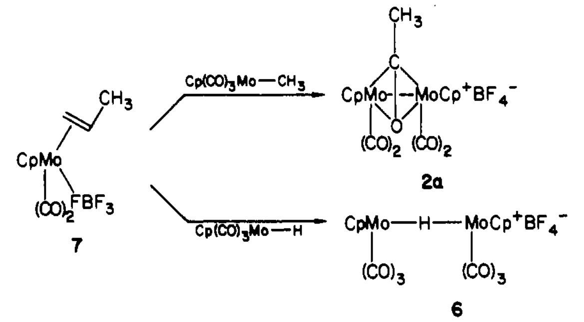
Scheme V



yield (42%) does not greatly improve on that obtained when we used $Cp(CO)_3MoFBF_3$ (**1a**) in place of **7** (36%). Both reactions are exceedingly messy (in terms of insoluble decomposition material), and neither produce the unsymmetric μ-(η^1-*C*,*O*)-acetyl compound **3**. The reaction between **7** and $Cp(CO)_3MoH$ (Scheme V) is even less promising. Essentially no reaction takes place, other than thermal degradation of **7** and generation of small amounts of $Cp(CO)_3Mo\text{-}H\text{-}Mo(CO)_3Cp^+$ (**6**).

We are at a loss to explain the rather disappointing conversion of $Cp(CO)_3MoCH_3$ to **2** by using **7** instead of $Cp(CO)_3MoFBF_3$ (**1a**). Clearly **7** functions as a Lewis acid precursor to $Cp(CO)_2Mo^+$ (as demonstrated by results of the reaction with iodide or PPh_3), but perhaps both ligated BF_4^- and propene are not sufficiently labile during the sequence of alkyl–CO migration and binding of the incipient acyl ligand (as η^2 complexation). We, of course, have no evidence for a metal Lewis acid even promoting hydride–CO insertion. Further mechanistic discussion is unwarranted until answers for at least three questions are forthcoming:

1. What is the mechanism for the reaction of $Cp(CO)_3MoCH_3$ and $Cp(CO)_3Mo^+$?
2. Will **7** interact with stable acetyl complexes and after CO loss give isolable μ-(η^2-*C*,*O*)-acetyl compounds?
3. Can **7** be altered (e.g., replacement of BF_4^- and propene by PF_6^- and isobutylene, respectively) in order to generate an even more labile/reactive Lewis acid precursor?

These and related questions concerning the reactions of organometallic Lewis acids with coordinated ligands are currently under investigation.

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Contribution from the Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, and Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Structural and Spectroscopic Study of $Mo_4(\mu_3\text{-}S)_4(\mu\text{-}S_2CN(C_2H_5)_2)_2(S_2CN(C_2H_5)_2)_4$, a Compound Containing a Cubane-like Cluster with Six Molybdenum–Molybdenum Bonds

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Refluxing $Mo_2(S_2CN(C_2H_5)_2)_6$ in toluene gave the tetranuclear complex $Mo_4(\mu_3\text{-}S)_4(\mu\text{-}S_2CN(C_2H_5)_2)_2(S_2CN(C_2H_5)_2)_4$, which usually contains solvent molecules of crystallization. Recrystallization of the complex from chloroform yielded $Mo_4(\mu_3\text{-}S)_4(\mu\text{-}S_2CN(C_2H_5)_2)_2(S_2CN(C_2H_5)_2)_4{\cdot}2CHCl_3$, which has been characterized by infrared, UV/vis, and NMR spectroscopy and single-crystal structural studies. Its crystals are tetragonal, of space group $P4_12_12$, with $a = 12.442$ (3) Å, $c = 40.30$ (1) Å, $D_o = 1.735$ (8) g cm^{-3}, $D_m = 1.746$ g cm^{-3}, and $Z = 4$. The structure was determined from 1099 reflections and refined by blocked-cascade least squares to an R factor of 0.094. The complex contains a cubane-like Mo_4S_4 cluster. Two of the dithiocarbamate ligands each form a bridge between the two Mo atoms on the opposite sides of the cube; the remaining four each coordinate to a Mo atom in a bidentate mode. The Mo_4S_4 cluster is similar to that of Fe_4S_4, but the four Mo atoms are mutually bonded via Mo–Mo single bonds ranging from 2.732 (5) Å for two Mo atoms bridged via the same dithiocarbamate to an average value of 2.861 (6) Å for the other four Mo–Mo distances.

Introduction

Molybdenum and iron are key metals in nitrogenase, an enzyme responsible for nitrogen fixation. The iron may be present as Fe_4S_4 clusters, yet the state of molybdenum is still to be identified. Over the years, many model studies were carried out to probe the function and state of the molybdenum atoms in the enzyme, and the available literature indicates that the enzyme consists of Fe- and Mo–Fe proteins.[1] Various Mo–Fe–S cubane-like clusters were proposed for the Mo–Fe protein, but no definite conclusion has ever been reached.[2] In our studies on molybdenum chemistry, the compound $Mo_4(\mu_3\text{-}S)_4(\mu\text{-}S_2CN(C_2H_5)_2)_2(S_2CN(C_2H_5)_2)_4$ was prepared, its crystal structure was determined, and other properties were measured. Although the present results have no direct connection with the study of nitrogenase, the existence of a cubane-like Mo_4S_4 cluster may prove to be highly significant in subsequent research on this enzyme.

The complex $Mo_2(S_2CN(C_2H_5)_2)_6$ was first reported by Brown et al.[3] by the method of oxidative decarbonylation of tricarbonyl(η^6-cycloheptatriene)molybdenum. Later, its preparation was reported by Mitchell and Scarle,[4] who suggested a distorted octahedral geometry around each Mo atom with four bidentate dithiocarbamate groups and two unidentate groups that bridge the Mo atoms. The former report was called into question by some workers.[5,6] One group of workers[7] doubted whether Mo(III) dithiocarbamates can be prepared by the above method, for their preparation always resulted in $Mo(S_2CN(C_2H_5)_2)_4$. Brown, Glass, and Jasim[8] reinvestigated the above system for dithiocarbamates with R = CH_3, C_2H_5, n-C_3H_7, and n-C_4H_9, and they suggested that the complexes may be formulated as dimeric species with

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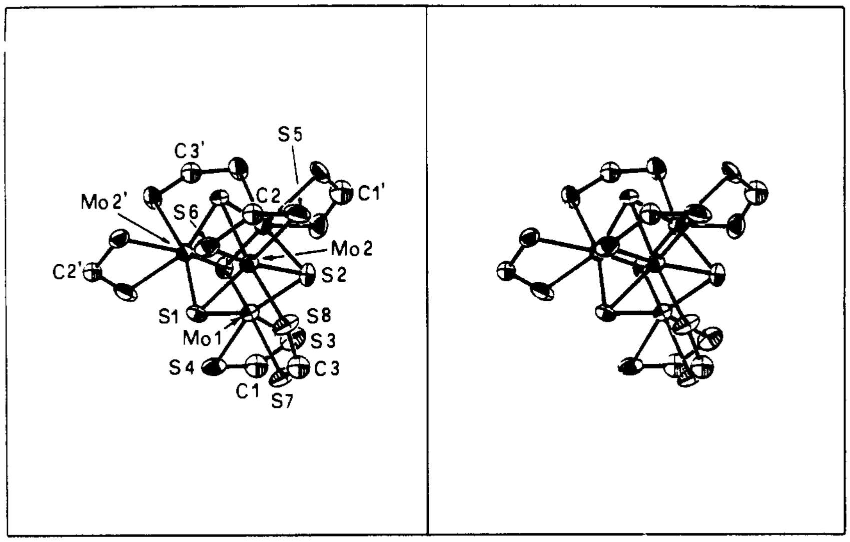

Figure 1. ORTEP plot of the cubane-like Mo_4S_4 cluster. For clarity, only the CS_2 moiety of each dithiocarbamate ligand is shown and the Mo–Mo bonds have been omitted.

four terminal and two bridging bidentate dithiocarbamate groups in a manner different from the one suggested earlier.[4] They mentioned that during the preparation of $Mo_2(S_2CN(C_2H_5)_2)_6$ from $Mo(CO)_6$ and tetraethylthiuram disulfide, some black byproduct was present.[9] We have now isolated these crystals in pure form and found that it can also be prepared by prolonged heating of $Mo_2(S_2CN(C_2H_5)_2)_6$ in a toluene solution.

Experimental Section

Infrared spectra were recorded as 2% KBr and CsBr disks on the following instruments: Beckman Acculab 10, Perkin-Elmer 457, and Perkin-Elmer 180. Ultraviolet and visible spectra were recorded as 0.04 mM $CHCl_3$ solutions on a Cary 118 instrument. Proton NMR studies were performed in deuterated chloroform solution on a Bruker WP-80 instrument. Elemental analyses were carried out by Guelph Chemical Laboratories Ltd. All chemicals were carefully purified and dried, and the reactions were carried out under a N_2 atmosphere in the dark for the preparation of $Mo_2(S_2CN(C_2H_5)_2)_6$.

The compound $Mo_4(\mu_3\text{-}S)_4(\mu\text{-}S_2CN(C_2H_5)_2)_2(S_2CN(C_2H_5)_2)_4$ was prepared in 25–35% yield (depending on the reaction time) by refluxing a toluene solution of $Mo_2(S_2CN(C_2H_5)_2)_6$ (2 g in 100 mL) for 20 h. The reaction mixture was then cooled to 333–343 K and the solvent evaporated under reduced pressure to 30 mL. The black crystals were obtained by filtration the next day. Anal. Calcd for $Mo_4(C_{37}H_{68}N_6S_{16})$: C, 29.76; H, 4.56; N, 5.63. Found: C, 30.04; H, 4.81; N, 5.68.

Crystallographic Studies. The square or rectangular black crystals of $Mo_4(\mu_3\text{-}S)_4(\mu\text{-}S_2CN(C_2H_5)_2)_2(S_2CN(C_2H_5)_2)_4 \cdot 2CHCl_3$ were grown over a period of >1 month, from $CHCl_3$. Upon exposure to air, these crystals lose $CHCl_3$ in a few minutes, emitting a strong odor of chloroform. Thus, a single crystal of dimensions 0.24 × 0.20 × 0.05 mm (plate with (001) well developed) was removed from the mother liquor, quickly covered with petroleum jelly, and lodged in a 0.5-mm Lindemann glass capillary partly filled with $CHCl_3$ at the tip portion. The crystal was thus kept in a chloroform atmosphere, and the petroleum jelly held it stationary against the wall of the glass capillary. Unit-cell and intensity data were measured on a Nicolet R3m automated four-circle diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.71069 Å) at 295 K. Three standard reflections were repeatedly measured between every fifty intensity measurements, and their intensities fluctuated within 2% of their mean values. The intensities of reflections declined rapidly with increasing Bragg angle, so a 2θ limit of 40° was used in the data collection. The raw data were processed with a learned-profile procedure,[10] and absorption correction was applied by using a pseudoellipsoidal treatment of reflection intensity measurements at different azimuthal angles.[11,12] Pertinent crystallographic and data processing parameters are given in Table I. Equivalent or multiply measured reflections are within 2% of their repective means.

Table I. Crystal Data and Parameters Used in the Structural Analysis

mol formula	$C_{39}H_{70}Cl_6Mo_4N_6S_{16}$
mol wt	1640.39
cell constants	a = 12.442 (3), c = 40.30 (1) Å; V = 6239 (3) Å^3; Z = 4
space group	$P4_12_12$ (No. 92)
density (obsd, calcd)	1.735, 1.746 g cm^{-3}
abs coeff	15.74 cm^{-1}
mean μ_r	0.11
transmission factors	0.648–0.873
scan type, speed	θ–2θ, 2.02–8.37° min^{-1}
scan range	1° below Kα_1 to 1° above Kα_2
bkgd counting	stationary counts for half of scan time at each end of scan
colln range; $2\theta_{max}$	$h, k > l$; 40°
no. of unique reflcns measd	1410
no. of data with $\lvert F_o\rvert > 3\sigma(F_o)$, n	1099
no. of variables, p	179
$R = \Sigma\lVert F_o\rvert - \lvert F_c\rVert / \Sigma\lvert F_o\rvert$	0.094
weighting scheme	$w = [\sigma_F{}^2 + 0.002F^2]^{-1}$
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \Sigma\lvert F_o\rvert^2]^{1/2}$	0.111
$S = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / (n - p)]^{1/2}$	1.72

Structure Solution and Refinement. A direct-phase determination based on negative quartets[13] yielded the locations of two Mo and six S atoms in the asymmetric unit. Subsequent difference Fourier maps gradually revealed the positions of most of the N and C atoms and also gave unequivocal indication that the $CHCl_3$ molecule is randomly oriented. The C atoms of the $CHCl_3$ and one of the terminal C atoms of the ethyl group were not located from the difference map. In the last stages of blocked-cascade[14] least-squares refinement, only the Mo and S atoms were allowed anisotropic temperature factors, while those of others remained isotropic. In addition, the occupancy factors for Cl atoms were allowed to vary, and the refinement converged to an R factor of 0.094. The sum of 2.84 for the occupancy factors was in fair agreement with the expected value of 3 for a chloroform molecule. The disordered Cl atoms lie at the corners of a tetrahedron of sides 2.53–2.87 Å.

All computations were performed on a Data General Corp. Nova 3/12 minicomputer with the SHELXTL program package.[15] Analytical ex-

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Table II. Atomic Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$)

atom	*x*	*y*	*z*	*U*
Mo(1)	398 (3)	772 (3)	345 (1)	55 (2)
Mo(2)	2455 (3)	906 (3)	111 (1)	52 (2)
S(1)	1592 (9)	2189 (9)	438 (3)	58 (5)
S(2)	1363 (9)	−637 (8)	111 (3)	64 (5)
S(3)	−1182 (10)	−474 (12)	453 (4)	97 (7)
S(4)	−1015 (10)	1669 (12)	695 (3)	87 (6)
S(5)	4004 (11)	−146 (12)	−133 (3)	93 (6)
S(6)	4126 (10)	2001 (10)	130 (3)	72 (5)
S(7)	966 (11)	40 (11)	897 (3)	87 (6)
S(8)	3277 (10)	132 (11)	643 (3)	78 (6)
C(1)	−1710 (43)	490 (41)	647 (12)	103 (18)
N(1)	−2789 (38)	303 (40)	804 (11)	114 (16)
C(11)	−3536 (63)	1527 (60)	855 (20)	199 (34)
C(12)	−3490 (62)	1419 (63)	1322 (21)	204 (35)
C(13)	−3110 (52)	−794 (55)	851 (16)	146 (25)
C(2)	4834 (34)	955 (32)	−51 (11)	61 (13)
N(2)	5902 (40)	1076 (39)	−168 (12)	134 (18)
C(21)	6527 (54)	−266 (54)	−238 (17)	147 (25)
C(22)	6476 (64)	−67 (60)	−587 (20)	183 (31)
C(23)	6530 (48)	2046 (50)	−28 (19)	149 (25)
C(24)	6737 (43)	2479 (43)	−370 (15)	123 (21)
C(3)	2238 (38)	−244 (38)	896 (11)	81 (16)
N(3)	2585 (36)	−881 (33)	1212 (11)	100 (13)
C(31)	3727 (56)	−1078 (59)	1365 (18)	158 (30)
C(32)	4047 (65)	−1755 (68)	1142 (21)	201 (37)
C(33)	1928 (53)	−1020 (52)	1507 (18)	168 (28)
C(34)	1374 (58)	−2073 (62)	1426 (19)	192 (33)
Cl(1)[a]	5755 (30)	5441 (31)	875 (10)	263 (28)
Cl(2)	7263 (37)	4501 (34)	438 (12)	357 (36)
Cl(3)	6119 (57)	6486 (58)	347 (18)	607 (84)
Cl(4)	5102 (46)	4622 (43)	307 (14)	235 (39)

[a] The occupancy factors for Cl(1)–Cl(4) are 0.75 (5), 0.83 (5), 0.80 (8), and 0.46 (5), respectively.

pressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[16] The atomic parameters are given in Table II.

Results

The compound $Mo_4(\mu_3\text{-}S)_4(\mu\text{-}S_2CN(C_2H_5)_2)_2(S_2CN(C_2H_5)_2)_4$ is insoluble in aliphatic and aromatic hydrocarbons, but it is sparingly soluble in cold acetone and chlorinated solvents. It is stable in air, and no changes in its IR and UV/vis spectra were detected even after air exposure for 1 month.

The key features of its molecular structure are shown in Figure 1, whereas the relevant bond distances and angles are listed in Table III. A novel feature of the molecular structure is that it contains a cubane-like Mo_4S_4 cluster, which is similar to that of Fe_4S_4 except that all four Mo atoms are mutually bonded to one another via single Mo–Mo bonds, whereas in the latter cluster, there is no metal–metal bond between the Fe atoms. The two Mo–Mo bonds involving metal atoms bridged by $S_2CN(C_2H_5)_2$ ligands are 2.732 (5) Å long, slightly shorter than the other four, which range from 2.858 (5) to 2.870 (7) Å, giving an average value of 2.861 (6) Å. Most Mo–S distances in the Mo_4S_4 cluster are close to 2.35 Å. The S–Mo–S angles are obtuse (101.6–107.8°), but the Mo–S–Mo angles are acute (71.5–75.2°).

If the Mo–Mo bonds are ignored, the coordination geometry about each metal center is a distorted octahedron, the S–Mo–S angles being constrained by the cubane-like arrangement and the "bite" of the $S_2CN(C_2H_5)_2$ group. The latter have values of 68.5 (5) and 70.0 (4)°, respectively, for angles centered at Mo(1) and Mo(2). Generally speaking, the Mo–S(from $S_2CN(C_2H_5)_2$) bonds are longer than the Mo–S(from μ_3-S) bonds, and the dithiocarbamate structural parameters are normal.[17]

The characteristic IR absorption bands of the title compound and those of $Mo_2(S_2CN(C_2H_5)_2)_6$ are given in Table IV. A single

Table III. Selected Bond Lengths (Å) and Angles (deg)

Mo_4S_4 Bond Lengths

Mo(1)–Mo(2)	2.732 (5) (twice)		
Mo(1)–Mo(1′)	2.859 (8)	Mo(1)–Mo(2′)	2.858 (5)
Mo(2)–Mo(1′)	2.858 (5)	Mo(2)–Mo(2′)	2.870 (7)
Mo(1)–S(1)	2.34 (1)	Mo(2)–S(1)	2.33 (1)
Mo(1′)–S(1′)	2.34 (1)	Mo(2)–S(2)	2.35 (1)
Mo(1)–S(2)	2.32 (1)	Mo(2′)–S(2′)	2.35 (1)
Mo(1)–S(2′)	2.36 (1)	Mo(2)–S(1′)	2.40 (1)

Mo_4S_4 Angles

S(1)–Mo(1)–S(2)	107.8 (4)	S(1)–Mo(2)–S(2)	107.0 (4)
S(1)–Mo(1)–S(2′)	103.7 (4)	S(1)–Mo(2)–S(1′)	102.3 (4)
S(2)–Mo(1)–S(2′)	101.6 (4)	S(2)–Mo(2)–S(1′)	102.2 (4)
Mo(1)–S(1)–Mo(2)	71.7 (4)	Mo(1)–S(2)–Mo(1′)	71.5 (3)
Mo(1)–S(1)–Mo(2′)	74.3 (4)	Mo(1)–S(2)–Mo(1′)	75.2 (4)
Mo(2)–S(1)–Mo(2′)	74.8 (4)	Mo(2)–S(2)–Mo(1′)	74.6 (3)
S(1)–Mo(1)–S(3)	157.7 (5)	S(1)–Mo(2)–S(5)	157.7 (5)
S(2)–Mo(1)–S(4)	157.4 (5)	S(2)–Mo(2)–S(6)	158.5 (1)
S(2′)–Mo(1)–S(7)	163.4 (4)	S(1′)–Mo(2)–S(8)	164.1 (4)
S(1)–Mo(1)–S(4)	91.2 (4)	S(1)–Mo(2)–S(6)	89.6 (4)
S(1)–Mo(1)–S(7)	87.3 (4)	S(1)–Mo(2)–S(8)	88.2 (4)
S(2)–Mo(1)–S(3)	90.5 (4)	S(2)–Mo(2)–S(8)	85.6 (4)
S(2)–Mo(1)–S(7)	86.6 (5)	S(2)–Mo(2)–S(5)	91.1 (4)
S(3)–Mo(1)–S(7)	81.1 (5)	S(5)–Mo(2)–S(8)	80.0 (5)
S(4)–Mo(1)–S(7)	82.0 (5)	S(6)–Mo(2)–S(8)	81.2 (4)
S(3)–Mo(1)–S(4)	68.5 (5)	S(5)–Mo(2)–S(6)	70.0 (4)

Mo–S (μ-$S_2CN(C_2H_5)_2$) Bond Lengths

Mo(1)–S(7)	2.51 (1)	Mo(2)–S(8)	2.56 (1)

Mo–S ($S_2CN(C_2H_5)_2$) Bond Lengths

Mo(1)–S(3)	2.54 (1)	Mo(2)–S(5)	2.53 (1)
Mo(1)–S(4)	2.51 (1)	Mo(2)–S(6)	2.49 (1)

$S_2CN(C_2H_5)_2$ Bond Lengths

C(1)–N(1)	1.50 (7)	C(1)–S(3)	1.58 (5)	C(1)–S(4)	1.71 (5)
C(2)–N(2)	1.42 (7)	C(2)–S(5)	1.75 (4)	C(2)–S(6)	1.73 (4)
C(3)–N(3)	1.56 (6)	C(3)–S(7)	1.62 (5)	C(3)–S(8)	1.71 (5)

C═S stretching vibration in the 1000-cm^{-1} region with no splitting suggests a bidentate mode of bonding for the $S_2CN(C_2H_5)_2$ groups.[18,19] However, the strong bands at 565 cm^{-1} and a shoulder at 551 cm^{-1} indicate that the C═S groups, although similar, are different. It is rather difficult to know whether these bands and shoulders result from different $S_2CN(C_2H_5)_2$ groups or from the C═S bond of the same $S_2CN(C_2H_5)_2$ group. The Mo–S stretching bands range between 300 and 360 cm^{-1}, in good agreement with some other reported values.[20] This broad peak can be resolved into a strong band at 360 cm^{-1} and two shoulders at 345 and 320 cm^{-1}. This broad or multiband spectrum for MoS is expected since there is a wide range of Mo–S distances, as revealed from the structural analysis. The chloroform molecule of crystallization can easily be detected from the band at 747 cm^{-1} attributable to C–Cl stretching.

The UV/vis spectrum of the title compound consists of four bands at 13.9 (ϵ = 1476), 17.9 (ϵ = 4180), 28.4 (ϵ = 2313), and 37.7 × 10^3 cm^{-1} (ϵ = 10448). According to Jørgensen,[21] the strong band at 37.7 × 10^3 cm^{-1} may be due to internal ligand transition, whereas the peaks between 13.9 and 28.4 × 10^3 cm^{-1} are assignable to ligand-to-metal charge-transfer absorptions. The d–d transitions were either very weak or obscured by the above intense bands.

The ^1H NMR spectrum of $Mo_4(\mu_3\text{-}S)_4(\mu\text{-}S_2CN(C_2H_5)_2)_2(S_2CN(C_2H_5)_2)_4\cdot C_7H_8$ (crystallized from toluene) showed two triplets for the CH_3 of the ethyl groups at 1.21 and 1.23 ppm with *J* = 6.8 and 7.2 Hz, respectively, the ratio of integrated intensities being 2:1. This indicated the nonequilvalence of the dithiocarbamate in the compound, as revealed by the structural study.

Discussion

Even though the coordination geometry around each Mo atom is an octahedron, if the Mo–Mo bonds are ignored, there is reason

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Table IV. Characteristic IR Bands (cm^{-1}) of Related Compounds[a]

compd	ν(RCN)	ν_s(C=S)	ν(C–Cl)	ν_{as}(C=S)	ν(Mo–S)
$Mo_4S_4 \cdot C_7H_8$	1497 (vs)	990 (s)		565 (s) 551 (sh)	360 (s) 345 (sh) 320 (sh)
$Mo_4S_4 \cdot 2CHCl_3$	1497 (vs)	990 (s)	747 (s)	565 (s) 551 (sh)	360 (s) 345 (sh) 320 (sh)
$Mo_2(dtc)_6$[8]	1495 (vs)	1005 (s)		580 (s) 558 (sh)	355 (s)
$Mo_2(dtc)_6 \cdot {}^2/_3CHCl_3$[8]	1520 (vs)	1000 (s)	743 (s)	580 (s) 560 (m)	355 (s)

[a] Abbreviations: vs, very strong; s, strong; m, medium; sh, shoulder; Mo_4S_4, $Mo_4(\mu_3\text{-}S)_4(\mu\text{-}S_2CN(C_2H_5)_2)_2(S_2CN(C_2H_5)_2)_4$; dtc, $S_2CN(C_2H_5)_2$.

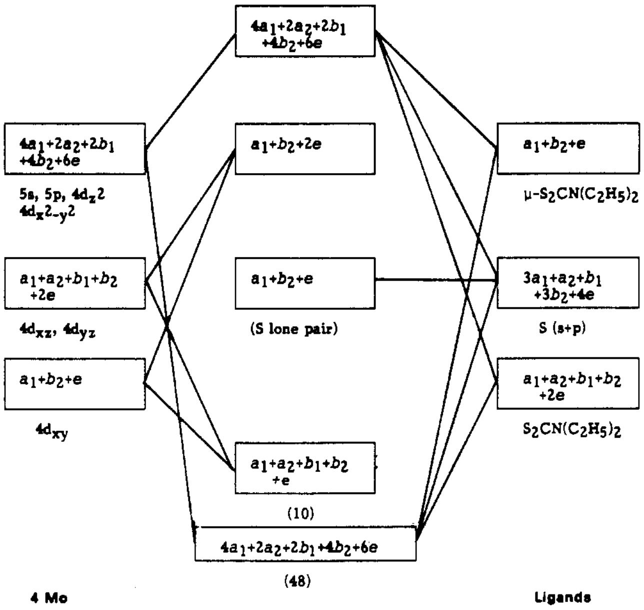

Figure 2. Molecular orbitals of the Mo_4S_4 cluster.

to believe that the distortion would warrant a splitting of the t_{2g} orbitals so that eight of the ten d electrons from the four Mo atoms occupy four orbitals, leaving the remaining two to wander among the four Mo atoms. This is an oversimplified view from the electrostatic crystal field theory, but a more elaborate molecular orbital treatment given later shows the same result.

From the crystallographic point of view, the 2-fold rotation axis of the molecule coincides with that of the unit cell; i.e., the molecule rigorously belongs to point group C_2, which is a subgroup of D_2, an approximate group for the central core of the molecule. Molecular orbitals can be derived from the atomic orbitals by assuming a D_2 symmetry for the Mo_4S_4 cluster and using a symmetry–adapted linear combination method. A right-handed coordinate system is imposed on each sulfur atom whereas a left-handed one is used for each Mo atom. In both cases, the coordinate axes coincide with the edges of the "cube". The irreducible representations of the molecular orbitals of the Mo_4S_4 cluster and their consituent atomic orbitals are given in Figure 2; the treatment is similar to that used for a similar compound.[22] The metal–ligand interaction yields 24 bonding orbitals, which accommodate 48 of the 58 electrons in the cluster. Four nonbonding orbitals ($a_1 + b_2 + e$) come from the four three-way-bridged S atoms, and the eight electrons in these orbitals are not included in the above electron count. Thus, only ten electrons are available for the six bonding orbitals ($a_1 + a_2 + b_1 + b_2 + e$) derived from the four Mo atoms. This bonding scheme agrees with the fact that there are six Mo–Mo bonds in the cluster, and the average length of 2.818 Å is longer than that that found for single Mo–Mo bonds, 2.765 (7) Å.[23,24]

Table V. Variation of Mo-Mo Bond Lengths (Å) with Number of Electrons per Mo_4S_4 Unit[a]

complex	no. of e	Mo-Mo dist	mean
dtc6	58	2.732 (5) twice, 2.858 twice, 2.859, 2.870	2.818 (67)
Cp0	58	2.790 (1), 2.820, 2.861, 2.879, 2.897, 2.902	2.858 (45)
Cp1	59	2.860 (1), 2.887, 2.893, 2.900, 2.901, 2.923	2.894 (21)
edta	59	2.755 (2), 2.775, 2.794, 2.796, 2.845, 2.880	2.808 (46)
Cp2	60	2.892 (1), 2.902 twice, 2.905, 2.912 twice	2.904 (7)
Ndp	68	2.861 (2), 2.862 (others >3.69)	
Ndtc	68	2.879 (3), 2.883 (others >3.66)	
NOCN	68	2.99 (3) twice, (others >3.5)	

[a] Only the standard deviation for the shortest Mo–Mo bond of each structure is given. Abbreviations for complexes: dtc6 = $Mo_4(\mu_3\text{-}S)_4(\mu\text{-}S_2CN(C_2H_5)_2)_2(S_2CN(C_2H_5)_2)_4$, Cp0–Cp2 = $Mo_4S_4(\eta\text{-}C_5H_4\text{-}i\text{-}Pr)_4{}^{n+}$ (n = 0, 1, 2), edta = $Mo_4S_4(EDTA)_2{}^{3-}$; Ndp = $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$, Ndtc = $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_4$, NOCN = $Mo_4S_4(NO)_4(CN)_8$.

To date, there are only a few reported compounds containing a cubane-like Mo_4S_4 central core, and these may be divided into two classes: one having a core with six Mo–Mo bonds and the other having two Mo–Mo bonds. A comparison of the Mo–Mo distances are given in Table V. Although there are distinctly two short and four long Mo–Mo bonds in the cluster of the present compound, this trend is not present in other compounds. Although the EDTA complex[25] has the shortest average Mo–Mo distance (2.81 (5) Å), the two short Mo–Mo bonds in the present compound are significantly shorter than those found in any other compounds. This feature may have been due to the effect of the bridging $S_2CN(C_2H_5)_2$ groups that pulled the two Mo atoms closer than those without bridging ligands other than S atoms. Within the three compounds of the same formula, but of different oxidation states, $[Mo(\mu\text{-}C_5H_4\text{-}i\text{-}Pr)(\mu\text{-}S)]_4{}^{n+}$ (n = 0, 1, 2),[26] the mean Mo–Mo distances decrease as the number of cluster electrons decrease due to oxidation. The standard deviations for the mean Mo–Mo distances in Table V are calculated from values used to calculate the mean, not those from structural analysis as given in the original publications.

However, the Mo_4S_4 moieties in $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$ and $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2CN(i\text{-}C_4H_9)_2)]_4$ are elongated, containing only two Mo–Mo bonds.[22,27,28]

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So also is the cluster with NO and CN ligands $[Mo_4(\mu_3\text{-}S)_4(NO)_4(CN)_8]^{8-}$, in which there are only two Mo–Mo bonds with a mean distance of 2.99 (5) A.[29] The clusters in these compounds have 60 electrons. If we assume the same bonding orbitals for the Mo_4S_4 cluster as shown in Figure 2, clusters with up to 60 electrons will have six Mo–Mo bonds. Clusters with 68 electrons fill the antibonding orbitals ($a_1 + b_2 + e$) with 8 electrons, resulting in four net metal–metal bonding electrons. Thus, these clusters have two Mo–Mo bonds. Aside from the compounds listed in Table V, Dahl mentioned a Mo_4S_4-containing cyclopentadienyl complex,[30] but no structural parameter is available in the literature.

Preliminary results for the title compound were published as a note.[31]

Since the structure of $Mo_2(S_2CN(C_2H_5)_2)_6$ is unknown, it is rather difficult even to speculate on the mechanism for the formation of the title compound, but that remains an interesting problem.

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Supplementary Material Available: Listings of observed and calculated structure factors and a packing diagram (14 pages). Ordering information is given on any current masthead page.

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Reversible Electrode Processes Involving Multistep Mechanisms for Cadmium Dithiocarbamates and Diselenocarbamates at Mercury Electrodes

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The electrochemistry of cadmium dithio- and diselenocarbamate complexes ($Cd(RR'dtc)_2$ and $Cd(RR'dsc)_2$, respectively) at mercury electrodes in dichloromethane solution is characterized by a series of chemically and electrochemically reversible processes. However, unlike the situation with other metal dithiocarbamates, the processes are not based solely on simple charge transfer, but rather on exchange reactions with electrode mercury and mercury(II) dithiocarbamates, and also involve dimer–monomer equilibria as well as formation of a bimetallic (Cd–Hg) species. The oxidation is an overall four-electron process consisting of the following reversible reactions: $Cd_2(RR'dtc)_4 \rightleftharpoons 2[Cd(RR'dtc)_2]$; $Cd(RR'dtc)_2 + Hg \rightleftharpoons Hg(RR'dtc)_2 + Cd^{2+} + 2e^-$; $Hg(RR'dtc)_2 + Hg \rightleftharpoons [Hg_2(RR'dtc)_2]^+ + e^-$; $[Hg_2(RR'dtc)_2]^+ + Hg \rightleftharpoons [Hg_3(RR'dtc)_2]^{2+} + e^-$. The reduction occurs in two major steps and is an overall two-electron process: $Cd(RR'dtc)_2 + Hg + 2e^- \rightleftharpoons Cd(Hg) + 2[RR'dtc]^-$. The first reduction step is controlled kinetically by the exchange reaction $Cd(RR'dtc)_2 + Hg \rightleftharpoons Hg(RR'dtc)_2 + Cd(Hg)$. In addition, the $Cd(RR'dtc)_2$ and $Hg(RR'dtc)_2$ species react with each other to produce a bimetallic complex that gives a reversible reduction response at potentials more positive than for reduction of either the cadmium or the mercury complex. ^{113}Cd NMR data confirm that all the exchange reactions are rapid on the NMR time scale and are consistent with the chemically reversible and diffusion-controlled nature of the electrode processes. Both negative ion and positive ion mass spectra have been obtained for $Cd(RR'dtc)_2$ compounds, and all data again show evidence of ligand exchange. The electrochemistry of $Cd(Et_2dsc)_2$ and $Hg(Et_2dsc)_2$ parallels that of the dithiocarbamate analogues.

Introduction

The redox chemistry of dithiocarbamate complexes has been studied extensively[3-5] and is noteworthy for the existence of unusually high oxidation states. In the case of $Cd(RR'dtc)_2$ (see Appendix for definition of symbols) the electrochemistry has received little attention with one of the few reports to date being that of Nieuwpoort et al.,[6] who examined the oxidation processes that occur for $Cd(Et_2dtc)_2$ and $[Cd(Et_2dtc)_3]^-$ in acetone at a platinum electrode. Complex cyclic voltammograms were reported, but little discussion of mechanism was provided. Chemical oxidation of $M(RR'dtc)_2$[7-9] with halogens leads to the formation of $M(R_4tds)X_2$ (M = Zn, Cd, Hg; X = Cl, Br, I; R = Me, Et; tds = thiuram disulfide). By analogy with this reaction, products for the electrochemical oxidation processes were postulated without proof to be thiuram disulfide complexes and/or ligand oxidation products.[6]

To date, electrochemical studies of cadmium dithiocarbamates at mercury electrodes have been confined to brief reports of reduction waves in DMF[10] and in ternary solvent mixtures.[11] In both cases only cursory discussion of possible mechanisms was presented. Furthermore, the selenium analogues, $Cd(RR'dsc)_2$, have not been examined electrochemically and the influence of the substituent groups R and R′ is unknown.

In the solid state the complexes $Cd(Et_2dtc)_2$[12,13] and cadmium hexamethylenedithiocarbamate[14] are dimeric, the cadmium environment being five-coordinate, with two bridging dithiocarbamate ligands. One Cd–S bond length is significantly longer

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