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Transition Metal Dithiolene Complexes. X[1]. Oxy-Metal Bis-1,2-Dithiolenes

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The reactions between several transition metal oxy-anion salts and $Na_2S_2C_2(CN)_2$ and $K_2S_2C_6Cl_4$ are reported. Oxy-metal bis-dithiolene complexes such as $[VOS_4C_4(CN)_4]^{2-}$, $[VO(S_2C_6Cl_4)_2]^{2-}$ and $[MoOS_4C_4(CN)_4]^{2-}$ have been isolated and are described, and voltammetric evidence for monoanionic species derived from these dianions is presented. The reactions between $[(C_6H_5)_2C_2S_2PS_2]_2$, and its toluoyl and anisoyl analogues, with ammonium paramolybdate is described and the nature of the products is discussed.

Introduction

Metal oxy-anions have frequently been used as precursors in the formation of tris-1,2-dithiolene metal complexes, $[MS_6C_6R_6]^z$, R = H or C_6H_5 and z = 0 or -1.[3] During our investigations of synthetic routes to tris-dicyano-[4] and tris-tetrachlorobenzene-dithiolene[5] complexes, we observed that some oxy-anions reacted with $Na_2S_2C_2(CN)_2$ and $K_2S_2C_6Cl_4$ to form the expected tris-complexes but that some, particularly vanadates and paramolybdates, afforded a different class of compounds containing metal-coordinated oxygen. We had previously noted[6] that vanadyl salts, on treatment with $Na_2S_2C_2(CN)_2$, gave either $[VOS_4C_4(CN)_4]^{2-}$ or $[VS_6C_6(CN)_6]^{2-}$ depending on the reaction conditions, and these observations, together with the report by Gray and his coworkers[7] that solutions believed to contain $[Cr(S_2C_6H_3CH_3)_3]^z$ (z probably -1 or -2) reacted with oxygen giving $[CrO(S_2C_6H_3CH_3)_2]^-$, suggested that we might profitably search for new five-coordinate oxy-metal dithiolenes, $[MO\text{–}(S\text{–}S)_2]^z$.[8]

The reaction of vanadyl salts or the vanadate ion, VO_3^{2-}, with $Na_2S_2C_2(CN)_2$ in hot water afforded $[VOS_4C_4(CN)_4]^{2-}$ together with small amounts of the tris-complex $[VS_6C_6(CN)_6]^{2-}$. The yields of the latter could be increased significantly by maintaining the reactants in near-boiling water for several hours. Hydrazine reduction of $[VS_6C_6(CN)_6]^{2-}$ is believed[4] to give $[VS_6C_6(CN)_6]^{3-}$ which reacts very quickly with aerial oxygen or with oxygenated solvents giving high yields of $[VOS_4C_4(CN)_4]^{2-}$. The vanadyl dithiolene was obtained by precipitation with heavy organic cations, and crystallised as green-brown, orange or orange-brown crystals, the colour apparently depending on the size of the crystals. The complex did not form adducts with pyridine or triethylamine. The V=O infrared stretching frequency was detected at *ca.* 940 cm^{-1} (Table I). The complex, as the $[(n\text{–}C_4H_9)_4N]^+$ salt, exhibited a magnetic moment consistent with one unpaired electron and gave a characteristic eight-line e.s.r. spectrum (^{57}V, I = 7/2) in dichloromethane solution.

If aqueous vanadyl sulphate or VCl_3 in an oxygen atmosphere or in ethanol under nitrogen was treated with $K_2S_2C_6Cl_4$, good yields of the red-brown $[VO(S_2C_6Cl_4)_2]^{2-}$ were obtained. This complex, which had the expected one unpaired electron, exhibited an eightline e.s.r. spectrum in solution, whose parameters (Table) are very similar to those of the bis-dicyano-dithiolene analogue. The V=O stretching frequency occurred at 950 cm^{-1}. Addition of iodine to acetone solutions containing the dianion caused the colour of the solutions to change from red-brown to green, and although we were unable to isolate solids from these solutions, we believe that they contain $[VO(S_2C_6Cl_4)_2]^-$; the infrared spectra of of these solutions exhibited a medium strong absorption at 980 cm^{-1}, the electronic spectrum of the green species in solution was significantly different from those of $[VO(S_2C_6Cl_4)_2]^{2-}$ and $[V(S_2C_6Cl_4)_3]^{-,2-}$,[5] and the species was apparently diamagnetic, all of which is not inconsistent with our formulation.

Treatment of ammonium paramolybdate, $[NH_4]_6[Mo_7O_{24}]\cdot 4H_2O$, with $Na_2S_2C_2(CN)_2$ in hot water/ethanol afforded the dianion $[MoOS_4C_4(CN)_4]^{2-}$ which was also formed, together with $[MoS_6C_6(CN)_6]^{2-}$, in the reactions of MoO_2Cl_2 and $MoOCl_3$ with $Na_2S_2C_2(CN)_2$. The colour of the complex, when isolated as the salt of a heavy organic cation, was dependent on the nature of the cation, being either green-brown or red-brown. The $[(C_6H_5)_4P]^+$ salt was isolated in two forms, green needles and red cubes, the later having a slightly higher melting point than the former. In solution, all salts were spectrally identical. The dianion is diamagnetic and exhibits one Mo=O stretching frequency (Table). In the reactions

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(8) The abbreviation S—S is used to denote bidentate dithiolate ligands, and not diatomic sulphur.

Table I. Physical and Chemical Data Obtained from Metal Oxy-dithiolene and Related Complexes

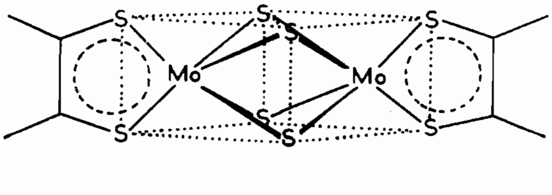
Complex	Cation	$\nu_{M=O}$ [a]	ESR Data $<g>$ [b]	$<a>$ [c]	Electrochemical Data $E_{1/2}$ [d]	R [e]	Process
$[VOS_4C_4(CN)_4]^{2-}$	Ph_4P^+	978 [i]	1.984 [g]	77 [h]	+0.40	+70	−2 −1
		970 [k]					
	Ph_4As^+	978 [f]					
		967 [j]					
$[VO(S_2C_6Cl_4)_2]^{2-}$	n—Bu_4N^+	950 [j]	1.9865	73 [h]	+0.13	+66	−2 −1
$[VO(S_2C_6Cl_4)_2]^{-}$ [l]	—	984 [j]	[m]	—	—	—	
		(950) [s]					
$[CrO(S_2C_6H_3CH_3)_2]^-$	n—Bu_4N^+	933 [j]	1.996	15 [n]	−1.13	—	−1 −2
$[MoOS_4C_4(CN)_4]^{2-}$	Ph_4P^+	940 [f]	dia.	—	+0.35	+59	−2 −1
		935 [j]					
		937 [p]					
	Et_4N^+	934 [f]					
		938 [p]					
	$Ph_3PhCH_2P^+$	943 [f]					
		940 [p]					
$[MoS_2(S_2C_2(C_6H_5)_2]_2$	—	—	dia.	—	−0.42 [q]	−60	0 −1
					−1.30 [q]	−70	−1 −2
					+1.0 [r]	—	0 +1?
$[MoS_2(S_2C_2(C_6H_4pOCH_3)_2]_2$	—	—	dia.	—	−0.51 [q]	−59	0 −1
					−1.35 [q]	−61	−1 −2
					−0.55	−59	0 −1
					−1.40 [r]	—	−1 −2?
					+0.89	+72	0 +1

[a] In cm^{-1}; [b] measured in CH_2Cl_2 solution at room temperature; [c] metal hyperfine splitting in gauss; [d] half-wave potential in volts, using a rotating Pt electrode except where otherwise stated; results *vs.* S.C.E.; [e] reversibility criterion: $E_{3/4}$—$E_{1/4}$ in mv.: for reversible one-electron wave, R = 56; [f] in KBr disc; g μ_{eff} = 1.78, consistent with one unpaired electron; [h] eight-line spectrum, ^{51}V, I = 7/2; [i] in nujol mull; [j] in CH_2Cl_2 solution; [k] in $CHCl_3$ solution; [l] complex generated in solution and not isolated; [m] no e.s.r. signal observed; [n] ^{53}Cr, I = 3/2, four-line spectrum; [p] in DMF solution; [q] measured using dropping mercury electrode, results *vs.* S.C.E.; [r] ill-defined wave diminished in height by electrode coating or reaction with base electrolyte; [s] weak peak due to presence of corresponding dianion.

between WO_2Cl_2 and $Na_2S_2C_2(CN)_2$ and $K_2S_2C_6Cl_4$ only the tris-complexes $[WS_6C_6(CN)_6]^{2-}$ [4] and $[W(S_2C_6Cl_4)_3]^{2-}$ [5] were formed, and WO_4^{2-} did not react at all with the dithiolates.

No dicyano-dithiolene complexes could be isolated from the reactions between $Na_2S_2C_2(CN)_2$ and chromate, permanganate and perrhenate. However, with the first two oxy-anions, $K_2S_2C_6Cl_4$ readily afforded[5] $[Cr(S_2C_6Cl_4)_3]^{2-}$ and $[Mn(S_2C_6Cl_4)_3]^{2-}$.

When paramolybdate was treated with $[(C_6H_5)_2C_2S_2PS_2]_2$[9] in dioxan, a black solution was formed from which small amounts of the known green $[MoS_6C_6(C_6H_5)_6]^0$ [3] could be obtained together with a large amount of a black solid which was soluble in dichloromethane giving purple solutions. Similar black solids, which dissolved in dichloromethane giving blue or blue-violet solutions, were obtained when paramolybdate was treated with $[(p\text{-}CH_3OC_6H_4)_2C_2S_2PS_2]_2$ and $[(p\text{-}CH_3C_6H_4)_2C_2S_2PS_2]_2$. Only the anisoyl derivative was sufficiently soluble in chloroform for molecular weight determinations to be carried out, and this, together with the available analytical data, suggests that these compounds could be formulated as $[MoS_2(S_2C_2R_2)]_2^0$. A possible structure is shown in the Figure, in which the coordination geometry around the metal atom is based on a trigonal prismatic arrangement of sulphur atoms. Trigonal prismatic coordination has been established in $[MoS_6C_6H_6]^0$ [10] and in MoS_2,[11] and is believed to be the coordination geometry in $[MoS_6C_6(C_6H_5)_6]^0$ [12] and in $[MoS(S_4C_4(C_6H_5)_4)]_2^0$;[13] in the last compound the bare sulphur atoms share a common edge between the two prisms whereas in our proposed structure, the four sulphur atoms share a common face.



The complexes described in this paper have been investigated by voltammetric techniques in dichloromethane solution, using a rotating platinum electrode, and the results are summarised in the Table. The vanadyl dianion, $[VOS_4C_4(CN)_4]^{2-}$, exhibits a nearly reversible anodic wave which we believe corresponds to a one-electron[14] oxidation step, and to generation of $[VOS_4C_4(CN)_4]^-$. The potential for this oxidation step proved to be too positive for iodine to be effective as an oxidising agent, and bromine in dichloromethane caused the decomposition of the compound. However, the potential of the corresponding wave in the voltammograms of $[VO(S_2C_6Cl_4)_2]^{2-}$ was in the range where iodine is useful synthetically, but, as previously described, we were unable to isolate the product for-

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(14) i_d/c for this process, and for the other described in this paper, are similar in value to that in the established one-electron oxidation of $[NiS_4C_4(CN)_4]^{2-}$, where the existence of the monoanion is proved.

med when the dianion was treated with iodine. The molybdenyl dianion, $[MoOS_4C_4(CN)_4]^{2-}$, was also oxidised in a one-electron step, but the monoanion could not be prepared. One-electron reduction of $[CrO(S_2C_6H_3CH_3)_2]^-$ proved to be irreversible in dichloromethane, and too negative to be effected by normal chemical reagents. No other waves were detected in the voltammograms of these oxy-bis-dithiolenes, which were investigated in the voltage range +2.00 to −2.00 v.

The proposed dinuclear species, $[MoS_2(S_2C_2R_2)]_2^0$, exhibited reduction waves, and the first reduction potential in the compound where R = C_6H_5 was such that BH_4^- might be expected to effect the reduction. Accordingly, treatment of the compound, suspended in THF, with sodium borohydride afforded unstable green-brown solutions which exhibited broad but irresolvable e.s.r. signals; the neutral dithiolene could not be regenerated from these solutions on re-oxidation.

Experimental Section

Voltammetric measurements were made using Heathkit Model EUW-401 and Sargent XV instruments, with a platinum electrode rotating at 620 r.p.m. Dichloromethane, previously dried and redistilled, was used as the solvent and $[(C_2H_5)_4N][ClO_4]$ (0.1 *M*) as the supporting electrolyte. The concentration of the complex in the solution was 10^{-3} *M*, and all results are quoted against a saturated calomel electrode containing 1 *M* aqueous LiCl. All results are corrected for iR drop and the estimated error in recording and reading the voltammograms is ±10 mv.

Conductivity measurements were made using a Phillips conductivity meter at room temperature (22°) and magnetic moments were determined by the Gouy method at room temperature. Electronic and infrared spectra were obtained using Unicam SP700, Carey 14 and Unicam SP100 spectrophotometers. Analytical determinations were carried out by the Microanalytical Laboratory of this Department, and melting points are uncorrected.

Reaction of $VOSO_4 \cdot 4H_2O$ *with* $Na_2S_2C_2(CN)_2$. $VOSO_4 \cdot 4H_2O$ (2.35 g) in hot water (15 ml) was treated with $Na_2S_2C_2(CN)_2$ (3.72 g) in water (30 ml) and warmed on a steam-bath for 5 min. The resulting green-brown solution was filtered, cooled and $[(C_6H_5)_4P]Br$ (8.4 g) in ethanol (30 ml) was added. The dark green precipitate which formed rapidly was collected by filtration, washed with water (50 ml) and ethanol (50 ml), and the two vanadium complexes which it contained were separated as follows.

$[(C_6H_5)_4P]_2[VS_6C_6(CN)_6]$. Extraction of the dark green precipitate with chloroform (50 ml) gave a green-brown solution which was treated with ethanol (30 ml). The volume of this solution was reduced using a water pump until crystallisation began, and the resulting black crystalline solid was twice recrystallised in the same way and the product washed with ethanol and ether, and air-dried. The yield of the complex, m.p. identical with an authentic sample, was 0.34 g (3% based on $VOSO_4$, $4H_2O$).

$[(C_6H_5)_4P]_2[VOS_4C_4(CN)_4]$. The light brown chloroform-insoluble residue which remained after removal of the soluble $[(C_6H_5)_4P]_2[VS_6C_6(CN)_6]$ was extracted with DMF (30 ml). To the red-brown extract was added water (50 ml) and after 45 min., crystallisation of a brown compound had occurred. These crystals were collected by filtration, washed with ethanol (50 ml) to remove an unidentified orange impurity, and recrystallised from DMF/water. The dark brown crystals were washed with ethanol and ether, and air-dried. The yield of the complex, m.p. 195-205°, was 6.44 g (63% based on $VOSO_4 \cdot 4H_2O$). The complex is moderately soluble in DMF, DMSO and dichloromethane, and sparingly soluble in chloroform and acetone, forming red-brown solutions. *Anal.* Calcd. for $C_{56}H_{40}N_4OP_2S_4V$: C, 65.6; H, 3.9; N, 5.5; S, 12.2. Found: C, 65.4; H, 3.9; N, 5.6; S, 12.7%.

Conductivity. $\Lambda = 292$ cm^2 ohm^{-1} mole^{-1} in 10^{-4} *M* at 23.5°, consistent with one unpaired electron.

Magnetic Susceptibility. $\chi^M_{cor} \times 10^6 = 1407$ c.g.s.u. at 23.5°, consitent with one unpaired electron.

Electronic Spectrum. In dichloromethane solution: λ = 10,500 (ε = 170); 17,400 (380); 26,400-(2160). (Frequencies in cm^{-1}, intensities in l . mole^{-1} cm^{-1}). The $[(C_6H_5)_4As]^+$ (m.p. 198°) and $[(C_6H_5)_3(CH_3)P]^+$ salts were prepared similarly.

Reaction of Ammonium Metavanadate with $Na_2S_2C_2(CN_2)$. NH_4VO_3 (1.17 g) was partially dissolved in hot water (100 ml) and treated with $Na_2S_2C_2(CN)_2$ (5.58 g). The mixture was heated on a steam-bath for 6 hr. after which time the deep yellow-green solution was filtered and $[(C_6H_5)_4P]Br$ (8.40 g) in ethanol (30 ml) added. The orange precipitate which separated was collected by filtration, washed thoroughly with water and ethanol, and recrystallised three times from DMF/water. After each recrystallisation, the crystals were collected by filtration, and washed with acetone (20 ml) to remove orange impurities. Finally, the crystals were washed with ethanol and ether, and air-dried. The yield of $[(C_6H_5)_4P]_2[VOS_4C_4(CN)_4]$ was 3.07 g (30% based on NH_4VO_3). The infrared and electronic spectrum, and the m.p. (mixed) of this specimen were identical with those of authentic samples.

$[(n\text{–}C_4H_9)_4N]_2[VO(S_2C_6Cl_4)_2]$. *Method 1.* $VOSO_4 \cdot 2H_2O$ (0.6 g) was dissolved in water (5 ml) and flushed with a stream of oxygen. The pale blue solution was treated dropwise, under oxygen, with $C_6Cl_4(SH)_2$ (1.68 g) dissolved in ethanol (20 ml) containing triethylamine (1.2 g). The resulting red-brown solution was refluxed under oxygen for 3.5 hr. After this time, the solution was treated with $[(n\text{–}C_4H_9)_4N]I$ (3.5 g) dissolved in ethanol (20 ml) and refluxed for a further 20 min. After filtration and partial evaporation of the solvent using a water pump, red crystals formed and were collected by filtration. Recrystallisation was effected from acetone/ethanol mixtures giving bright-red crystals which were washed with ether and air-dried. The yield of the complex, m.p. 210-212°, was 2.1 g (64% based on $VOSO_4 \cdot 2H_2O$).

Method 2. VCl_3 (0.48 g) in ethanol (15 ml) was treated with $C_6Cl_4(SH)_2$ (2.52 g) dissolved in ethanol (25 ml) containing potassium metal (0.72 g). HCl gas was evolved and the solution developed a red-brown colour. After refluxing for 10 min., the solution was treated with $[(n\text{–}C_4H_9)_4N]I$ (4.0 g) disolved in ethanol (25 ml) and the mixture then refluxed for a further 30 min. On cooling, a red solid was precipitated and was collected by filtration, recrystallised from acetone/ethanol mixtures giving 1.8 g of the complex as red microcrystals, m.p. 212° (yield 53% based on VCl_3).

The complex dissolves in acetone and dichloromethane affording red-brown solutions. *Anal.* $C_{44}H_{72}N_2OS_4Cl_8V$ requires C, 47.7; H, 6.5; N, 2.5; S, 11.6; Cl, 25.4%.

Conductivity. $\Lambda = 211$ cm^2 ohm^{-1} mole^{-1} in $10^{-4}\,M$ acetone solution, consistent for a 2:1 electrolyte.

Electronic Spectrum. Recorded in dichloromethane: λ = 11,900 (4); 18,300 (65); 23,400 (520); 28,000 (8,400); 34,100 (26,100); 37,000 (41,900.

Treatment of dichloromethane solutions containing this salt with iodine results in the formation of green solutions.

Electronic Spectrum of Green Solutions obtained by Iodine Oxidation of $[VO(S_2C_6Cl_4)_2]^{2-}$. Recorded in dichloromethane: λ = 11,300 (20,100); 15,400 (10,900); 29,300 (10,800); 38,000 (56,800).

$[(C_6H_5)_4P]_2[MoOS_4C_4(CN)_4]$. Ammonium paramolybdate, $[NH_4]_6[Mo_7O_{24}]\,.\,4H_2O$ (1. g) was dissolved in water (20 ml) and heated with $Na_2S_2C_2(CN)_2$ (2.11 g) in ethanol (30 ml) on a steam-bath for 3 hr. After this time, $[(C_6H_5)_4P]Br$ (4.1 g) dissolved in the minimum volume of ethanol, was added giving a brown crystalline precipitate. The mixture was cooled and filtered, the precipitate being washed with methanol and then recrystallised from acetone/methanol over a period of 2 days. The yield of the complex, m.p. 205-225°, was 1.4 g (23% based on $[NH_4]_6[Mo_7O_{24}]\,.\,4H_2O$). Four subsequent recrystallisations gave red cubes, m.p. 220-226°. The compound is soluble in DMF, DMSO, dichloromethane and acetone giving pale green-brown solutions. *Anal.* Calcd. for $C_{56}H_{40}N_4OS_4P_2Mo$: C, 62.8; H, 3.7; N, 5.2; S, 12.0. Found: C, 62.7; H, 4.2; N, 4.9; S, 12.9%.

Conductivity. $\Lambda = 310$ cm^2 ohm^{-1} mole^{-1} in $10^{-4}\,M$ acetone, consistent for a 2:1 electrolyte.

Electronic Spectrum. Recorded in dichloromethane: λ = 15,00 (120); 16,100 (170); 20,100 (260); 27,100 (4,430).

The $[(C_6H_5CH_2)(C_6H_5)_3P]^+$, $[(C_2H_5)_4N]^+$, $[(n\text{–}C_4H_9)_4N]^+$, and $[C_5H_5NCH_3]^+$ salts were prepared and isolated in the same way as the $[(C_6H_5)_4P]^+$ salt. *Anal.* Calcd. for $[C_6H_5CH_2)(C_6H_5)_3P]^+$ salt: C, 63.4; H, 4.0; N, 5.1; S, 11.6. Found: C, 63.5; H, 3.9; N, 5.3; S, 11.3%. Calcd. for $[(C_2H_5)_4N]^+$ salt: C, 44.1; H, 6.2; N, 12.9; S, 19.6. Found: C, 44.0; H, 5.9; N, 12.8; S, 19.6%. Calcd. for $[(n\text{–}C_4H_9)_4N]^+$ salt: C, 54.8; H, 8.3; N, 9.6. Found: C, 54.7; H, 8.0; N, 9.3%. Calcd. for $[C_5H_5NCH_3]^+$ salt: C, 41.9. Found: C, 41.4%.

Reaction of MoO_2Cl_2 *with* $Na_2S_2C_2(CN)_2$. MoO_2Cl_2 (1.0 g) was dissolved in methanol (30 ml) and treated with $Na_2S_2C_2(CN)_2$ (2.0 g) under nitrogen. The mixture was refluxed for 10 min. giving a green solution to which was added $[(C_6H_5)_4P]Br$ (4.0 g). A grey-green precipitate formed and this was removed by filtration from the solution while it was still hot. The solid was dissolved in ethanol and chromatographed on alkaline alumina using ethanol/methanol mixtures as eluant. Two bands separated, one green from which green-brown crystals were obtained on evaporation, and the other dark green from which deep blue-green crystals were isolated on evaporation. The green-brown crystals were $[(C_6H_5)_4P]_2[MoOS_4C_4(CN)_4]$, m.p. 212-225°, and the blue-green crystals $[(C_6H_5)_4P]_2[MoS_6C_6(CN)_6]$, m.p. *ca.* 265°.

The same products were obtained from a similar reaction between $MoOCl_3$ and $Na_2S_2C_2(CN)_2$; yields were not recorded in either case.

$[MoS_2(S_2C_2(C_6H_5)_2)]_2$. A solution containing ammonium paramolybdate (2.3 g) in water (20 ml) was added to a dioxan solution (70 ml) containing $[(C_6H_5)_2C_2S_2PS_2]_2$,[9] obtained by refluxing together benzoin (10 g) and P_4S_{10} (15.0 g) for 2 hr. The mixture was heated on a steam-bath for 1.5 hr., and the black crystalline compound which had formed during this time was collected by filtration and recrystallised from dichloromethane. The yield of the complex, m.p. 270°, was 3.0 g (45% based on $[NH_4]_6[Mo_7O_{24}]\cdot 4H_2O$). The compound is sparingly soluble in dichloromethane giving deep purple solution, but is barely soluble in other common organic solvents. *Anal.* Calcd. for $C_{28}H_{20}S_8Mo_2$: C, 41.8; H, 2.5; S, 31.9. Found: C, 41.7; H, 2.7; S, 32.5%.

$[MoS_2(S_2C_2(C_6H_4p\text{–}OCH_3)_2]_2$. This complex was prepared in the same way as the phenyl compound described above,, and was purified by Soxhlet-extraction using dichloromethane which gave a deep blue solution from which a black microcrystalline solid was precipitated on addition of an equal volume of ether. This compound was collected by filtration, reprecipitated from hot chloroform using ether, and was obtained as a dark blue solid, m.p. 255-257°. The complex is soluble in dichloromethane and chloroform, sparingly soluble in ether and acetone, but insoluble in hydrocarbon and aromatic solvent. *Anal.* Calcd. for $C_{32}H_{32}O_4S_8Mo_2$: C, 41.6; H, 3.0; S, 27.7; M = 978. Found: C, 44.7; H, 3.6; S, 27.8, M (osmometric) = 924.

Electronic Spectrum. Recorded in dichloromethane: λ = 13,800, 17,150 sh; 21,750 sh.

$[MoS_2(S_2C_2JC_6H_4p\text{–}CH_3)_2]_2$. The complex was prepared in the same way as its phenyl analog, and was recrystallised from dichloromethane. The compound was isolated as a dark blue-violet solid, m.p. 350°. *Anal.* Calcd. for $C_{32}H_{32}S_8Mo_2$: C, 44.7; H, 3.3; S, 29.8. Found: C, 42.3; H, 3.4; S, 34.4%.

Electronic Spectrum. Recorded in dichloromethane: λ = 12,900 sh; 17,800; 30,000 sh.