A trinuclear Mo-Fe-Mo cluster compound $[Et_4N]\{[Me_2dtcMoO(\mu\text{-}S)_2]_2Fe\}$ containing dialkyldithiocarbamate ligand

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A trinuclear linear Mo-Fe-Mo dialkyldithiocarbamate complex $[Et_4N]\{[Me_2dtcMoO(\mu\text{-}S)_2]_2Fe\}$ has been obtained and structurally characterized, which contains two $Me_2dtcMoO(\mu\text{-}S)_2$ units coordinated to a central tetrahedral Fe atom. A comparison of the structural parameters indicates the metal oxidation states of $2Mo^{(V)} + Fe^{(III)}$. The ^1H NMR shows chemical shifts of Me_2dtc ligands at δ 10.14 and δ 9.40 with the intensity ratio of 1:1. The cyclic voltammogram displays a reversible couple at −1.41 V/−1.36 V responsible for 1-/2- anions of the complex and an irreversible oxidation at 0.5 V, which seems to show the apparent lack of stability for its neutral species $(Me_2dtcMoOS_2)_2Fe$.

Keywords Iron complex, molybdenum complex, dialkyldithiocarbamate, crystal structure, spectrum, electrochemistry

Introduction

Over the last two decades, the inorganic modeling of the structure and function of active centers of metalloproteins has been of an increased interest. Much effort has been focused on the Mo/Fe/S cluster contained in FeMo-cofactor of nitrogenase. Trinuclear Mo-Fe-Mo cluster $[(MoS_4)_2Fe]^{3-}$ with $Mo(\mu\text{-}S)_2Fe$ structural units was one of the early modeling compounds and was intensively studied[1] in order to mimic the spectral properties of this natural active center. Up to now, a trinuclear linear Mo/Fe/S cluster family has appeared to contain Mo-Fe-Mo,[1,2] Fe-Mo-Fe,[3] and Fe-Fe-Mo[4] complexes, of which $Mo(\mu\text{-}S)_2Fe(\mu\text{-}S)_2Mo$ complexes have become an important type. However, none of these linear complexes contains dialkyldithiocarbamate (R_2dtc) ligand though a tetranuclear Mo-Fe-Fe-Mo cluster[5] and a series of Mo/Fe/S cubane-like clusters[6] have been reported to contain R_2dtc ligands. This paper reports a novel member of trinuclear Mo-Fe-Mo cluster family, which is the first trinuclear linear Mo-Fe-S cluster containing R_2dtc ligand.

Experimental

All manipulations were carried out under dinitrogen atmosphere. The solvents were dried with molecular sieves and degassed prior to use. Ferrous chloride and Et_4NCl are commercially available without further purification. Compound $(NH_4)_2MoO_2S_2$ was obtained by literature method.[7] Me_2dtcNa was synthesized by the reaction of Me_2NH with NaOH and CS_2 in water.

Preparation of $[Et_4N]\{[Me_2dtcMoO(\mu\text{-}S)_2]_2Fe\}$ (1)

A solution of $FeCl_2$ (0.76 g, 6 mmol), Me_2dtcNa (1.71 g, 12 mmol) and Et_4NCl (0.33 g, 2 mmol) in 16 mL of DMF was stirred vigorously for one hour, then $(NH_4)_2MoS_2O_2$ (0.46 g, 2 mmol) was added. The solution was stirred for 34 h. After filtration, 12 mL of MeCN was added to the filtrate, and the solution was allowed to stand at 4℃ for two days. After filtration to remove precipitates, 10 mL of acetonitrile was added to the solution and the solution was allowed to stand for several days. Black crystals were collected, washed with ace-

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tonitrile, and dried *in vacuo*, affording 0.34 g (yield 43.7%) of product. ν_{max}(KBr): 1538(C-N, dtc), 933 (Mo = O), 436(Mo-μ_2S), 322, 375(Mo-Sdtc) cm^{-1}. δ_H (DMSO-d_6); 1.16 (CH_3, Et_4N), 3.14 (CH_2, Et_4N), 9.40, 10.14(CH_3, Me_2dtc). Anal. $C_{14}H_{32}FeMo_2N_3O_2S_8$. Calcd: C, 21.56; H, 4.11; Fe, 7.19; Mo, 24.65; N, 5.39. Found: C, 21.24; H, 3.99; Fe, 6.88; Mo, 24.04; N, 5.15.

Crystal structure determination

A black prism crystal of the title complex with approximate dimensions of 0.60 × 0.35 × 0.30 mm was coated with epoxy resin and mounted on a glass fibre. Data collection was performed with Mo K_α radiation (λ = 0.071073 nm) on an Enraf Nonium CAD_4 diffractometer at 20℃ using ω-2θ scan mode with the maximum 2θ of 50°. A total of 5946 reflections were collected and the corrections of Lorentz polarization and empirical absorption were applied to the data. Summary of the crystal data, data collection and structure refinement of (Et_4N)-[($Me_2dtcMoOS_2$)$_2$Fe] is listed in Table 1.

Table 1 Summary of crystal data, data collection and structure refinement of (Et_4N)[($Me_2dtcMoOS_2$)$_2$Fe]

Formula	$C_{20}H_{46}FeMo_2N_4O_2S_8$
Mr	878.85
Color and habit	black prism
Crystal size/mm	0.60 × 0.35 × 0.30
System	monoclinic
Space group	*C*2/c
a/nm	1.8382(7)
b/nm	1.9782(7)
c/nm	2.0296(8)
β/°	116.87(3)
Z	8
D_c/g·cm^{-3}	1.77
μ/cm^{-1}	16.8
F(000)	3128
Total reflections	5946
Observed reflections	1808 ($I > 3.0\sigma(I)$)
R^a	0.0888
R_w^b	0.0929
No. of variables	266
S (goodness of fit)	1.00
Residual peak/e·nm^{-3}	500 to − 170

$^a R = \sum|F_o - F_c| / \sum|F_o|$

$^b R_w = [(\sum w(F_o - F_c)^2 / \sum wF_o^2)]^{1/2}$

The structure of complex **1** was solved by direct methods with MULTAN-83 program followed by successive difference Fourier syntheses. The structure was refined in full-matrix least-squares method using anisotropic thermal parameters for all the non-hydrogen atoms. All hydrogen atoms were geometrically located and included in the structure factor calculations, but their positions were not refined. The final cycle of refinement included 266 variable parameters for 1536 reflections with $I > 3.0\sigma(I)$ and converged to R = 0.089 and R_W = 0.093. The highest peak in the final difference Fourier map had a maximum height of 500 e/nm^3, and the minimum negative peak of − 170 e/nm^3. All calculations were performed on a COMPAQ computer using MolEN/PC program.[8]

Other physical measurement

Infrared spectrum was recorded on a Bio-Rad FTS-40 model spectrophotometer. ^{1}H NMR spectrum was recorded on a Bruker-Am 500 spectrometer with TMS as standard. Electrochemical measurement was performed in cyclic voltammetric mode on a CV-1B cyclic voltammeter in DMF solution with an SCE reference electrode, Pt plate working electrode and Pt auxiliary electrode. The supporting electrolyte was Et_4NBF_4.

Result and discussion

Synthesis

Complex **1** was obtained from an assembly system composed of $MoO_2S_2^{2-}$, $FeCl_2$, Me_2dtc^- and Et_4N^+. The formation of **1** passes through coordination of $MoO_2S_2^{2-}$ and redox of the metal centers. In the reaction $MoO_2S_2^{2-}$ acts as a bidentate ligand chelating to the Fe center, accompanying with the reduction of $MoO_2S_2^{2-}$. A series of reactions of MoS_4^{2-} and Fe^{2+} with reducing agents (R_2dtc^-, $ROCSS^-$, PhS^- *etc.*) have resulted in the trinuclear cluster $[(MoS_4)_2Fe]^{3-}$,[1] such as the following reaction reported by Newton.[1b]

$$2Fe(C_5H_{10}dtc)_2 + 2MoS_4^{2-} \longrightarrow [(MoS_4)_2Fe]^{3-} + Fe(C_5H_{10}dtc)_3 + C_5H_{10}dtc^-$$

It is believed that a similar trianion [(MoO_2S_2)$_2$-

$Fe]^{3-}$ would become a possible intermediate in our reaction system and then undergoes a replacement of Me_2dtc group leading to the production of the title complex as shown in the following mechanism:

$$2Me_2dtc^- + FeCl_2 \longrightarrow Fe(Me_2dtc)_2$$

$$2MoO_2S_2^{2-} + 2Fe(Me_2dtc)_2 \longrightarrow [O_2Mo(S_2)Fe(S_2)MoO_2]^{3-} + Fe(Me_2dtc)_3 + Me_2dtc^-$$

$$[O_2Mo(S_2)Fe(S_2)MoO_2]^{3-} \xrightarrow{2Me_2dtc^-} [(Me_2N{=}C(S_2)Mo(O)(S_2)Fe(S_2)Mo(O)(S_2)C{=}NMe_2)]^-$$

Though the Mo = O bonding is strong in $Mo^{(V)}$ complex, the example in which the terminal oxygen atom is substituted by nucleophilic sulfur ligand has been reported and discussed.[9]

Structure

The structure of compound **1** is composed of a monoanion shown in Fig. 1 and one $[Et_4N]^+$ cation. Selected bond distances and angles are listed in Table 2. A tetrahedrally coordinated Fe atom is bounded to two $[(Me_2dtc)MoOS_2]^{2-}$ units through two bridging sulfido-groups, forming a nearly linear trinuclear backbone with the Fe-Mo-Fe bond angle of 168.6°. The Fe—S bond distances range from 0.2183(6) to 0.2233 (8) nm with the mean value of 0.2217(10) nm, which is consistent with the $Fe^{(III)}$—S distances in compounds $[Me_4N]_3\{[SCH_2CH_2S)MoS_3]_2Fe\}$ (0.2221(6) nm)[2a] and $[Et_4N]_3\{[(SCH_2CH_2S)MoS_3]_2Fe\}$ (0.2225 nm)[2b]

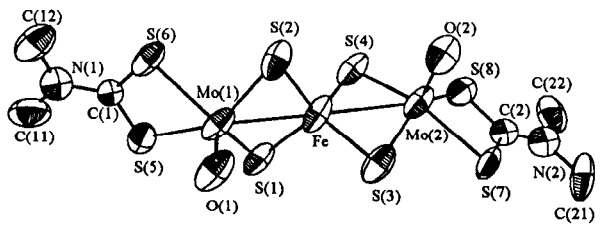

Fig. 1 Structure and labeling of $\{[Me_2dtcMoO(\mu\text{-}S)_2]_2\text{-}Fe\}^{3-}$. Thermal ellipsoids as drawn by ORTEP represent the 30% probability surfaces.

Table 2 Selected bond distances (nm) and angles (°)

Distance			
Mo(1)—Fe	0.2697(4)	Mo(2)-Fe	0.2691(4)
Mo(1)—S(1)	0.2316(6)	Mo(2)—S(3)	0.2305(7)
Mo(1)—S(2)	0.2299(9)	Mo(2)—S(4)	0.2297(9)
Mo(1)—S(5)	0.246(1)	Mo(2)—S(7)	0.2449(7)
Mo(1)—S(6)	0.2472(7)	Mo(2)—S(8)	0.2442(7)
Mo(1)—O(1)	0.170(2)	Mo(2)—O(2)	0.165(2)
Fe—S(1)	0.2232(9)	Fe—S(2)	0.2233(8)
Fe—S(3)	0.222(1)	C(1)—N(1)	0.144(3)
Fe—S(4)	0.2183(6)	C(2)—N(2)	0.126(3)
Angle			
Mo(1)-Fe-Mo(2)	168.6(2)		
S(1)-Mo(1)-S(2)	102.8(3)	S(5)-Mo(1)-S(6)	70.3(3)
S(1)-Mo(1)-S(6)	140.4(3)	S(1)-Mo(1)-S(5)	81.1(3)
S(2)-Mo(1)-S(6)	85.0(3)	S(2)-Mo(1)-S(5)	141.9(3)
S(1)-Mo(1)-O(1)	108.5(6)	S(2)-Mo(1)-O(1)	107.2(8)
S(5)-Mo(1)-O(1)	107.2(8)	S(6)-Mo(1)-O(1)	105.9(6)
S(3)-Mo(2)-S(4)	101.7(3)	S(7)-Mo(2)-S(8)	69.9(2)
S(3)-Mo(2)-S(7)	85.1(2)	S(3)-Mo(2)-S(8)	141.6(3)
S(4)-Mo(2)-S(7)	140.5(3)	S(4)-Mo(2)-S(8)	82.2(3)
S(3)-Mo(2)-O(2)	106.6(5)	S(4)-Mo(2)-O(2)	109.5(7)
S(7)-Mo(2)-O(2)	105.4(7)	S(8)-Mo(2)-O(2)	107.9(5)
S(1)-Fe-S(2)	107.8(3)	S(1)-Fe-S(3)	110.2(3)
S(1)-Fe-S(4)	106.1(3)	S(2)-Fe-S(3)	114.8(3)
S(2)-Fe-S(4)	109.5(3)	S(3)-Fe-S(4)	108.2(3)

indicating that the Fe oxidation state in **1** is the same as those of the complexes containing a tetrahedral FeS_4 unit. Both the five-coordinate Mo sites possess distorted tetragonal pyramid coordination geometry with S(1)-

S(2)-S(5)-S(6) and S(3)-S(4)-S(7)-S(8) based planes for Mo(1) and Mo(2), respectively. The Mo—S bond distances can be divided into two sets one of which is Mo—S_{core} (0.2297(9)—0.2316(6) nm) and the other Mo—S_{dtc} (0.2442(7)—0.2472(7) nm). The Mo coordination geometry is identical to that found in the binuclear $Mo^{(V)}$ complexes, $Mo_2O_2(\mu\text{-}S)_2(dtc)_2$[10] and $Mo_2O_2(\mu\text{-}S)_2(C_4H_8dtc)_2$,[11] and the corresponding bond lengths are similar to each other in these complexes (Table 3), indicating that Mo^{5+} and Fe^{3+} are reasonable oxidation states for **1**. Electron transfer from $Fe^{(II)}$ to $Mo^{(VI)}$ through the double sulfido bridges gives rise to the reduction of $MoO_2S_2^{2-}$ moiety with the formation of the complex and explains the variation of metal oxidation state. The mean Mo—Fe bond length is 0.2695 nm, showing significant metal-metal interaction between Mo and Fe atoms. Interestingly, distinguishable structural features were observed between the two Mo atoms. For example, Mo(1)—S_{dtc} and Mo(1)—O bond distances are longer than Mo(2)—S_{dtc} and Mo(2)—O by 0.002 nm and 0.005 nm, respectively, and C(1)—N(1) (0.144(3) nm) is obviously longer than C(2)—N(2) (0.126(3) nm). This may lead to some differences in the spectral features for the two Mo atoms.

Table 3 Comparison of bond distances (nm) and angles (°) for related Mo/Fe/S complexes

Compound	Mo—S_{core}	Mo—S_{dtc}	Fe—S_{core}	Mo = O	Mo-Fe-Mo	Ref.
$[(Me_2dtcMoOS_2)_2Fe]^{3-}$	0.2304(8)	0.246(1)	0.2217(10)	0.168(2)	168.6(2)	*a*
$\{[(C_2H_4S_2)MoS_3]_2Fe\}^{3-}$	0.232(1)		0.2221(6)		155.7(2)	[2a]
$\{[Mo_2O_2S_2(S_2)]_2Fe\}^{3-}$	0.231(1)		0.225(1)	0.168(2)	160.3(2)	[2b]
$Mo_2O_2S_2(dtc)_2$	0.2325(1)	0.2461(1)		0.1677(3)		[10]
$Mo_2O_2S_2(C_4H_8dtc)_2$	0.2318(3)	0.2464(2)		0.1660(5)		[11]

[a] This work.

Infrared spectra

The R_2dtc ligands have very characteristic absorption in the vicinity of 1500 cm^{-1} corresponding to the stretching vibration of C—N.[12] The C—N stretching vibration of compound **1** was observed at 1538 cm^{-1} showing considerable double-bond character. This is consistent with the short C—N bond distance (< 0.140 nm) in the compound. The vibrations of Mo = O and Mo—μ_2S occur at 933 cm^{-1} and 436 cm^{-1}, respectively. The absorptions at 322 cm^{-1} and 375 cm^{-1} are attributed to the Mo—S_{dtc} vibration.[12]

^{1}H NMR *spectrum*

The ^{1}H NMR spectrum of **1** in DMSO-d_6 is depicted in Fig. 2. It is noticed that Me_2dtc ligand coordinating to the metal atom forms a $MS_2C = NMe_2$ conjugation system through which the paramagnetic metal site affects the proton chemical shift of the Me_2dtc group by the contact mechanism. This has been observed in some Mo[6] and V[13] complexes, which contain paramagnetic metal center linking to Me_2dtc group. In the spectrum of **1**, two peaks at δ 10.14 and δ 9.40 with the intensity ratio of 1:1 can be assigned to the Me_2dtc groups that coordinate to the $Mo^{(V)}$ sites, showing obviously downfield shift relative to the corresponding signal of Me_2dtcNa (δ 3.5, DMSO-d_6). The two peaks with i-

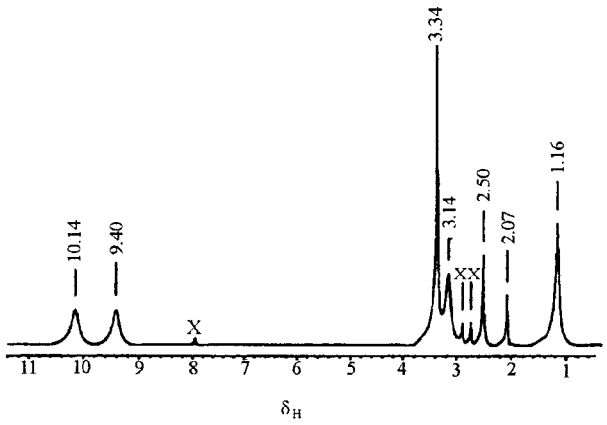

Fig. 2 ^{1}H NMR spectrum of $[Et_4N]\{[Me_2dtcMoO(\mu\text{-}S)_2]_2Fe\}$ in DMSO-d_6 solution at room temperature. δ_H: 1.16(CH_3, Et_4N), 2.07(CH_3CN), 2.50(DMSO), 3.14(CH_2, Et_4N), 3.34(H_2O), 9.40, 10.14(Me_2dtc). The mark X represents DMF (HCO, 7.98; CH_3, 2.73, 2.89).

dentical intensity imply that there are two types of distinguishable CH_3 groups in the complex. This can be considered to stem from either the two Mo sites having aforementioned significantly different structural parameters or the C = N double bond restricting free rotation around the bond and making the two CH_3 groups of the same Mo site different from each other in ^1H NMR spectrum. However, the latter seems unlikely since the environments of the two methyl groups are almost identical. Therefore, it is reasonable to assign the two peaks as the contribution of Me_2dtc^- groups of Mo(1) and Mo(2), respectively.

Electrochemical study

The cyclic voltammogram diagram of **1** in DMF displays irreversible oxidation at 0.5 V and a reversible redox process at − 1.41 V/ − 1.36 V as shown in Fig. 3. Interestingly, this electrochemical behavior has somewhat similarity to that of $[(MoS_4)_2Fe]^{3-}$[1a,b] which shows its irreversible oxidation at − 0.10 V and quasireversible redox at − 1.798 V/ − 1.688 V in CH_3CN. Similarly,

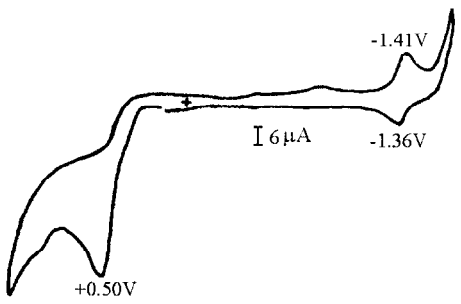

Fig. 3 Cyclic voltammogram for complex **1**, 0.002 mol/L in DMF with scan speed of 100 mV/s.

we tentatively assign the latter couple (− 1.41 V/ − 1.36 V) to the reduction of $[(Me_2dtcMoOS_2)_2Fe]^-$. It is shown that the $Mo(\mu\text{-}S)_2Fe(\mu\text{-}S)_2Mo$ backbone has its ability to delocalize charge by accepting electron in unoccupied Mo-d orbitals. Such reductions have also been reported for $[M'\text{-}(MS_4)_2]^{2-}$ complexes[14] (M' = Ni, Pd, Pt, Co; M = Mo, W). However, the irreversibility of the oxidation at 0.5 V seems to show the apparent lack of stability for its neutral species ($Me_2dtcMoOS_2)_2Fe$.

$$[(Me_2dtcMoOS_2)_2Fe]^{2-} \underset{-1.41\ V}{\overset{-1.36\ V}{\rightleftharpoons}} [(Me_2dtcMoOS_2)_2Fe]^{1-} \xrightarrow{+0.50\ V} (Me_2dtcMoOS_2)_2Fe$$

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