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Diethyldithiocarbamate triangular thio complexes of molybdenum: synthesis and an X-ray structural study of $[Mo_3S_7(S_2CNEt_2)_3]Cl$

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Abstract

Heating of $Mo_3S_7(S_2CNEt_2)_4$ (**1**) in 1,2-dichloroethane has afforded the $[Mo_3S_7(S_2CNEt_2)_3]Cl$ (**2**) complex which was characterized by elemental analysis, IR, Raman and PMR data. The structure of **2** was established by X-ray structural analysis. The average Mo–Mo distance is 2.721(2) Å, and the S–S distance of the μ_2-S_2 ligand is 2.041(6) Å. The outer sphere chlorine atom is separated from the axial sulfurs of the μ_2-S_2 ligands by 2.97–3.05 Å. Complexes **1** and **2** are 1:1 electrolytes in DMF (**1**) and in 1,2-dichloroethane (**2**).

Introduction

Since the discovery of $Mo_3S_7Cl_4$ [1] and the establishment of its structure [2] a series of cationic and anionic triangular cluster thio complexes of molybdenum have been obtained by different methods and their structures characterized: $(NH_4)_2Mo_3S_{13}$ [3], $(PPh_4)_2Mo_3S_7Cl_6$ [4], $(Et_4N)_3Mo_3S_7Cl_7$ [5], $(C_{18}H_{30}N_3)_2[Mo_3S_7(Hmsa)_3][Mo_3S_7(Hmsa)_2(msa)]Br\cdot 6H_2O$ (H_3msa = mercaptosuccinic acid) [6], $[Mo_3S_7(S_2PEt_2)_3](S_2PEt_2)$ [7], $\{Mo_3S_7[S_2P(OEt)_2]_3\}Cl$ [8]. All these compounds have triangular cluster fragments $Mo_3(\mu_3\text{-}S)_3(\mu_2\text{-}S_2)_3^{4+}$. In ref. 9 there was a brief mention of the synthesis of $[Mo_3S_7(S_2CNEt_2)_3]I$ from $(NH_4)_2Mo_3S_{13}$ and tetraethylthiuramdisulfide. In our previous study we have proposed [10] an alternative route to the $Mo_3S_7^{4+}$ tetraalkyldithiocarbamate complexes via nucleophilic substitution of the bromide atoms in $Mo_3S_7Br_6^{2-}$ by dithiocarbamate ligands which enabled us to obtain $Mo_3S_7(S_2CNEt_2)_4$ (**1**). During an attempt to recrystallize this complex from boiling 1,2-dichloroethane the $[Mo_3S_7(S_2CNEt_2)_3]Cl$ (**2**) complex was obtained, the structure of which was established by X-ray structure analysis.

Experimental

The syntheses were carried out in air. The solvents were purified and dried using the established procedures. The $(Et_4N)_2Mo_3S_7Br_6$ and $Mo_3S_7(S_2CNEt_2)_4$ compounds were synthesized by the procedures described in refs 10 and 11. Raman spectra were recorded on a Triplemate Spex spectrometer. IR spectra were recorded in KBr pellets on an IR-75 instrument. PMR spectra were recorded on an SXP-4-100 instrument. Electrical conductivity of 10^{-3} mol/l solutions was measured on an OP-210 conductometer.

Red–brown prismatic crystals of **2** suitable for X-ray analysis were obtained by slow cooling to room temperature of a concentrated solution of $[Mo_3S_7(S_2CNEt_2)_3]Cl$ in 1,2-dichloroethane. The details of the X-ray experiment are shown in Table 1. The unit cell parameters and reflection intensities were obtained by standard procedures. The structure was solved by the direct method using the SHELX-86 program [12] and refined by full-matrix least-squares using the YANX package of programs [13] in the anisotropic approximation for the non-hydrogen atoms with a unit weighting scheme. The absorption was taken into account using the azimuthal scanning curve around the $1\bar{2}0$ reflection ($2\theta = 15.59°$). The hydrogen atoms were located from a difference Fourier synthesis and included in the refinement with fixed coordinates and $U_{iso} = 0.07$ Å^2.

Preparation of $[Mo_3S_7(S_2CNEt_2)_3]Cl$ (2)

Complex **1** (0.80 g) was boiled in 1,2-dichloroethane for 5 min and then cooled to −5 °C. The separated crystals were filtered off and dried *in vacuo*. Yield 0.69 g (89%) of complex **2**.

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TABLE 1. Crystallographic data for complex 2

Formula	$C_{15}H_{30}ClN_3S_{13}Mo_3$
Formula weight	992.53
Space system	monoclinic
Space group	$P2_1/n$
a (Å)	14.497(3)
b (Å)	12.361(2)
c (Å)	18.117(2)
β (°)	90.13(1)
V (A^3)	3246.5(9)
Z	4
Density (calc.) (g cm^{-3})	2.030
Dimensions (mm)	0.06×0.10×0.15
Diffractometer	Syntex $P2_1$
Radiation	Cu Kα
Monochromator	graphite
Scan mode	$\theta/2\theta$, $V_{min}=4°$/MNH
2θ (°)	3–100
μ (cm^{-1})	182.4
Temperature	room
Total reflections	3708
Independent reflections	2214 ($I>3\sigma(I)$)
R_F	0.0416

Anal. Found: C, 18.30; H, 3.01; N, 4.06. Calc. for $C_{15}H_{30}ClN_3S_{13}Mo_3$: C, 18.02; H, 3.02; N, 4.20%.

Λ (10^{-3} M solution in 1,2-dichloroethane): 7.5 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (CD_2Cl_2; δ, ppm): 3.83 (quadruplet, 2H); 3.78 (quadruplet 2H); 1.35 (triplet, 3H); 1.30 (triplet, 3H).

Results and discussion

Preparation and properties of [$Mo_3S_7(S_2CNEt_2)_3$]Cl (2)

The interaction of $(Et_4N)_2Mo_3S_7Br_6$ with sodium diethylthiocarbamate results in replacement of all the bromine atoms [10] (eqn. (1)).

$$(Et_4N)_2Mo_3S_7Br_6 + 4NaS_2CNEt_2 \longrightarrow \underset{\mathbf{1}}{Mo_3S_7(S_2CNEt_2)_4} + 2Et_4NBr + 4NaBr \quad (1)$$

In an attempt to recrystallize **1** from boiling 1,2-dichloroethane we unexpectedly obtained complex **2** which was probably formed by the following reaction (eqn. (2)).

$$\underset{\mathbf{1}}{Mo_3S_7(S_2CNEt_4)_4} + ClCH_2CH_2Cl \longrightarrow \underset{\mathbf{2}}{[Mo_3S_7(S_2CNEt_2)_3]Cl} + Et_2NCS_2CH_2CH_2Cl \quad (2)$$

β-Chloroethylcarbamate which first forms in reaction (2) may further give rise to the 1,3-dithiolanium salt as it is formed by the interaction of NaS_2CNMe_2 with 1,2-dichloroethane [14].

Complex **2** is a red crystalline substance stable in air and well soluble only in methylene chloride and hot 1,2-dichloroethane. The intense bands ν(C=S) at 1501 and 1508 cm^{-1} observable in the IR spectra indicate the presence of bidentate S_2CNEt_2 ligands. The Raman spectrum is particularly characteristic. Figure 1 shows the Raman spectrum of complex **2** measured for the same single crystal that had been used in the X-ray analysis. The intense bands at 543 and 536 cm^{-1} in the Raman spectra are due to the S–S valence vibrations in the μ_2-S_2 ligands. The band at 457 cm^{-1} of low intensity is due to the vibrations involving μ_3-S [15, 16].

In the PMR spectrum of complex **2** in CD_2Cl_2 the methylene protons of the S_2CNEt_2 ligands coordinated to molybdenum appear in the spectrum as two quadruplets of equal intensity while the methyl protons appear as two triplets of equal intensity. Such a complex picture of the spectrum is a result from non-equivalence of the ethyl groups of each of the dithiocarbamate ligands which is due to an asymmetry of the $Mo_3S_7^{4+}$ fragment in the presence of a substantial rotational barrier around the C–N bonds in the dithiocarbamate complexes (58–75 kJ/mol) [17].

According to the X-ray analysis data (a detailed description of the structure is given below) a characteristic feature of the structure of **2** is the presence of rather short (2.8–2.9 Å) contacts of the Cl$^-$ counterion and the axial sulfurs of the μ_2-S_2 ligands. In spite of this, in a 10^{-3} mol/l solution in 1,2-dichloroethane complex **2** is a 1:1 electrolyte [18], which suggests that in solution there probably occurs dissociation of complex **2** to form Cl$^-$ ions and $Mo_3S_7(S_2CNEt_2)_3^+$. Complex **1** is also a 1:1 electrolyte. Therefore, the present work does not completely solve the question of the structure of complex **1**. The powder diffractogram for complex **2** completely coincides with the theoretical one calculated from X-ray analysis data for a single crystal of **2**.

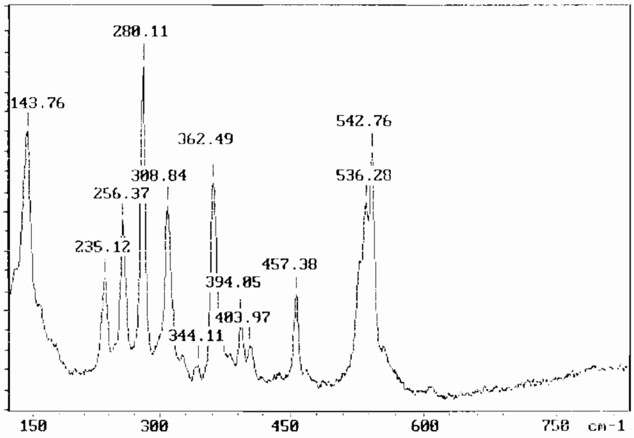

Fig. 1. The Raman spectrum of [$Mo_3S_7(dtc)_3$]Cl.

Structure of 2

The structure of **2** is shown in Fig. 2. The $Mo_3S_7^{4+}$ cluster fragment geometry is analogous to that described in the literature [2–8]. It is worth noting that the Mo–Mo bond lengths in this cluster (average 2.721(2) Å) are somewhat shorter than the value 2.75 Å typical for such complexes. The average S–S distance is 2.041(6) Å, a value typical for $Mo_3S_7^{4+}$ complexes. Asymmetrical coordination of the μ_2-S_2 ligands shows itself in the fact that the average distance of the molybdenum atoms to the equatorial sulfurs (2.478(4) Å) is approximately 0.07 Å longer than their separation from the axial sulfurs (2.404(4) Å). Another asymmetrical feature is that the equatorial sulfur atoms practically lie in the Mo_3 plane, the corresponding deviations not exceeding 0.15 Å. The μ_3-S ligand is symmetrically coordinated to all three molybdenum atoms and the average Mo–μ_3-S distance is 2.365(4) Å.

Dithiocarbamate ligands coordinate the Mo atoms in a bidentate fashion to form practically planar four-membered chelate rings perpendicular to the Mo_3 plane. Sulfurs of the chelate ring reside in semi-axial non-symmetrical positions relative to the Mo_3 plane. The average MoMoS angle is 125.3(1)° for the sulfur atoms occupying the same side as the capping μ_3-S ligand and 143.5(1)° for S on the opposite side. Their separations from the Mo_3 plane are 0.94 and 1.83 Å, respectively.

The bond lengths in the MoS_2CNEt_2 fragment are within the normal values (according to CBSD [19] the average bond lengths are 1.72(4) for S–C, 1.33(4) for $C(CS_2)$–N and 1.50(5) Å for C(Et)–N on the basis of 193 structures; Mo–S is 2.50(3) Å for 13 structures).

A characteristic feature in the structure of **2** is the presence of short (2.97–3.05 Å) contacts of the outer sphere chlorine atom and the axial sulfur atoms of the μ_2-S_2 ligands. The trend to an additional interaction of this type was noted earlier in ref. 8 for $\{Mo_3S_7[S_2P(OEt)_2]_3\}Cl$ (S...Cl ~ 2.9 Å) and for the salt $(Et_4N)_3[Mo_3S_7Cl_6]Cl$ (S...Cl ~ 2.9 Å) [5]. For the binary salt $(C_{18}H_{30}N_3)_2[Mo_3S_7(Hmsa)_3][Mo_3S_7(Hmsa)_2(msa)]Br$ the bromine atom at the distance 3.20–3.35 Å from the axial sulfur atoms acts as a kind of a bridge connecting two cluster fragments [6]. In the $(PPh_4)_2Mo_3S_7Cl_6$ salt the trend to realize such an interaction results in an arrangement where the $Mo_3S_7Cl_6^{2-}$ anions become linked to each other to form centrosymmetrical dimers through the short S...Cl contacts (3.2–3.5 Å) which produce pairs of anionic neighbours in the crystal lattice that are not quite usual

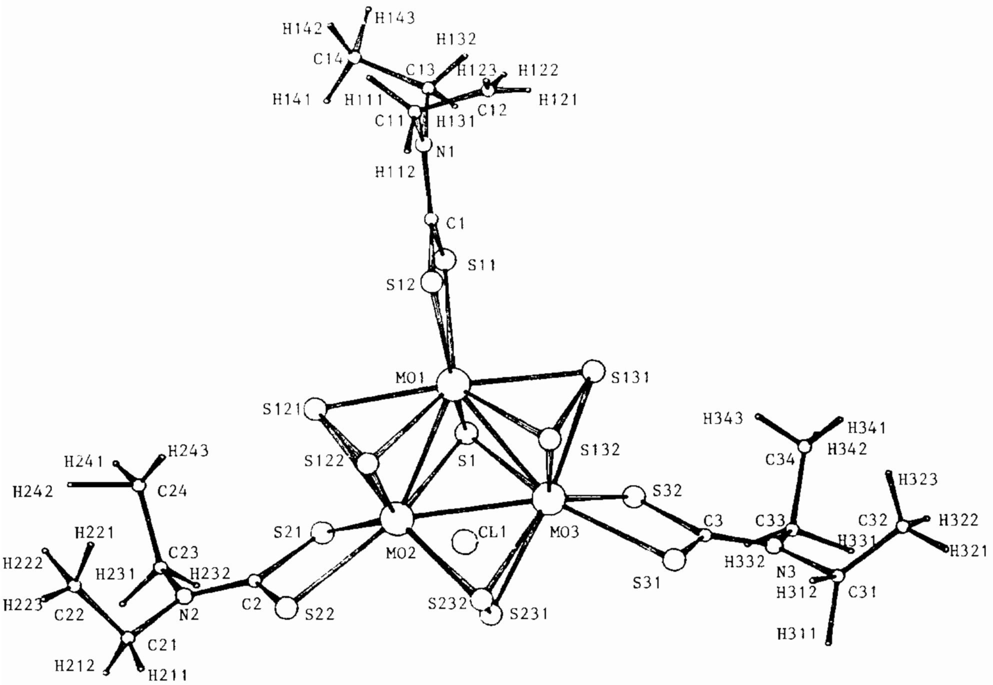

Fig. 2. The structure of $[Mo_3S_7(dtc)_3]Cl$. Selected bond distances (Å): Mo(1)–Mo(2), 2.721(2); Mo(1)–Mo(3), 2.722(2); Mo(2)–Mo(3), 2.719(2); Mo(1)–S(1), 2.371(4); Mo(2)–S(1), 2.360(4); Mo(3)–S(1), 2.374(3); Mo(1)–S(121), 2.495(4); Mo(1)–S(122), 2.410(4); Mo(1)–S(131), 2.489(4); Mo(1)–S(132), 2.415(4); Mo(2)–S(121), 2.472(4); Mo(2)–S(122), 2.402(4); Mo(2)–S(231), 2.480(4); Mo(2)–S(232), 2.418(4); Mo(3)–S(131), 2.481(4); Mo(3)–S(132), 2.401(4); Mo(3)–S(231), 2.467(4); Mo(3)–S(232), 2.410(4); Mo(1)–S(11), 2.480(4); Mo(1)–S(12), 2.517(4); Mo(2)–S(21), 2.477(4); Mo(2)–S(22), 2.534(4); Mo(3)–S(31), 2.455(4); Mo(3)–S(32), 2.531(4); S(121)–S(122), 2.040(5); S(131)–S(132), 2.043(6); S(231)–S(232), 2.041(6).

for ionic compounds. It should be noted that all these contacts are shorter than the sum of the van der Waals radii of S and Cl (3.65 Å) [4].

It can be suggested that this interaction is due to the interaction of the unshared pairs of the halogen atom with σ^* MO of the S_2 ligand similar to what takes place in the halogen complexes $X_2 \cdot L$ [20]. This is a consequence of the isolobality of the X_2 molecules and the chalcogenide dianions Y_2^{2-}.

$$X_2 \longleftrightarrow Y_2^{2-}$$

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