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Synthesis and Structure of a Novel Molybdenum–Iron–Sulfur Cluster with Mo_2Fe_2 Core and All-disulfide Chelate Ligands, $[Mo_2Fe_2(\mu_3\text{-}S)_4(S_2CNEt_2)_5]CH_3CN$

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Abstract

The cluster compound $[Mo_2Fe_2(\mu_3\text{-}S)_4(S_2CNEt_2)_5]CH_3CN$ has been prepared from the reaction system containing $(NH_4)_2MoS_4$, $FeCl_3$, NaS_2CNEt_2, PhSH and $NaOCH_3$. The crystal and molecular structure have been determined by the low temperature X-ray diffraction technique. The compound crystallizes in space group $P2_1/c$ of the monoclinic system with $a = 19.397(7)$, $b = 10.891(7)$, $c = 24.302(8)$ Å, $\beta = 108.95(2)°$ and $Z = 4$. With use of 2647 reflections ($I > 2.5\sigma(I)$) the structure was refined to $R(R_w) = 0.045(0.036)$. The cluster $Mo_2Fe_2S_4(S_2CNEt_2)_5$ has a cubane-like skeleton $[Mo_2Fe_2S_4]^{5+}$. Each metal atom is coordinated by three μ_3-S atoms and a disulfide chelate terminal ligand. The fifth S_2CNEt_2 group as a bridging ligand coordinates to two Mo atoms. In a molecule of the compound, the two Mo atoms are equivalent but the two Fe atoms are unequivalent.

Introduction

Molybdenum–iron–sulfur cluster chemistry has developed under the stimulation of modeling biological nitrogen fixation [1]. To date, synthesized Mo–Fe–S cluster compounds can be divided in principle into two classes [2], one is cubane-like, the other is linear. Mo–Fe–S cluster compounds with other structure types have also been reported recently [3]. The single cubane-like Mo–Fe–S cluster compounds have been synthesized by Holm and his coworkers through the reaction of catechols with double cubane-like one [4]. We have successfully synthesized the single cubane-like Mo–Fe–S cluster compound, $[Mo_2Fe_2(\mu_3\text{-}S)_4(S_2CNEt_2)_5]CH_3CN$, with a Mo_2Fe_2 core and all-disulfide chelate ligands through a self-assembly reaction.

Experimental

Preparation

All manipulations were performed under pure dinitrogen atmosphere with water-free and degassed solvents.

To a solution of CH_3ONa (30 mmol) in 20 ml of CH_3OH was added a solution of $(NH_4)_2MoS_4$ (6 mmol) in 10 ml of DMF. The mixture was stirred until it became a transparent solution. Two ml of PhSH, a solution of CH_3ONa (15 mmol) in 10 ml of CH_3OH and a solution of NaS_2CNEt_2 (15 mmol) in 20 ml of CH_3OH were in turn added to the above mentioned solution, and the reaction solution was stirred for 20 h. A solution of $FeCl_3$ (15 mmol) in 20 ml of CH_3OH was added, and the reaction solution was stirred for another 72 h. Addition of a solution of Et_4NBr (14 mmol) in 10 ml of CH_3OH immediately resulted in a large amount of black precipitate. The precipitate was dissolved in 50 ml of CH_3CN and refluxed for 8 h. The system was filtered and the filtrate was kept at 0 °C. Black–brown needle-like crystals were obtained from the solution. This is the title compound **1**. Yield is about 18% (according to amount of Mo added). *Anal.* Calc. for $Mo_2Fe_2S_{14}N_6C_{27}H_{53}$: Mo, 15.81; Fe, 9.21; S, 36.99; N, 6.92; C, 26.70; H, 4.37. Found: Mo, 15.32; Fe, 9.96; S, 37.73; N, 6.52; C, 26.20; H, 4.57%.

UV–Vis spectrum

The UV–Vis spectrum of the title compound was measured in DMF on a UV-240 spectrophotometer. Only one characteristic absorption (shoulder) is displayed, which may be assigned to charge transfer of RS ($R = Et_2NCS$) $\rightarrow$ $[Mo_2Fe_2S_4]^{5+}$ [5].

Determination of Crystal Structure

A single crystal sample of edge 0.4 X 0.4 X 0.3 mm^3 was mounted on a Nicolet R3m/E four-circle diffractometer with an LT-1 low temperature device at about –80 °C to collect crystallography and intensity data measured using graphite-monochromated

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0020-1693/89/$3.50

TABLE 1. Crystal data

$Mo_2Fe_2S_4(S_2CNEt_2)_5CH_3CN$
Molecular weight 1213.42
Monoclinic system
Space group $P2_1/c$
$\mu = 17.0\ \mathrm{cm}^{-1}$ (Mo Kα)
$\lambda = 0.71069$ Å
$a = 19.397(7)$ Å
$b = 10.891(7)$ Å
$c = 24.302(8)$ Å
$\beta = 108.95(2)°$
$V = 4855.6$ Å^3
$Z = 4$
$D_c = 1.66\ \mathrm{g/cm^3}$

TABLE 2. Coordinates ($\times 10^4$) and equivalent temperature factors (Å^2 $\times 10^3$) of non-hydrogen atoms

	x	y	z	U
Mo(1)	2959(1)	5510(1)	5212(1)	29(1)
Mo(2)	2079(1)	7536(1)	4995(1)	27(1)
Fe(1)	3286(1)	7421(2)	5994(1)	30(1)
Fe(2)	2075(1)	5940(2)	5869(1)	31(1)
S(1)	3310(2)	7523(5)	5088(2)	30(2)
S(2)	1690(2)	5489(3)	4915(1)	31(1)
S(3)	3285(2)	5427(3)	6217(2)	33(2)
S(4)	2162(2)	8031(3)	5948(1)	32(2)
S(5)	2947(2)	3211(4)	5128(2)	37(2)
S(6)	4219(2)	4740(4)	5321(2)	38(2)
S(7)	775(2)	8192(3)	4579(2)	34(2)
S(8)	2012(2)	9816(3)	4788(2)	38(2)
S(9)	2829(2)	5195(4)	4141(2)	44(2)
S(10)	1896(2)	7513(4)	3896(1)	39(2)
S(11)	4402(2)	8365(4)	6176(2)	43(2)
S(12)	3671(2)	7932(4)	6973(2)	42(2)
S(13)	1899(2)	4398(4)	6499(2)	59(2)
S(14)	776(2)	6049(4)	5876(2)	57(2)
N(1)	4251(5)	2303(9)	5164(4)	42(5)
N(2)	647(5)	10627(10)	4420(4)	42(5)
N(3)	2349(6)	6342(10)	3146(5)	44(6)
N(4)	4977(5)	9051(10)	7301(4)	45(5)
N(5)	553(6)	4321(11)	6582(5)	59(6)
N(6)	4234(7)	3388(14)	1598(6)	126(9)
C(1)	3854(6)	3264(11)	5196(5)	29(6)
C(11)	5024(6)	2369(12)	5240(5)	46(6)
C(12)	5503(7)	2285(16)	5864(5)	66(8)
C(13)	3911(7)	1083(11)	5018(5)	60(7)
C(14)	3654(8)	838(13)	4365(5)	71(8)
C(2)	1087(7)	9679(12)	4580(5)	35(6)
C(21)	928(7)	11902(12)	4461(5)	52(7)
C(22)	1004(7)	12363(14)	5069(6)	84(9)
C(23)	−151(6)	10482(13)	4215(5)	50(7)
C(24)	−478(8)	10427(16)	3556(5)	84(9)
C(3)	2361(6)	6330(12)	3694(5)	35(6)
C(31)	1993(8)	7260(15)	2721(6)	72(9)
C(32)	2476(11)	8378(15)	2767(8)	121(13)
C(33)	2749(7)	5395(12)	2936(6)	59(8)
C(34)	2306(8)	4224(15)	2740(7)	86(9)
C(4)	4438(7)	8525(11)	6893(5)	41(6)
C(41)	4959(7)	9183(13)	7886(5)	54(7)
C(42)	4674(7)	10416(12)	8009(6)	62(8)
C(43)	5614(6)	9608(12)	7173(5)	50(7)
C(44)	6217(7)	8668(13)	7264(6)	62(8)
C(5)	1004(6)	4848(12)	6346(5)	39(6)
C(51)	−208(7)	4677(14)	6429(5)	67(8)
C(52)	−368(11)	5552(20)	6838(8)	150(14)
C(53)	781(8)	3265(15)	6999(7)	106(10)
C(54)	1100(11)	3622(22)	7602(7)	183(17)
C(6)	3628(9)	3571(15)	1466(6)	83(9)
C(7)	2796(8)	3767(18)	1335(8)	128(12)

TABLE 3. Main bond lengths (Å)

Mo(1)–Mo(2)	2.734(2)	Fe(1)–Fe(2)	2.784(3)
Mo(1)–Fe(1)	2.751(2)	Mo(1)–Fe(2)	2.737(3)
Mo(2)–Fe(1)	2.775(2)	Mo(2)–Fe(2)	2.748(2)
Mo(1)–S(1)	2.344(5)	Mo(1)–S(2)	2.329(3)
Mo(1)–S(3)	2.318(4)	Mo(2)–S(1)	2.323(5)
Mo(2)–S(2)	2.341(4)	Mo(2)–S(4)	2.334(4)
Fe(1)–S(1)	2.221(5)	Fe(1)–S(3)	2.238(4)
Fe(1)–S(4)	2.249(4)	Fe(2)–S(2)	2.246(4)
Fe(2)–S(3)	2.291(4)	Fe(2)–S(4)	2.288(4)
Mo(1)–S(5)	2.511(4)	Mo(1)–S(6)	2.515(5)
Mo(1)–S(9)	2.556(4)	Mo(2)–S(7)	2.504(3)
Mo(2)–S(8)	2.527(3)	Mo(2)–S(10)	2.573(3)
Fe(1)–S(11)	2.306(4)	Fe(1)–S(12)	2.319(4)
Fe(2)–S(13)	2.370(5)	Fe(2)–S(14)	2.528(4)

Mo Kα radiation. The ω scan mode, scan speed of 5.86°/min and scan width of 1.6° were used. A total of 5060 independent reflections were collected within the range of $3° < 2\theta < 40°$, of which 2647 reflections with $I > 2.5\ \sigma(I)$ were considered observed. The intensities were corrected for Lorentz and polarization factors. The crystal data are listed in Table 1.

The coordinates of the two Mo atoms were obtained from Patterson function analysis. Further Fourier synthesis provided coordinates of all non-hydrogen atoms. The atomic coordinates and anisotropic temperature factors for all non-hydrogen atoms were refined by using the block-matrix least-squares method. All hydrogen coordinates were added theoretically, and the final agreement factors are $R = 0.045$, $R_w = 0.036$. All calculations were performed using SHELXTL programs. The coordinates and equivalent isotropic temperature factors for non-hydrogen atoms, selected bond lengths and bond angles are presented in Tables 2, 3 and 4 respectively.

TABLE 4. Main bond angles (°)

Fe(1)–Mo(1)–Mo(2)	60.8(1)	Fe(2)–Mo(1)–Mo(2)	60.3(1)
Fe(1)–Mo(1)–Fe(2)	61.0(1)	Fe(1)–Mo(2)–Mo(1)	59.9(1)
Fe(2)–Mo(2)–Mo(1)	59.9(1)	Fe(1)–Mo(2)–Fe(2)	60.5(1)
Mo(1)–Fe(1)–Fe(2)	59.3(1)	Mo(2)–Fe(1)–Fe(2)	59.3(1)
Mo(1)–Fe(1)–Mo(2)	59.3(1)	Mo(1)–Fe(2)–Fe(1)	59.8(1)
Mo(2)–Fe(2)–Fe(1)	60.2(1)	Mo(1)–Fe(2)–Mo(2)	59.8(1)
Mo(1)–S(1)–Mo(2)	71.7(1)	Mo(1)–S(1)–Fe(1)	74.0(2)
Mo(2)–S(1)–Fe(1)	75.2(2)	Mo(1)–S(2)–Mo(2)	71.7(1)
Mo(1)–S(2)–Fe(2)	73.5(1)	Mo(2)–S(2)–Fe(2)	73.6(1)
Fe(1)–S(3)–Fe(2)	75.8(1)	Fe(1)–S(3)–Mo(1)	74.3(1)
Fe(2)–S(3)–Mo(1)	72.9(1)	Fe(1)–S(4)–Fe(2)	75.7(1)
Fe(1)–S(4)–Mo(2)	74.5(1)	Fe(2)–S(4)–Mo(2)	73.0(1)
S(1)–Mo(1)–S(2)	106.9(1)	S(1)–Mo(1)–S(3)	100.4(1)
S(1)–Mo(1)–S(5)	156.6(2)	S(1)–Mo(1)–S(6)	90.7(2)
S(1)–Mo(1)–S(9)	86.1(1)	S(2)–Mo(1)–S(3)	103.0(1)
S(2)–Mo(1)–S(5)	89.1(1)	S(2)–Mo(1)–S(6)	157.3(1)
S(2)–Mo(1)–S(9)	86.5(1)	S(3)–Mo(1)–S(5)	92.2(1)
S(3)–Mo(1)–S(6)	87.3(1)	S(3)–Mo(1)–S(9)	166.2(1)
S(5)–Mo(1)–S(6)	70.1(1)	S(5)–Mo(1)–S(9)	77.8(1)
S(6)–Mo(1)–S(9)	80.4(1)	S(1)–Mo(2)–S(2)	107.2(2)
S(1)–Mo(2)–S(4)	99.7(1)	S(1)–Mo(2)–S(7)	155.8(2)
S(1)–Mo(2)–S(8)	90.6(2)	S(1)–Mo(2)–S(10)	83.9(1)
S(2)–Mo(2)–S(4)	102.6(1)	S(2)–Mo(2)–S(7)	89.0(1)
S(2)–Mo(2)–S(8)	157.6(1)	S(2)–Mo(2)–S(10)	88.5(1)
S(4)–Mo(2)–S(7)	94.0(1)	S(4)–Mo(2)–S(8)	87.3(1)
S(4)–Mo(2)–S(10)	166.7(1)	S(7)–Mo(2)–S(8)	70.1(1)
S(7)–Mo(2)–S(10)	78.6(1)	S(8)–Mo(2)–S(10)	79.8(1)
S(1)–Fe(1)–S(3)	106.9(2)	S(1)–Fe(1)–S(4)	105.6(2)
S(1)–Fe(1)–S(11)	81.2(2)	S(1)–Fe(1)–S(12)	154.5(2)
S(3)–Fe(1)–S(4)	102.8(1)	S(3)–Fe(1)–S(11)	117.4(1)
S(3)–Fe(1)–S(12)	90.6(1)	S(4)–Fe(1)–S(11)	135.5(2)
S(4)–Fe(1)–S(12)	87.9(1)	S(11)–Fe(1)–S(12)	74.1(1)
S(2)–Fe(2)–S(3)	106.5(2)	S(2)–Fe(2)–S(4)	107.2(1)
S(2)–Fe(2)–S(13)	116.3(2)	S(2)–Fe(2)–S(14)	91.1(1)
S(3)–Fe(2)–S(4)	100.0(1)	S(3)–Fe(2)–S(13)	86.2(1)
S(3)–Fe(2)–S(14)	155.9(2)	S(4)–Fe(2)–S(13)	132.3(2)
S(4)–Fe(2)–S(14)	89.9(1)	S(13)–Fe(2)–S(14)	71.1(1)

Results and Discussion

Synthesis

The synthetic reaction was performed under reducing conditions. Oxidation numbers of both Mo and Fe decrease in the reaction process. The total of oxidation numbers of the metal cluster core Mo_2Fe_2 in compound **1** is +13, but that of Mo_2Fe_2 calculated according to the oxidation numbers of metals in reactants is +18. The total of oxidation numbers decreases by 5. Reductants in the reaction are PhS^- and $Et_2NCS_2^-$ with their corresponding dimerization providing electrons

$$2PhS^- \longrightarrow PhSSPh + 2e$$

$$2Et_2NCS_2 \longrightarrow Et_2NC(S)SS(S)CNEt_2 + 2e$$

In the reaction system it was found that S_8 crystals formed. In the previous report [6] we have shown that $[Fe_4S_4(S_2CNEt_2)_4]^{2-}$ was synthesized from $(NH_4)_2WS_4$, $FeCl_2$ and NaS_2CNEt_2 with a by-product of S_8 crystals produced simultaneously, which has been demonstrated by determination of the crystal structure. The C–S bond is comparatively strong and cannot be broken under general conditions. The simple substance S_8 can only come from MS_4^{2-} (M = Mo or W). The following reaction probably occurs.

$$MS_4^{2-} \longrightarrow MS_3^{2-} + S \ (M = Mo \text{ or } W)$$

Muller *et al.* have shown that an intramolecular redox reaction of MS_4^{2-} may occur [7]

$$Mo^r(S^{2-}) \longrightarrow Mo^{r-2}(S^0)$$

Our results indicate that an intramolecular redox process may also take place for WS_4^{2-} [6] in addition to MoS_4^{2-}.

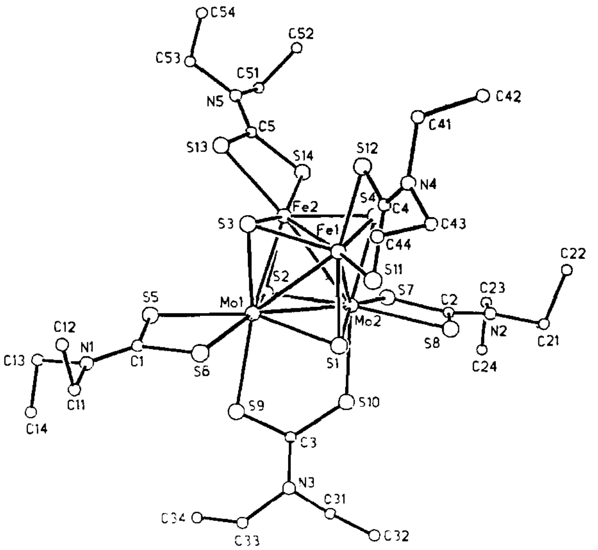

Fig. 1. Structure of $Mo_2Fe_2S_4(S_2CNEt_2)_5$.

Crystal Structure

The structure of $Mo_2Fe_2(\mu_3\text{-}S)_4(S_2CNEt_2)_5$ is shown in Fig. 1. The cluster skeleton $Mo_2Fe_2(\mu_3\text{-}S)_4$ has a cubane-like structure. Each metal atom is coordinated with three μ_3-S atoms and a disulfide chelating terminal ligand. In addition, the fifth S_2CNEt_2 group as a bridging ligand coordinates to two Mo atoms. The two Mo atoms are both deformation-octahedrally coordinated. On the other hand, coordination polyhedra of Fe atoms are all irregular triangular bipyramids. The cluster skeleton, $Mo_2Fe_2S_4$, has a formal valence of +5 and a twice-axis symmetry. The twice axis passes through the midpoints of Mo(1)–Mo(2) and Fe(1)–Fe(2).

The average distances of M–S (M = Mo or Fe) of cubane-like cluster compounds containing S_2CNEt_2 ligands, and Fe_4S_4, $MoFe_3S_4$ and $Mo_2Fe_2S_4$ cores respectively, are presented in Table 5. It may be discovered that average bond lengths of $Mo-S_b$ (triply bridging sulfur atom) and $Mo-S_t$ (dithiocarbamate sulfur atom) are all **1** > **4** > **3**, but **2** > **3** > **1** > **4** for that of $Fe-S_b$ and $Fe-S_t$.

It is found that in **1** the differences of average bond lengths between Mo_1-S_b (2.330 Å) and Mo_2-S_b (2.333 Å), and between Mo_1-S_t (2.527 Å) and Mo_2-S_t (2.535 Å), are very small, but quite remarkable for the differences between Fe_1-S_b (2.236 Å) and Fe_2-S_b (2.275 Å), and between Fe_1-S_t (2.313 Å) and Fe_2-S_t (2.449 Å). This shows that, according to the comparison of the bond lengths, the two Mo atoms are equivalent but the two Fe atoms are unequivalent.

TABLE 5. Comparison of $\overline{M-S}$ distances (Å) in cluster compounds **1**, **2**, **3** and **4**

Compound	**1**	**2**[a]	**3**[b]	**4**[c]
$Mo-S_b$	2.332		2.271	2.277
$Mo-S_t$	2.531		2.467	2.515
$Fe-S_b$	2.256	2.293	2.274	2.222
$Fe-S_t$	2.381	2.449	2.497	2.341

[a] **2** = $(Et_4N)_2(Fe_4S_4(S_2CNEt_2)_4]$ [6]. [b] **3** = $(Et_4N)[MoFe_3S_4(S_2CNEt_2)_5]\cdot CH_3CN$ [8]. [c] **4** = $MoFe_3S_4(S_2CNEt_2)_5\cdot CH_3CN$ [9].

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