Inorganica Chimica Acta, 116 (1986) L25–L27

Structures and Properties of Cubane-type Clusters of $[Mo_4S_4(edta)_2]^{n-}$ (n = 2, 3, and 4) and $[Mo_4S_4(H_2O)_{12}]^{n+}$ (n = 4 and 5)

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(Received January 20, 1986)

We have recently reported the preparation, properties, and X-ray structure determination of a mixed-valence complex $[Mo_4S_4(edta)_2]^{3-}$ (**1**) (edta = ethylenediaminetetraacetate(4−)) in which a cubane-type $Mo_4S_4^{5+}$ core is contained and the reversible cyclic voltammogram shows up [1]. Several clusters with the cubane-type Mo_4S_4 core have been reported [2]. However, $[Mo_4S_4(\eta\text{-}C_5H_4Pr^i)_4]^{n+}$ (**2**) (n = 0, 1, and 2) is the only case so far found to form a set of consecutive oxidation numbers of molybdenum [3]. Furthermore, no discussion has appeared about the electronic spectral change accompanied by the change of oxidation state of molybdenum.

We describe here the preparations, X-ray structure determinations and electronic spectra of $[Mo_4S_4(edta)_2]^{n-}$ (n = 2 and 4), and the preparations and properties of cubane-type aqua ions $[Mo_4S_4(H_2O)_{12}]^{n+}$ (n = 4 and 5).

The oxidized form of **1**, $[Mo_4S_4(edta)_2]^{2-}$ (**3**), was prepared by the oxidation of **1** with bromine. A few drops of bromine were added to the green aqueous solution (10 ml) containing sodium salt of **1** (0.1 g), $Na_3[Mo_4S_4(edta)_2]\cdot 10H_2O$ (**1′**). Dark red crystals were deposited by the addition of sodium chloride (0.1 g) to the resultant solution. The crystals were analyzed to be $Na_2[Mo_4S_4(edta)_2]\cdot 6.5H_2O$ (**3′**). The reduced form of **1**, $[Mo_4S_4(edta)_2]^{4-}$ (**4**), was obtained by the reduction of **1** with $NaBH_4$ under dinitrogen atmosphere. 0.1 g of **1′** in 5 ml of water was transferred into a flask containing $NaBH_4$ (0.1 g). The addition of $MgCl_2$ (0.05 g) gave orange crystals, which were analyzed to be $Mg_2[Mo_4S_4(edta)_2]\cdot 22H_2O$ (**4′**). The clusters **3** and **4** can also be prepared by the controlled potential electrolyses of **1**; one electron per four molybdenum was transferred for each case.

X-ray crystal structure analyses* of **3′** and **4′** revealed that the structures of the three complex anions **1**, **3**, and **4** are very similar. Some notable differences, however, can be found if bond distances and volumes of the tetrahedra consisting of four Mo atoms are compared among these three complex anions (Table I). The mean values for the Mo–Mo bond lengths and volumes of Mo_4 and Mo_4S_4 decrease in the order of **3**, **1**, and **4**. The Mo–O(edta) bond lengths, on the contrary, increase in the order of **3**, **1**, and **4**; this agrees with the general tendency that the lower the oxidation state of the metal, the longer the metal–ligating atom distances. The Mo–S and Mo–N bond lengths show no distinct tendency

TABLE I. Volumes and Bond Distances of $[Mo_4S_4(edta)_2]^{n-}$

	$[Mo_4S_4(edta)_2]^{4-}$ (4)	$[Mo_4S_4(edta)_2]^{3-}$ (1)	$[Mo_4S_4(edta)_2]^{2-}$ (3)
Oxidation state of molybdenum	3.00	3.25	3.50
Volume (Å^3)			
Mo_4	2.540(5)	2.601(6)	2.655(5)
Mo_4S_4	10.78(2)	10.87(3)	10.97(2)
Octahedron[a]	15.08	15.03	14.59
Bond distance (Å)[b]			
Mo–Mo	2.783	2.807	2.826
Mo–S	2.355	2.356	2.355
Mo–N	2.28	2.29	2.27
Mo–O	2.18	2.14	2.09

[a] Mean value of four coordination octahedra around respective Mo atoms. [b] Mean value.

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*Crystal data: **3′**; monoclinic, space group $P2_1/n$, a = 25.171(4), b = 11.231(3), c = 13.417(3) Å, β = 98.28(1)°, Z = 4, $\max_{2\theta}$ = 50°, number of reflections used ($F_o^2 \geqslant 3\sigma(F_o^2)$) = 4532, R = 0.046. **4′**; monoclinic, space group $P2_1/m$, a = 14.358(6), b = 13.680(6), c = 12.990(5) Å, β = 96.56(2)°, Z = 2, $\max_{2\theta}$ = 50°, number of reflections used ($F_o^2 \geqslant 3\sigma(F_o^2)$) = 3152, R = 0.056. Intensity data were collected and structures were solved for both crystals as stated in ref. 1. No crystallographically imposed symmetry exists in **3**. A mirror plane passes through the anion **4** and introduce disorder in the ethylenediamine moiety of edta^{4-} in **4**.

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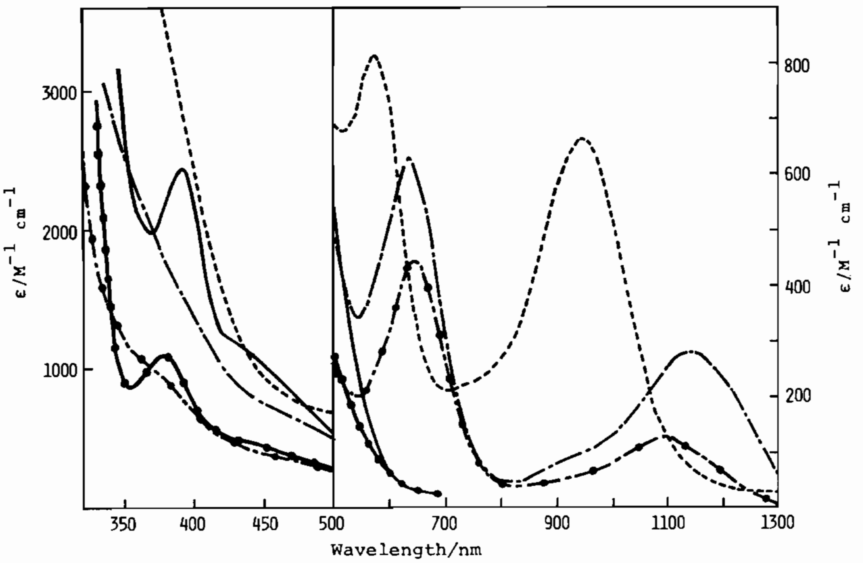

Fig. 1. Electronic spectra (ϵ values are per tetramer): $[Mo_4S_4(edta)_2]^{4-}$ in water, ——; $[Mo_4S_4(edta)_2]^{3-}$ in water, – - –; $[Mo_4S_4(edta)_2]^{2-}$ in water, - - -; $[Mo_4S_4(H_2O)_{12}]^{4+}$ in 2 M HPTS, –●–; $[Mo_4S_4(H_2O)_{12}]^{5+}$ in 2 M HPTS, –●– - –●–.

of becoming shorter or longer in the order of **3**, **1**, and **4**.

Although the Mo–Mo bond lengths range from 2.741 to 2.872 Å in **3** and 2.769 to 2.791 Å in **4**, the volumes* of coordination octahedra around respective Mo atoms in **3** are almost equal within the limit of e.s.d.s as in the case of **1** [1], and it is also the case with **4**; therefore the Mo_4 tetramers can approximately be regarded as belonging to T_d symmetry. Under this symmetry six bonding orbitals, $(a_1 + e + t_1)$ [4] are filled with twelve 4d-electrons from four Mo(III) cations in **4**, and removal of one or two electrons from the bonding orbitals in **4** will afford **1** and **3**, respectively, resulting in weaker, accordingly longer Mo–Mo bond length and larger Mo_4 volume. Full occupation of Mo_4 bonding orbitals with 12 electrons as in the case of **4** gives rise to the loss of absorption peaks of electronic spectra in visible and near infrared regions, while **1** and **3** have ones in these regions (Fig. 1); energy difference between bonding and antibonding orbitals seems to be relatively large. The volume of Mo_4 in **2** decreases as the oxidation number of molybdenum increases, being in remarkable contrast to the present case of $[Mo_4S_4(edta)_2]^{n-}$. This can be explained by the presence of back-bonding in the former and its lack in the latter [5].

A solution of a cubane-type aqua ion, $[Mo_4S_4(H_2O)_{12}]^{5+}$ (**5**) was prepared by the aquation of **1**. Sodium salt of **1** (0.2 g) was dissolved in concentrated HCl (10 ml) and allowed to stand for a couple of days. After dilution the solution was absorbed on a Dowex 50W-X2 cation exchanger, which was washed with 1 M HCl. A green eluent was obtained by the use of 2 M HCl. The presence of cubane-type Mo_4S_4 core has been confirmed by the reproduction of **1** from the solution **5** and $edta^{4-}$. An HPTS (p-toluenesulfonic acid) solution of the ion was obtained as described elesewhere [6].

The cyclic voltammogram of **5** (17 mM in 2 M HPTS) at a glassy carbon electrode *vs.* SCE and a scan rate of 0.1 V/s shows two quasi-reversible, one-electron waves ($E_{pc,1} = 0.621$ V, $E_{pa,1} = 0.690$; $E_{pc,2} = -0.045$, $E_{pa,2} = 0.012$). E_p values are shifted toward the positive as compared to the corresponding ones of **1** [1]. Controlled potential electrolysis of **5** at −0.12 V gives the reduced form of **5**, $[Mo_4S_4(H_2O)_{12}]^{4+}$ (**6**), whereas oxidation of **5** at 0.8 V produces a mixture of several oxidation products including $[Mo_3S_4(H_2O)_9]^{4+}$ aqua ion [7]; $[Mo_4S_4(H_2O)_{12}]^{6+}$ seems unstable. The electronic spectra of **5** ($\lambda_{max} = 643$ nm, $\epsilon = 445$ M^{-1} cm^{-1} per tetramer; 1100 nm, $\epsilon = 128$) and **6** (378 nm, $\epsilon = 1090$) are included in Fig. 1. The result of coulometric measurement of **5** (e/Mo = 1/4) and the similarity of the spectra (**1** and **5**; **4** and **6**) support that the average oxidation states of molybdenum in **5** and **6** are 3.25 and 3.00, respectively.

Contradictory reports have appeared on the spectra of cubane-type aqua ions with Mo_4S_4 core from the two groups; $[Mo_4S_4(H_2O)_{12}]^{5+}$ by Sykes *et al.* [2c] and $[Mo_4S_4(H_2O)_{12}]^{6+}$ by Cotton *et al.* [2d]. Electronic spectra of these complexes can be seen as nearly identical. It now becomes clear that the spectrum which shows absorption peaks at 643 nm is originated from $[Mo_4S_4(H_2O)_{12}]^{5+}$ **.

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*3′: Mo1, 14.61(9) Å^3; Mo2, 14.66(8) Å^3; Mo3, 14.62(8) Å^3; Mo4, 14.47(9) Å^3. 4′: Mo1, 14.94(10) Å^3; Mo2, 15.09(9) Å^3; Mo3, 15.12(8) Å^3.

We have found that the coordination of NCS^- ions to **5 gives $[Mo_4S_4(NCS)_{12}]^{6-}$, air oxidation being accompanied (unpublished results).

Supplementary Material

Tables of atomic coordinates, thermal parameters, bond distances, bond angles, and ORTEP figures for **3**′ and **4**′ and the cyclic voltammogram of **5**.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (No. 59470039) from the Ministry of Education, Science and Culture.

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