Influence of a Neutral Terminal Ligand on the Structure and Redox Potential of the Hexamolybdenum(12+) Cluster Ion with Mixed Capping Ligand

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Synopsis. A hexamolybdenum cluster complex of (n-$Bu_4N)_2[(Mo_6Br_7S)Cl_5(CH_3CN)]$ was synthesized, and its crystal structure was determined. The Mo–Mo distance (2.637(7) Å) is similar to that of $(Et_4N)_3[(Mo_6Br_7S)Cl_6]$. The oxidation potential is higher than that of $[(Mo_6Br_7S)Cl_6]^{3-}$ by 0.21 V. The shift of potential may be caused by change of net charge of the cluster anion.

Bivalent molybdenum gives a stable Mo_6 core, which is capped with eight μ_3-halo ligands and oxidized or reduced with difficulty.[1,2] We have shown that substitution of one sulfide or selenide ion for the capping halide decreases the oxidation potential by ca. 0.8 V.[3] Stable cluster complexes with oxidized Mo_6^{13+} core such as $(n\text{-}Bu_4N)_2[(Mo_6X_7Y)Cl_6]$ ($X_7Y = Cl_7S$, Cl_7Se, and Br_7S) were obtained in crystalline state. X-Ray diffraction studies with single crystals disclosed that the change in bond lengths Mo–Mo, Mo–capping halide/chalcogenide, and Mo–terminal halide is rather modest on the oxidation.[4]

The terminal halides are very labile, and their systematic change is difficult.[5] We have compared the redox potential, Mo_6^{12+}/Mo_6^{13+}, in dichloromethane and acetonitrile between $[(Mo_6X_7Y)Cl_6]^{n-}$ and $[(Mo_6X_7Y)Br_6]^{n-}$ ($X_7Y = Cl_7S$ and Cl_7Se).[4] A slight change (0.05 V) of the redox potential was found. Several complexes with $(Mo_6Cl_8)^{4+}$ core having mixed terminal ligands were synthesized mostly in disubstituted form,[6] including those with neutral terminal ligand, e.g. *trans*-$[(Mo_6Br_8)Br_4(H_2O)_2]$,[7] *cis*- and *trans*-$[(Mo_6Cl_8)Cl_4(Bu_3P)_2]$.[8] No information is available, however, as to their redox potential.

We have succeeded in synthesizing a mixed capping and mixed terminal ligand cluster complex with Mo_6^{12+} core, $(n\text{-}Bu_4N)_2[(Mo_6Br_7S)Cl_5(CH_3CN)]$, determined the crystal structure and the redox potential, and compared them with those of related complexes.

Experimental

Synthesis. A cluster complex with $(Mo_6Br_7S)^{3+}$ core was prepared and chromatographically separated with hexaaqua terminal ligand by the same method as for $(n\text{-}Bu_4N)_3[(Mo_6Br_7S)Cl_6]$,[3] The eluate from Dowex 50W-X2 column was treated with n-Bu_4NCl solution in 6 M HCl (1 M=1 mol dm^{-3}) to give orange precipitate, which was filtered off and dried in vacuo. The product (1 g) was dissolved in a mixture (3/10 v/v, 5 cm^3) of CH_3CN and CH_3OH, set aside for 30 min and passed through a column of Sephadex LH-20 (2.5 cmϕ, 30 cm long). Some orange bands and some red bands were observed. The column was eluted with the same solvent to collect the orange bands. Slow evaporation of the eluate gave two kinds of red crystal. One easily lost crystalline solvent, and the other did not. The latter was collected, washed with CH_3CN and dried in vacuo. Anal. Calcd for $C_{34}H_{75}N_3Br_7Cl_5Mo_6S$: C, 21.84; H, 4.04; N, 2.25%. Found: C, 21.81; H, 3.94; N, 2.36%. ^1H NMR (vs. TMS) in CD_3CN/ppm δ=0.99 (t, 24H), 1.38 (m, 16H), 1.62 (m, 16H), 1.98 (s, 3H), 3.11 (t, 16H). IR ν(CN) 2296 cm^{-1}.

X-Ray Structure Determination. Intensity data were collected on a Rigaku AFC7R four circle diffractometer at 23 °C by use of ω–2θ scan technique and graphite monochromated Mo $K\alpha$ radiation (λ=0.71069 Å). Structure was solved and refined using the teXsan® crystallographic software package on an IRIS Indigo computer. The cell dimensions were determined by a least squares calculation of 25 well-centered peaks in the 2θ range of 25° to 30°. The unit cell was tetragonal system, $I4/mmm$, a=14.389(1), c=14.152(2) Å, V=2930.2(5) Å^3. An empirical absorption correction DIFABS[9] was applied. The structure was solved with three dimensional Patterson maps and refined by the full matrix least-squares. All non-hydrogen atoms were located from the successive Fourier syntheses and included in the refinement. Because there is only one capping site in an asymmetric unit, it was refined as 1/8S+7/8Br. Terminal acetonitrile was on a 4-fold axis and disordered at two sites related by inversion center. Trial was made to refine the locations of N atom of acetonitrile and terminal Cl^- at separate positions, but not successful. Then this terminal position was refined as 1/2N+1/2Cl. The methyl carbon atom of n-butyl group was disordered at two sites concerned with mirror plane. All non-hydrogen atoms were refined anisotropically except methyl carbon atom of acetonitrile, C(2), which was refined isotropically. The scattering factors and anomalous scattering correction were taken from Ref. 10. Other crystal data and refinement parameters were as follows: d_{calcd}=2.12 g cm^{-3}, μ=63.2 cm^{-1}, crystal size 0.2×0.15×0.1 mm^3, reflection measured ($+h$, $+k$, $+l$, 2θ<60°) 2388, unique reflection ($I>3\sigma(I)$) 688, R0.035, R_w0.034.[11] Positional parameters are listed in Table 1.

Measurements. Absorption spectra were measured with a Hitachi 3400 spectrophotometer. ^1H NMR spectra were recorded on a JEOL GX-400 spectrometer. Electrochemical measurements were carried out with a Hokuto HA-501G potentiostat/galvanostat and HB-105 function generator. Working and counter electrodes were glassy carbon and platinum, respectively. The reference electrode was $Ag/AgNO_3$ (0.1 M) in acetonitrile. The supporting electrolyte was 0.1 M n-Bu_4NClO_4, and the sample concentration was 1×10^{-3} M. The ferrocene/ferricenium (Fc/Fc^+) couple was used as a standard.

Table 1. Positional Parameters and B_{eq} Values of $(n\text{-}Bu_4N)_2[(Mo_6Br_7S)Cl_5(CH_3CN)]$[a)]

Atom	x	y	z	B_{eq}
Mo(1)	0	0	0.1307(1)	2.38(4)
Mo(2)	0.13008(8)	0	0	2.41(5)
Br,S(1)	0.12821(5)	0.12821	0.12956(7)	3.24(3)
Cl,N(1)	0	0	0.3000(5)	3.1(2)
Cl(2)	0.3029(2)	0	0	3.6(2)
N(2)	0	1/2	1/4	3.3(4)
C(1)	0	0	0.359(4)	4(1)
C(2)	0	0	0.468(4)	8(1)[b)]
C(3)	0	0.4181(7)	0.3179(7)	4.1(5)
C(4)	0	0.3227(7)	0.2690(8)	5.5(7)
C(5)	0	0.249(1)	0.342(1)	7.7(9)
C(6)	0.117(2)	0.242(1)	0.378(1)	9(1)

a) $B_{eq}=(8\pi^2/3)\sum_i\sum_j U_{ij}a_i^* a_j^* \boldsymbol{a}_i\cdot\boldsymbol{a}_j$. b) Isotropic thermal parameter.

Results and Discussion

Synthesis. The chloride ion is a common terminal ligand for many kinds of stable hexamolybdenum clusters with mixed capping ligands.[3)] The yellow eluate from the Dowex 50W-X2 column containing $[(Mo_6Br_7S)(H_2O)_6]^{3+}$ was treated with n-Bu$_4$NCl in 6 M HCl, and submitted to gel permeation chromatography with a Sephadex LH-20 column and a mixed eluant CH_3CN–CH_3OH to give a mixture of complexes with different terminal ligands, hexachloro, pentachloro-monoacetonitrile, etc. Tetra-n-butylammonium salt of the complex with terminal pentachloro-monoacetonitrile, $(n\text{-}Bu_4N)_2[(Mo_6Br_7S)Cl_5(CH_3CN)]$ was obtained in crystalline state. Once formed it is stable and remains unchanged in acetonitrile solution. Tetra-n-butylammonium salts of other complexes with other terminal ligands including hexachloro lose crystalline acetonitrile easily.

X-Ray Structure. Figure 1 shows the structure of $[(Mo_6Br_7S)Cl_5(CH_3CN)]^{2-}$ with atomic numbering. The important bond distances are as follows: Mo(1)–Mo(2), 2.632(1); Mo(2)–Mo(2′), 2.647(2); Mo(1)–Br, S(1), 2.609(1); Mo(2)–Br,S(1), 2.6011(9); Mo(1)–Cl, N(1), 2.396(8); Mo(2)–Cl(2), 2.487(4); Cl,N(1)–C(1), 0.83(5); C(1)–C(2), 1.55(7) Å. The average Mo–Mo distance of this salt (2.637(7) Å) is quite similar to that of $(Et_4N)_3[(Mo_6Br_7S)Cl_6]$ (2.638(6) Å). The capping sulfide is completely disordered on eight capping sites. For $[(Mo_6Br_7S)Cl_5(CH_3CN)]^{2-}$ there are two possible isomers depending on whether the molybdenum atom connected to acetonitrile is also connected with sulfur or not. Because of the disorder it is unknown whether the crystal contains one particular isomer or a mixture of these two isomers.

Properties. The electronic absorption spectrum of the new complex in CH_3CN has an absorption peak at 303 nm with ε value 4370 M^{-1} cm^{-1} and two shoulder bands at 330 and 390 nm. This pattern remains unchanged for 24 h and is very similar to that of $(n\text{-}Bu_4N)_3[(Mo_6Br_7S)Cl_6]$ (a peak at 307 nm with ε value 4250 M^{-1} cm^{-1} and two shoulder bands at 330 and 390 nm) which also remains unchanged. The absorption bands in this region are due to charge transfer from the ligand to the metal ion. The change of one terminal ligand should give only a small influence on the electronic structure.

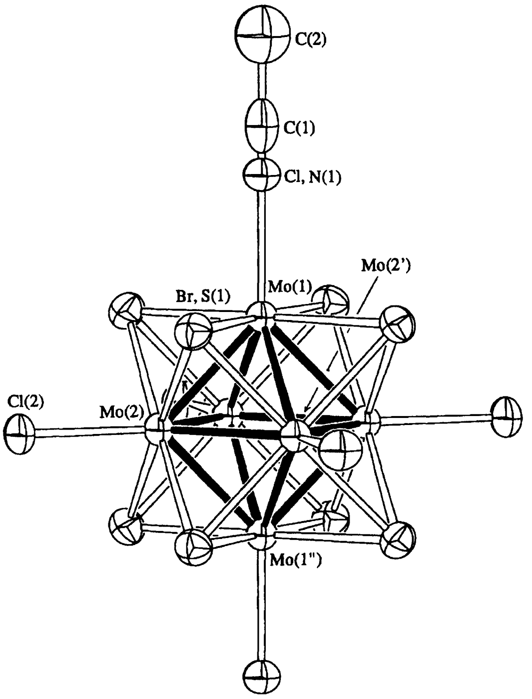

Fig. 1. Structure of the cluster anion $[(Mo_6Br_7S)Cl_5(CH_3CN)]^{2-}$. The C atoms of CH_3CN ligand at one of the disordered sites are omitted. The crystallographically equivalent atoms are marked as follows; ′ y, x, z; ″ x, y, $-z$.

The cyclic voltammogram of the new complex in CH_3CN gives a quasi-reversible oxidation wave with $E_{1/2}=0.35$ V vs. Fc/Fc$^+$, which corresponds to the oxidation Mo_6^{12+}/Mo_6^{13+}. This potential is more positive than that of $[(Mo_6Br_7S)Cl_6]^{3-}$ (0.14 V) by 0.21 V. When all the terminal chlorides of the cluster ions, $[(Mo_6Cl_7S)Cl_6]^{3-}$ and $[(Mo_6Cl_7Se)Cl_6]^{3-}$, were replaced by bromide, the positive shift of the redox potential was only 0.05 V.[3,4)] The substitution of one CH_3CN molecule for the terminal chloride gives much larger change than that of six bromide ions for the whole chloride. If acetonitrile acted as a π acceptor ligand, the CN vibration frequency should shift to lower field[12)] and the oxidation potential may shift higher. The CN vibration peak of $[(Mo_6Br_7S)Cl_5(CH_3CN)]^{2-}$ was observed at 2296 cm^{-1} a higher field than that of free acetonitrile (2253 cm^{-1}). This result suggests π back-donation is not the reason for the positive shift of oxidation potential. Thus we consider that the difference in electrode potential is due to the change of overall charge of the cluster anion.

We found that the substitution of one capping chalcogenide for the capping halides brought about a decrease of the oxidation potential by ca. 0.8 V.[3] We ascribed the reason to the introduction of a soft base, chalcogenide. However the change of overall electric charge should have been also partly responsible for the change in the redox potential.

Comparison of the Mo–Mo and Mo–capping ligand distances and electronic absorption spectra indicated very modest difference between the cluster anions having different terminal ligands. This fact tells that the perturbation from terminal ligands to the overall electronic state of the Mo_6 cluster through the given Mo atom is small. Nevertheless, the introduction of one CH_3CN molecule at the terminal site gives a very significant change of electrode potential.

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