Reactivity of Organometallic Molybdate toward Lanthanide Cations. Synthesis and Structure of Polynuclear Lanthanide−Molybdate Complexes

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Introduction

The study of the chemistry of polyoxoanions has developed tremendously during the last quarter of the 20th century. Polyoxoanions attracted interest not only from basic inorganic chemists but also from researchers in many other fields, such as catalysis, materials science, and medicine.[1,2] The current studies of the chemistry of polyoxocations, on the other hand, are anything but well-developed. This is not because such compounds do not exist. In fact, polyoxocations—molecular cations made up of metal and oxygen atoms—are known to exist for virtually all metals on the periodic table.[3] They have potentially much richer chemistries than polyoxoanions, whose chemistries are largely restricted to early transition elements such as V, Mo, and W. The problem lies in isolation. While polyoxoanions have oxygen-rich composition, polyoxocations have metal-rich composition and are expected to have metal atoms exposed on their surface. Those surface metal sites are supposedly very reactive and vulnerable to further uncontrollable condensation, which leads to the formation of insoluble (usually amorphous) solids. To isolate polyoxocations, we need to protect those surface metal sites.

The pentamethylcyclopentadienyl derivative of the molybdate anion, $Cp^*MoO_3^-$, is perfect for this purpose. Reactivity of MoO oxygens toward different metals has been well demonstrated by the flourished chemistry of polyoxometalates. Also, $Cp^*MoO_3^-$ itself has been proved to be reactive toward many metals.[4] Once $Cp^*MoO_3^-$ is coordinated to the surface metal sites, the bulky Cp* group would effectively protect the metals sites from further reaction. The surface of the resulting “protected polyoxocation” would be covered with Cp* groups. Such a compound is expected to have high solubility in different solvents and would have a rich solution chemistry. Here, we report the first results of our effort to isolate polyoxocations using $Cp^*MoO_3^-$ as a protective group.

Experimental Section

Reagents, Solvents, and General Procedures. The following were purchased from commercial sources and used without further purification: $Mo(CO)_6$ (Strem); $La(NO_3)_3\cdot 6H_2O$, $Ce(NO_3)_3\cdot 6H_2O$, P_2O_5, and acetone (Kishida); and 10% aqueous $(n\text{-}C_4H_9)_4NOH$ (Kanto). THF (tetrahydrofurane) and toluene were dried over 4 Å molecular sieves prior to use. The complex $[(n\text{-}C_4H_9)_4N][Cp^*MoO_3]$ was prepared through literature procedures.[5]

Analytical Procedures. Elemental analyses were performed by Toray Research Center, Shiga, Japan. Infrared spectra were recorded from mineral oil (Nujol) mulls between KBr plates on a Hitachi I-3000 spectrometer. Absorptions are described as follows: strong (s), medium (m), weak (w), and shoulder (sh). ^1H NMR spectra were recorded on a Varian Unity-Plus 300 (300 MHz) spectrometer and referenced against TMS.

Synthesis of $[La_3(Cp^*MoO_3)_2(OH_2)_7](NO_3)_7$. $La(NO_3)_3\cdot 6H_2O$ (0.360 g, 0.831 mmol) was dissolved in 10 mL of THF, and 3.6 mL of this solution was added to a solution of $[(n\text{-}C_4H_9)_4N][Cp^*MoO_3]$ (0.240 g, 0.460 mmol, in 10.0 mL of THF) dropwise for over 1 min with stirring. After the $[(n\text{-}C_4H_9)_4N]NO_3$ that formed had been filtered off, the rest of the lanthanum solution was added to the filtrate over 1 min with stirring. White precipitate formed again during the addition, but it redissolved, and the solution was clear when the addition was complete. Toluene was added to this yellow solution to the point of saturation (ca. 54 mL), and the mixture was allowed to stand at −10 °C for 18 h. Crystals of $[(n\text{-}C_4H_9)_4N]NO_3$ that appeared were filtered off, and 22.9 mL of toluene was added to the filtrate. The cloudy solution was filtered, and the yellow filtrate was allowed to stand at ambient temperature to yield yellow, somewhat hygroscopic, plate-shaped crystals of the product, which had a mass of 0.115 g (0.0715 mmol, 31.1% based on Mo) and was analyzed as $[La_3(Cp^*MoO_3)_2(OH_2)_7](NO_3)_7\cdot THF$ after being dried under vacuum over P_2O_5. Anal. Calcd for $C_{24}H_{52}N_7La_3Mo_2O_{35}$: C, 17.93; H, 3.26; N, 6.10. Found: C, 17.34; H, 3.11; N, 5.75. IR (Nujol, 400−1000 cm^{-1}): 958 (w), 916 (w), 856 (s), 814 (s), 800 (s), 734 (m), 666 (w), 620 (w), 564 (w), 414 (w). ^1H NMR (CD_3CN): δ 1.80 (m, THF), 2.04 (s, Cp*), 2.44 (s, H_2O), 3.65 (m, THF). Different types of crystals were obtained after a slight change of the preparatory procedures. When the final filtration was skipped, thin needlelike crystals appeared from the initially cloudy solution. Those gave the same IR and ^1H NMR spectra as the plate-shaped crystals mentioned above, but they were analyzed as $[La_3(Cp^*MoO_3)_2](NO_3)_7\cdot 2THF\cdot 5H_2O$ after being dried under vacuum over P_2O_5. Anal. Calcd for $C_{28}H_{56}N_7La_3Mo_2O_{34}$: C, 20.46; H, 3.43; N, 5.97; La, 25.4; Mo, 11.7. Found: C, 20.81; H, 3.71; N, 5.97; La, 25.2; Mo, 11.7. The yield improved to 55.0%. When those needlelike crystals were left to stand in the mother liquor in a capped vial for about a week, block-shaped crystals appeared. These crystals also exhibited the same spectroscopic features as the plate-shaped crystals mentioned above.

Synthesis of $[Ce_3(Cp^*MoO_3)_2](NO_3)_7$. $Ce(NO_3)_3\cdot 6H_2O$ (0.360 g, 0.829 mmol) was dissolved in 10.0 mL of THF, and 4 mL of this solution was added to a solution of $[(n\text{-}C_4H_9)_4N][Cp^*MoO_3]$ (0.240 g, 0.460 mmol, in 10.0 mL of THF) dropwise over 1 min with stirring. After the $[(n\text{-}C_4H_9)_4N]NO_3$ that formed had been filtered off, the rest of the cerium solution was added to the filtrate over 1 min with stirring. Toluene was added to this mixed solution to the point of saturation (ca. 74 mL), and the mixture was allowed to stand for 18 h at −10 °C. The oily substance that formed on the bottom of the container was removed by decantation. Toluene was added once again to the solution, thus reaching the point of saturation (ca. 9 mL). The mixture was stored at −10 °C for 18 h before it was allowed to stand at ambient temperature. Yellow crystals of a compound analyzed as $[Ce_3(Cp^*MoO_3)_2](NO_3)_7\cdot 3THF\cdot 4H_2O$ after being dried under vacuum started to appear in 1 day (88 mg, 0.052 mmol, 23% yield based on Mo). Anal. Calcd for $C_{32}H_{62}N_7Ce_3Mo_2O_{34}$: C, 22.59; H, 3.67; N, 5.76; Ce, 24.7; Mo, 11.3. Found: C, 22.39; H, 3.42; N, 5.56; Ce, 24.6; Mo 11.5. IR (Nujol, 400−1000 cm^{-1}): 968 (w), 866 (s), 834 (s), 810 (s), 778 (m), 736 (s), 694 (m), 672 (w), 660 (w), 644 (w), 618 (m), 584 (w), 544 (w), 466 (w), 428 (sh), 414 (m). ^1H NMR (CD_3CN): δ −1.21

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10.1021/ic991221c CCC: $19.00

Table 1. Crystallographic Data for $[La_3(OH_2)_7(Cp^*MoO_3)_2(NO_3)_7]\cdot 4THF$ and $[\{La_3(OH_2)_5(THF)(Cp^*MoO_3)_2(NO_3)_6\}_2(NO_3)_2]\cdot 4THF$

	$[La_3(OH_2)_7(Cp^*MoO_3)_2(NO_3)_7]\cdot 4THF$	$[\{La_3(OH_2)_5(THF)(Cp^*MoO_3)_2(NO_3)_6\}_2(NO_3)_2]\cdot 4THF$
formula	$C_{36}H_{76}N_7O_{38}La_3Mo_2$	$C_{64}H_{128}N_{14}O_{70}La_6Mo_4$
formula weight	1823.62	3430.97
crystal system	monoclinic	triclinic
space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a (Å)	12.647(6)	12.661(3)
b (Å)	23.554(5)	22.168(3)
c (Å)	24.523(6)	11.691(4)
α (deg)	90.0	94.44(2)
β (deg)	104.30(3)	115.41(2)
γ (deg)	90.0	86.45(2)
V (Å^3)	7079(4)	2954(1)
ρ(calcd) (g cm^{-3})	1.711	1.929
Z	4	1
μ (mm^{-1})	2.21	2.63
$R[F_o > 4.0\sigma(F_o)]^a$	0.0532	0.0584
$R_w[F_o > 4.0\sigma(F_o)]^b$	0.1515^c	0.1465^d

[a] $R = 3||F_o| - |F_c||/3|F_o|$. [b] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [c] $w = 1/[\sigma^2(Fo^2) + (0.099P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. [d] $w = 1/[\sigma^2(Fo^2) + (0.090P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

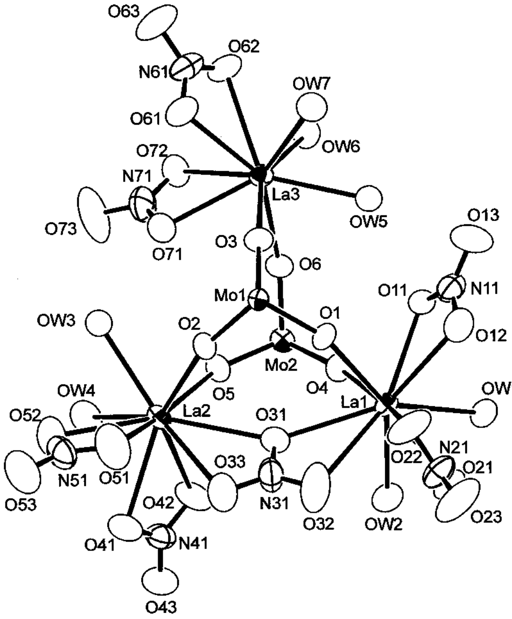

Figure 1. Perspective drawing of $[La_3(OH_2)_7(Cp^*MoO_3)_2(NO_3)_7]$. The Cp* groups are omitted for clarity. Displacement ellipsoids are scaled to enclose 30% probability levels. The oxygen atoms of the coordinated water molecules are labeled as OW with a numerical suffix. Other atoms are labeled with their elemental symbols plus numerical suffixes.

($\upsilon_{1/2} \approx 140$ Hz, H_2O), 1.71 (m, THF), 1.81 ($\upsilon_{1/2} \approx 16$ Hz, Cp*), 3.51 (m, THF), 3.75 ($\upsilon_{1/2} \approx 13$ Hz, H_2O).

Crystal Structure Determination. The crystals of $[La_3(OH_2)_7(Cp^*MoO_3)_2(NO_3)_7]\cdot 4THF$ and $[\{La_3(OH_2)_5(THF)(Cp^*MoO_3)_2(NO_3)_6\}_2(NO_3)_2]\cdot 4THF$ were mounted on glass capillaries and covered with epoxy resin. The diffraction data were collected on a RIGAKU AFC-5R automated four-circle diffractometer at ambient temperature (296 ± 2 K) with graphite monochromated MoKα radiation ($\lambda = 0.71069$ Å). Cell parameters were refined through 25 reflections. Lorenz polarization, empirical absorption correction based on Ψ-scans for three reflections, and decay correction for $[La_3(OH_2)_7(Cp^*MoO_3)_2(NO_3)_7]\cdot 4THF$ were applied by using the TEXSAN program package.[6] The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELX97[7] program at the Computer Center of the Institute for Molecular Science, Okazaki, Japan. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were neither located nor included in the calculations. Crystallographic data are summarized in Table 1.

Structure determination of the Ce compound has also been attempted but has not been successful so far because of a large unit cell and the poor quality of the crystals. The crystallographic parameters for the Ce compound are triclinic, $P\bar{1}$, $a = 21.387(6)$ Å, $b = 30.37(2)$ Å, $c = 12.441(6)$ Å, $\alpha = 97.65(4)°$, $\beta = 102.74(3)°$, $\gamma = 102.52(4)°$, and $V = 7553(6)$ Å^3. Some THF molecules of crystallization could not be located. The tentative formula from the current structural analysis is $[Ce_3(Cp^*MoO_3)_2(NO_3)_6(OH_2)_7]_2\cdot 2[Ce_3(Cp^*MoO_3)_2(NO_3)_8(OH_2)_5]\cdot n$THF. The former unit is a polycation with a charge of +2 and the latter a polyanion with a charge of −1. The current refinement gives R1 = 0.0936 for 9874 reflections with $F_o < 4.0\sigma(F_o)$.

Results

When $[(n\text{-}C_4H_9)_4N][Cp^*MoO_3]$ is reacted with $La(NO_3)_3\cdot 6H_2O$ in THF at ambient temperature, a novel lanthanum−molybdate adduct is formed.

$$2[Cp^*MoO_3]^- + 3La(NO_3)_3 \rightarrow [La_3(Cp^*MoO_3)_2](NO_3)_7 + 2NO_3^-$$

Three different types of crystals of this compound are isolated, depending on the crystallization conditions (see Experimental Section). Although one type, the needlelike crystals, was too thin for an X-ray structural analysis, two others, plate- and block-shaped crystals, were suitable for the crystal structure analyses. X-ray structural analysis revealed that the plate-shaped crystals are composed of neutral $[La_3(OH_2)_7(Cp^*MoO_3)_2(NO_3)_7]$ units (**1**, Figure 1) and THF molecules from crystallization. X-ray structural analysis on the block-shaped crystals revealed that they are composed of THF molecules of crystallization and dimeric $\{La_3(OH_2)_5(THF)(Cp^*MoO_3)_2(NO_3)_6\}_2(NO_3)_2$ units (**2**) with the structure shown in Figure 2. In this dimer, two nitrate groups with different coordination modes link the two $[La_3(OH_2)_5(THF)(Cp^*MoO_3)_2(NO_3)_6]$ units, related by a crystallographic inversion center (see Discussion). The bridging nitrate groups are located close to the inversion center and disordered over two equally occupied positions. In Figure 2, only one of the settings of the nitrate groups is shown for clarity.

The Ce analogue is obtained when $[(n\text{-}C_4H_9)_4N][Cp^*MoO_3]$ is reacted with $Ce(NO_3)_3\cdot 6H_2O$. The analysis of the diffraction data revealed that the crystals are composed of both monomeric $[Ce_3(OH_2)_5(Cp^*MoO_3)_2(NO_3)_8]^-$ and dimeric $[Ce_3(OH_2)_7$-

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(6) *TEXSAN, single-crystal structure analysis software*; Molecular Structure Corporation: The Woodlands, TX, 1993, and the programs therein.

(7) Sheldrick, G. M. *SHELX-97*; Universität Göttingen: Göttingen, Germany, 1997.

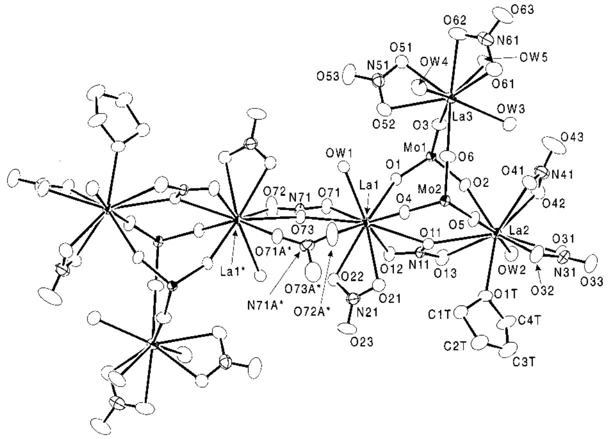

Figure 2. Perspective drawing of $[La_3(OH_2)_5(THF)(Cp^*MoO_3)_2(NO_3)_6]_2(NO_3)_2$. The Cp* groups are omitted for clarity. Displacement ellipsoids are scaled to enclose 30% probability levels. Atoms are labeled in the same manner as in Figure 1. Carbon and oxygen atoms in the THF molecules are given a suffix T in addition to the numerical suffix. Atoms with * are generated by the symmetry operation $1 - x$, $1 - y$, $-z$. The two NO_3 groups bridging two $[La_3(OH_2)_5(THF)(Cp^*MoO_3)_2(NO_3)_6]$ moieties are disordered, and only one pair of them is drawn in the figure.

$(Cp^*MoO_3)_2(NO_3)_6]_2^{2+}$ units with the same basic structural framework as those of the La compounds.

Discussion

X-ray structural analyses revealed that the current lanthanum−molybdate adduct exists in two forms in the solid state. In both forms, metal atoms arrange themselves into trigonal bipyramids. The La atoms occupy the equatorial positions and the Mo atoms the axial positions. The Mo and La atoms are connected by six μ^2 oxygen atoms. Two La atoms, La1 and La2, are further bridged by a NO_3 group. The La1···La2 distance is significantly shorter than the La1···La3 and La2···La3 distances as a consequence of this third bridge. In the dimeric form, two $La_3(Cp^*Mo)_2O_6$ units are linked by two NO_3 groups. One of the NO_3 groups lies on the plane defined by the N atom and two La atoms bridged, and coordinates to both La atoms as a bidentate. The other NO_3 group locates itself out of this plane and functions as a monodentate toward both La atoms. This double bridge results in a relatively short La···La distance (5.153 Å). In fact, this La···La distance between the monomeric Ln_3Mo_2 units is significantly shorter than the La···La distances within the Ln_3Mo_2 unit (see Table 3). The Ce analogue has the same basic structural features as the La compound. However, the low quality of the diffraction data precludes further discussion on its structure.

Table 2. Selected Interatomic Distances (Å) for **1**

La1−O1	2.426(5)	Mo1−O1	1.760(5)
La1−O4	2.437(5)	Mo1−O2	1.768(5)
La2−O2	2.439(5)	Mo1−O3	1.753(5)
La2−O5	2.442(5)	Mo2−O4	1.756(5)
La3−O3	2.420(5)	Mo2−O5	1.763(5)
La3−O6	2.444(5)	Mo2−O6	1.760(5)
La1···La2	5.287(1)	La1···Mo1	4.078(1)
La1···La3	6.232(1)	La2···Mo1	4.135(1)
La2···La3	6.157(1)	La3···Mo1	4.141(1)
La1···Mo2	4.120(1)	OW5···O11	2.785(8)
La2···Mo2	4.108(2)	OW3···O71	2.792(9)
La3···Mo2	4.137(1)		

Table 3. Selected Interatomic Distances (Å) for **2**[a]

La1−O1	2.452(5)	Mo1−O1	1.759(5)
La1−O4	2.383(5)	Mo1−O2	1.759(5)
La2−O2	2.413(5)	Mo1−O3	1.774(6)
La2−O5	2.438(5)	Mo2−O4	1.770(5)
La3−O3	2.410(6)	Mo2−O5	1.765(5)
La3−O6	2.407(6)	Mo2−O6	1.766(6)
La1···La2	5.261(2)	La2···Mo1	4.091(2)
La1···La3	6.168(1)	La2···Mo2	4.110(1)
La1···La1[1]	5.153(2)	La3···Mo1	4.124(1)
La2···La3	6.185(2)	La3···Mo2	4.158(1)
La1···Mo1	4.126(1)	OW1···O52	2.822(9)
La1···Mo2	4.024(1)	OW3···O41	2.82(1)

[a] Symmetry operation: $1 - x$, $1 - y$, $-z$.

In addition to the extensive intermolecular hydrogen bonds holding the lattice of the crystal of **1** together, there seems to exist a couple of intramolecular hydrogen bonds between water molecules and NO_3 groups coordinated to the La atoms (2.79 Å, OW3−O71 and OW5−O11). These intramolecular hydrogen bonds are weaker in dimeric **2** (2.82 Å, OW1−O52 and OW3−O41).

Another interesting feature of the current compounds is the shortness of the La−O bonds. The average La−O distances of **1** and **2** are 2.44 and 2.42 Å, respectively. These are much shorter than the La−O distances observed in $[La(Mo_8O_{24})_2]^{5-}$ and $[\{La(NO_3)_3\}_2(Mo_8O_{24})]^{4-}$,[8] and they are comparable to those observed for La_2O_3.[9] The shortest La−O distance in **2** (2.382 Å) is equal to the shortest La−O distance in La_2O_3 (2.38 Å). The short La−O distances of **1** and **2** indicate that relatively strong bonds are formed between Cp^*MoO_3 groups and La atoms, as we have anticipated. The current results have proved the potential of $Cp^*MoO_3^-$ as a protective group for polyoxocations.

Supporting Information Available: X-ray crystallographic files in CIF format for the structures of $[La_3(OH_2)_7(Cp^*MoO_3)_2(NO_3)_7]\cdot 4THF$, $[\{La_3(OH_2)_5(THF)(Cp^*MoO_3)_2(NO_3)_6\}_2(NO_3)_2]\cdot 4THF$, and $[Ce_3(Cp^*MoO_3)_2(NO_3)_6(OH_2)_7]_2\cdot 2[Ce_3(Cp^*MoO_3)_2(NO_3)_8(OH_2)_5]\cdot n$THF. This material is available free of charge via the Internet at http://pubs.acs.org.

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