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The True Nature of the Green Product from the Reaction of Molybdenum(II) Acetate with Xanthate Ion

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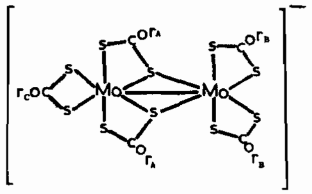
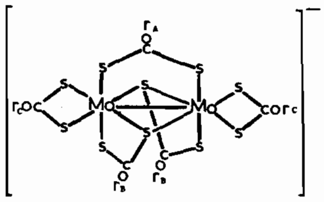
Several years ago [1, 2] it was reported that reaction of molybdenum(II) acetate with an excess of K[S_2COEt] in degassed alcohol led to the precipitation of the red crystalline solid [$Mo_2(S_2COEt)_4$], shown by X-ray analysis [2] to have the well known 'acetate-type' structure. This red compound was isolated from a green solution, claimed by Weiss *et al.* [2] to contain another complex of probable composition [$Mo_2(S_2COEt)_4$], which reacted in the manner expected of an alkoxycarbonyl complex and whose nmr spectrum indicated the presence of two electronically non-equivalent ligands. Recently, Cotton *et al.* [3] mentioned this green 'impurity' and showed that it was *not* formed when equivalent amounts of xanthate ion were used in the preparation of [$Mo_2(S_2COR)_4$] (R = Et, ^{i}Pr).

In this preliminary communication, we now wish to report that this green compound is neither an impurity nor an isomeric form of [$Mo_2(S_2COEt)_4$] but in fact contains an anion of *empirical* formula [$Mo_2(S_2COEt)_5]^-$ which can be readily precipitated from solution by addition of either $AsPh_4ClHCl$ or $Ph_3(PhCH_2)PCl$.

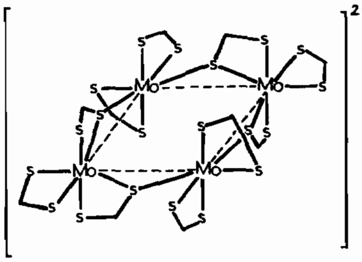
The complex $M_n[\xi Mo_2(S_2COEt)_5\xi_n]$ (M = $AsPh_4^+$, $Ph_3(PhCH_2)P^+$) is best synthesised by reaction of [$Mo_2(S_2COEt)_4$] with K[S_2COEt] (1:1 molar ratio) in degassed acetone followed by precipitation on addition of an ethanolic solution of $AsPh_4ClHCl$ or $Ph_3(PhCH_2)PCl$. Similarly, $M_n[\xi Mo_2(S_2COR)_5\xi_n]$ (R = Me, ^{i}Pr) were synthesised and by reaction of [$Mo_2(S_2COR)_4$] with K[S_2COR^1] (1:1 molar ratio), the mixed xanthato complexes $M_n[\xi Mo_2(S_2COR)_4(S_2COR^1)\xi_n]$ (R = Me, R^1 = Et; R = Et, R^1 = Me) could also be made.



(1a)



(1b)



(2)

The compounds have been characterised by elemental analyses and high resolution ^{1}H nmr spectroscopy (Table I). For $M_n[\xi Mo_2(S_2COR)_5\xi_n]$ (R = Me, Et), three sets of alkyl resonances of relative intensity 1:2:2 were clearly observed, consistent with either structure (1a) or (1b) (assuming n = 1)*. For R = ^{i}Pr, three methyl doublets also of relative intensity 1:2:2 were found but the methine proton region was too weak and complicated to analyse fully. Since two of the nmr signals are very close together such that at lower resolution, (or for the $[\xi Mo_2(S_2COEt)_5\xi_n]^{n-}$ anion, when M = $Ph_3(PhCH_2)P^+$), two peaks of relative intensity 3:2 were initially observed, (*cf.* the observation in reference 2), structure (1a) in which alkyl groups R_B and R_C are in very similar environments was believed to be the more likely. For $[Ph_3(PhCH_2)P]_n[\xi Mo_2(S_2COMe)_4(S_2COEt)\xi_n]$, since it was the resonance assigned to the methyl of the bridging $^-S_2COMe$ groups in (1a) (R_A) which halved in intensity (see Table I), this suggested that the $^-S_2COEt$ ligand occupied one of the bridging positions in structure (1a). However, although conductivity measurements in nitromethane or acetone (*ca.* 10^{-3} dm^{-3} mol, assuming n = 1) gave values expected for 1:1 electrolytes (75–95 S cm^2 mol^{-1}) [7], measurements over a wide range of concentrations for all these compounds and subsequent plots of $\Lambda_o - \Lambda$ (equivalent conductance) *vs.* $C^{1/2}$ (concentration in equiv-

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*It is of interest to note that cations of formulae $[M_2(S_2CNR_2)_5]^+$ (M = Co[4], Ru[5], Rh[6]) which have structures analogous to (1a) or (1b) have been synthesised in recent years.

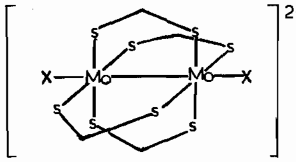
TABLE I. Some Analytical and Physical Data.

Complex	Analysis (%)[a]		^{1}H nmr (δ)[b,c]					Gradient of $\Lambda_o - \Lambda_d$ vs. $C^{1/2}$ plot[d]
	C	H	CH_3	CH_2	CH	Ph	$Ph_3(PhCH_2)P^+$	
$[Ph_3(PhCH_2)P]_n[\{Mo_2(S_2COEt)_5\}_n]$[e]	41.5(41.7)	4.0(4.1)	1.17(t)[2] 1.42(t)[1] 1.43(t)[2]	4.17(q)[2] 4.62(q)[3]		7.0–8.0 (m)	5.02(d)	650[f] 780[g]
$[AsPh_4]_n[\{Mo_2(S_2COEt)_5\}_n]$	39.8(39.7)	3.7(3.8)	1.17(t)[2] 1.41(t)[1] 1.43(t)[2]	4.17(q)[2] 4.60(q)[1] 4.62(q)[2]		7.86(5)		
$[Ph_3(PhCH_2)P]_n[\{Mo_2(S_2COMe)_5\}_n]$	38.4(38.9)	3.5(3.4)	3.77(s)[2] 4.22(s)[1] 4.25(s)[2]			7.0–8.0(m)	5.12(d)	600[f] 646[g]
$[Ph_3(PhCH_2)P]_n[\{Mo_2(S_2COCH\{Me\}_2)_5\}_n]$	44.0(44.2)	4.4(4.7)	1.35(d)[2] 1.36(d)[2] 1.41(d)[1]		5.43[h]	6.7–7.8(m)	4.66(d)	
$[Ph_3(PhCH_2)P]_n[\{Mo_2(S_2COMe)_4(S_2COEt)\}_n]$	39.8(39.5)	3.4(3.6)	1.46(t)[1] 3.75(s)[1] 4.22(s)[1] 4.25(s)[2]	4.67(q)[1]		7.0–8.0(m)	5.02(d)	
$[Ph_3(PhCH_2)P]_n[\{Mo_2(S_2COEt)_4(S_2COMe)\}_n](CH_2Cl_2)_n$	39.3(39.3)	3.8(3.8)	4.21(s)[1] 1.17(t)[1] 1.43(t)[2] 1.42(t)[1]	4.18(q)[1] 4.62(q)[2] 4.64(q)[1]		7.0–8.0(m)	5.03(d)	500[f]
$[Ph_3(PhCH_2)P]_n[\{Mo_2(S_2COEt)_4Cl\}_n]$[i]	41.9(41.7)	3.9(3.9)	1.40(t)	4.54(q)		7.0–8.0(m)	4.97(d)	
$[Ph_3(PhCH_2)P]_2[Mo_2(S_2COEt)_4Br_2]$[j]	28.0(28.2)	4.1(4.2)	1.44(t)	4.59(q)		7.0–8.0(m)	5.18(d)	400[g]

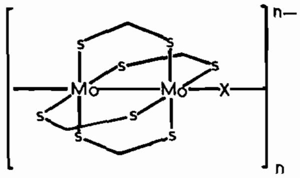
[a] Calculated percentages in parentheses. [b] ±0.01. [c] Relative intensities in parentheses. [d] Measured at 291 K. [e] Found: Mo, 16.7; P, 2.8; S, 27.5%; Required: Mo, 16.7; P, 2.7; S, 27.8%. [f] In acetone. [g] In notromethane. [h] ^{1}H n.m.r. of this compound is very poor due to rapid decomposition in solution; value of 5.43 for CH resonance is largest peak in a very complex multiplet. [i] Found: Cl, 3.4% Required: 3.3%. [j] Found: Br, 10.4% Required: 10.4%.

alents dm^{-3}) revealed unequivocally that all the compounds were *2:1* and *not* 1:1 electrolytes**. Thus, these complexes should be formulated as *tetrameric*.

$[M_2[Mo_4(S_2COR)_{10}]$ and $M_2(Mo_4(S_2COR)_8(S_2COR^1)_2]$ (*i.e.* n = 2) compounds and a possible structure which maintains the xanthato group arrangement shown in (1a) is (2). Although X-ray structural analyses are now essential to verify the details of these tetrameric structures, the recent X-ray determination [9] of the related $[Mo_4Cl_8(PEt_3)_4]$ complex, showing it to be a rectangular cluster containing two short and two long Mo–Mo bonds is most encouraging.



(3)



(4)
a) n>> 1
b) n = 1

Preliminary work shows that reaction of $[Mo_2(S_2COR)_4]$ with other dithio- and monothio-acid anions $[S–S(0)^-]$ leads to the formation of $[\xi Mo_2(S_2COR)_4(S–S(O)\xi_n]^{n-}$ anions (S–S = $^-S_2CNR_2$; S–O = $^-$SOCPh) which can be trapped out with large cations and are also 2:1 electrolytes (*i.e.* n = 2).

In contrast, reaction of $[Mo_2(S_2COR)_4]$ with a large excess of LiX (X = Br, I) followed by addition of $Ph_3(PhCH_2)P^+$ gave the compounds $[Ph_3(PhCH_2)P]_2[Mo_2(S_2COR)_4X_2]$ of probable structure (3) (*cf.* $[Mo_2(O_2CCF_3)_4X_2]^{2-}$ [10]). With LiCl however, anions of formulae $[\xi Mo_2(S_2COR)_4Cl\xi_n]^{n-}$ were formed which might have the polymeric, single chloride bridged structure (4a) (*cf.* $[Ru(OCOR)_4Cl]$ [11]) and/or a discrete dimeric structure (4b) (*cf.* $[Mo_2(O_2CCF_3)_4X]^-$ [10]).

Acknowledgement

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**In CH_3NO_2, plots of $\Lambda_o - \Lambda$ *vs.* $C^{1/2}$ give slopes of *ca.* 190–250 for 1:1 electrolytes and *ca.* 350–700 for 2:1 electrolytes [8].