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Solvent extraction syntheses and ^{1}H NMR spectra of incomplete cubane-type sulfur/oxygen-bridged molybdenum clusters with 8-quinolinolato ligands – Anomalous chemical shifts

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Abstract

Solvent extraction technique gave six incomplete cubane-type sulfur/oxygen-bridged molybdenum clusters with 8-quinolinol or 5-chloro-8-quinolinol ligands, $[Mo_3S_4(C_9H_5ClNO)_3(H_2O)_3]^+$, $[Mo_3S_4(C_9H_6NO)_3(H_2O)_3]^+$, $[Mo_3OS_3(C_9H_6NO)_3(H_2O)_3]^+$, $[Mo_3O_2S_2(C_9H_6NO)_3(H_2O)_3]^+$, $[Mo_3O_3S(C_9H_6NO)_3(H_2O)_3]^+$, and $[Mo_3O_4(C_9H_6NO)_3(H_2O)_3]^+$ from corresponding aqua clusters, $[Mo_3O_{4-n}S_n(H_2O)_9]^{4+}$ ($n = 0$–4). Hydrogen bonding of C–H···(μ-S) caused large downfield chemical shifts in the ^{1}H NMR spectra of the sulfur-bridged clusters.

Keywords: 8-Quinolinol; Solvent extraction; Molybdenum cluster; Sulfur-bridge; Hydrogen bond

8-Quinolinol (Hqn = C_9H_7NO) and its derivatives have been widely used as chelating and solvent extraction agents for the spectrophotometric determination of metal ions [1], however, application of the solvent extraction technique to the synthesis of metal complexes, to our knowledge, has not been reported yet.

Solvent extraction technique, i.e., shaking a mixture of an aqueous solution of $[Mo_3S_4(H_2O)_9]^{4+}$ and a dichloromethane solution of 5-chloro-8-quinolinol (HClqn = C_9H_6ClNO) after pH adjustment of the aqueous phase to ca. 1 gave crystalline product $[Mo_3S_4(Clqn)_3(H_2O)_3](pts) \cdot CH_2Cl_2 \cdot 3H_2O$ (**1′**).[1] Similar procedures gave $[Mo_3S_4(qn)_3(H_2O)_3](pts) \cdot 2H_2O$ (**1**), $[Mo_3OS_3(qn)_3(H_2O)_3]Cl \cdot 0.5CH_2Cl_2 \cdot H_2O$ (**2**), $[Mo_3O_2S_2(qn)_3(H_2O)_3]Cl \cdot 1.5H_2O$ (**3**), $[Mo_3O_3S(qn)_3(H_2O)_3]Cl \cdot H_2O$ (**4**), and $[Mo_3O_4(qn)_3(H_2O)_3]Cl \cdot$

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[1] To an aqueous solution of $[Mo_3S_4(H_2O)_9]^{4+}$ (3.67×10^{-3} M, 10 mL, 0.0367 mmol) in 0.5 M *p*-toluenesulfonic acid was added sodium hydroxide solution (0.1 M, ca. 30 mL) to adjust pH ca. 1. A mixture of the resultant solution and a dichloromethane solution of HClqn (3.59×10^{-2} M, 10 mL, 0.359 mmol) was vigorously shaken for 5 min and allowed to stand for 5 min in a separatory funnel. The aqueous solution turned gradually from the green to the light yellow, while the organic solution turned gradually from colorless to the intense red-brown: extraction was close to 100%. The organic phase was kept at room temperature overnight. Brown plate like crystals of **1′** deposited were filtered by suction and air-dried; yield, 43.2 mg (89%). Anal. Found (calcd. for $Mo_3Cl_5S_5O_{12}N_3C_{35}H_{36}$): C, 32.09 (31.94); H, 2.53 (2.76); N, 3.18 (3.19)%.

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$CH_2Cl_2 \cdot H_2O$ (**5**), which were obtained by the reaction of the corresponding aqua complexes, $[Mo_3O_{4-n}S_n(H_2O)_9]^{4+}$ ($n = 0$–4) [2] with Hqn in 0.5 M Hpts or 0.5 M HCl. Elemental analyses of these complexes agreed with these formulae: **1′**, **1**, **2**, **3**, **4**, **5**.[2]

Not only antibacterial and antifungal properties [3] of Hqn and its derivatives, but also the first report by Tang et al. [4] in 1987 on the electroluminescence of a bilayer device using $[Al(qn)_3]$ as electron transfer and luminance material has stimulated studies of a variety of complexes with the ligands [5]. This new synthetic method of solvent extraction using Hqn and its derivatives may give another route for the synthesis of complexes with the ligands. Although a number of mononuclear [6] or binuclear [7] molybdenum complexes containing the ligands have been reported, no report on tri- or more nuclear sulfur-bridged molybdenum clusters with the ligands has appeared except that the presence of $[Mo_3S_7(qn)_3]^+$ was suggested by FAB-MASS [8]. In addition, the synthesis of the complexes enabled us to find anomalous chemical shifts.

The structure of **1′** was determined by X-ray crystallography, and an ORTEP drawing of the cation of **1′** is shown in Fig. 1 together with the relevant bond distances. The cation of **1′** has neither crystallographic nor non-crystallographic symmetry elements. The nitrogen atom of each ligand coordinates to molybdenum atom so that the atom locates *trans* to μ_3-S.

^{1}H NMR spectra of the six kinds of clusters (**1′**, **1**, **2**, **3**, **4**, **5**) and two kinds of ligands (HClqn and Hqn) in DMSO-d_6 are shown in Fig. 2 together with their assignments [9]. The HH correlation spectra of **1′** and **1** support their assignments. Although there are three kinds of Clqn$^-$ ligands in **1′**, the ^{1}H NMR spectrum shows only one kind of signals. This phenomenon indicates that **1′** has a structure with a threefold rotation axis in DMSO solution as shown in the inset (together with names of protons) of Fig. 2, though the X-ray structure analysis shows that **1′** does not have the symmetry element. The ^{1}H NMR spectra of **1′** and **1** are very similar to each other except that H^e signal of **1′** appears as a doublet due to a coupling only to H^f, while H^e signal of **1** appears as doublet of doublets due to a coupling to H^d and H^f. Therefore, **1** also has a structure with a threefold rotation axis in DMSO solution as shown in the inset of Fig. 2. Each of the spectra of **4** and **5** also shows only one kind of qn$^-$ signal, which indicates that these clusters also have structures with threefold rotation axes in DMSO solution as shown in the inset of Fig. 2. In the solution, solvent DMSO molecules probably replace the coordinated water molecules of the clusters.

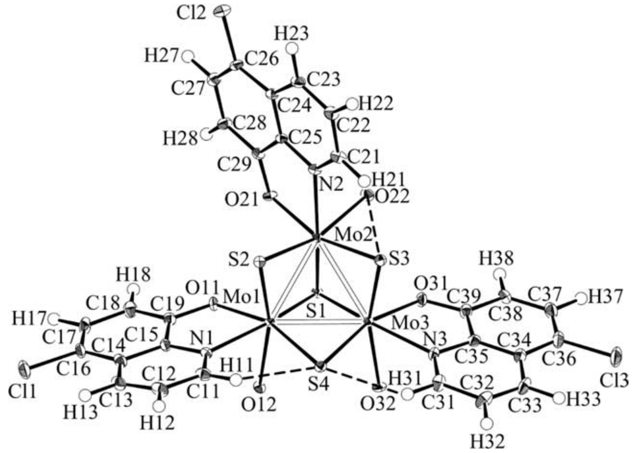

Fig. 1. The ORTEP drawing of the $[Mo_3S_4(Clqn)_3(H_2O)_3]^+$ (**1′**). Selected bond lengths (Å) and bond angles (°): Mo1–Mo2, 2.7403(5); Mo1–Mo3, 2.7869(7); Mo2–Mo3, 2.7720(5); Mo1–S1, 2.341(1); Mo2–S1, 2.353(1); Mo3–S1, 2.341(1); Mo1–S2, 2.287(1); Mo1–S4, 2.315(1); Mo2–S2, 2.298(1); Mo2–S3, 2.303(1); Mo3–S3, 2.280(1); Mo3–S4, 2.3234(9); Mo1–O11, 2.062(3); Mo2–O21, 2.083(3); Mo3–O31, 2.066(3); Mo1–N1, 2.225(3); Mo2–N2, 2.233(4); Mo3–N3, 2.228(3); Mo1–O12, 2.258(3); Mo2–O22, 2.207(3); Mo3–O32, 2.196(3) and Mo2–Mo1–Mo3, 60.20(1); Mo1–Mo2–Mo3, 60.74(2); Mo1–Mo3–Mo2, 59.07(1).

The assignments of the proton signals of **1′**, **1**, **4**, and **5** are rather straightforward and they are noted in Fig. 2. Their chemical shifts depend very much on the kinds of the bridging atoms, i.e., sulfur or oxygen. Among them, H^a signal in each spectrum is distinctly separated from other signals and the chemical shift dependence on the bridging atoms is very large. Therefore, we will mainly discuss the chemical shift dependence of H^a protons on the bridging atoms.

H^a signals of **1′** (10.29 ppm (3H, d))[3] and **1** (10.17 ppm (3H, d)) appear at very low magnetic fields compared to those of the free ligands, HClqn (8.95 ppm (1H, d)) and Hqn (8.85 ppm (1H, d)). A large upfiled chemical shift of H^a was observed when three μ_2-Ss of **1** were replaced by three μ_2-Os to give **4**. The direction of the chemical-shift-change is opposite to the direction deduced from the electronegativity change from sulfur to oxygen [10]. There is a report on the XPS spectra of the incomplete cubane type sulfur/oxygen-bridge clusters $[Mo_3O_{4-n}S_n(NCS)_9]^{5-}$ ($n = 0$–3) and $[Mo_3S_4(NCS)_8(H_2O)]^{4-}$, where the number of sulfurs in the $Mo_3O_{4-n}S_n^{4+}$ core increased, and the binding energies of Mo-3d$_{5/2}$ and Mo-3d$_{3/2}$ decreased. That the bridging sulfur attracts fewer electrons from the molybdenum atoms than the bridging oxygen explains the XPS spectra [11]. The explanation

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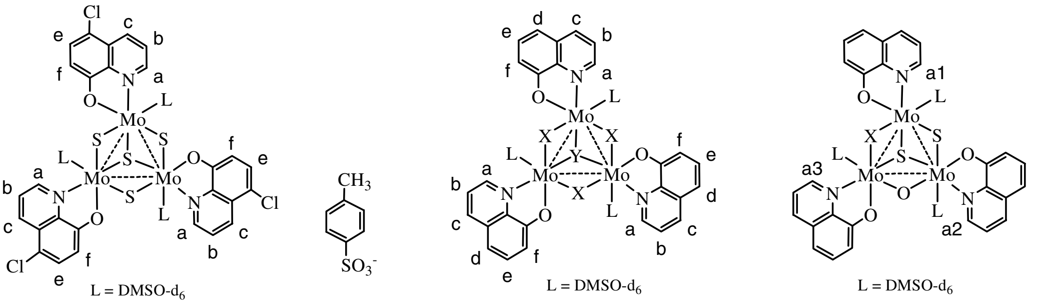
[2] All of the electronic spectra of the clusters in dichloromethane have strong peaks in the near ultraviolet region. The peak positions are: **1′**, 428 nm; **1**, 415 nm; **2**, 410 nm; **3**, 403 nm; **4**, 397 nm; and **5**, 384 nm. In strictly dehydrated dichloromethane, the peaks of the electronic spectra of **1′** and **1** show relatively large splits, and that of **2** shows a shoulder. Remaining clusters show no split.

[3] In addition to the splitting (the coupling constant $^3J_{HH} = 4.96$ Hz), a further splitting with a smaller coupling constant ($^4J_{HH} =$ ca. 1 Hz) was observed, but was not described here. Almost all the signals in Fig. 2 showed this kind of further splitting.



1' **pts⁻** **1** (X = S, Y = S) **4** (X = O, Y = S), **5** (X = O, Y = O) **2** (X = S), **3** (X = O)

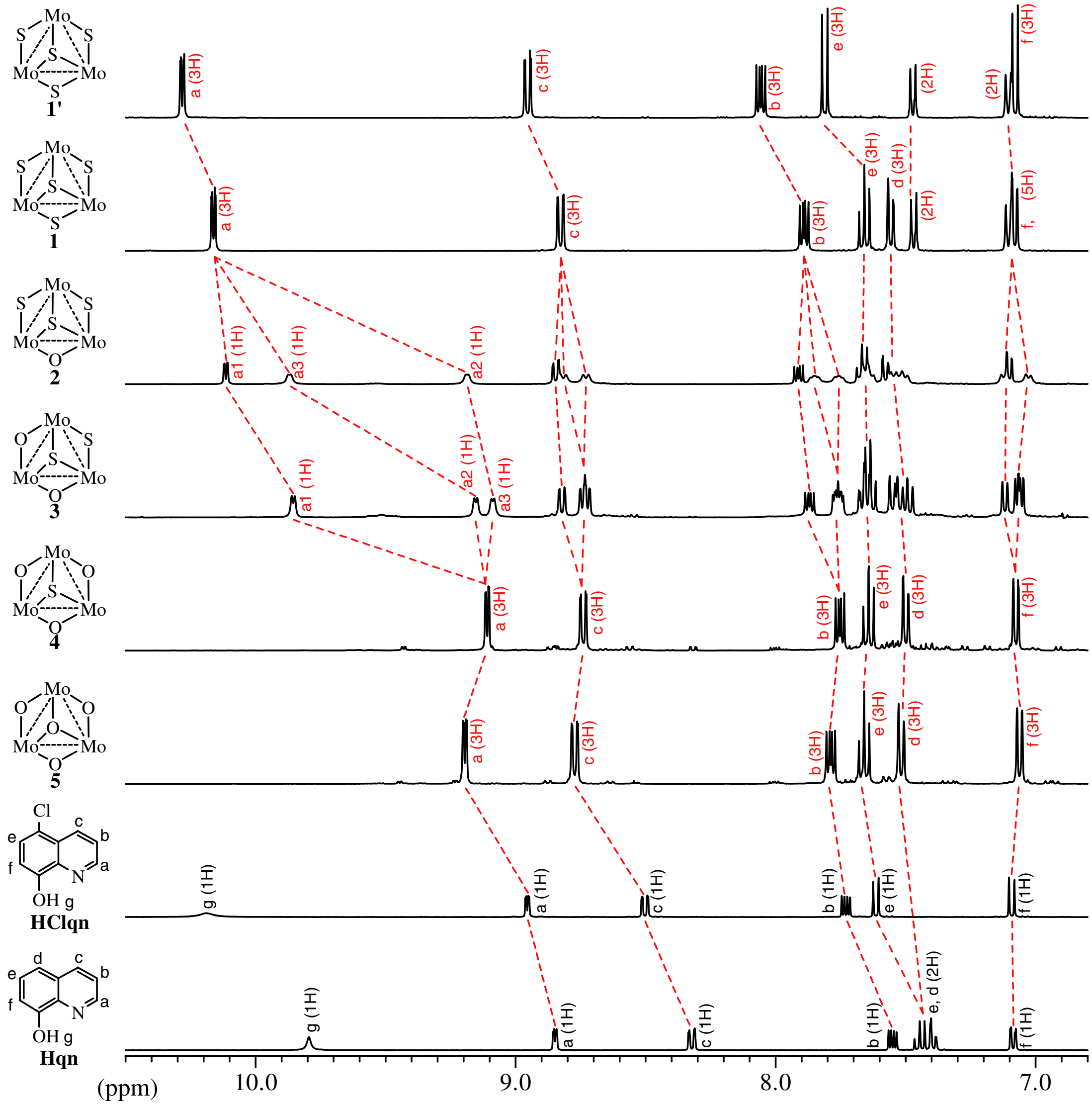


Fig. 2. ^{1}H NMR Spectra of **1′**, **1**, **2**, **3**, **4**, **5**, HClqn, and Hqn (20 °C, 400 MHz, DMSO-d_6, TMS = 0.0 ppm).

of the chemical shifts is as follows: the X-ray analysis of **1′** showed that the H^a–(μ-S) distances are in the range of 2.63–2.81 Å,[4] which is clearly shorter than the sum (3.05 Å) of the van der Waals radii of hydrogen (1.20 Å) and sulfur (1.85 Å) atoms, and the existence of the hydrogen bonds C–H$^a\cdots$(μ-S) [12] is deduced as shown in Fig. 1. The structure of **1** will be very close to that of **1′**, and hydrogen bonds C–H$^a\cdots$(μ-S) should exist. On the other hand, the X-ray analysis of

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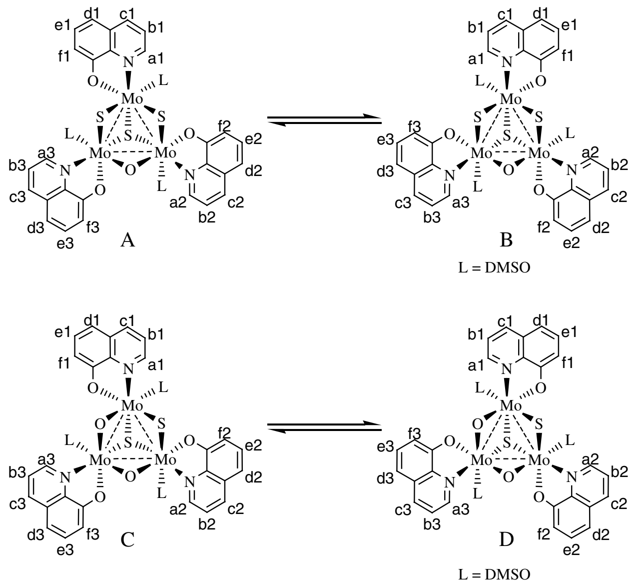
[4] **1′**: C11–S4, 3.409(4); C21–S3, 3.268(5); C31–S4, 3.396(4); H11–S4, 2.809(1); H21–S3, 2.626(1); H31–S4, 2.771(1) Å.



Scheme 1.

$[Mo_3O_4(qn)_3(H_2O)_3](pts) \cdot 2CH_2Cl_2 \cdot 4H_2O$ (**5′**) showed that the H^a–(μ-O) distances are in the range of 2.58–2.62 Å,[5] which is comparable to the sum (2.60 Å) of the van der Waals radii of hydrogen (1.20 Å) and oxygen (1.40 Å) atoms, and no definite C–$H^a \cdots$(μ-O) hydrogen bonds will exist. Therefore, the existence of the hydrogen bonding of C–$H^a \cdots$(μ-S) is the main factor in the downfield shift of H^a in **1′** and **1**.

On the basis of the above arguments, we assigned the ^1H NMR spectra of **2** (with two μ-Ss and a μ-O) and **3** (with a μ-S and two μ-Os), both having oxygen and sulfur bridges. Obviously, they have no threefold rotation axes contrary to the case of **1′**, **1**, **4**, and **5**, and we think that an isomerization occurs as shown in Scheme 1. As for **2**, the signal at 10.12 ppm (1H, d) is assigned to H^{a1}, since the proton belongs to the qn^- coordinated to the molybdenum atom bridged by two μ-Ss. The assignment of the remaining two signals, 9.87 ppm (1H, d) and 9.19 ppm (1H, d), to either H^{a2} or H^{a3} is rather complicated. If the complex takes the structure of A (the same as the inset in Fig. 2) in Scheme 1, H^{a2} is far from μ-S, and H^{a3} is close to μ-S, while if the complex takes the structure of B in Scheme 1, H^{a2} is close to μ-S, and H^{a2} is far from μ-S. Therefore, it is impossible to assign the two signals to either H^{a2} or H^{a3}. The following fact also supports the isomerization in Scheme: ^1H NMR spectra of **2** at higher temperatures show coalescence of the signals, while the signal at 10.12 ppm moves little. The assignment of **3** is similar to the case of **2**. The signal at 9.09 ppm (1H, d) is assigned to H^{a3}, since the proton belongs to the qn^- coordinated to the molybdenum atom bridged by two μ-Os, and the signal should show a chemical shift similar to that of H^a of **4**. The assignment of the remaining two signals, 9.86 ppm (1H, d) and 9.16 ppm (1H, d), to either H^{a1} or H^{a2} is impossible as discussed above due to the rotation (see Scheme 1C and D). ^1H NMR spectra of **3** at higher temperatures show coalescence of the signals, while the signal at 9.09 ppm moves little.

As for **4** (with μ_3-S) and **5** (with μ_3-O), the signal of H^a (**4**) appears at slightly higher magnetic field than that of H^a (**5**), which is explained by the electronegativity change from sulfur to oxygen. The chemical shift dependence of H^fs on the bridging atoms is different from that of H^as in **4** and **5**, which indicates that there are other minor factors influencing the chemical shifts of protons in the complexes discussed.

Acknowledgments

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Appendix A. Supplementary data

Crystallographic data of **1′** (CCDC No. 266069) and **5′** (CCDC No. 266068) and ^1H NMR spectra of **1′**, **1**, **2**, **3**, **4**, and **5**. Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.inoche.2005.05.021.

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