Inorg. Chem. **1997,** *36,* 4275−4279

β-Octamolybdate as a Building Block. Synthesis and Structural Characterization of Rare Earth−Molybdate Adducts

A. Kitamura,[1a] T. Ozeki,*,[1b] and A. Yagasaki*,[1a]

Departments of Chemistry, Kwansei Gakuin University, Uegahara, Nishinomiya 662, Japan, and Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

Received March 20, 1997⊗

Reaction of $[(n\text{-}C_4H_9)_4N]_4[Mo_8O_{26}]$ with nitrate salts of rare earth metals yields two different series of new compounds $[Ln(Mo_8O_{26})_2]^{5-}$ and $[\{Ln(NO_3)_3\}_2(Mo_8O_{26})]^{4-}$ (Ln = Y, La, Ce, Pr, Nd, Gd, Yb) as tetra-*n*-butylammonium salts. X-ray structural analyses of $[(n\text{-}C_4H_9)_4N]_5[La(Mo_8O_{26})_2]\cdot CH_3CN$ [monoclinic, space group $P2_1/c$, $a = 25.8332(6)$ Å, $b = 17.5054(7)$ Å, $c = 32.6565(12)$ Å, $\beta = 91.699(2)°$, $Z = 4$] and $[(n\text{-}C_4H_9)_4N]_4[\{La(NO_3)_3\}_2(Mo_8O_{26})]\cdot 2CH_3CN$ [monoclinic, space group $P2_1/n$, $a = 17.702(2)$ Å, $b = 17.2646(12)$ Å, $c = 18.965(2)$ Å, $\beta = 102.132(3)°$, $Z = 2$] revealed that these compounds contain the Mo_8O_{26} unit as their building block.

Introduction

One of the major challenge in polyoxometalate chemistry is the "rational" synthesis of new compounds. Many research groups are trying to establish synthetic methods to obtain novel and larger polyoxometalates systematically.[2] Some have approached this problem by replacing hexavalent metal centers with one or more lower valent metals such as V^{5+}, Nb^{5+}, or $CpTi^{3+}$.[3] This substitution results in highly charged nucleophilic compounds. Polyoxometalates activated in this manner can then be reacted with cationic complexes to produce new polyoxometalates with extended metal−oxygen frameworks.

Apparently, this is not the only solution to the problem. We should be able to work the other way around. If conventional polyoxometalates are not basic enough to react with ordinary cations, we should be able to use cations of high oxophilicity to promote the adduct-forming reaction. Since rare earth elements are known to be highly oxophilic, we initiated a project to build up new polyoxometalates by reacting rare earth metals with conventional nonactivated polyoxometalates. Here we report the first results of this effort.

Experimental Section

Reagents, Solvents, and General Procedures. The following were purchased from commercial sources and used without further purification: hydrochloric acid, ethanol, $Na_2MoO_4\cdot 2H_2O$, $Gd(NO_3)_3\cdot 5H_2O$, $Pr(NO_3)_3\cdot 6H_2O$, and $Yb(NO_3)_3\cdot 3H_2O$ (Kishida), $[(n\text{-}C_4H_9)_4N]Br$ (Tokyo Kasei), and 10% ^{17}O-enriched water (Cambridge Isotope Laboratories). Acetonitrile and diethyl ether (Kishida or Wako) and deuterated acetonitrile (Isotec) were dried over molecular sieves. The following were dried under vacuum for 24 h before use: $Y(NO_3)_3\cdot 6H_2O$ and $Nd(NO_3)_3\cdot xH_2O$ (Wako) and $La(NO_3)_3\cdot 6H_2O$ (Kishida). Procedures described in the literature[4] were followed for the preparation of $[(n\text{-}C_4H_9)_4N]_4[\alpha\text{-}Mo_8O_{26}]$.

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). ^{17}O NMR spectra were recorded at 40.67 MHz on a Varian Unity-Plus spectrometer and referenced externally to D_2O.

Preparation of $[(n\text{-}C_4H_9)_4N]_5[Y(Mo_8O_{26})_2]$. A solution of $Y(NO_3)_3\cdot 6H_2O$ (0.0713 g, 0.186 mmol) in 4.5 mL of acetonitrile was added dropwise to a solution of $[(n\text{-}C_4H_9)_4N]_4[\alpha\text{-}Mo_8O_{26}]$ (0.809 g, 0.376 mmol) in 30 mL of acetonitrile with stirring. After the mixed solution was stirred for 1 h, 50 mL of diethyl ether was added to the solution. The colorless precipitate formed was collected by filtration and dried under vacuum overnight to yield 0.424 g of crude product. Purification was accomplished by dissolving 0.40 g of the crude product in 9 mL of acetonitrile and adding 12 mL of diethyl ether gently to form a second layer. The vial that contained the mixture was capped and allowed to stand overnight, and the colorless needle-like crystals that formed were collected by filtration and dried under vacuum overnight to yield 0.20 g (0.055 mmol, 31% based on Y) of analytically pure compound. Anal. Calcd for $C_{80}H_{180}N_5YMo_{16}O_{52}$: C, 26.19; H, 4.95; N, 1.91; Y, 2.42; Mo, 41.9. Found: C, 26.04; H, 4.73; N, 1.92; Y, 2.39; Mo, 42.0. IR (Nujol, 1000−400 cm^{-1}): 977 (m), 954 (s), 936 (m), 920 (m), 877 (sh), 864 (s), 798 (m), 747 (sh), 702 (s), 672 (m), 634 (m), 589 (w), 552 (w), 526 (m), 482 (w), 455 (w), 422 (m). The compound was soluble in acetone, acetonitrile, and *N,N*-dimethylformamide but insoluble in ethanol, chloroform, and dichloromethane.

Preparation of $[(n\text{-}C_4H_9)_4N]_5[La(Mo_8O_{26})_2]$. A solution of $La(NO_3)_3\cdot 6H_2O$ (0.0867 g, 0.200 mmol) in 10 mL of acetonitrile was added dropwise to a solution of $[(n\text{-}C_4H_9)_4N]_4[\alpha\text{-}Mo_8O_{26}]$ (0.863 g, 0.401 mmol) in 40 mL of acetonitrile with stirring. After the mixed solution was stirred for 1 h, 150 mL of diethyl ether was added to the solution. The white precipitate formed on addition was collected by filtration, washed with 50 mL of diethyl ether, and dried under vacuum to yield 0.554 g of crude product. Purification was accomplished by dissolving 0.40 g of the crude product in 16 mL of acetonitrile, filtering off a small amount of insoluble material, and adding 44 mL of diethyl

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⊗ Abstract published in *Advance ACS Abstracts,* August 15, 1997.

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S0020-1669(97)00335-2 CCC: $14.00

Table 1. Crystallographic Data for $[(n\text{-}C_4H_9)_4N]_5[La(Mo_8O_{26})_2]\cdot CH_3CN$ and $[(n\text{-}C_4H_9)_4N]_4[\{La(NO_3)_3)\}_2(Mo_8O_{26})]\cdot 2CH_3CN$

	$[(n\text{-}C_4H_9)_4N]_5[La(Mo_8O_{26})_2]\cdot CH_3CN$	$[(n\text{-}C_4H_9)_4N]_4[\{La(NO_3)_3\}_2(Mo_8O_{26})]\cdot 2CH_3CN$
empirical formula	$C_{82}H_{183}LaMo_{16}N_6O_{52}$	$C_{68}H_{150}La_2Mo_8N_{12}O_{44}$
formula weight	3759.3	2885.3
space group	$P2_1/c$	$P2_1/n$
a/Å	25.8332(6)	17.702(2)
b/Å	17.5054(7)	17.2646(12)
c/Å	32.6565(12)	18.965(2)
β/°	91.699(2)	102.132(3)
V/Å^3	14761.4(9)	5666.8(10)
Z	4	2
T/K	293	293
λ/Å	0.7107	0.7107
ρ_{calcd}/g cm^{-3}	1.69	1.69
μ/mm^{-1}	1.66	1.67
$R[F_o^2 > 2\sigma(F_o^2)]^a$	0.0565	0.0359
$R_w[F_o^2 > 2\sigma(F_o^2)]^b$	0.1683^c	0.0982^d

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [c] $w = 1/[\sigma^2(F_o^2) + (0.11P)^2 + 30.0P]$, where $P = (F_o^2 + 2F_c^2)/3$. [d] $w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 5.0\ P]$, where $P = (F_o^2 + 2F_c^2)/3$.

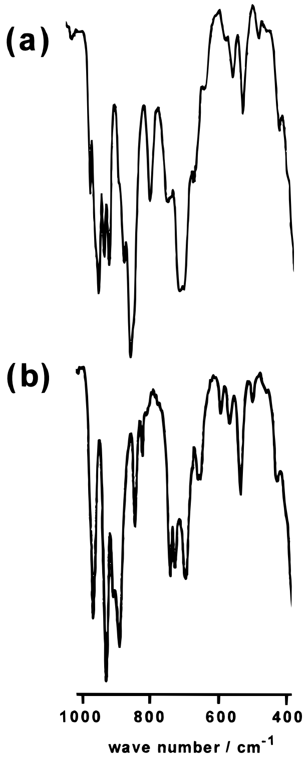

Figure 1. Infrared spectra measured from Nujol mulls of tetra-*n*-butylammonium salts of (a) $[La(Mo_8O_{26})_2]^{5-}$ and (b) $[\{La(NO_3)_3\}_2(Mo_8O_{26})]^{4-}$. See Experimental Section for numerical data.

ether gently to the filtrate to make a second layer. Colorless needle-like crystals that appeared the next day were collected by filtration and dried under vacuum to yield 0.22 g (0.059 mmol, 41%) of analytically pure compound. Anal. Calcd for $C_{80}H_{180}N_5LaMo_{16}O_{52}$: C, 25.84; H, 4.88; N, 1.88; La, 3.74; Mo, 41.3. Found: C, 25.83; H, 4.90; N, 1.84; La, 3.62; Mo, 40.7. IR (Nujol, 1000−400 cm^{-1}; see Figure 1): 978 (m), 954 (s), 936 (m), 922 (m), 887 (sh), 877 (m), 860 (s), 802 (m), 747 (m), 708 (s), 673 (w), 634 (w), 554 (w), 524 (w), 473 (w), 411 (m).

^{17}O-Enriched material was prepared by dissolving 0.100 g (0.0269 mmol) of crystalline $[(n\text{-}C_4H_9)_4N]_5[La(Mo_8O_{26})_2]$ in 10 mL of acetonitrile, adding 13 μL of ^{17}O-enriched water, stirring the solution for 1 h, adding 40 mL of diethyl ether, collecting the precipitate then formed by filtration, and drying under vacuum for 24 h (0.0772 g, 0.0208 mmol, 77.2%). ^{17}O NMR (40.67 MHz, CH$_3$CN): δ −6.3, 41.8, 77.6, 272.5, 338.6, 422.1, 490.3, 772.8, 804.4, 818.1, 924.0, 947.9 ppm.

Preparation of $[(n\text{-}C_4H_9)_4N]_5[Pr(Mo_8O_{26})_2]$ and Other $[(n\text{-}C_4H_9)_4N]_5[Ln(Mo_8O_{26})_2]$ Compounds. A solution of $Pr(NO_3)_3\cdot 6H_2O$ (0.0875 g, 0.201 mmol) in 5 mL of acetonitrile was added dropwise to a solution of $[(n\text{-}C_4H_9)_4N]_4[\alpha\text{-}Mo_8O_{26}]$ (0.862 g, 0.400 mmol) in 40 mL of acetonitrile with stirring. After the mixed solution was stirred for 1 h, 180 mL of diethyl ether was added to the solution to produce an oily substance. The mixture was allowed to stand for 3 h before the oily substance was separated by decantation. The substance was washed with 50 mL of diethyl ether, and the solid then formed was collected by filtration and dried under vacuum for 24 h to yield 0.66 g (0.18 mmol, 89%) of the product as a green powder. Crystallization was accomplished by dissolving 0.30 g of the product in 12 mL of acetonitrile and adding 14 mL of diethyl ether gently to make a second layer. Green plate-shaped crystals (0.18 g) appeared from the mixture in 2 days. IR (Nujol, 1000−400 cm^{-1}): 978 (m), 954 (s), 938 (m), 922 (m), 876 (m), 858 (s), 850 (s), 798 (m), 750 (m), 714 (sh), 698 (s), 668 (sh), 634 (m), 576 (w), 554 (w), 526 (m), 478 (w), 454 (w), 416 (m). The Ce, Nd, Gd, and Yb analogs were prepared in a similar manner. See Supporting Information for details.

Preparation of $[(n\text{-}C_4H_9)_4N]_4[\{La(NO_3)_3\}_2(Mo_8O_{26})]$ and Its Ce and Pr Analogs. A solution of $La(NO_3)_3\cdot 6H_2O$ (0.173 g, 0.400 mmol) in 3 mL of acetonitrile was added dropwise to a solution of $[(n\text{-}C_4H_9)_4N]_4[\alpha\text{-}Mo_8O_{26}]$ (0.431 g, 0.200 mmol) in 20 mL of acetonitrile with stirring. After the mixed solution was stirred for 1 h, 50 mL of diethyl ether was added gently to make a second layer. The mixture was allowed to stand for 2 days, and colorless block-shaped crystals that appeared were collected by filtration and dried under vacuum overnight to yield 0.412 g (0.147 mmol, 73.5%) of analytically pure compound. Anal. Calcd for $C_{64}H_{144}N_{10}La_2Mo_8O_{44}$: C, 27.42; H, 5.18; N, 5.00; La, 9.91; Mo, 27.4. Found: C, 27.14; H, 4.81; N, 4.93; La, 9.62; Mo, 27.5. IR (Nujol, 1000−400 cm^{-1}; see Figure 1): 962 (s), 924 (s), 900 (m), 884 (s), 838 (m), 816 (w), 734 (m), 720 (m), 690 (m), 652 (m), 586 (w), 558 (w), 526 (m), 490 (w), 418 (m). The Ce and Pr analogs were prepared in a similar manner. See Supporting Information for details.

Crystal Structure Determination. Extremely efflorescent crystals of $[(n\text{-}C_4H_9)_4N]_5[La(Mo_8O_{26})_2]\cdot CH_3CN$ and $[(n\text{-}C_4H_9)_4N]_4[\{La(NO_3)_3\}_2(Mo_8O_{26})]\cdot 2CH_3CN$ were sealed in glass capillaries. Diffraction data were collected on a Rigaku RAXIS IICS imaging plate diffractometer[5] using screenless Weissenberg methods.[6] The structures were solved by the direct method using the SHELXS-86 program[7] and refined by the full-matrix least-squares method on F^2 using the SHELXL-93 program.[8] In $[(n\text{-}C_4H_9)_4N]_5[La(Mo_8O_{26})_2]\cdot CH_3CN$, anisotropic displacement parameters were applied to La, Mo, and O atoms. All non-hydrogen atoms were refined anisotropically in $[(n\text{-}C_4H_9)_4N]_4[\{La(NO_3)_3\}_2(Mo_8O_{26})]\cdot 2CH_3CN$. Hydrogen atoms were generated at idealized positions and refined with the riding model. Crystallographic parameters are summarized in Table 1. Selected bond distances for the $[La(Mo_8O_{26})_2]^{5-}$ and $[\{La(NO_3)_3\}_2(Mo_8O_{26})]^{4-}$ anions are listed in Tables 2 and 3.

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Table 2. La−O Distances (Å) and O···O Contacts within 4.0 Å in the LaO_8 and LaO_{10} Coordination Spheres in **1** and **2**

1		**2**	
La−O1$_A$	2.507(5)	La−O1	2.624(3)
La−O2$_A$	2.505(6)	La−O2	2.645(3)
La−O3$_A$	2.480(5)	La−O3	2.618(3)
La−O4$_A$	2.568(5)	La−O4	2.665(3)
La−O1$_C$	2.513(5)	La−O14	2.602(3)
La−O2$_C$	2.522(5)	La−O15	2.603(3)
La−O3$_C$	2.507(6)	La−O17	2.577(3)
La−O4$_C$	2.561(5)	La−O18	2.538(3)
		La−O20	2.544(4)
		La−O21	2.557(4)
O1$_A$−O3$_C$	3.078(7)	O1−O20	3.025(5)
O1$_A$−O4$_C$	3.333(7)	O1−O21	3.120(5)
O2$_A$−O4$_C$	3.107(7)	O2−O21	3.004(6)
O2$_A$−O1$_C$	3.303(7)	O2−O18	3.062(5)
O3$_A$−O1$_C$	3.230(7)	O3−O14	2.884(4)
O3$_A$−O2$_C$	3.328(8)	O3−O18	3.178(5)
O4$_A$−O2$_C$	3.197(7)	O4−O14	2.906(4)
O4$_A$−O3$_C$	3.340(7)	O4−O15	2.973(4)
		O14−O17	3.033(5)
		O14−O18	3.555(5)
		O15−O20	2.775(6)
		O15−O17	3.035(5)
		O17−O20	3.173(6)
		O17−O21	3.217(6)
		O18−O21	3.246(6)

Table 3. Mo−O Distances (Å) in **1** and **2**

	1				**2**
	A	B	C	D	
Mo1−O1	1.731(5)	1.694(6)	1.739(5)	1.694(6)	1.726(3)
Mo1−O5	1.685(6)	1.701(7)	1.678(6)	1.674(7)	1.688(3)
Mo1−O9	1.882(6)	1.897(6)	1.876(5)	1.883(6)	1.883(3)
Mo1−O12	1.996(5)	2.036(5)	2.006(5)	2.030(5)	2.024(3)
Mo1−O13	2.303(5)	2.371(5)	2.310(5)	2.353(5)	2.326(2)
Mo1−O11^a	2.237(5)	2.337(5)	2.233(5)	2.331(5)	2.263(3)
Mo2−O2	1.747(5)	1.694(8)	1.741(5)	1.685(6)	1.724(3)
Mo2−O6	1.670(6)	1.696(8)	1.681(5)	1.700(6)	1.686(3)
Mo2−O9	1.926(6)	1.905(7)	1.924(6)	1.921(6)	1.921(3)
Mo2−O10	1.921(6)	1.912(7)	1.927(7)	1.910(7)	1.926(3)
Mo2−O13	2.433(4)	2.544(5)	2.424(4)	2.521(5)	2.464(2)
Mo2−O8^a	2.166(5)	2.405(5)	2.178(5)	2.396(5)	2.265(3)
Mo3−O3	1.739(5)	1.695(6)	1.735(5)	1.687(6)	1.734(3)
Mo3−O7	1.685(6)	1.689(7)	1.684(6)	1.681(7)	1.680(3)
Mo3−O10	1.885(6)	1.884(6)	1.876(5)	1.895(5)	1.886(3)
Mo3−O11	2.018(5)	2.029(5)	2.014(5)	2.028(5)	2.031(2)
Mo3−O13	2.322(5)	2.338(5)	2.321(5)	2.358(5)	2.340(2)
Mo3−O12^a	2.235(5)	2.373(5)	2.232(5)	2.356(4)	2.247(2)
Mo4−O4	1.725(5)	1.662(5)	1.718(5)	1.671(5)	1.707(3)
Mo4−O8	1.719(5)	1.768(5)	1.723(5)	1.758(5)	1.742(2)
Mo4−O11	1.939(5)	1.976(6)	1.935(5)	1.963(6)	1.946(2)
Mo4−O12	1.937(5)	1.954(5)	1.936(5)	1.960(6)	1.967(2)
Mo4−O13	2.161(5)	2.100(5)	2.179(4)	2.111(5)	2.159(2)
Mo4−O13^a	2.292(5)	2.369(4)	2.289(5)	2.346(4)	2.246(2)

[a] Belong to adjacent Mo_4O_{13} subunit of the Mo_8O_{26} structure. In the case of **2**, it is the atom generated by the symmetry operation −*x*, −*y*, −*z*.

Results

When $[(n\text{-}C_4H_9)_4N]_4[\alpha\text{-}Mo_8O_{26}]$ is reacted with $La(NO_3)_3\cdot 6H_2O$ in acetonitrile at ambient temperature in a 2:1 molar ratio, a compound which after recrystallization from acetonitrile/diethyl ether analyzes as $[(n\text{-}C_4H_9)_4N]_5[La(Mo_8O_{26})_2]$ is formed.

$$2[Mo_8O_{26}]^{4-} + La(NO_3)_3 \rightarrow [La(Mo_8O_{26})_2]^{5-} + 3NO_3^{-}$$

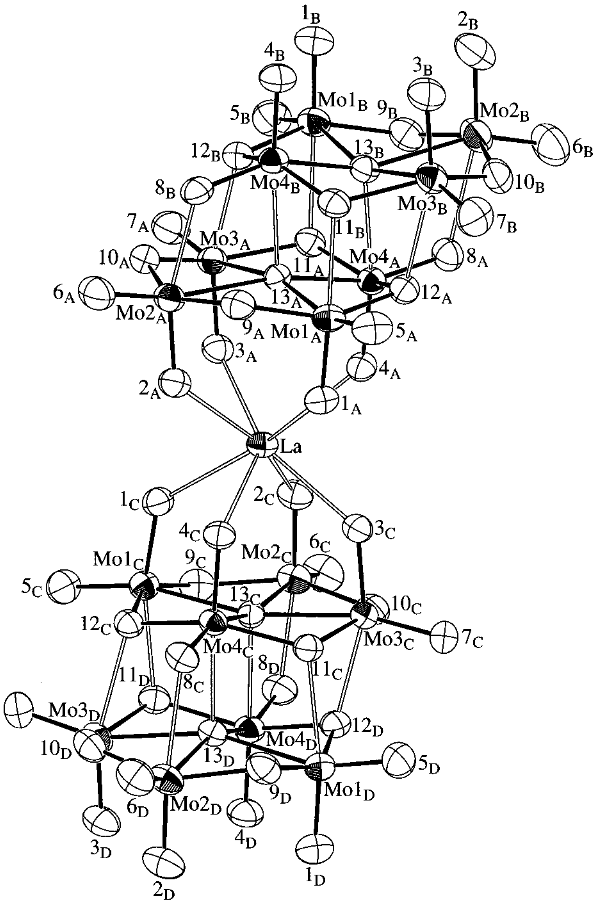

Figure 2. Perspective drawing of the $[La(Mo_8O_{26})_2]^{5-}$ anion. Displacement ellipsoids are scaled to enclose 30% probability levels. Metal atoms are labeled with their elemental symbols plus, in the case of molybdenum, a numerical suffix and alphabetical subscript. Oxygen atoms are labeled only with their suffixes and subscripts.

X-ray structural analysis revealed that single crystals of $[(n\text{-}C_4H_9)_4N]_5[La(Mo_8O_{26})_2]$ are composed of $[(n\text{-}C_4H_9)_4N]^+$ cations, acetonitrile molecules of crystallization, and discrete $[La(Mo_8O_{26})_2]^{5-}$ anions having the structure shown in Figure 2. Metal−oxygen distances in the $[La(Mo_8O_{26})_2]^{5-}$ anion (**1**) are given in Tables 2 and 3.

Heteropolymolybdates that contain other rare earth elements such as Y, Ce, Pr, Nd, Gd, and Yb can be prepared in a similar manner. Their IR spectra in the 1000−400 cm^{-1} region are virtually identical to that of $[(n\text{-}C_4H_9)_4N]_5[La(Mo_8O_{26})_2]$ (see Figure 1a and Supporting Information), strongly suggesting a common structure for all those compounds.

When $[(n\text{-}C_4H_9)_4N]_4[\alpha\text{-}Mo_8O_{26}]$ is reacted with $La(NO_3)_3\cdot 6H_2O$ in a 1:2 ratio, on the other hand, a compound that gives a totally different IR spectrum is obtained (see Figure 1b). This compound analyzes as $[(n\text{-}C_4H_9)_4N]_4[\{La(NO_3)_3\}_2(Mo_8O_{26})]$.

$$[Mo_8O_{26}]^{4-} + 2La(NO_3)_3 \rightarrow [\{La(NO_3)_3\}_2(Mo_8O_{26})]^{4-}$$

X-ray structural analysis revealed that single crystals of $[(n\text{-}C_4H_9)_4N]_4[\{La(NO_3)_3\}_2(Mo_8O_{26})]$ are composed of $[(n\text{-}C_4H_9)_4N]^+$ cations, acetonitrile molecules of crystallization, and discrete $[\{La(NO_3)_3\}_2(Mo_8O_{26})]^{4-}$ anions having the structure shown in Figure 3. Metal−oxygen distances in the $[\{La(NO_3)_3\}_2(Mo_8O_{26})]^{4-}$ anion (**2**) are listed in Tables 2 and 3.

Compounds that give IR spectra virtually identical to that of $[(n\text{-}C_4H_9)_4N]_4[\{La(NO_3)_3\}_2(Mo_8O_{26})]$ can be obtained for Ce and Pr in a similar manner. The Ce and Pr compounds are most likely to have the same structure as $[(n\text{-}C_4H_9)_4N]_4[\{La(NO_3)_3\}_2(Mo_8O_{26})]$. Attempts to prepare Y, Nd, Gd, and Yb

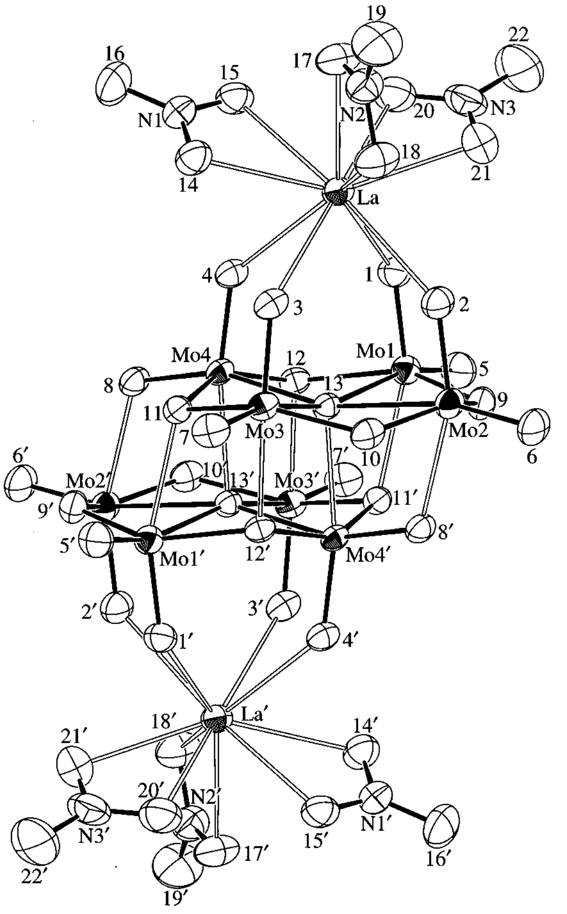

Figure 3. Perspective drawing of the $[\{La(NO_3)_3\}_2(Mo_8O_{26})]^{4-}$ anion. Displacement ellipsoids are scaled to enclose 30% probability levels. Metal and nitrogen atoms are labeled with their elemental symbols plus, in the cases of molybdenum and nitrogen, a numerical suffix. Oxygen atoms are labeled only with their suffixes. Atoms labeled with a prime (′) are related to those without a prime by the crystallographic inversion center at (0, 0, 0) in the unit cell.

analogs, however, failed. Reaction of $[(n\text{-}C_4H_9)_4N]_4[\alpha\text{-}Mo_8O_{26}]$ with nitrates of these metals always yielded $[(n\text{-}C_4H_9)_4N]_5[Ln(Mo_8O_{26})_2]$ compounds even if the molybdate and the rare earth metals were mixed in a 1:2 ratio.

Discussion

Both anions **1** and **2** contain the $[\beta\text{-}Mo_8O_{26}]^{4-}$ [9] unit as their main building block (see Figures 2 and 3). The atoms in those units are labeled in a manner that reflects the fact that the β-octamolybdate structure is composed of two Mo_4O_{13} subunits stacked together by relatively long Mo−O bonds.[9,10] The Mo−O bonds within those subunits are depicted by filled thick lines in both Figures 2 and 3. There are four such subunits in the structure of **1**, and they are named A, B, C, and D, respectively. The atoms in each subunit are given corresponding subscripts. Subunits A and B make up one complete β-Mo_8O_{26} unit and C and D another. The La atom in **1** is sandwiched between these two octamolybdate units and achieves 8-fold square-antiprismatic coordination. This mode of coordination of lanthanide and actinide elements is also found in $[M(W_5O_{18})_2]^{n-}$,[11] $[U(GeW_{11}O_{39})_2]^{12-}$,[12] and $[Ce(P_2W_{17}O_{61})_2]^{16-}$.[13] The average La−O bond length of 2.52 Å in **1** is comparable to that observed for $La(C_5H_7O_2)_3(H_2O)_2$ (2.50 Å),[14] where the La atom also assumes square-antiprismatic coordination.

In **2**, on the other hand, it is the β-octamolybdate moiety that is sandwiched between two $La(NO_3)_3$ units. Each NO_3^- group functions as a bidentate ligand here, and the La atom achieves 10-fold coordination. The coordination polyhedron of the La atom in this compound is very similar to that observed for the Th atom in $Na_6[Th(CO_3)_5]\cdot 12H_2O$.[15]

This difference of the La coordination modes in **1** and **2** gives us one explanation for the unsuccessful preparation of the heavier lanthanide and Y analogs of **2**. The shortest distances between the O atoms of two different β-Mo_8O_{26} units in **1** are no shorter than 3.078 Å. On the other hand, some of the O···O distances between different NO_3^- groups and between a NO_3^- group and the β-Mo_8O_{26} moiety in **2** are as short as 2.775 Å (O15···O20), 2.884 Å (O3···O14), and 2.906 Å (O4···O14). Heavy lanthanide elements and Y have much smaller ionic radii than La. Substituting the La atoms in **2** with these smaller atoms would result in still shorter O···O distances, and the repulsion would make the structure unfavorable.

The basic metal−oxygen framework of the Mo_8O_{26} moieties in the current complexes is the same as that of uncomplexed β-Mo_8O_{26}.[9,16] However, some significant differences can be noticed on a closer inspection (Table 3). In both **1** and **2**, La atoms are bound to the terminal oxygen atoms of the β-Mo_8O_{26} unit. The Mo−O bonds for these oxygens are significantly elongated compared to the corresponding bonds in uncomplexed

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β-Mo_8O_{26} as a direct consequence of coordination to the La atoms. The *trans* influence of those lengthened "terminal" Mo−O bonds is expected to make the Mo−O bonds *trans* to them shorter. Such bonds are in fact shortened in both structures. As is mentioned above, the $[\beta\text{-}Mo_8O_{26}]^{4-}$ structure can be considered to be composed of two Mo_4O_{13} subunits stacked together by relatively long Mo−O bonds. Since the β-Mo_8O_{26} unit is sandwiched between two La atoms in **2**, the *trans* influence just mentioned results in shortening of all these originally long eight Mo−O bonds that hold two Mo_4O_{13} units together. In **1**, on the other hand, the La atom is bound to only one side of the β-Mo_8O_{26} unit, and only four of those long Mo−O bonds are shortened.

Another significant structural difference between the β-Mo_8O_{26} units in the current complexes is observed for the 5-coordinated oxygen atoms (O13). Of the eight Mo atoms in the β-Mo_8O_{26} structure, two are not connected to the triply bridging oxygen atoms (O11 and O12). The bond length between this kind of Mo, labeled Mo2, and the 5-coordinated O13 oxygen is 2.464 Å in **2**. There are four Mo_4O_{13} subunits and hence four Mo2−O13 bonds in **1** ($Mo2_A$−$O13_A$, $Mo2_B$−$O13_B$, $Mo2_C$−$O13_C$, and $Mo2_D$−$O13_D$). Two of them, those in the subunits A and C which face the La atom (2.433 and 2.424 Å), are significantly shorter than the Mo2−O13 bonds of **2**. The other two that are in the subunits B and D which are not connected to the La atom directly (2.544 and 2.521 Å), on the other hand, are significantly longer than the Mo2−O13 bonds of **2**. It is interesting to note that while the Mo2−O13 bond lengths of **2** and the shorter two of **1** ($Mo2_A$−$O13_A$ and $Mo2_C$−$O13_C$) lie in the range observed for different salts of $[\beta\text{-}Mo_8O_{26}]^{4-}$, the lengths of the longer two Mo2−O13 bonds of **1** ($Mo2_B$−$O13_B$ and $Mo2_D$−$O13_D$) are well outside of this range. (The average Mo2−O13 length for 25 different $[\beta\text{-}Mo_8O_{26}]^{4-}$ structures is 2.453 Å, and the standard deviation is 0.029 Å.)[16]

Complexes **1** and **2** are also interesting from a synthetic point of view. Successful isolation of **1** and other $[Ln(Mo_8O_{26})_2]^{5-}$ complexes has proven that it is indeed possible to connect two β-Mo_8O_{26} units with rare earth metals. The result of preliminary ^{17}O NMR measurement suggests that **1** maintains its framework and does not dissociate in solution. The anion **2** and its analogs tell us that it is also possible to bind two lanthanide cations on opposite faces of β-Mo_8O_{26}. These findings imply that it may be feasible to synthesize larger polyoxometalates such as $[(Mo_8O_{26})Ln(Mo_8O_{26})Ln(Mo_8O_{26})]^{6-}$ by using β-Mo_8O_{26} as a building block and lanthanide metals as "glue". An attempt to synthesize such a polyoxometalate is in progress in our laboratory.

Acknowledgment. This work was supported in part by Grants-in-Aid for Scientific Research No. 08232276, 08874084, 09218256, and 60214136 from Monbusho (Ministry of Education, Science, and Culture of Japan). We thank Prof. Y. Ohashi of TIT for the use of the X-ray diffractometer.

Supporting Information Available: Experimental details of the preparations of $[(n\text{-}C_4H_9)_4N]_5[Ln(Mo_8O_{26})_2]$ (Ln = Ce, Nd, Gd, Yb) and $[(n\text{-}C_4H_9)_4N]_4[\{Ln(NO_3)_3\}_2(Mo_8O_{26})]$ (Ln = Ce, Pr) and attempted preparations of $[(n\text{-}C_4H_9)_4N]_4[\{Ln(NO_3)_3\}_2(Mo_8O_{26})]$ (Ln = Y, Nd, Gd, Yb), tables of crystal structure reports, complete atomic coordinates and anisotropic displacement parameters, and complete bond lengths and angles for non-hydrogen atoms, packing diagrams for $[(n\text{-}C_4H_9)_4N]_5[La(Mo_8O_{26})_2]\cdot CH_3CN$ and $[(n\text{-}C_4H_9)_4N]_4[\{La(NO_3)_3\}_2\text{-}(Mo_8O_{26})]\cdot 2CH_3CN$, and IR spectra of $[(n\text{-}C_4H_9)_4N]_5[Ln(Mo_8O_{26})_2]$ (Ln = Y, La, Ce, Pr, Nd, Gd, Yb) and $[(n\text{-}C_4H_9)_4N]_4[\{Ln(NO_3)_3\}_2(Mo_8O_{26})]$ (Ln = Ln, Ce, Pr) (51 pages). Ordering information is given on any current masthead page.

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