit of 15 reflections (26° ≤ 2θ ≤ 34°) for **1** and 25 reflections (26° ≤ 2θ ≤ 32°) for **2**. Other general procedures for data collection have been detailed elsewhere.[8,9] Specific data collection parameters and crystallographic data are summarized in Table I. For each crystal, Lorentz and polarization corrections were applied. In addition, the measurement of three intensity standards every 50 reflections revealed that a significant amount of decomposition of the crystal of compound **1** was occurring during data collection.

Plots of intensity vs. time for these three reflections, which were essentially identical, were linear with a slope of −1.69%/h and a total loss in intensity of 31.4% over the 18.6-h period of data collection. A linear decay correction was applied to the data with use of the above parameters.

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