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Syntheses and Characterization of the Cobalt Bis(tetrathiomolybdate) Trianion, $Co(MoS_4)_2^{3-}$

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The anion MoS_4^{2-} forms a number of interesting bimetallic metal sulfide complexes by acting as a bidentate ligand [1]. For example in the series $M(MoS_4)_2^{2-}$, M can be Zn, Ni, Pd, Pt or Mo=S (the latter in the special case of the recently isolated $Mo_3S_9^{2-}$ anion [2]). In the case of Fe–Mo–S systems, the presence of an Fe–Mo–S center in nitrogenase has inspired the preparation of the trianion $Fe(MoS_4)_2^{3-}$ [3, 4]. Further, MoS_4^{2-} can serve as a bridging group as in $MoS_4(FeCl_2)_2$ [2–5, 6] or as a starting material to form clusters such as $Mo_2Fe_6S_8(SR)_9^{3-}$ [7].

In the series $M(MoS_4)_2^{2-,3-}$, the species with M = Co are notably absent from the literature. Our initial efforts to prepare $Co(MoS_4)_2^{2-}$ led invariably to black–grey solid materials insoluble in common organic solvents. Failure to prepare a stable Co complex with MoS_4^{2-} was reminiscent of the situation first observed with the Fe system. In the Fe system, although the dianionic complex $Fe(MoS_4)_2^{2-}$ was briefly reported [8], MacDonald *et al.* [3] and Coucouvanis *et al.* [4] independently discovered that the reduced complex, $Fe(MoS_4)_2^{3-}$, could be isolated in stable form. Cyclic voltammetry of this compound shows an irreversible oxidation wave at –0.075 V *vs.* SCE, consistent with the failure to isolate the dianion $Fe(MoS_4)_2^{2-}$. $Fe(MoS_4)_2^{3-}$ can be regarded as having formally Fe(I) wherein Fe(I) to MoS_4^{2-} charge delocalization presumably plays a central role in stabilizing the trianion** [9].

The stability of the trianionic Fe complex suggested that the trianionic Co complex might also be most amenable to synthesis. This is indeed the case. Reacting a solution of $CoCl_2$ and $[N(C_2H_5)_3H](SC_6H_5)$ in CH_3CN with a suspension of an MoS_4^{2-} salt in CH_3CN provides a simple route to salts of the trianion $Co(MoS_4)_2^{3-}$ in high yield†. The dark grey–green compounds are air-sensitive and decompose completely in aerobic solutions within 15 minutes. The IR spectrum (KBr pellet of $N(C_2H_5)_4^+$ salt) is similar to that of $Fe(MoS_4)_2^{3-}$ [3, 4], showing bands at 481(s) cm^{-1}, 466(s) cm^{-1} and 445(m) cm^{-1}. The first peak is assigned to a terminal Mo–S stretching vibration while the last two peaks are assigned to bridging Mo–S stretching modes. The UV–VIS–NIR spectrum in DMF (Fig. 1) displays peaks at 825 nm (4,400), 645 nm (6,600), 545 nm (5,300), 453 nm(sh) and 394 nm (19,500 M^{-1} cm^{-1}). The complex is paramagnetic in DMSO solution having a magnetic moment of 3.3 B.M. (Evans NMR method) [11].

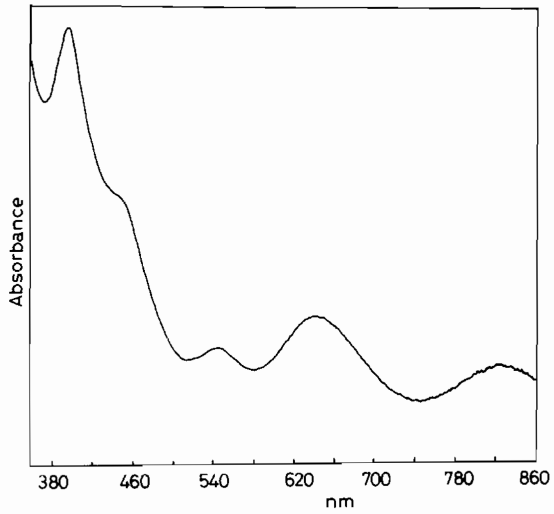

Fig. 1. Electronic spectrum of $[N(C_2H_5)_4]_3Co(MoS_4)_2$ in DMF.

The magnetic susceptibility of $[N(C_2H_5)_4]_3Co(MoS_4)_2$ was measured with the Faraday technique from 4 K to 300 K in magnetic fields below 6.3 kG. After correcting for small ferromagnetic impurity contributions and for temperature independent

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**Similar charge delocalization leads to an electron deficient central metal in the W complex $Fe(WS_4)_2^{2-}$, and results in adduct formation with coordinating solvents such as DMF, DMSO or pyridine. See ref. 10.

†In a typical preparation, 1.3 ml HSPh and 1.75 ml $N(C_2H_5)_3$ were added to a suspension of 0.66 g $CoCl_2$ in CH_3CN; the resulting dark green solution was added to a suspension of 4.9 g $[N(C_2H_5)_4]_2MoS_4$ in CH_3CN. The mixture was stirred and a dark green solution resulted. Within 30 min, the reaction was complete and the solution was filtered. The product was precipitated by adding diethylether to the filtrate. Yields upwards of 70% could be obtained. *Anal.* Calcd. for $C_{24}H_{60}N_3CoMo_2S_8[N(C_2H_5)_4]_3[Co(MoS_4)_2]$; C, 32.1%; H, 6.73%; N, 4.68%; found: C, 32.3%; H, 6.63%; N, 4.55%.

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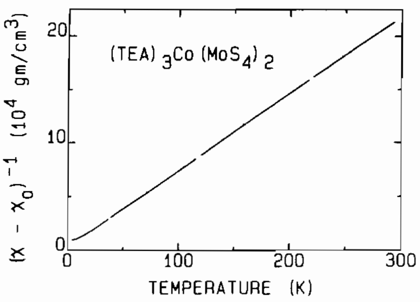

Fig. 2. Inverse magnetic susceptibility $(\chi - \chi_0)^{-1}$ *vs.* temperature for (TEA)$_3$Co(MoS$_4$)$_2$; χ_0 is the computed temperature independent (diamagnetic) orbital susceptibility.

diamagnetism ($\chi^{\text{dia.}}_{\text{calc.}} = -4.49 \times 10^{-7}$ cm^3/gm), the inverse susceptibility was plotted *vs.* temperature (Fig. 2). Above about 100 K, the data follow a Curie–Weiss law $[\chi = C/(T - \theta)]$ with $C = 1.38 \times 10^{-3}$ cm^3 K/gm, $\mu_{\text{eff}} = 3.15$ μ_B/Co and $\theta = -2.2$ K leading to $g = 2.23$ assuming $S = 1$. Departure of the data from the Curie–Weiss behavior below 100 K is consistent with an axial crystal field splitting of the $S = 1$ triplet ground state; in this case, one expects χ to follow the relation

$$(\chi T)_{\text{calc.}} = \frac{C\left[1 - \dfrac{2k_BT}{D}(1 - e^{D/k_BT})\right]}{2 + e^{D/k_BT}} \qquad (1)$$

where D is the usual anisotropy parameter. Analyzing the data in Fig. 2 in terms of eqn. (1) yielded a good fit with $D/k_B = 30$ K; this corresponds to the non-magnetic triplet $M_s = 0$ state being the ground state, with the $M_s = \pm 1$ levels lying 30 K above it (in zero magnetic field). The derived value of C (1.34×10^{-3} cm^3-K/gm) is in good agreement with the value obtained above 100 K and leads to $\mu_{\text{eff}} = 3.10$ μ_B/Co and $\langle g \rangle = 2.19$. The value for μ_{eff} is in reasonable agreement with the value found from the NMR measurements above. If we assume the presence of Co(I) (3d^8), the magnetic data suggest a tetrahedral configuration around the central Co atom.

The likelihood of a tetrahedral Co in Co(MoS$_4$)$_2^{3-}$ also finds support in the reported crystal structures of the analogs, Co(WS$_4$)$_2^{3-}$ [12] and Fe(MoS$_4$)$_2^{3-}$ [4], where both the Co and Fe were found to be tetrahedral. The powder X-ray diffraction pattern from [N(C$_2$H$_5$)$_4$]$_3$[Co(MoS$_4$)$_2$] is nearly identical to that of the Fe analog, indicating that these two compounds are isomorphous.[††]

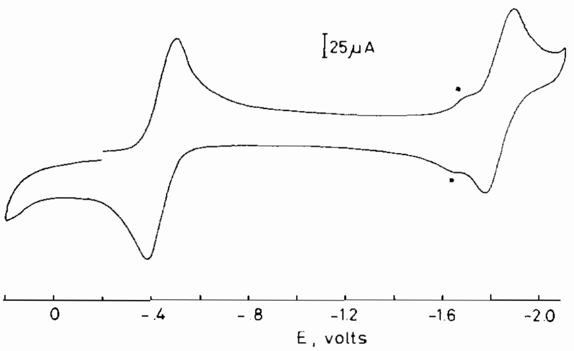

Fig. 3. Cyclic voltammogram of [N(C$_2$H$_5$)$_4$]$_3$Co(MoS$_4$)$_2$ (3 mM in DMF containing 0.1 M [N(C$_4$H$_9$)$_4$]PF$_6$ at 100 mV/sec scan rate. The weak redox wave marked by an asterisk is attributed to an impurity.

Cyclic voltammetry of Co(MoS$_4$)$_2^{3-}$ in DMF shows two reversible waves at −0.44 V and −1.83 V (*vs.* SCE) (Fig. 3). In comparison, the cyclic voltammetry of Co(WS$_4$)$_2^{2-}$ shows reversible redox waves at −0.52 V and −2.04 V assigned to the $2^-/3^-$ and $3^-/4^-$ couples respectively [13]. In view of previous voltammetric trends [2, 13, 14] of M′(MS$_4$)$_2^{2-}$ (M = Mo, W; M′ = Ni, Pd, Pt, Co, Mo = S) complexes, we assign the two waves observed in Co(MoS$_4$)$_2^{3-}$ to the $2^-/3^-$ and $3^-/4^-$ couples, respectively. In Fe(MoS$_4$)$_2^{3-}$, the irreversible $2^-/3^-$ wave is consistent with the instability of Fe(MoS$_4$)$_2^{2-}$. In contrast, the reversible $2^-/3^-$ wave in the Co complex suggests the existence of Co(MoS$_4$)$_2^{2-}$ which nonetheless has not been isolated in stable form.

The low formal valence of the central cobalt calls attention to the need for a source of reducing equivalents in the preparative procedure. For example, we have found that either (η^5-C$_5$H$_5$)Co(CO)$_2$ or Co(S$_2$CN(C$_2$H$_5$)$_2$)$_3$ can serve as the Co starting material in the synthesis of Co(MoS$_4$)$_2^{3-}$. In using the Co(I) organometallic complex (η^5-C$_5$H$_5$)Co(CO)$_2$, no added reductant is required and, remarkably, both the CO and cyclopentadienyl ligands are displaced by MoS$_4^{2-}$. When the starting material contains divalent or trivalent Co, the presence of a reducing agent is required. When Co(S$_2$CN(C$_2$H$_5$)$_2$)$_3$, containing Co(III), is used as the starting material, the reducing agent S$_2$CN(C$_2$H$_5$)$_2^-$ is released from the Co coordination sphere upon substitution by MoS$_4^{2-}$. In our preferred preparation, C$_6$H$_5$S$^-$ is added as the reductant for divalent Co with oxidation to C$_6$H$_5$S–SC$_6$H$_5$ presumed to occur. The successful isolation of Co(MoS$_4$)$_2^{3-}$ may be a further manifestation of the importance of charge delocalization from the central metal to MoS$_4^{2-}$ in stabilizing complexes of the type M(MoS$_4$)$_2^{n-}$ (n = 2, 3) [9].

[††] The powder X-ray diffraction patterns of [N(C$_2$H$_5$)$_4$]$_3$Co(MoS$_4$)$_2$ and [N(C$_2$H$_5$)$_4$]$_3$Fe(MoS$_4$)$_2$ are practically identical with major peaks at (for Co) 2θ = 10.27, 10.95, 17.89 and 18.46° and (for Fe) 2θ = 10.55, 11.22, 18.07 and 18.70° (λ = 1.5418 Å).

Note Added in Proof

The X-ray crystal structure of $[N(C_2H_5)_4][Ph_3PNPh_3]_2[Co(MoS_4)_2]$ has recently been solved [15]. The central Co atom is indeed tetrahedrally coordinated confirming the structural assignment arrived at in the current note.

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