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Synthesis, Structure, and Reactivity of the Substitution-Labile Metal Cluster $[Bu_4N]_2[Ta_6Cl^i_{12}(OSO_2CF_3)^a_6]$

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The synthetic utility of metal cluster compounds with labile anions such as$[Bu_4N]_2[Mo_6Cl^i_8(OSO_2CF_3)^a_6]$[1] and $[Bu_4N]_2[Mo_6Cl^i_8(CO_2CF_3)^a_6]$ was demonstrated recently.[2−4] These compounds undergo ligand substitution reactions with stronger coordinating anions such as OAc^- and neutrals such as PR_3 or pyridine and unusual ligands such as $[(NC)Mn(CO)_2Cp]^-$.[2,3] The wide variety of new metal cluster derivatives that are accessible through this route should greatly expand the photochemically induced redox chemistry of the six-metal molybdenum and tungsten clusters.[5]

In the present note we report the preparation of analogous lightly coordinated tantalum cluster compounds $[Bu_4N]_n[Ta_6Cl^i_{12}(OSO_2CF_3)^a_6]$ ($n = 2-4$) from $[Bu_4N]_n[Ta_6Cl_{12}Cl_6]$ and demonstrate their facile substitution to produce a 12-metal supercluster. The clusters $[M_6Cl^i_8(OSO_2CF_3)^a_6]^{2-}$ (M = Mo, W) were synthesized by metathesis of $[M_6Cl_8Cl_6]^{2-}$ (M = Mo, W) with $AgOSO_2CF_3$,[2] but this type of reaction did not lead to pure products with $[Bu_4N]_n[Ta_6Cl_{12}Cl_6]$ ($n = 2-4$). By contrast, the reaction of the tantalum chloride cluster with $HOSO_2CF_3$ provided well defined cluster metathesis with high yields:[6−8]

$$[Bu_4N]_2[Ta_6Cl_{12}Cl_6] + 6HOSO_2CF_3 \rightarrow [Bu_4N]_2[Ta_6Cl^i_{12}(OSO_2CF_3)^a_6] + 6HCl$$

Experimental Section

All manipulations were performed under a dry N_2 atmosphere employing standard Schlenk and syringe techniques.[9] The solvents CH_2Cl_2 and Et_2O were dried over P_2O_5 and CaH_2, respectively, and distilled prior to use. The IR spectra were obtained either as solution spectra using 0.1 mm path length CaF_2 solution cells (with rubber septa caps) or as Nujol mulls between KBr plates. The spectrometer employed was a Bomem MB-100 FT-IR set at a resolution of 2 cm^{-1}. UV−vis spectra were obtained on a Cary 1E UV−vis spectrophotometer in 1.0 cm path length cells designed for air-sensitive work. The mass spectra were obtained either from the Midwest Center for Mass Spectrometry (University of Nebraska−Lincoln) or from the Analytical Services Laboratory (ASL) at Northwestern University. The conditions used at ASL were reported previously.[2,3] Elemental analyses were performed by Elbach Analytical Laboratories, Gummersbach, Germany.

Table 1. Crystallographic Data for $[Bu_4N]_2[Ta_6Cl^i_{12}(OSO_2CF_3)^a_6]$

formula: $C_{38}H_{72}Cl_{12}F_{18}N_2O_{18}S_6Ta_6$
fw: 2890.44
cryst syst: monoclinic
space group: $P2_1/c$ (No. 14)
$a = 14.955(6)$ Å
$b = 15.683(4)$ Å
$c = 18.567(5)$ Å
$\beta = 110.69(3)°$
$V = 4074(4)$ Å^3
$Z = 2$
$d_{calcd} = 2.356$ g/cm^3
λ(Mo Kα) = 0.71069 Å
μ(Mo Kα) = 85.7 cm^{-1}
temp = −120 °C
$T_{min}, T_{max} = 0.84, 1.36$
$R^a = 0.034$
$R_w{}^b = 0.036$

$^a\ \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b\ [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Synthesis of $[Bu_4N]_2[Ta_6Cl^i_{12}(OSO_2CF_3)^a_6]$. In a typical synthesis, $HOSO_2CF_3$ (1.6 mL) was added to $[Bu_4N]_2[Ta_6Cl_{12}Cl_6]$[10] (300 mg) in CH_2Cl_2 (25 mL) under a dry N_2 atmosphere and the resulting mixture was stirred overnight in the absence of light. Gases were purged from the reaction vessel to remove HCl several times during a 24 h period, and then all the volatile components were removed under vacuum. The resulting oily brown residue was heated to ca. 80 °C under vacuum to remove the last traces of $HOSO_2CF_3$, leaving a brown solid which was recrystallized from CH_2Cl_2/Et_2O to yield 255 mg (64%) of product. This product appears to be a mixture of two components, the desired $[Bu_4N]_2[Ta_6Cl^i_{12}(OSO_2CF_3)^a_6]$ (brown), along with a small impurity of $[Bu_4N]_4[Ta_6Cl^i_{12}(OSO_2CF_3)^a_6]$ (green). These compounds were separated by growing large crystals in a diffusion tube and manually separating the crystals. IR (Nujol; cm^{-1}): 1340 ($\nu_{as}(SO_3)$) 1235 ($\nu_s(CF_3)$), 1203 ($\nu_{as}(SO_3)$), 1004 ($\nu_s(SO_3)$), 1165 ($\nu_{as}(CF_3)$), 631 ($\delta_s(SO_3)$). Anal. Calcd for $C_{38}H_{72}Cl_{12}F_{18}N_2O_{18}S_6Ta_6$: C, 15.79; H, 2.51; N, 0.97; Cl, 14.72; Ta, 37.56. Found: C, 15.75; H, 2.37; N, 1.00; Cl, 15.01; Ta, 37.30.

The analogous niobium cluster system $[Bu_4N]_n[Nb_6Cl^i_{12}(OSO_2CF_3)^a_6]$ ($n = 2-4$) can be obtained in a manner similar to that for the tantalum compound.

Synthesis of $[Bu_4N]_2[Ta_6Cl^i_{12}\{(\mu\text{-}NC)Mn(CO)_2Cp\}^a_6]$. A 30-mL Schlenk flask was charged with 15 mg (0.0052 mmol) of $[Bu_4N]_2[Ta_6Cl^i_{12}(OSO_2CF_3)^a_6]$ and 15 mg (0.034 mmol) of $[Bu_4N][CpMn(CO)_2CN]$.[11] In the dark, 7.0 mL of CH_2Cl_2 was added to the solids and the resulting solution was stirred overnight. To this solution was added slowly 10.0 mL of Et_2O, and the resulting microcrystals were isolated by filtration and dried *in vacuo* to yield 7 mg (40%) of product. IR (CH_2Cl_2; cm^{-1}): 2055 (ν(CN)), 1919, 1856 (ν(CO)).

X-ray Structure Determination. The single deep red-brown crystals of $[Bu_4N]_2\ [Ta_6Cl^i_{12}(OSO_2CF_3)^a_6]$ were grown by slow diffusion of ether into a concentrated CH_2Cl_2 solution of the cluster at room temperature in the absence of light. The selected crystal (0.3 × 0.2 × 0.2 mm) was immersed in Paratone-N (Exxon) oil and mounted on a glass fiber and transferred to the N_2 cold stream of an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo Kα radiation. Cell constants and an orientation matrix for data collection were obtained from a least squares refinement of the setting angles of 25 carefully centered reflections ($21.0 < 2\theta < 21.9°$). Based on the systematic absences of $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$) and the successful solution and refinement of the structure, the space group was determined to be $P2_1/c$ (No. 14). The data were collected ($\pm h, -k, -l$) at -120 ± 1 °C using the $\omega-\theta$ scan type to a maximum 2θ of 48.0°. There were a total of 6874 reflections measured of which 6653 were considered unique ($R_{int} = 0.055$) and 4411 ($I > 3.00\sigma(I)$) were considered observed. A summary of relevant crystallographic data is provided in Table 1. The intensities of three representative reflections

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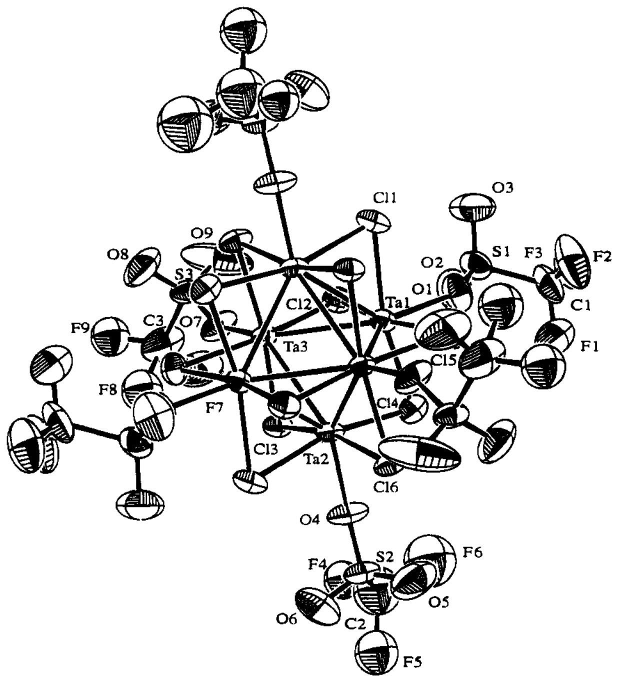

Figure 1. ORTEP drawing of the anion of $[Bu_4N]_2[Ta_6Cl^i_{12}(OSO_2CF_3)^a_6]$ with hydrogen atoms omitted. Thermal ellipsoids are drawn at 50% probability.

which were measured after every 90 min of X-ray exposure time remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied). The data were corrected for Lorentz and polarization effects. Am empirical absorption correction, using the program DIFABS,[12] was applied which resulted in transmission factors ranging from 0.84 to 1.36.

All calculations were carried out with the TEXSAN crystallographic software package.[13] The structure was solved by direct methods.[14] Neutral atom scattering factors were taken from Cromer and Waber.[15] Anomalous dispersion effects were included in F_c;[16] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[17] The rotationally disordered fluorines atoms were refined isotropically and the remaining non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement[18] included 443 variable parameters and converged (largest parameter shift was 0.49 times its esd) to an R value of 0.034 (R_w = 0.036). The standard deviation of an observation of unit weight[19] was 1.30. The weighting scheme was based on counting statistics and included a factor (p = 0.03) to downweight the intense reflections. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $(\sin \theta)/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.07 and −0.95 e/Å^3, respectively and were in the vicinity of the metal positions.

Table 2. Atomic Coordinates and B(eq) Values (Å^2) for $[Bu_4N]_2[Ta_6Cl^i_{12}(OSO_2CF_3)^a_6]$

atom	x	y	z	B(eq)[a]
Ta1	0.03539(3)	0.12265(3)	0.47712(3)	2.78(2)
Ta2	−0.08802(3)	0.05114(3)	0.55464(3)	2.72(2)
Ta3	0.11383(3)	0.00021(3)	0.60390(2)	2.59(2)
Cl1	0.1443(2)	0.0825(2)	0.4121(2)	3.9(1)
Cl2	0.1739(2)	0.1409(2)	0.5937(2)	3.5(1)
Cl3	0.0302(2)	0.0591(2)	0.6831(1)	3.2(1)
Cl4	−0.0585(2)	0.2004(2)	0.5382(2)	3.8(1)
Cl5	−0.0902(2)	0.1407(2)	0.3534(2)	4.0(1)
Cl6	−0.2334(2)	0.0587(2)	0.4423(2)	3.7(1)
S1	0.1376(2)	0.3159(2)	0.4736(2)	4.5(1)
S2	−0.2671(2)	0.1172(2)	0.6191(2)	4.2(1)
S3	0.3246(2)	−0.0113(2)	0.7577(2)	3.8(1)
F1	−0.0091(6)	0.4161(6)	0.4432(6)	8.1(5)
F2	0.1174(8)	0.4756(5)	0.4392(6)	8.8(5)
F3	0.0369(9)	0.3914(7)	0.3482(6)	9.9(6)
F4	−0.174(1)	0.186(1)	0.751(1)	6.9(5)
F4B	−0.192(3)	0.114(3)	0.764(2)	15(1)
F5	−0.325(1)	0.196(2)	0.714(1)	9.1(6)
F5B	−0.315(2)	0.243(2)	0.692(2)	8.0(8)
F6	−0.222(2)	0.275(2)	0.650(2)	13(1)
F6B	−0.187(3)	0.248(3)	0.705(3)	12(1)
F7	0.2836(7)	0.0673(8)	0.8634(5)	8.9(6)
F8	0.220(2)	−0.064(1)	0.839(1)	8.4(6)
F8B	0.287(1)	−0.055(1)	0.875(1)	6.1(5)
F9	0.369(1)	−0.062(1)	0.901(1)	7.7(6)
F9B	0.414(1)	0.021(1)	0.901(1)	6.8(6)
O1	0.0647(6)	0.2479(5)	0.4491(5)	4.9(4)
O2	0.1633(7)	0.3366(6)	0.5525(5)	6.5(5)
O3	0.2108(8)	0.3042(7)	0.4436(7)	8.1(6)
O4	−0.1731(5)	0.1052(6)	0.6130(5)	4.9(4)
O5	−0.3322(8)	0.155(1)	0.5531(7)	10.4(8)
O6	−0.2986(9)	0.0491(8)	0.6492(9)	10.8(8)
O7	0.2254(5)	0.0034(6)	0.7119(4)	5.1(4)
O8	0.3530(8)	−0.0947(8)	0.7460(6)	8.6(6)
O9	0.384(1)	0.055(1)	0.7556(9)	13(1)
N1	0.3996(6)	0.1835(6)	0.3200(5)	3.6(4)
C1	0.064(1)	0.405(1)	0.422(1)	6.3(8)
C2	−0.235(2)	0.204(2)	0.697(2)	11.0(7)
C3	0.315(1)	−0.002(2)	0.8512(9)	8(1)
C10	0.2974(9)	0.2180(9)	0.2903(8)	4.4(6)
C11	0.2212(9)	0.1513(8)	0.2559(7)	4.1(6)
C12	0.1216(8)	0.195(1)	0.2358(8)	5.1(6)
C13	0.0422(9)	0.131(1)	0.1965(8)	5.6(7)
C14	0.4195(9)	0.129(1)	0.3921(8)	6.4(7)
C15	0.418(1)	0.173(2)	0.4620(8)	11(1)
C16	0.429(1)	0.093(2)	0.521(1)	16(2)
C17	0.433(2)	0.117(2)	0.591(1)	15(2)
C18	0.4183(9)	0.128(1)	0.262(1)	5.6(7)
C19	0.399(1)	0.170(2)	0.185(1)	11(1)
C20	0.424(2)	0.133(3)	0.108(4)	27(4)
C21	0.391(2)	0.066(1)	0.103(3)	19(3)
C22	0.4632(8)	0.2625(8)	0.3379(8)	4.4(6)
C23	0.5719(8)	0.244(1)	0.3709(7)	4.6(6)
C24	0.623(1)	0.328(1)	0.385(1)	8(1)
C25	0.732(1)	0.315(1)	0.421(1)	9(1)

[a] $B(\mathrm{eq}) = (4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos \gamma)B_{12} + ac(\cos \beta)B_{13} + bc(\cos \alpha)B_{23}]$.

Results and Discussion

An X-ray single crystal determination of a brown crystal reveals an essentially octahedral Ta_6 cluster, Figure 1, where $[Ta_6Cl^i_{12}(OSO_2CF_3)^a_6]^{2-}$ is situated on an inversion center and the two $[Bu_4N]^+$ cations are related by the center of symmetry.[19] The Ta_6 core is a slightly distorted octahedron, in agreement with the essentially octahedral metal array in other $[Ta_6Cl_{12}L_6]^{n-}$ systems.[20-26] The average Ta−Ta bond length, 2.940 Å, is also

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(19) Standard deviation of an observation of unit weight: $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o = number of observations and N_v = number of variables.

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Table 3. Selected Bond Distances (Å) and Angles (deg) for $[Bu_4N]_2[Ta_6Cl^i_{12}(OSO_2CF_3)^a_6]$

Ta1−Ta2	2.935(1)	Ta2−Cl1′	2.419(3)
Ta1−Ta2′	2.9536(9)	Ta2−Cl3	2.419(3)
Ta1−Ta3	2.942(1)	Ta2−Cl4	2.421(3)
Ta1−Ta3′	2.930(1)	Ta2−Cl6	2.427(3)
Ta1−Cl1	2.428(3)	Ta2−O4	2.118(7)
Ta1−Cl2	2.426(3)	Ta3−Cl2	2.415(3)
Ta1−Cl4	2.423(3)	Ta3−Cl3′	2.425(3)
Ta1−Cl5	2.416(3)	Ta3−Cl5′	2.416(3)
Ta1−O1	2.118(8)	Ta3−Cl6′	2.422(3)
Ta2−Ta3	2.939(1)	Ta3−O7	2.107(7)
Ta2−Ta3′	2.943(1)		

Ta1−Ta2−Ta1′	89.85(3)	Ta1−Ta3−Ta1′	90.17(4)
Ta1−Ta2−Ta3	60.11(3)	Ta1−Ta3−Ta2	59.90(3)
Ta1−Ta2−Ta3′	59.81(3)	Ta1−Ta3−Ta2′	60.26(3)
Ta1−Ta2−Cl1′	142.38(8)	Ta1−Ta3−Cl2	52.60(8)
Ta1−Ta2−Cl3	95.50(7)	Ta1−Ta3−Cl3	95.19(8)
Ta1−Ta2−Cl4	52.67(8)	Ta1−Ta3−Cl5′	142.79(8)
Ta1−Ta2−Cl6	94.96(8)	Ta1−Ta3−Cl6′	95.80(9)
Ta1−Ta2−O4	133.8(3)	Ta1−Ta3−O7	134.8(3)
Ta1−Ta2′−Ta3	59.66(2)	Ta1−Ta3′−Ta2	60.43(3)
Ta1−Ta2′−Ta3′	59.86(2)	Ta1−Ta3‘−Ta2′	59.98(3)
Ta1−Ta2′−Cl1	52.54(8)	Ta1−Ta3′−Cl2′	142.76(8)
Ta1−Ta2′−Cl3′	95.19(8)	Ta1−Ta3′−Cl3′	95.64(8)
Ta1−Ta2′−Cl4′	142.51(8)	Ta1−Ta3′−Cl5	52.63(8)
Ta1−Ta2′−Cl6′	95.38(8)	Ta1−Ta3′−Cl6	95.20(8)
Ta1−Ta2′−O4′	136.3(3)	Ta1−Ta3′−O7′	134.9(3)
Ta3−Ta2−Ta3′	89.68(4)	Ta2−Ta3−Ta2′	90.32(4)
Ta2−Ta1−Ta2′	90.15(3)	Ta2−Ta1′−C15′	95.17(8)
Ta2−Ta1−Ta3	59.99(3)	Ta2−Ta1′−O1′	135.6(3)
Ta2−Ta1−Ta3′	60.21(3)	Ta3−Ta1−Ta3′	89.83(4)
Ta2−Ta1−Cl1	142.34(9)	Ta3−Ta1−Cl1	94.53(9)
Ta2−Ta1−Cl2	95.34(8)	Ta3−Ta1−Cl2	52.38(8)
Ta2−Ta1−Cl4	52.69(8)	Ta3−Ta1−Cl4	95.00(8)
Ta2−Ta1−Cl5	95.67(8)	Ta3−Ta1−Cl5	142.49(8)
Ta2−Ta1−O1	134.3(3)	Ta3−Ta1−O1	138.0(2)
Ta2′−Ta1−Ta3	59.88(2)	Ta3′−Ta1′−Cl1′	95.51(8)
Ta2′−Ta1−Ta3′	59.91(3)	Ta3−Ta1′−Cl2′	142.20(8)
Ta2−Ta1′−Cl1′	52.20(8)	Ta3−Ta1′−Cl4′	96.23(8)
Ta2−Ta1′−Cl2′	94.79(8)	Ta3−Ta1′−Cl5′	52.66(8)
Ta2−Ta1′−Cl4′	142.83(8)	Ta3−Ta1′−O1′	132.1(2)

as expected for a $[Ta_6Cl_{12}L_6]^{2-}$ core. The nearest neighbor Ta−Cl distances range from 2.428 to 2.416 Å. The narrow Ta−Ta−Ta angles range from 59.66 to 60.11°, while the wide ones range from 89.68 to 90.17°. The CF_3 portions of the $OSO_2CF_3^-$ groups are rotationally disordered with respect to the pseudo 3-fold CF_3 axis. Table 2 lists the atomic coordinates and *B*(eq) values, while Table 3 lists selected bond distances and angles for the cluster. The IR (Nujol) data shows a band at 1004 cm^{-1} which is assigned as the metal bound O—S stretching frequency and two bands assigned as O═S at 1203 and 1340 cm^{-1}, with additional C—F bands at 1165 and 1235 cm^{-1} which correlate well with the data for the Mo_6 derivative.[2,27] MS-FAB⁻ data show a complex parent peak envelope at a maximum *m/z* of 2889 amu, which agrees well (*R* = 13.5 over a *m/z* range of 2886−2896) with the calculated peak envelope. The loss of the expected fragments assignable as OTf, Cl and $[Bu_4N]$ was also observed. The UV−vis (CH_2Cl_2) data, λ_{max} 235, 341, and 1153 nm, are in agreement for that expected for a $[Ta_6Cl_{12}L_6]^{2-}$ core structure.

The $[Bu_4N]^+$ salt of $[Ta_6Cl^i_{12}(OSO_2CF_3)^a_6]^{2-}$ was found to react with 6 equiv of the$[Bu_4N]^+$ salt of $[(NC)Mn(CO)_2Cp]^-$ in CH_2Cl_2 to provide the 12-metal supercluster $[Bu_4N]_2[Ta_6Cl^i_{12}\{\mu\text{-}(NC)Mn(CO)_2Cp\}^a_6]$. This compound (in CH_2Cl_2) displays IR absorptions for ν(CN) at 2055 cm^{-1} and for ν(CO) at 1919 and 1856 cm^{-1}, which are shifted from 2122, 2046 and 1797 cm^{-1} in $[Bu_4N][CpMn(CO)_2CN]$ and 2028, 1916 and 1866 cm^{-1} in $[(Mo_6Cl_8)\{\mu\text{-}(NC)Mn(CO)_2Cp\}_6]^{2-}$.[3] The MS-FAB⁻ data for the compound show a parent broad envelope with a maximum *m/z* of 3210 amu, which agrees well with the calculated peak envelope with a maximum *m/z* of 3209 amu,[28] further the loss of fragments assignable as $[(NC)Mn(CO)_2Cp]$ and $[Bu_4N]$ were observed.

The $[Ta_6Cl_{12}Cl_6]^{n-}$ cluster has several readily accessible oxidation states and their redox chemistry has been investigated extensively;[25,29] therefore, this labile tantalum cluster should expand the substitution chemistry of these clusters and facilitate the formation of new ligand bridged metal systems that may undergo intervalence charge transfer reactions.

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Supplementary Material Available: Tables of X-ray crystallographic details, hydrogen atom coordinates, anisotropic thermal parameters, and interatomic bond distances and angles (17 pages). Ordering information is given on any current masthead page.

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