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Synthesis and reactivity of molybdenum–sulfur cubes

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Abstract

A series of tetranuclear $Mo_4S_4(R_2NCS_2)_6$ complexes has been prepared by using the 'self-assembly' route as well as by synthesis from well-defined molecular building blocks. A variety of mononuclear, dinuclear and trinuclear building blocks have been successfully used to prepare the tetranuclear $Mo_4S_4^{6+}$ complexes. These thiocubanes have been prepared with mono-anionic 1,1-dithiolate ligands, which provide each of the Mo atoms with a pseudo-octahedral coordination geometry and result in the formation of neutral species. $Mo_4S_4L_6$ complexes with dialkyldithiocarbamate (DTC), R_2NCS_2; dialkyldithiophosphate (DDP), $(RO)_2PS_2$; alkylxanthate (XAN), $ROCS_2$; and alkylthioxanthate (THIOXAN), $RSCS_2$ ligands have been prepared. The structure of the $Mo_4S_4(DDP)_6$ complex was determined by single crystal X-ray structure analysis and is compared with the structures of other known Mo_4S_4 thiocubane complexes. The synthesis, electrochemistry, reactivity and bonding of the tetranuclear clusters are presented.

Introduction

Complexes containing transition metal sulfur cores are of interest as models of the active sites in a variety of metalloenzymes [1, 2] and for their use as catalyst precursors [3, 4] and lubricant additives [5, 6]. This paper concentrates on the important group of M_4S_4 thiocubane complexes. Tetranuclear complexes that contain mixed-metal cubes have been shown to be precursors for the formation of very active hydrotreating catalysts [7]. Moreover, the tetranuclear $Mo_4S_4^{6+}$ complexes have been shown to reduce wear, friction and oxidation in a variety of bench and engine tests [8].

The tetranuclear M_4S_4 complexes are important as active site models for a variety of enzymes that have been shown to contain thiocubane clusters. Tetranuclear iron–sulfur centers, Fe_4S_4, are present as electron transfer components in a wide variety of proteins and enzymes, including ferredoxins [9], the nitrogenase Fe proteins [10] and possibly, hydrogenase [2], the enzyme responsible for biological hydrogen uptake and production. Tetranuclear MFe_3S_4 mixed-metal cubes, where M is Mo or V, have also been proposed as models for the FeMo cofactor or FeV cofactor active sites in the nitrogenase enzymes, which are responsible for the six-electron reduction of dinitrogen to ammonia in biological systems [11, 12].

The original thiocubane complexes were prepared by what is referred to as a 'self-assembly' mechanism [2a]. More recent studies have focused on the synthesis of these complexes from discrete molecular building blocks. In the case of the mixed-metal thiocubane, $Mo_2Co_2S_4L_2L'_2$, where L and L' are a variety of ligands, the complex can be prepared by the addition of a low valent cobalt complex such as $Co_2(CO)_8$ to the dinuclear building block, $Mo_2(\mu\text{-}S)_2(S)_2L_2$ [13]. More recently, Curtis and co-workers have shown that a sulfur-deficient $Mo_2Co_2S_3$ cube is capable of desulfurizing thiophene in a homogeneous reaction [14].

Tetranuclear $Mo_4S_4^{6+}$ complexes have been prepared with a variety of ligands, including water [15, 16], the monodentate cyanide [17] and thiocyanate [18], the bidentate dialkyldithiocarbamate [19, 20] and dialkyldithiophosphinate [21], the tetradentate ethylenediamine tetraacetic acid [22], as well as cyclopentadienyl ligands [23–25]. We are particularly interested in the bidentate mono-anionic ligands as six of these ligands provide each of the Mo atoms with a pseudo-octahedral coordination geometry and result in the formation of neutral coordinatively saturated complexes. We have prepared a series of $Mo_4S_4^{6+}$ complexes with dialkyldithiocarbamate (DTC), R_2NCS_2; dialkyldithiophosphate (DDP), $(RO)_2PS_2$; xanthate (XAN), $ROCS_2$; and thioxanthate (THIOXAN), $RSCS_2$, ligands. The $Mo_4S_4(R_2NCS_2)_6$ complexes have been prepared by 'self-assembly' routes as well as by synthesis from well-defined molecular building blocks. Mononuclear,

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dinuclear and trinuclear building blocks have been successfully used to prepare the homonuclear as well as mixed-metal complexes. The $Mo_4S_4(R_2NCS_2)_6$ thiocubanes can be prepared either by the oxidation of lower valent molybdenum complexes or by reduction starting with higher valent molybdenum starting materials.

The solid-state structure of the $Mo_4S_4[(C_2H_5O)_2PS_2]_6$ complex was determined by single crystal X-ray structure analysis and is compared with the structures of other known $Mo_4S_4L_6$ cubes, where L is a mono-anionic, bidentate ligand. The synthesis, electrochemistry reactivity, and bonding of these tetrameric clusters will be discussed in detail.

Experimental

Molybdenum hexacarbonyl, sodium diethyldithiocarbamate, tetraethylthiuram disulfide, molybdenum(V) chloride, sodium borohydride, lithium triethylborohydride, potassium t-butoxide, magnesium sulfate, potassium ferricyanide, phosphorous pentasulfide, ammonium diethyldithiophosphate, isobutyraldehyde and MoO_3 were purchased from Aldrich and used without further purification. Dimethylformamide, acetone, hexane and acetonitrile were purchased from Burdick and Jackson. Toluene, CH_2Cl_2, diethyl ether and various alcohols were purchased from J. T. Baker and used as received. Absolute ethanol was purchased from Quantum Chemical. The potassium salts of dialkyldithiocarbamic acids were either purchased from Aldrich or prepared as previously reported [26]. The potassium salts of alkylxanthates and alkylthioxanthates were prepared in a similar manner by substitution of alcohol or thiol for the amine. The tetraalkylthiuram disulfides and the disulfides of alkylxanthate and alkylthioxanthate salts were prepared as previously described using ferricyanide as the oxidant rather than ammonium persulfide [26]. The $Mo_2(\mu\text{-}S)_2(S)_2(DTC)_2$ starting materials were prepared as previously described [27].

The disulfide of diethyldithiophosphate was prepared *in situ* by the slow addition of a solution of 0.01 mol of $K_3Fe(CN)_6$ in water to a solution of 0.01 mol of ammonium diethyldithiophosphate in water. The resulting red–brown solution and yellow oil were stirred at room temperature until all the water evaporated. Methylene chloride was added to the solid and the solution was filtered. The filtrate was dried over $MgSO_4$ and the methylene chloride was evacuated to produce a yellow oil.

The tetranuclear $Mo_4S_4^{6+}$ complexes are air stable as isolated. Cyclic voltammograms were obtained with a BAS 100 electrochemical analyzer and an IBM voltammetric cell consisting of a glassy-carbon working electrode (area 16 mm^2), a platinum wire auxiliary electrode, and a saturated calomel reference electrode. The samples were run anaerobically in dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate purchased from Southwestern Analytical Chemicals as a supporting electrolyte. Elemental analyses were performed by Galbraith Laboratories.

Synthesis of Mo_4S_4 complexes from mononuclear starting materials

Synthesis of $Mo_4S_4[(C_2H_5)_2NCS_2]_6$ from $Mo(CO)_6$

Tetraethylthiuram disulfide (5.90 g, 0.02 mol) was dissolved in a solution consisting of toluene (12 ml) and heptane (3 ml). This solution was degassed and added dropwise via cannula to a solution of (0.01 mol, 2.64 g) of molybdenum hexacarbonyl in 10 ml degassed toluene. The solution was refluxed for 6 h during which time the solution darkened to a purple color. Upon cooling to 0 °C a dark purple solid was isolated and recrystallized from CH_2Cl_2/ether. Yield 60%.

Synthesis of $Mo_4S_4[(C_8H_{17})_2NCS_2]_6$ from $Mo(CO)_6$

Tetraoctylthiuram disulfide (42.48 g, 0.067 mol) was dissolved in 80 ml toluene and a small amount of heptane. This solution was degassed and added dropwise via cannula to a solution (0.038 mol, 10.12 g) of molybdenum hexacarbonyl in 80 ml degassed toluene. The solution was refluxed for 7 days during which time the solution darkened to a purple color. The solution was evacuated to dryness and the pure product was separated on a silica gel column eluted with methylene chloride. The product was the first fraction collected and was recrystallized from CH_2Cl_2/hexane.

Synthesis of $Mo_4S_4(C_2H_5OCS_2)_6$ from $Mo(CO)_6$

A solution containing 0.01 mol of molybdenum hexacarbonyl and 0.02 mol of ethylxanthogen disulfide, $(C_2H_5OCS_2)_2$, in 25 ml of toluene was refluxed for 6 h. On cooling, the black crystalline solid was filtered, washed with toluene, and dried in vacuum. The complex can be recrystallized from CH_2Cl_2/hexane. *Anal.* Calc. for $Mo_4S_4(C_2H_5OCS_2)_6$: Mo, 30.97; S, 41.39; O, 7.75. Found: Mo, 29.95; S, 40.57, O, 8.22%.

Synthesis of $Mo_4S_4(C_8H_{17}OCS_2)_6$ from $Mo(CO)_6$

A solution containing 10 mmol of molybdenum hexacarbonyl and 20 mmol of octylxanthogen disulfide, $(C_8H_{17}OCS_2)_2$, in 25 ml of toluene was refluxed for 6 h. The toluene is removed to produce a black oil. The complex can be further purified from CH_2Cl_2/hexane. *Anal.* Calc. for $Mo_4S_4(C_8H_{17}OCS_2)_6$: Mo, 22.04; S, 29.39; C, 37.20; H, 5.86. Found: Mo, 22.49; S, 29.42, C, 37.26; H, 6.09%.

Synthesis of $Mo_4S_4[(C_2H_5O)_2PS_2]_6$ from $Mo(CO)_6$

Molybdenum hexacarbonyl (2.64 g, 0.01 mol) was suspended in 30 ml toluene and degassed. The disulfide of diethyldithiophosphate (7.41 g, 0.02 mol) was dissolved in 30 ml toluene, degassed and added to the suspension of $Mo(CO)_6$. A clear red solution was produced after 15 min of refluxing. The reaction was refluxed for 6 h at which time the IR spectra indicated the absence of a CO stretch at ~ 2000 cm^{-1}. The solution was evaporated to dryness, and the two products were separated on a silica gel column eluted with methylene chloride. The first fraction eluted was $Mo(DDP)_3$ and the second was $Mo_4S_4(DDP)_6$. The product was recrystallized using CH_2Cl_2/hexane to yield 20% pure tetramer.

Synthesis of $Mo_4S_4(C_{12}H_{25}SCS_2)_6$ from $Mo(CO)_6$

Molybdenum hexacarbonyl (1.3 g, 0.005 mol) and 6.0 g of the disulfide of dodecylthioxanthate, $(C_{12}H_{25}SCS_2)_2$, were dissolved in 50 ml toluene and 15 ml hexane. The solution was degassed and refluxed. After 2 h, the reaction was cooled to room temperature and the solvent was stripped under vacuum. The product was purified on a 5×50 cm silica gel column using hexane/CH_2Cl_2. The middle green band was collected and applied to a second 2.5×30 cm silica gel column using hexane/CH_2Cl_2. The product was then recrystallized from hexane/acetone to yield 300 mg of the green complex. Yield 11%. *Anal.* Calc. for $Mo_4S_4(C_{12}H_{25}SCS_2)_6$: C, 43.06; H, 6.89; S, 32.40; Mo, 17.65. Found: C, 43.05; H, 6.93; S, 32.50; Mo, 17.20%.

Synthesis of $Mo_4S_4[(C_2H_5)_2NCS_2]_6$ from molybdenum(V) chloride

Molybdenum pentachloride (20 g, 0.073 mol) was reacted with acetonitrile (100 ml) to produce $MoCl_4(CH_3CN)_2$ [28]. One gram of $MoCl_4(CH_3CN)_2$ was reacted with isobutyraldehyde (0.57 ml) to form $MoCl_3(CH_3CN)_3$ [29]. One mol of $MoCl_3(CH_3CN)_3$ was refluxed with 4 mol of dry potassium diethyldithiocarbamate in absolute ethanol to produce the $Mo_4S_4[(C_2H_5)_2NCS_2]_6$ thiocubane complex in greater than 50% yield.

Synthesis of $Mo_4S_4[(C_8H_{17})_2NCS_2]_6$ from molybdenum(V) chloride

$MoCl_3(CH_3CN)_3$ (250 mg, 0.77 mmol) was prepared as described above and dissolved in 20 ml of degassed, anhydrous ethanol. In a separate flask, potassium t-butoxide (346 mg, 3.08 mmol), dioctylamine (774 mg, 3.08 mmol) and CS_2 (234 mg, 3.08 mmol) were added to 20 ml anhydrous ethanol and degassed. This solution was then added to the molybdenum solution and the mixture was refluxed for several days. The reaction mixture was filtered to remove a precipitate and the remaining filtrate was evacuated to dryness. The residue was dissolved in methylene chloride. Acetonitrile was added to isolate a dark purple oil. After drying at 105 °C for 1 h in a vacuum drying oven, a 53% yield of $Mo_4S_4[(C_8H_{17})_2NCS_2]_6$ was obtained.

Synthesis of $Mo_4S_4[(C_2H_5)_2NCS_2]_6$ from $(NH_4)_2MoCl_5(H_2O)$

$(NH_4)_2MoCl_5(H_2O)$ (0.231 g, 0.706 mmol) was reacted with sodium diethyldithiocarbamate, $Na[(C_2H_5)_2NCS_2]\cdot 3H_2O$ (0.9 g, 4 mmol) in degassed absolute ethanol (50 ml) and refluxed for 18 h. The ethanol was evaporated and the resulting residue extracted with methylene chloride (15 ml). The $Mo_4S_4[(C_2H_5)_2NCS_2]_6$ complex was isolated in approximately 25% yield after column chromatography on a 3×6 cm silica gel column with CH_2Cl_2.

Synthesis of $Mo_4S_4[(C_2H_5)_2NCS_2]_6$ from MoO_3

MoO_3 can be converted to $(NH_4)_2MoCl_5(H_2O)$ by the procedure previously reported [30] and $Mo_4S_4[(C_2H_5)_2NCS_2]_6$ can be prepared from $(NH_4)_2[MoCl_5(H_2O)]$ by the procedure outlined above.

Synthesis of $Mo_4S_4[(C_2H_5)_2NCS_2]_6$ from $Mo[(C_2H_5)_2NCS_2]_4$

Mo(diethyldithiocarbamate)$_4$ can be synthesized in high yield from a variety of readily available starting materials such as MoO_3 and $MoCl_5$. MoO_3 can be converted electrochemically to K_3MoCl_6 [31] and then reacted with the appropriate salt of the diethyldithiocarbamate to produce Mo(diethyldithiocarbamate)$_4$. Alternatively, molybdenum(V) chloride can be quantitatively converted to $MoCl_4(CH_3CN)_2$ [28], which further reacts with a salt of diethyldithiocarbamate to produce $Mo[(C_2H_5)_2NCS_2]_4$ in nearly stoichiometric yield. $Mo[(C_2H_5)_2NCS_2]_4$ (250 mg, 0.36 mmol) was added to 25 ml of degassed toluene and refluxed for 5 days. A 60% yield of the black solid, $Mo_4S_4[(C_2H_5)_2NCS_2]_6$, was isolated by filtration, as confirmed by cyclic voltammetry and UV–Vis spectroscopy.

Synthesis of $Mo_4S_4(C_8H_{17}OCS_2)_6$ from $Mo(C_8H_{17}OCS_2)_4$

$Mo(C_8H_{17}OCS_2)_4$ was prepared by reacting $MoCl_4(CH_3CN)_2$ (1.0 g, 3.125 mmol) with the potassium salt of octylxanthate (3.12 g, 1.28 mmol) in 50 ml of toluene in an inert atmosphere dry box overnight at room temperature. The reaction was filtered to remove KCl, and solvent removed under vacuum. The compound was purified on a silica gel column and eluted with hexane/methylene chloride (9:1) to yield 0.44 g of $Mo(C_8H_{17}OCS_2)_4$ (15% yield).

$Mo(C_8H_{17}OCS_2)_4$ (200 mg, 0.2 mmol) was added to 15 ml of degassed toluene and refluxed for 4 h. The solvent was removed under reduced pressure and the residue was extracted with 10 ml methylene chloride. The product, $Mo_4S_4(C_8H_{17}OCS_2)_6$, was purified by column chromatography with silica as the support and 7:1 hexane/methylene chloride as the eluent and isolated in a 37% yield.

Synthesis of Mo_4S_4 complexes from dinuclear starting materials

Synthesis of $Mo_4S_4[(C_4H_9)_2NCS_2]_6$ by reduction of $Mo_2(\mu\text{-}S)_2(S)_2[(C_4H_9)_2NCS_2]_2$ with $NaBH_4$

$Mo_2(\mu\text{-}S)_2(S)_2[(C_4H_9)_2NCS_2]_2$ (50 mg, 0.7 mmol) and tetraisobutylthiuram disulfide (14 mg, 0.35 mmol) were dissolved in DMF (4 ml). This solution was combined with a solution of $NaBH_4$ (10 mg, 0.094 mmol) in 4 ml DMF and the resultant dark solution was refluxed for 1 h. The purple $Mo_4S_4[(C_4H_9)_2NCS_2]_6$ was isolated in 35% yield after column chromatography on a silica gel column with CH_2Cl_2: hexane (3:1) as the eluent.

Synthesis of $Mo_4S_4[(C_4H_9)_2NCS_2]_6$ by reduction of $Mo_2(\mu\text{-}S)_2(S)_2[(C_4H_9)_2NCS_2]_2$ with $LiB(C_2H_5)_3H$

$Mo_2(\mu\text{-}S)_2(S)_2[(C_4H_9)_2NCS_2]_2$ (100 mg, 0.14 mmol) was dissolved in THF (7 ml) and degassed. $LiB(C_2H_5)_3H$ (0.15 ml of a 1 M solution) was added via syringe and the resultant solution was stirred for 30 min at room temperature. The purple $Mo_4S_4[(C_4H_9)_2NCS_2]_6$ was isolated in 12–15% yield after column chromatography on a silica gel column with CH_2Cl_2: hexane (3:1) as the eluent.

Synthesis of $Mo_4S_4[(C_8H_{17})_2NCS_2]_6$ by reduction of $Mo_2(\mu\text{-}S)_2(S)_2[(C_8H_{17})_2NCS_2]_2$ with $NaBH_4$

$Mo_2(\mu\text{-}S)_2(S)_2[(C_8H_{17})_2NCS_2]_2$ (50 mg, 0.052 mmol) and $NaBH_4$ (8 mg, 0.075 mmol) were dissolved in DMF (4 ml). The resulting brown solution was refluxed for 1 h. A low yield of the purple $Mo_4S_4[(C_8H_{17})_2NCS_2]_6$ was evident by thin layer chromatography.

Synthesis of $Mo_4S_4[(C_8H_{17})_2NCS_2]_6$ by reduction of $Mo_2(\mu\text{-}S)_2(S)_2[(C_8H_{17})_2NCS_2]_2$ with $NaBH_4$ in the presence of dioctyldithiocarbamate

$Mo_2(\mu\text{-}S)_2(S)_2[(C_8H_{17})_2NCS_2]_2$ (50 mg, 0.052 mmol) and the sodium salt of dioctyldithiocarbamate (8 mg, 0.024 mmol) were dissolved in DMF (3 ml) and added to a solution of $NaBH_4$ (8 mg, 0.075 mmol) in DMF (2 ml). The resulting solution was refluxed for 1 h. A low yield of the purple $Mo_4S_4[(C_8H_{17})_2NCS_2]_6$ was evident by thin layer chromatography.

Synthesis of $Mo_4S_4[(C_8H_{17})_2NCS_2]_6$ by reduction of $Mo_2(\mu\text{-}S)_2(S)_2[(C_8H_{17})_2NCS_2]_2$ with $NaBH_4$ in the presence of tetraoctylthiuram disulfide

$Mo_2(\mu\text{-}S)_2(S)_2[(C_8H_{17})_2NCS_2]_2$ (50 mg, 0.052 mmol), tetraoctylthiuram disulfide (17 mg, 0.027 mmol) and $NaBH_4$ (8 mg, 0.024 mmol) were refluxed in DMF (5 ml) for 1 h. A 40% yield of the purple $Mo_4S_4[(C_8H_{17})_2NCS_2]_6$ was isolated after column chromatography on a silica gel column with CH_2Cl_2 as the eluent.

Synthesis of $Mo_4S_4[(C_3H_7)_2NCS_2]_6$ by reduction of $Mo_2(\mu\text{-}S)_2(S)_2[(C_3H_7)_2NCS_2]_2$ with tetrabutylammonium borohydride in the presence of tetrapropylthiuram disulfide

$Mo_2(\mu\text{-}S)_2(S)_2[(C_3H_7)_2NCS_2]_2$ (100 mg, 0.15 mmol), tetrapropylthiuram disulfide (105 mg, 0.30 mmol) and tetrabutylammonium borohydride (191 mg, 0.59 mmol) were refluxed in toluene (20 ml) for 4 h. A 10% yield of the purple $Mo_4S_4[(C_3H_7)_2NCS_2]_6$ was isolated after column chromatography on a silica gel column with CH_2Cl_2 as the eluent.

Synthesis of Mo_4S_4 complexes from trinuclear starting materials

Synthesis of $Mo_4S_4[(C_3H_7)_2NCS_2]_6$ from $Mo_3S_4[(C_3H_7)_2NCS_2]_4$

A toluene solution (5 ml) containing $Mo_3S_4[(C_3H_7)_2NCS_2]_4$ (0.05 g, 0.045 mmol), molybdenum hexacarbonyl (0.012 g, 0.045 mmol) and tetrapropylthiuram disulfide (0.016 g, 0.045 mmol) was refluxed for 5 h, producing a brown solution containing a purple precipitate. The solid was isolated by filtration and washed with hexane and ethanol to produce 0.044 g of purple, crystalline $Mo_4S_4[(C_3H_7)_2NCS_2]_6$. This is a 62.9% yield based on the Mo_3S_4 complex.

Ligand exchange reactions on Mo_4S_4 complexes

The mixed-ligand complexes, $Mo_4S_4[(C_2H_5)_2NCS_2]_4(C_2H_5OCS_2)_2$ and $Mo_4S_4[(C_2H_5)_2NCS_2]_5(C_2H_5OCS_2)$, can be prepared by ligand substitution reactions by ethylxanthate on $Mo_4S_4[(C_2H_5)_2NCS_2]_6$. $Mo_4S_4[(C_2H_5)_2NCS_2]_6$ (100 mg, 0.071 mmol) and potassium diethyldithiocarbamate (68 mg, 0.426 mmol) were dissolved in methylene chloride (~20 ml). The diethyl ether complex of tetrafluoroboric acid, $HBF_4 \cdot O(C_2H_5)_2$, (~0.6 ml) was added to the stirring purple reaction mixture. The mixed-ligand complexes were purified by silica gel chromatography. The first band that eluted from the column with methylene chloride was $Mo_4S_4[(C_2H_5)_2NCS_2]_4(C_2H_5OCS_2)_2$ and the second band was $Mo_4S_4[(C_2H_5)_2NCS_2]_5(C_2H_5OCS_2)_2$ as determined by ^1H NMR.

Preliminary structural data on $Mo_4S_4(C_2H_5OCS_2)_6$

A dark, rectangular-shaped purple crystal of $Mo_4S_4(C_2H_5OCS_2)_6$, having approximate dimensions of 0.34×0.13×0.024 mm was isolated from a solution of methylene chloride and hexane and mounted on a glass fiber. Preliminary examination and data collection were performed with Mo Kα radiation ($\lambda = 0.71073$ Å) on an Enraf-Nonius CAD4 computer controlled kappa axis diffractometer equipped with a graphite crystal incident beam monochromator. The orthorhombic cell parameters and calculated volume are: $a = 10.492(6)$, $b = 25.011(10)$, $c = 8.711(6)$ Å, $V = 2285.9$ Å^3, respectively. Although extensive disorder in the ethyl groups prevented a full structural determination, preliminary evidence is consistent with the presence of an Mo_4S_4 thiocubane with approximate distances and angles that very closely resemble those observed for the DDP cube.

Solution and refinement of the structure of $Mo_4S_4[(C_2H_5O)_2PS_2]_6$

Dark, rectangular-shaped, purple crystals of $Mo_4S_4[(C_2H_5O)_2PS_2]_6$ were grown by addition of hexane to a methylene chloride solution of the complex, followed by storage at 4 °C. A single crystal of approximate dimensions 0.12×0.34×0.38 mm was mounted in a glass capillary with its longest edge nearly parallel to the phi axis of the diffractometer. Graphite-monochromated Mo Kα radiation was used for the X-ray diffraction study which was conducted on a computer-controlled four-circle Nicolet autodiffractometer. A total of 8252 independent reflections was collected with full ω-scans and a range of $3.0 < 2\theta < 45.8$ and 4181 reflections were observed with $I > 3\sigma$. Other details of the data collection and refinement are given in Table 1.

The data collection, solution and refinement were conducted by C. Day of the Crystalytics Company. The structure was solved using direct methods with Siemens SHELXTL-Plus software package as modified by Crystalytics Company. Intensity data were corrected empirically for absorption effects by using Ψ scans for seven reflections. A relative range of transmission factors of 0.81 to 1.0 was used. The data were reduced to relative squared amplitudes, F_o^2, by means of standard Lorentz and polarization corrections. Six standard reflections exhibited no significant loss of intensity throughout the course of data collection and therefore no time-dependent intensity corrections were necessary. Anomalous dispersion corrections were applied to all non-hydrogen atoms in the complex.

TABLE 1. Summary of crystallographic parameters

Formula	$Mo_4S_4[(C_2H_5O)_2PS_2]_6$
Molecular weight	1633.30
a (Å)	17.374(4)
b (Å)	17.354(4)
c (Å)	19.963(4)
β (°)	93.20(2)
V (Å^3)	6010(2)
Z	4
Space group	$P2/c$
Crystal dimensions (mm)	0.12×0.34×0.38
Radiation	Mo Kα ($\lambda = 0.71073$ Å)
Scan speed (°/min)	6 ($3 < 2\theta < 31.3$)
	3 ($31.3 < 2\theta < 39.7$)
	1 ($39.7 < 2\theta < 43.0$)
	1 ($43.0 < 2\theta < 45.8$)
Data collected	8252
Unique data	4181
Check collection	6/300
R (%)	7.2
R_w (%)	8.0

The final structural model was refined with all non-hydrogen atoms having anisotropic thermal parameters. There was significant disorder remaining on one of the ethyl groups on O31 and on O62. The structure of the complex is shown in Fig. 1 with the carbon atoms removed for clarity. The counter-weighted full matrix least-squares refinement converged with final residuals of $R = 7.2\%$ and $R_w = 8.0\%$ and a goodness of fit indicator equal to 2.17.

Extended Hückel calculations

The molecular orbitals and energy levels were calculated via Extended Hückel treatment implemented on a Mac II-fx by Tektronix using the CAChe Scientific system with coordinates obtained from the crystal structure for $Mo_4S_4[(C_2H_5O)_2PS_2]_6$. The parameters for sulfur were those of Hoffmann and co-workers [32].

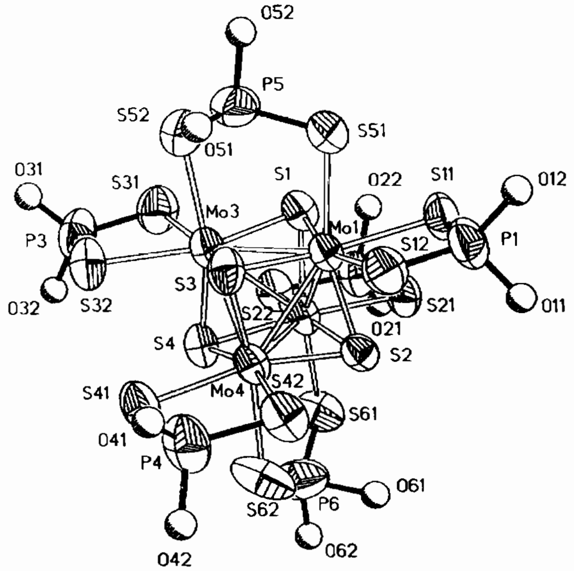

Fig. 1. Molecular representation of the crystal structure of $Mo_4S_4[(C_2H_5O)_2PS_2]_6$ with the numbering scheme. The thermal elipsoids are drawn at 50% probability level. Carbon atoms have been eliminated for clarity.

Results and discussion

A series of tetranuclear $Mo_4S_4(R_2NCS_2)_6$ complexes has been prepared by the 'self-assembly' route as well as by synthesis from well-defined molecular building blocks. Mononuclear, dinuclear and trinuclear building blocks have been successfully used to prepare the homonuclear complexes as shown in Fig. 2. The $Mo_4S_4L_6$ thiocubanes can be prepared by the oxidation of lower valent Mo(0) species as well as the reduction of higher valent Mo(IV), Mo(V) and Mo(VI) species. The formal oxidation state of the Mo in the neutral $Mo_4S_4(R_2NCS_2)_6$ cube consists of two Mo(IV) and two Mo(III) atoms.

The lower valent molybdenum complexes such as $Mo(CO)_6$ are oxidized by the disulfides of DTC, DDP, XAN or THIOXAN to produce the corresponding $M_4S_4L_6$ cubes. This reaction has been effected by refluxing the two neutral starting materials in toluene. The reaction time is a function of the ligand type and the solubility of the reagents and products. For example, the diethyldithiocarbamate complex requires approximately 6 h to prepare, while the dioctyldithiocarbamate complex requires approximately 7 days. In all of these reactions the sulfide in the $M_4S_4L_6$ cubes is apparently obtained from the decomposition of the ligands as no additional source of sulfide was provided.

The tetranuclear clusters have also been prepared by reduction of mononuclear Mo(IV), Mo(V) and Mo(VI) complexes in the presence of the appropriate ligand. The $Mo_4S_4(R_2NCS_2)_6$ complex has been synthesized from a Mo(IV) starting material by reaction of Mo(dialkyldithiocarbamate)$_4$ with the appropriate salt of the dialkyldithiocarbamate ligand. The stepwise reduction of $MoCl_5$ to $Mo(IV)Cl_4(CH_3CN)_2$ and $Mo(III)Cl_3(CH_3CN)_3$ followed by addition of the appropriate ligand has also been shown to result in the synthesis of the $Mo_4S_4L_6$ complex. Similarly, the Mo(VI) compound, MoO_3, can be reduced to $[NH_4]_2[Mo(III)Cl_5H_2O]$ by a variety of procedures that have been previously reported [30, 31]. This Mo(III) complex can then be reacted with the appropriate ligand to produce the desired $M_4S_4L_6$ cubes.

The step-wise synthesis of these $Mo_4S_4L_6$ complexes from dinuclear building blocks has also been achieved. Previous work by Sykes and co-workers [18] has indicated that mixtures of the water-soluble, trinuclear $[Mo_3S_4(H_2O)_9]^{4+}$ and tetranuclear $[Mo_4S_4(H_2O)_{12}]^{5+}$ clusters can be prepared from $[Mo_2O_2X_2(\text{cysteinato})_2]^{2-}$ dimers in HCl. We have shown that the neutral Mo(V) complex, $Mo_2(\mu\text{-}S)_2(S)_2(DTC)_2$, can be reduced in organic solvent electrochemically and by a variety of reductants including sodium borohydride to produce the Mo_4S_4 cube. The structure of the dinuclear building block is shown in Fig. 3, together with a possible association scheme. The two molybdenum atoms and four sulfide sulfur atoms in this complex occupy positions that approximate six of the eight vertices of a cube. The reduction of these dinuclear building blocks allows two of them to associate, with the elimination of excess sulfur to form the $Mo_4S_4(DTC)_6$ cubes.

The $Mo_4S_4(DTC)_6$ cubes can also be prepared from trinuclear building blocks. Previous work has indicated that the dithiophosphinate complex, $Mo_4S_4(R_2PS_2)_6$, can be prepared by reaction of $Mo(CO)_6$ with trinuclear building blocks [21]. The Mo(IV) dialkyldithiocarbamate complex, $Mo_3S_4(DTC)_4$, also reacts with 1 equiv. of a Mo(0) species such as $Mo(CO)_6$ in the presence of tetraalkylthiuram disulfide to produce the $Mo_4S_4(DTC)_6$ cube. The structure of the trinuclear building block is

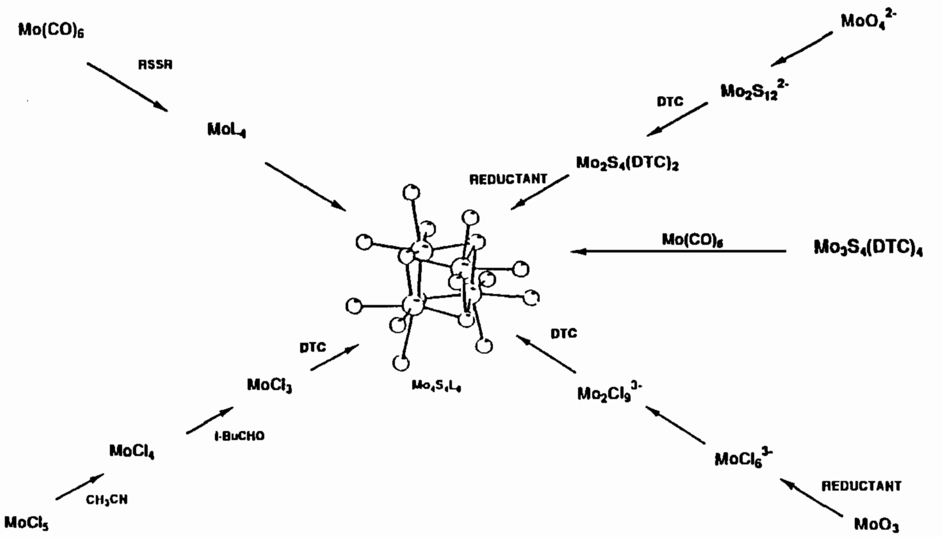

Fig. 2. Scheme outlining a variety of synthetic routes for the preparation of $Mo_4S_4L_6$.

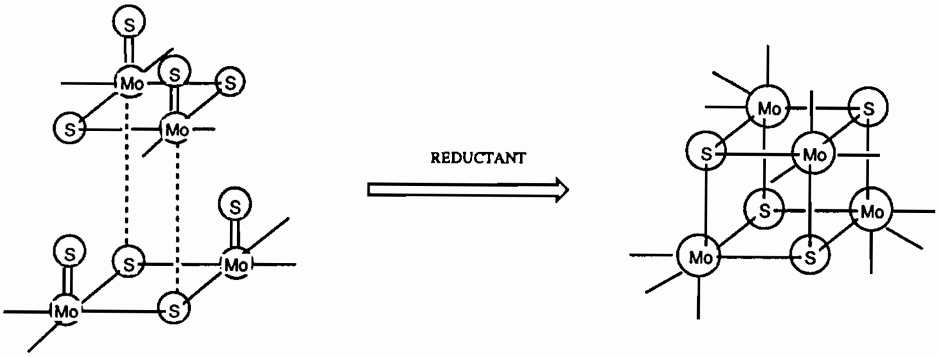

Fig. 3. Possible reaction pathway for the synthesis of $Mo_4S_4L_6$ from $Mo_2(\mu\text{-}S)_2(S)_2L_2$ dimers.

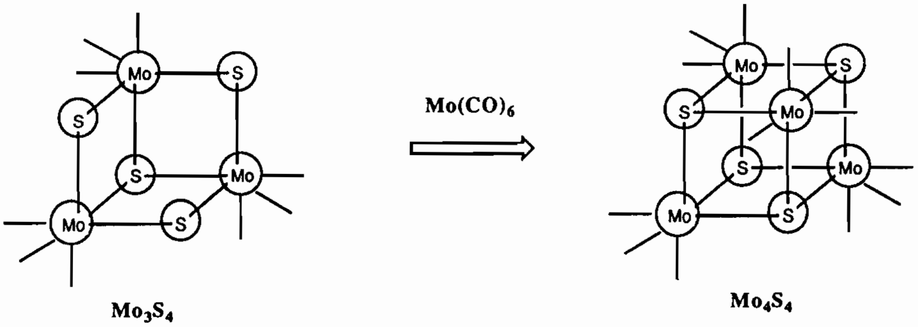

Fig. 4. Possible reaction pathway for the synthesis of $Mo_4S_4L_6$ from $Mo_3S_4L_4$ trimers.

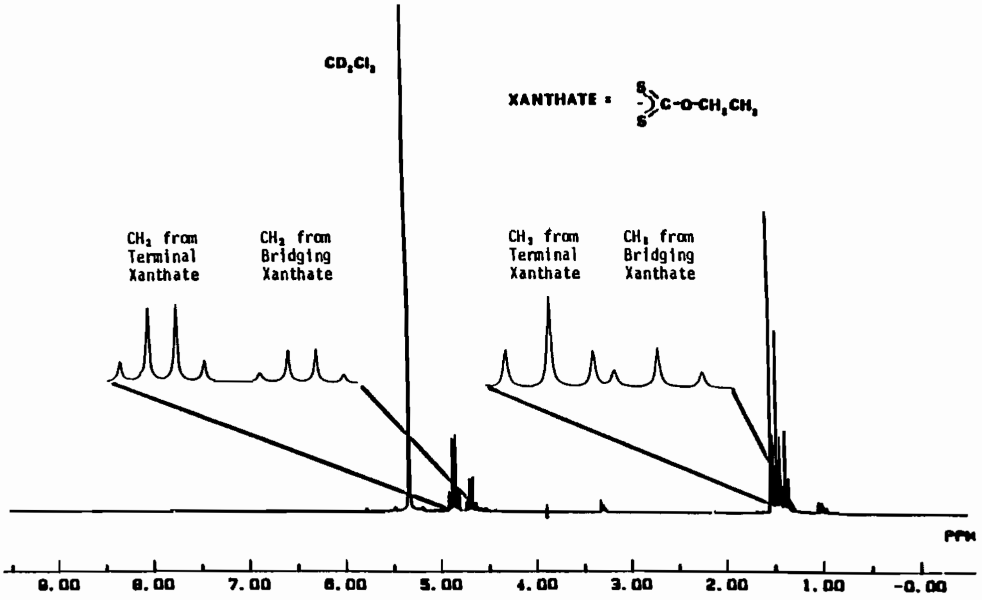

Fig. 5. Proton NMR of $Mo_4S_4(C_2H_5OCS_2)_6$.

presented in Fig. 4, together with a possible assembly scheme. The three molybdenum atoms and four sulfide atoms in this complex occupy positions that approximate seven of the eight vertices of a cube. The reaction of these trinuclear building blocks with a low valent mononuclear Mo(0) species results in the formation of the $Mo_4S_4(DTC)_6$ cubes.

The ^1H NMR of $Mo_4S_4(C_2H_5OCS_2)_6$, shown in Fig. 5, indicates that there are two different types of ethyl groups present in the complex which correspond to two different types of xanthate ligands. The two ligands are present in a two-to-one ratio as shown by NMR. These results are consistent with the presence of two bridging and four chelating xanthate ligands. This result is consistent with preliminary X-ray structural data that has been obtained for the $Mo_4S_4(C_2H_5OCS_2)_6$ complex as well as the structural data presented for the $Mo_4S_4[(C_2H_5O)_2PS_2]_6$ complex.

X-ray crystal structure of $Mo_4S_4[(C_2H_5O)_2PS_2]_6$

The structure of $Mo_4S_4[(C_2H_5O)_2PS_2]_6$ was determined by X-ray crystallography. The dark purple rectangular crystals crystallized in the space group *P2/c* with $a = 17.3740$, $b = 17.3540$, $c = 19.9630$ Å, $\beta = 93.2°$ and $Z = 4$. The structure of the complex, shown in Fig. 1, indicates that the four molybdenum and four sulfide sulfur atoms in the complex occupy positions that approximate the vertices of a distorted cube. Each of the molybdenum atoms is coordinated to three of the sulfide sulfur ligands and one chelating diethyldithiophosphate ligand. The pseudo-octahedral coordination around each Mo is completed by two additional diethyldithiophosphate ligands which bridge Mo atoms.

The structure of the $Mo_4S_4[(C_2H_5O)_2PS_2]_6$ complex is similar to that previously determined for the $Mo_4S_4[(C_2H_5)_2NCS_2]_6$ and $Mo_4S_4[(C_2H_5)_2PS_2]_6$ thiocubane complexes [20, 21]. The structure is also similar to the preliminary structural data obtained for the $Mo_4S_4(C_2H_5OCS_2)_6$ complex. Selected bond distances and angles are presented in Table 2. The two Mo–Mo bonds in $Mo_4S_4[(C_2H_5O)_2PS_2]_6$ that are connected by bridging ligands are at 2.767 and 2.811 Å with an average distance of 2.789 Å as compared to 2.732 Å for the diethyldithiocarbamate complex and 2.786 Å for the diethyldithiophosphinate complex. The other four Mo–Mo distances involving metal atoms that are not bridged by chelating ligands have an average value of 2.873 Å as compared to 2.861 Å for the diethyldithiocarbamate complex and 2.879 Å for the diethyldithiophosphinate complex. The average Mo–S distance in the Mo_4S_4 core of the complex is 2.359 Å, which agrees well with the average Mo–S distances in the diethyldithiocarbamate and diethyldithiophosphinate complexes of approximately 2.35 Å. Additional structural data are included in Table 2. See also 'Supplementary material'.

Redox properties

The oxidation states of the Mo atoms in the cube are described as formally two Mo(IV) and two Mo(III). However, several other oxidation states of the clusters are quite stable and can be accessed electrochemically [33]. The cyclic voltammograms of $Mo_4S_4^{6+}$ clusters reveal two quasi-reversible one-electron reduction waves to form $Mo_4S_4^{5+}$ and $Mo_4S_4^{4+}$ cores and one or two quasi-reversible one-electron oxidation waves to form $Mo_4S_4^{7+}$ and $Mo_4S_4^{8+}$ cores. The cyclic voltammogram of $Mo_4S_4[(C_2H_5)_2NCS_2]_6$ is shown in Fig. 6. The redox potentials of the $Mo_4S_4^{6+}$ clusters can vary as much as 670 mV depending on the ligand binding the cube. The relative ease of reduction is as follows THIOXAN > XAN > DDP > DTC.

The reduction potentials for these complexes are shown in Table 3. The dialkyldithiocarbamate complex

TABLE 2. Selected bond distances (Å) and bond angles (°)

Distances			
Mo1–Mo2	2.874(3)		
Mo1–Mo3	2.810(3)		
Mo1–Mo4	2.861(3)		
Mo2–Mo3	2.871(3)		
Mo2–Mo4	2.769(3)		
Mo3–Mo4	2.893(3)		
Mo1–S1	2.349(6)		
Mo1–S2	2.360(6)		
Mo1–S3	2.351(6)		
Mo2–S1	2.372(6)		
Mo2–S2	2.366(6)		
Mo2–S4	2.372(6)		
Mo3–S1	2.353(6)		
Mo3–S3	2.335(6)		
Mo3–S4	2.397(6)		
Mo4–S2	2.347(6)		
Mo4–S3	2.358(6)		
Mo4–S4	2.351(6)		
Angles			
S1–Mo1–S2	102.8	S1–Mo1–S3	105.2
S2–Mo1–S3	102.8		
S1–Mo2–S2	101.9	S1–Mo2–S4	103.5
S2–Mo2–S4	106.3		
S1–Mo3–S3	105.6	S1–Mo3–S4	103.3
S3–Mo3–S4	101.2		
S2–Mo4–S3	103.0	S2–Mo4–S4	107.6
S3–Mo4–S4	101.9		
Mo1–S3–Mo3	73.7	Mo2–S2–Mo4	72.0
Mo3–S1–Mo1	73.4	Mo4–S4–Mo2	71.8

Numbers in parentheses are e.s.d.s. in the least significant digits.

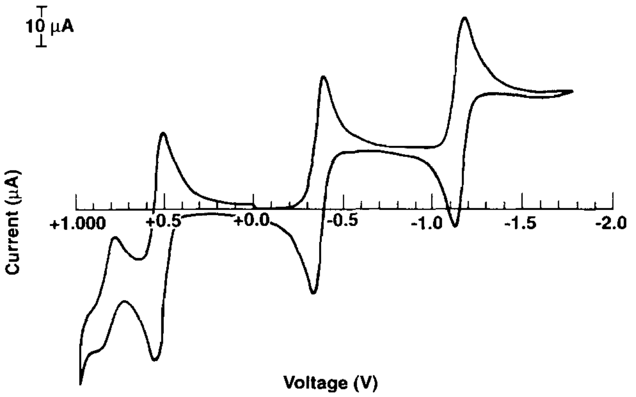

Fig. 6. Cyclic voltammetry of $Mo_4S_4[(C_2H_5)_2NCS_2]_6$.

TABLE 3. Electrochemical potentials of $Mo_4S_4L_6$ complexes in CH_2Cl_2 with 0.1 M Bu_4NPF_6 versus SCE

Ligand	$E_{1/2}$° (V)		
C12-THIOXAN		+0.260	−0.430
Ethyl XAN	+1.112	+0.176	−0.603
Ethyl DDP	+1.059	+0.164	−0.671
Octyl XAN		+0.147	−0.640
$(EtXAN)_2(EtDTC)_4$	+0.722	−0.211	−0.779
$(EtXAN)(EtDTC)_5$	+0.622	−0.306	−1.084
Ethyl DTC	+0.534	−0.426	−1.230
i-Butyl DTC	+0.516	−0.461	−1.202

is the hardest to reduce with a redox potential of −413 mV versus SCE while the alkylthioxanthate complex is the easiest to reduce with a redox potential of +260 mV versus SCE. Despite this range, the tetranuclear $Mo_4S_4^{6+}$ complexes are all air stable. The effect of chain length on the potential has also been examined and the results, which are summarized in Table 3, indicate that the increase in chain length can account for a decrease in the reduction potential of approximately 30 mV. $M_4S_4^{6+}$ cubes have also been prepared with mixed ligands including $Mo_4S_4(DTC)_5(XAN)$ and $Mo_4S_4(DTC)_4(XAN)_2$. As expected, the redox potentials of the mixed-ligand complexes are between those reported for complexes with all dithiocarbamate and all xanthate ligands.

The reversible electrochemical behavior of the complexes suggests that it may be possible to isolate stable reduced forms of the cubes. The fully reduced form of the cube would contain formally four Mo(III) atoms. The one and two electron reduced species, $[Mo_4S_4(L)_6]^n$, where L = diethyldithiocarbamate and ethylxanthate and $n = 1^-$ and 2^- have been prepared by controlled potential coulometry. The reaction and potentials are shown below for the ethylxanthate complex. The UV–Vis spectra of each of these $[Mo_4S_4(C_2H_5OCS_2)_6]^n$ species,

$$[Mo_4S_4(L)_6]^0 \underset{-0.2\ V}{\longleftrightarrow} Mo_4S_4(L)_6]^{1-} \underset{-0.8\ V}{\longleftrightarrow} [Mo_4S_4(L)_6]^{2-}$$

blue–purple green green

where $n = 0, 1^-, 2^-$, is shown in Fig. 7 and the absorption maxima are summarized in Table 4 for thiocubanes with other ligands.

Extended Hückel calculations

Extended Hückel calculations were carried out primarily to elucidate the bonding nature of the four metals in the $Mo_4S_4[(C_2H_5O)_2PS_2]_6$ cube. The focus was therefore on the molecular orbitals that are metal–metal bonding in nature. The calculations indicated that there were five filled metal–metal bonding molecular orbitals (HOMO to HOMO-4) and one unoccupied metal–metal bonding (LUMO) orbital. All six molecular orbitals are principally σ in nature. These orbitals are grouped together as shown in the energy level diagram in Fig. 8. The molecular orbitals above and below these six are primarily ligand or sulfur centered in nature and will not be discussed further.

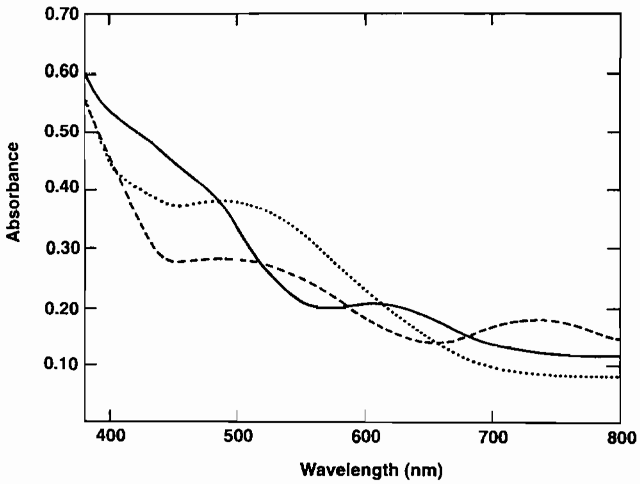

Fig. 7. Electronic spectra of $[Mo_4S_4((C_2H_5)_2NCS_2)_6]^n$, where $n = 0$, – – –; 1^-, ——; 2^-, · · · · ·.

TABLE 4. Absorption maxima (nm) in electronic spectra of $[Mo_4S_4L_6]^n$ complexes, where $n = 1^+$, 0, 1^-, 2^-

Ligand	Complex charge			
	1^+	0	1^-	2^-
$C_2H_5OCS_2$	735 475	735	610 460(sh)	490
$C_8H_{17}OCS_2$	720 500(sh)	735 480(sh)	610	485
$C_{12}H_{25}SCS_2$		765 570		
$(C_2H_5)_2NCS_2$	550	568	555 418	675 412

The LUMO is best described as having σ bonding character between the metals that are not bridged by the DDP ligand. The HOMO is 0.038 eV lower energy than the LUMO and has σ bonding between the metals that are not bridged by the DDP. The HOMO-1 molecular orbital is σ in character between the metal centers that are bridged by the DDP ligand. The HOMO-2 orbital is primarily σ in nature between the metals that are not bridged by the ligand. The HOMO-3 orbital has strong σ bonding character between the metals bridged by the DDP ligand. The HOMO-4 molecular orbital is best described as σ bonding between all four metal atoms. All of the overlap from the four molybdenum atoms for this molecular orbital is within the

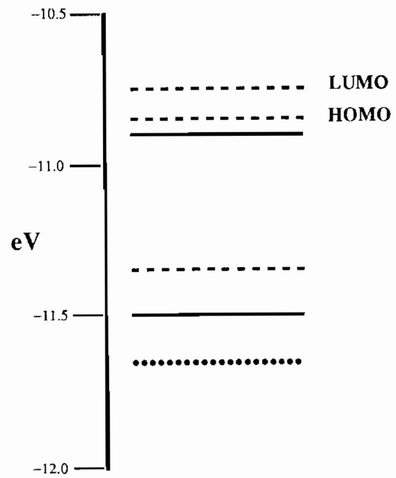

Fig. 8. The energy level diagram for $Mo_4S_4[(C_2H_5O)_2PS_2]_6$. The overall bonding of the orbital is indicated as follows: ——, orbitals involving Mo atoms bridged by the DDP ligand; – – –, orbitals involving Mo atoms not bridged by the DDP ligand; · · · · ·, orbital involving all four Mo atoms. This diagram was obtained by examining the eigen values and visualizing each molecular orbital.

cube. An apt description of this orbital is a four-center-two-electron bond.

The relatively small HOMO–LUMO gap and the bonding character of the LUMO suggests that the mono- and di-anion of the parent complex should both be easily accessible. This is consistent with the observed electrochemistry reported here.

Taken together, the results of the Extended Hückel calculations are summarized as follows; five occupied metal–metal bonding orbitals of the cube have been identified, one less than to be expected for a fully metal–metal bonded cube. The sixth molecular orbital is the LUMO which is both bonding in nature and accessible. Consistent with our observations that the mono- and di-anion are accessible by electrochemical reduction. The Extended Hückel calculations clearly show that there is delocalized metal–metal bonding distributed throughout the cube framework and that there are no localized oxidation states in this formally mixed valent [2Mo(III), 2Mo(IV)] complex. Harris has published a more comprehensive review of the electronic structure of similar M_4S_4 clusters [34].

Conclusions

A series of tetranuclear $Mo_4S_4(R_2NCS_2)_6$ complexes has been prepared by using the 'self-assembly' route as well as by syntheses from well-defined molecular building blocks. A variety of mononuclear, dinuclear and trinuclear building blocks has been successfully used to prepare the tetranuclear $Mo_4S_4^{6+}$ complexes. The complexes have also been prepared with a variety of bidentate mono-anionic ligands that would provide each of the Mo atoms with a pseudo-octahedral coordination geometry and result in the formation of neutral species. The $Mo_4S_4^{6+}$ complexes with dialkyldithiocarbamate (DTC), R_2NCS_2; dialkyldithiophosphate (DDP), $(RO)_2PS_2$; alkylxanthate (XAN), $ROCS_2$; and alkylthioxanthate (THIOXAN), $RSCS_2$, ligands have all been prepared. The structure of the $Mo_4S_4[(C_2H_5O)_2PS_2]_6$ complex was determined by single crystal X-ray structure analysis and is compared with the structures of other known $Mo_4S_4L_6$ cubes. Extended Hückel calculations indicate that the LUMO has significant metal–metal bonding character. Coupled with a relatively small HOMO–LUMO gap this suggests that the mono- and di-anion of the parent complex should be both easily accessible and thermodynamically stable which is consistent with the electrochemical results.

Complexes containing M_4S_4 cores are of interest for a number of reasons including their use as catalyst precursors, lubricant additives, and models for the active sites in a variety of metalloenzymes. Additional work on the preparation of a variety of mixed-metal cubes will follow in a subsequent report. The reactivity of these complexes is currently being investigated.

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