Ligand Substitution

DOI: 10.1002/anie.200700151

Synthesis and Ligand-Exchange Kinetics of the Solvated Trigonal-Prismatic Clusters $[W_6CCl_{12}L_6]^{2+}$ (L = dmf, py)**

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A variety of hexanuclear transition-metal clusters have found use in solution-based syntheses of porous coordination solids, certain of which behave as molecular sieves, chemical sensors, or ion-exchange materials.[1] These clusters possess rigid, metal–metal-bonded core structures, typically consisting of an octahedron of metal atoms with eight face-capping or twelve edge-bridging ligands. Each metal center is additionally coordinated by an outer terminal ligand, for which the exchange chemistry and bridge-forming capability are of critical importance in the generation of solid frameworks. The recent discovery of high-temperature routes to the Z-centered clusters $[W_6ZCl_{18}]^{n-}$ (Z = C, N; n = 1–3) has provided a new, highly redox-active building unit, wherein six terminal chloride ligands are arranged in a trigonal prism instead of an octahedron.[2] As a step toward utilizing these $[W_6ZCl_{18}]^{n-}$ species in the synthesis of extended-framework materials, we herein report some initial ligand-substitution reactions, together with a detailed study of the self-exchange kinetics for a pyridine-solvated cluster.

A triflate-terminated (triflate = $CF_3SO_3^-$) variant of the trigonal-prismatic cluster was sought, since prior work had demonstrated the versatility of octahedral clusters such as $[W_6Cl_8(CF_3SO_3)_6]^{2-}$ in ligand-substitution reactions.[3] Solid $(Bu_4N)_2[W_6CCl_{18}]$ was heated in neat triflic acid at 100 °C under a stream of nitrogen. After 8 h, the resulting black solution was reduced to dryness under an increased nitrogen flow. Recrystallization from a 1:25 mixture of nitromethane and diethyl ether at −28 °C afforded black, distorted tetrahedron-shaped crystals of $(Bu_4N)_2[W_6CCl_{12}(CF_3SO_3)_6]$ (**1**) in 91 % yield. X-ray analysis of a crystal of **1** indeed revealed a structure in which all six terminal chloride ligands have been replaced with oxygen-bound triflate anions (Figure 1).[4] With an unperturbed count of 24 W_6C-based valence electrons, the geometry of the cluster core is essentially the same as that observed in $(Bu_4N)_2[W_6CCl_{18}]$,[2a] consisting of a central carbon atom surrounded by a regular trigonal prism of tungsten atoms and twelve edge-bridging chloride anions.

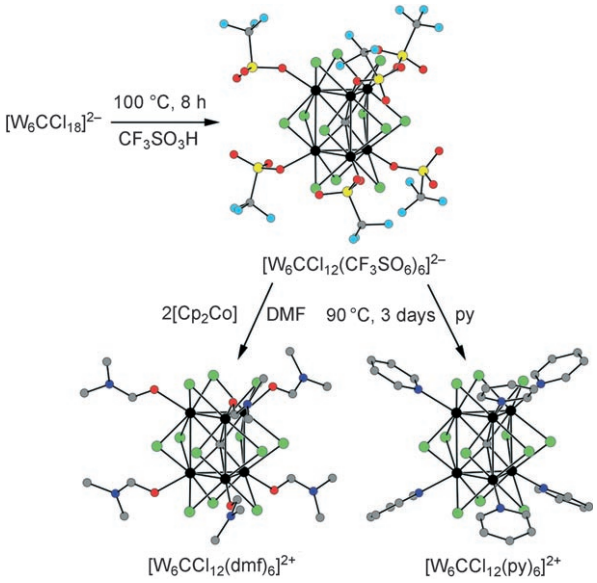

Figure 1. Synthetic scheme and crystal structures for the ligand-substituted clusters in **1** (upper), **2** (lower left), and **3** (lower right). W black, S yellow, Cl green, C gray, N blue, O red, F light blue; H atoms are omitted for clarity. Selected mean interatomic distances [Å] and angles [°] for the clusters in **1**, **2**, and **3**, respectively (△ = triangle edge, | = longer rectangle edge, L = coordinating atom of terminal ligand): W-W△ 2.632(2), 2.6618, 2.67(3); W-W| 3.037(5), 2.9562, 3.00(6); W-C 2.15(3), 2.1323, 2.15(2); W-L 2.08(1), 2.140, 2.248(9); W-Cl△ 2.395(8), 2.416(2), 2.408(6); W-Cl| 2.455(8), 2.471(4), 2.48(1); W-C-W△ 75.5(6), 77.24, 77(1); W-C-W| 90(2), 87.77, 88(2); W-Cl-W△ 66.6(2), 66.85, 67.3(9); W-Cl-W| 76.44(8), 73.48, 74(1).

Similar to $[W_6CCl_{18}]^{2-}$, $[W_6CCl_{12}(CF_3SO_3)_6]^{2-}$ exhibits a rich electrochemistry. The cyclic voltammogram of **1** in nitromethane solution displays a reversible one-electron oxidation event at $E_{1/2}$ = 1.130 V (ΔE_p = 71 mV) versus $[Cp_2Fe]/[Cp_2Fe]^+$ ($Cp^- = C_5H_5^-$), and two reversible one-electron reduction processes at $E_{1/2}$ = 0.117 V (ΔE_p = 74 mV) and −0.460 V (ΔE_p = 78 mV). In DMF solution, the couples for the oxidation and first reduction events are shifted to the more negative potentials of $E_{1/2}$ = 0.149 V (ΔE_p = 66 mV) and −0.565 V (ΔE_p = 78 mV), while the second reduction at −0.949 V now shows no reversibility. This last result suggests that, upon reduction of the cluster by two electrons, the triflate ligands become labile and are readily displaced by the strongly coordinating DMF solvent. In distinct contrast, the cyclic voltammogram of $[W_6CCl_{18}]^{2-}$ in DMF gives no indication of such lability.[2a]

Consistent with the above hypothesis, chemical reduction of $[W_6CCl_{12}(CF_3SO_3)_6]^{2-}$ in DMF generates the solvated cluster $[W_6CCl_{12}(dmf)_6]^{2+}$. Addition of two equivalents of $[Cp_2Co]$ to a solution of **1** in DMF at room temperature

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[**] The authors thank Prof. Robert G. Bergman and Dr. Dennis H. Leung for helpful discussions. This research was funded by DOE Grant No. DE-FG03-01ER15257. dmf = *N*,*N*-dimethylformamide, py = pyridine.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

induces an immediate color change from black to red-brown. Salt metathesis with $(Bu_4N)BF_4$ in water with subsequent recrystallization gives brown cube-shaped crystals of $[W_6CCl_{12}(dmf)_6](BF_4)_2{\cdot}dmf$ (**2**) in 83% yield. A similar reduction in pyridine promptly affords the pyridine-ligated cluster, and it is expected that a variety of other solvated species can be produced analogously. Although the exchange reaction in pyridine can be carried out without use of a reductant, complete substitution was found to require 3 days of heating at 90°C. Crystallization of the product from hot pyridine gave black block-shaped crystals of $[W_6CCl_{12}(py)_6](CF_3SO_3)_2{\cdot}2py$ (**3**) in 72% yield.

X-ray analyses of single crystals of **2** and **3** revealed the structures of the two solvated cluster cations, as depicted in Figure 1.[4] In each case, the connectivity of the cluster core is retained, but each terminal triflate ligand has been replaced with a dmf or py ligand. The mean planes of the dmf ligands are canted 32° away from the (approximate) vertical mirror planes associated with the central trigonal prism, while the pyridine rings are perpendicular to these planes. These structures represent new trigonal-prismatic members in a limited family of hexanuclear clusters that have been structurally characterized and are fully solvated by a common solvent. This family also includes the face-capped octahedral clusters $[Mo_6Cl_8(MeCN)_6]^{4+}$ and $[Re_6Se_8(MeCN)_6]^{2+}$, and the edge-bridged octahedral clusters $[M_6Cl_{12}(EtOH)_6]^{2+}$ (M = Nb, Ta).[5]

Unlike the dmf-ligated cluster, which resides on a D_3-symmetry site within the crystal, the 26-electron core structure of $[W_6CCl_{12}(py)_6]^{2+}$ shows significant deviation from the near-ideal D_{3h} symmetry of the parent 24-electron $[W_6CCl_{12}]^{4+}$ core. As shown at the left in Figure 2, the

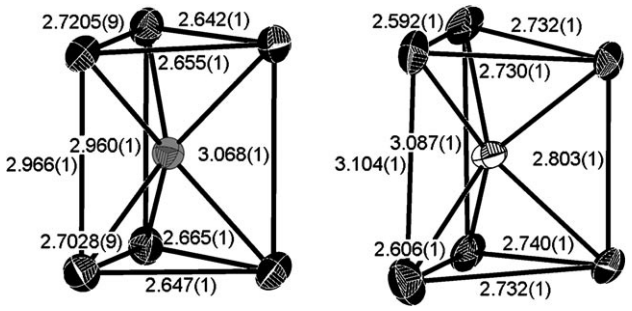

Figure 2. Structures and W–W distances for the 26-electron W_6Z trigonal prisms within $[W_6CCl_{12}(py)_6]^{2+}$ (left) and $[W_6NCl_{18}]^{3-}$ (right).[2c] The distortions approximate C_{2v} symmetry and are consistent with population of two different e′ orbitals of the corresponding 24-electron, D_{3h}-symmetric parent species.

distortion corresponds to elongating the rightmost W–W$_{\|}$ edge and the two opposing W–W$_{\triangle}$ edges of the trigonal prism, thereby lowering the symmetry to C_{2v}. Interestingly, this is opposite to the distortion previously observed in the isoelectronic cluster core of $[W_6NCl_{18}]^{3-}$, wherein the same edges are pinched closer together (Figure 2, right). These two different distortions are consistent with addition of two electrons into one of the two complementary e′ orbitals calculated for the $[W_6CCl_{18}]^{2-}$ or $[W_6NCl_{18}]^{1-}$ parent species.[2a,c] A similar but much more subtle case of electronically driven, complementary distortions has been observed within the octahedral core of the one-electron-oxidized species $[Re_6S_8(CN)_6]^{3-}$.[6] Interestingly, a ^{1}H NMR spectrum collected on a solution of **3** in [D$_6$]acetone at −80°C maintained D_{3h} symmetry, indicating that the distortion in $[W_6CCl_{12}(py)_6]^{2+}$ is dynamic under these conditions.

To gauge the suitability of the solvated clusters for direct use in ligand-substitution and solid-formation reactions, the lability of the py ligands of $[W_6CCl_{12}(py)_6]^{2+}$ was assessed. Compound **3** was dissolved in [D$_5$]pyridine, and ^{1}H NMR spectra collected at 30, 40, 50, and 60°C were used to monitor the rate of the self-exchange reaction (Figure 3). Rigorous

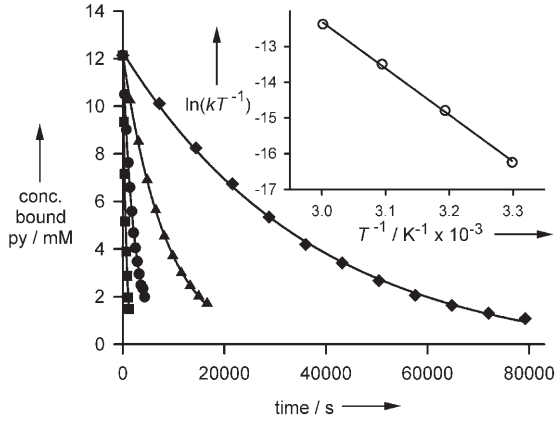

Figure 3. Plots showing the change in concentration of bound py ligands over time at temperatures of 30 (◆), 40 (▲), 50 (●), and 60°C (■), as determined by monitoring the ^{1}H NMR spectrum of **3** in [D$_5$]pyridine. Concentrations were determined by integrating the area of a doublet of ^{1}H NMR resonances at $\delta = 8.08$ ppm relative to an internal standard of hexamethylbenzene. The inset shows the Eyring plot used to determine the activation parameters.

exclusion of water was found to be essential, as even trace amounts were observed to inhibit the reaction significantly. Each data set fit an exponential decay model to at least three half-lives, indicating that the solvent exchange reaction is pseudo-first-order. Clean conversion to $[W_6CCl_{12}([D_5]py)_6]^{2+}$ at the end of each run was verified by UV/Vis spectroscopy and mass spectrometry. A least-squares fit of the Eyring equation to the combined data gave activation parameters $\Delta H^{\ddagger} = 25.9 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = 6.0 \pm 1.7$ cal mol^{-1} K, suggesting a dissociative mechanism with a substantial activation barrier. Extrapolation of the data to 298 K results in a rate constant of $k = 1.4 \times 10^{-5}$ s^{-1}, enabling classification of the $[W_6CCl_{12}]^{2+}$ cluster core as inert.

Surprisingly few quantitative experiments of this type have been carried out on solvated cluster species. Similar measurements performed on the site-differentiated clusters $[Re_6Se_8(PEt_3)_5L]^{4-}$ revealed somewhat larger activation barriers, with self-exchange rate constants of 3.9×10^{-7} and 7.5×10^{-8} s^{-1} at 298 K for L = MeCN and dmso, respectively.[7] Comparisons with hydrated transition-metal ions at 298 K show the pyridine exchange for $[W_6CCl_{12}(py)_6]^{2+}$ to be slightly

faster than the water exchange for $[Cr(H_2O)_6]^{3+}$ ($k = 3.5 \times 10^{-6}\ s^{-1}$) and $[Ru(H_2O)_6]^{3+}$ ($k = 3.5 \times 10^{-6}\ s^{-1}$).[8]

The results described herein provide the first quantitative assessment of the lability of a hexasolvated cluster core. The observed kinetics suggest that ligand-exchange reactions for $[W_6CCl_{12}L_6]^{2+}$-type species should be rapid in dry solvents at temperatures of 60 °C and above. Attempts are underway to utilize compounds **2** and **3** under these conditions in the generation of clusters terminated by good bridge-forming ligands, and even in the direct formation of ligand-bridged cluster frameworks.

Experimental Section

Experimental details are provided in the Supporting Information.

Received: January 12, 2007
Published online: March 27, 2007

Keywords: cluster compounds · Jahn–Teller distortion · kinetics · ligand substitution

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[4] Crystallographic analysis: **1** ($C_{39}H_{72}Cl_{12}F_{18}N_2O_{18}S_6W_6$): $M_r = 2919.85$, monoclinic, space group $C2/c$ (No. 15), $a = 24.099(3)$, $b = 15.7926(17)$, $c = 21.109(2)$ Å, $\beta = 93.314(2)°$, $V = 8020.3(15)$ Å^3, $Z = 4$, black crystal, crystal dimensions $0.13 \times 0.12 \times 0.06$ mm^3, $F(000) = 5480$, $\rho_{calcd} = 2.418$ g cm^{-3}, $\mu Mo_{K\alpha} = 9.225$ mm^{-1}, radiation $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $T = 142$ K, 17538 reflections collected ($2\theta_{max} = 49.5°$), of which 6610 are independent ($R_{int} = 0.0650$). Data/restraints/parameters of 6610/0/463, $R_1 = 0.0471$ ($wR_2 = 0.1085$, $I > 2\sigma(I)$), $R_1 = 0.0940$ ($wR_2 = 0.1373$, all data), GOF = 1.028. **2** ($C_{22}H_{49}B_2Cl_{12}F_8N_7O_7W_6$): $M_r = 2225.80$, trigonal, space group $R32$ (No. 155), $a = 12.359(2)$, $c = 30.041(11)$ Å, $V = 3974.1(18)$ Å^3, $Z = 3$, black crystal, crystal dimensions $0.12 \times 0.11 \times 0.11$ mm^3, $F(000) = 3048$, $\rho_{calcd} = 2.790$ g cm^{-3}, $\mu Mo_{K\alpha} = 13.649$ mm^{-1}, radiation $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $T = 161$ K, 6459 reflections collected ($2\theta_{max} = 52.66°$), of which 1746 are independent ($R_{int} = 0.0477$). Data/restraints/parameters of 1746/0/93, $R_1 = 0.0264$ ($wR_2 = 0.0620$, $I > 2\sigma(I)$), $R_1 = 0.0334$ ($wR_2 = 0.0643$, all data), GOF = 1.016. **3** ($C_{43}H_{40}Cl_{12}F_6N_8O_6S_2W_6$): $M_r = 2225.80$, monoclinic, space group $P2_1/c$ (No. 14), $a = 11.916(4)$, $b = 27.206(9)$, $c = 19.892(6)$ Å, $\beta = 105.991(5)°$, $V = 6200(3)$ Å^3, $Z = 4$, black crystal, crystal dimensions $0.20 \times 0.13 \times 0.12$ mm^3, $F(000) = 4544$, $\rho_{calcd} = 2.648$ g cm^{-3}, $\mu Mo_{K\alpha} = 11.741$ mm^{-1}, radiation $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $T = 170$ K, 29864 reflections collected ($2\theta_{max} = 52.82°$), of which 11913 are independent ($R_{int} = 0.0848$). Data/restraints/parameters of 11913/18/743, $R_1 = 0.0448$ ($wR_2 = 0.0712$, $I > 2\sigma(I)$), $R_1 = 0.1213$ ($wR_2 = 0.0871$, all data), GOF = 0.882. Additional details are provided in the Supporting Information. CCDC-632207 (**1**), CCDC-632208 (**2**), and CCDC-632209 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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