Notes

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Effect of μ-Sulfido Ligands on Substitution at Molybdenum(V). A Temperature-Jump Study of the 1:1 Equilibration of Thiocyanate with Di-μ-sulfido-bis[aquooxalatooxomolybdenum(V)]

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Received April 17, 1977

It is known that molybdenum–sulfur bonds are present in molybdo enzymes,[1] and the effect of sulfur-donor ligands in a variety of different situations on the chemistry of molybdenum is therefore of considerable interest. Spivack and Dori[2] have reported the separation of the aquo ion $Mo_2S_2O_2^{2+}$, which is the analogue of the now well-characterized di-μ-oxo ion $Mo_2O_4^{2+}$, and commented on the unusual stability of the di-μ-sulfido complex in acidic solutions. From the aquo ion we have generated the oxalato complex $[Mo_2S_2O_2(C_2O_4)_2(H_2O)_2]^{2-}$ in solution at pH ca. 3.0 and studied the kinetics of the replacement of one H_2O by NCS^-. The corresponding 1:1 equilibration of NCS^- with $[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2-}$ has already been reported,[3] thus enabling a comparison of the effectiveness of di-μ-sulfido ligands on the lability of coordinated water molecules to be made.

Experimental Section

Preparation of Sodium Di-μ-oxo-bis[(L-cysteinato)oxomolybdate(V)] Pentahydrate, $Na_2[Mo_2O_4(L\text{-}cyst)_2]\cdot 5H_2O$. A modification of the literature method[4] was used. L-Cysteine hydrochloride (19.2 g, 0.12 mol) in distilled water (30 mL) was added to a solution of sodium molybdate dihydrate (30.4 g, 0.12 mol) in H_2O (50 mL). To the stirred solution sodium dithionite (10 g, 0.057 mol) in H_2O (50 mL) was added and the solution cooled in ice. Orange crystals formed which were filtered off. A second crop of crystals was obtained after rotary evaporation. The combined products were dissolved in a minimum of air-free H_2O (50 °C). Air-free methanol was added until the solution just turned cloudy, when it was cooled in ice. The product was filtered, washed with methanol and diethyl ether, and dried in a current of air; found ϵ 12 500 M^{-1} cm^{-1} (per dimer) at the 308-nm peak in good agreement with the literature value (ϵ 12 000 M^{-1} cm^{-1}).

Conversion to Sodium Di-μ-sulfido-bis[(L-cysteinato)oxomolybdate(V)] Trihydrate, $Na_2[Mo_2O_2S_2(L\text{-}cyst)_2]\cdot 3H_2O$. Literature procedures[4] were modified as follows. The di-μ-oxo complex (see above, 4 g, 0.006 mol) was dissolved in H_2O (200 mL). Hydrogen sulfide (B.D.H., A.R. cylinder) was passed through the solution for ca. 5 min, after which the flask was stoppered. The dark colored solution was shaken intermittently over ca. 5 h. It was then evaporated to dryness on a rotary evaporator (50 °C) and the product stored in vacuo over silica gel. The solid (not recrystallized) gave a peak at λ 228 nm, ϵ 2.9 × 10^4 M^{-1} cm^{-1} (per dimer).

Preparation of a Solution of Di-μ-sulfido-bis[triaquooxomolybdenum(V)], $Mo_2S_2O_2^{2+}$. The method used was similar to that described by Spivack and Dori.[2] The di-μ-sulfido complex (see above) (2 g, 0.003 mol) was dissolved in H_2O (40 mL), and $HClO_4$ (5 M, 10 mL) was added slowly with stirring. After 10 min the black suspension was filtered (Whatman No. 42 paper). The orange-yellow aquo ion was obtained pure in 1.0 M $HClO_4$ by gel filtration through a Sephadex G10 column (4-cm diameter, 30-cm long) preequilibrated with 1.0 M $HClO_4$. Molar absorption coefficients (per dimer) were obtained on the basis of Mo and S analyses (see below). Peak positions, nm (ϵ, M^{-1} cm^{-1}), were 225 (5800), 245 (4120) 280 (5510), 300 (sh, 4360), and 370 (1940), Figure 1. The shape of the spectrum is in agreement with that of Spivack and Dori (no ϵ's quoted),[2] although peak ratios are somewhat different and the peak at 225 nm is more clearly defined in our case.

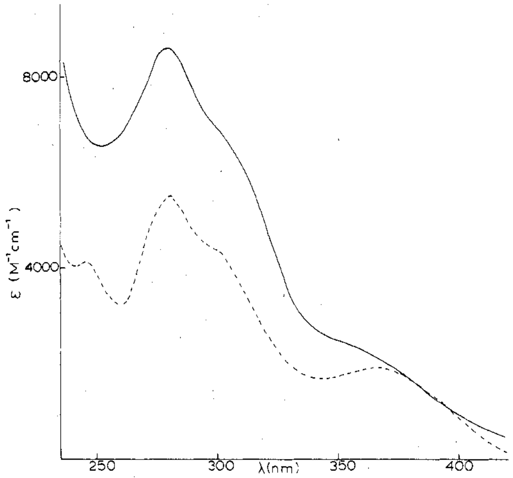

Figure 1. UV–visible spectra of the di-μ-sulfido molybdenum(V) aquo dimer, $Mo_2S_2O_2^{2+}$, in 1.0 M $HClO_4$ (···) and the related oxalato complex $[Mo_2S_2O_2(C_2O_4)_2(H_2O)_2]^{2-}$ at pH 3, I = 1.0 M ($NaClO_4$) (—).

Preparation of the Di-μ-sulfido-bis[aquooxalatooxomolybdate(V)] Complex, $[Mo_2S_2O_2(C_2O_4)_2(H_2O)_2]^{2-}$. For temperature-jump studies a solution of 0.01 M oxalic acid in 1.0 M $NaClO_4$ (both Analar) was added to the aquo ion (4 × 10^{-3} M, 2.0 mL) to give a 2.1:1 ratio of oxalate to Mo dimer. No spectrophotometric evidence was obtained for formation of a trisoxalato dimer with higher oxalate concentrations. The pH was adjusted to 3.0 by addition of first 1.0 M NaOH and then more dilute NaOH and made up to I = 1.0 M ($NaClO_4$). A Radiometer PHM 4d meter calibrated with perchloric acid solutions of known concentration, I = 1.0 M ($NaClO_4$), was used with glass (Type 202C) and calomel (Type K401) electrodes. Solutions were made up to the required volume with perchloric acid, pH 3, I = 1.0 M ($NaClO_4$). Stock solutions were generally (8–40) × 10^{-5} M in $[Mo_2S_2O_2(C_2O_4)_2(H_2O)_2]^{2-}$.

Isolation of a Cesium Salt. To prepare a crystalline sample of the cesium salt, KOH was first used to adjust the pH of a 10^{-2} M solution of $Mo_2S_2O_2^{2+}$ containing a slight excess of oxalate to 3.0. The resultant $KClO_4$ was filtered off and the volume of the filtrate decreased on a rotary evaporator. A solution of CsCl (ca. 0.2 M, 5 mL) was added, and an unidentified yellow solid filtered off and discarded. Solid CsCl (ca. 3 g) was then added a little at a time and the solution left overnight at 0 °C. Recrystallization was from water at 40 °C (35 mL for 0.07 g), to which CsCl (0.5 g) was added. The crystals were washed with water and then ethanol. Yield 0.035 g of orange-red crystals. Anal. Calcd for $Cs_2[Mo_2S_2O_2(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$: Mo, 23.9; C, 5.99; H, 1.01. Found: Mo, 24.2; C, 5.62; H, 0.92. Peak positions, nm (ϵ M^{-1} cm^{-1}), were 280 (8690), 310 (sh, 6200), and 370 (sh, 1930), Figure 1. Comparison of the IR spectrum of a sample of $K_2[Mo_2O_4(C_2O_4)_2(H_2O)_2]\cdot 3H_2O$, bands at 960 and 910 cm^{-1} (Mo=O) and 735 cm^{-1} (μ-oxo), with that for $Cs_2[Mo_2O_2S_2(C_2O_4)_2]\cdot 2H_2O$, bands at 940 and 915 cm^{-1} (Mo=O), no band 700–750 cm^{-1}, and additional bands ca. 500 and 355 cm^{-1}, are consistent with a di-μ-sulfido structure having two terminal oxo ligands.[4,5]

Analysis for Mo and S. The following procedure was used for $Mo_2S_2O_2^{2+}$ solutions in 1 M $HClO_4$. To remove $HClO_4$ small amounts of HNO_3 and H_2SO_4 (both concentrated) were added and the solution was heated almost to dryness. After cooling, HCl (concentrated) was added and the solution again heated almost to dryness. This procedure was repeated. Finally the Mo was determined by Rao's method.[6] To determine the sulfur, KOH was added to neutralize the $HClO_4$ and make the solution alkaline. To oxidize the sulfur a tenfold excess of H_2O_2 (30%) was added and the solution heated until colorless. After

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Table I. Reciprocal Relaxation Times [λ 330 nm, pH 3.0 (Except As Stated)] Given as $10^{-4}\tau^{-1}$ (s^{-1}) for the 1:1 Equilibration of NCS^- with $Mo_2S_2O_2(C_2O_4)_2(H_2O)_2{}^{2-}$ (4.1×10^{-5} M) [$I = 1.0$ M ($NaClO_4$)][c]

	[NCS⁻], M								
Temp, °C	0.025	0.040	0.050	0.065	0.075	0.085	0.100	0.125	0.150
3.0	0.94	1.11	1.14[a]	1.26	1.32	1.43	1.60	1.74	1.89
6.0	1.19	1.31	1.42	1.47	1.62[b]	1.74	1.82	1.99	2.25
9.0	1.42	1.58	1.71	1.77		2.06	2.29	2.46	
12.0	1.67	1.94	2.05		2.28		2.56	2.96	3.38

[a] $10^{-4}\tau^{-1} = 1.14$ s^{-1} (pH 2.8) and 1.15 s^{-1} (pH 3.3). [b] $10^{-4}\tau^{-1} = 1.57$ s^{-1} ($10^5[(Mo^V)_2] = 8.2$ M), 1.55 s^{-1} ($10^5[Mo^V)_2] = 12.3$ M), and 1.58 s^{-1} ($10^5[(Mo^V)_2] = 16.4$ M) with λ 363 nm. [c] Each τ^{-1} value is generally the average of three to six runs.

Table II. A Comparison of Rate Constants and Activation Parameters for the Formation and Aquation of 1:1 NCS^- Complexes of Mo(V) at 25.0 °C

	$10^{-4}k$, M^{-1} s^{-1}	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, cal K^{-1} mol^{-1}	Ref
	Formation (k_c)			
$[Mo_2S_2O_2(C_2O_4)_2(H_2O)_2]^{2-}$	21[a,b]	7.5	−9.2	This work
$[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2-}$	0.5[a]	11.2	−4.2	3
$Mo_2O_4{}^{2+}$ [c]	2.9[d]	11.3	0.3	*e*
	Aquation (k_b)			
$[Mo_2S_2O_4(C_2O_4)_2(H_2O)(NCS)]^{3-}$	3.5[a,b]	10.1	−4.1	This work
$[Mo_2O_4(C_2O_4)_2(H_2O)(NCS)]^{3-}$	0.092[a]	15.1	5.6	3
$[Mo_2O_4(NCS)]^+$ [c]	0.012[d]	13.7	−3.0	*e*

[a] $I = 1.00$ M ($NaClO_4$). [b] Extrapolated value from activation parameters, 3–12 °C. [c] Aquo ion. [d] $I = 2.00$ M ($LiClO_4$). [e] Y. Sasaki, R. S. Taylor, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 396 (1975).

heating for a further 10 min it was cooled in ice and $KClO_4$ filtered off. The sulfate was then determined as $BaSO_4$. The sulfate to Mo ratio was 1.01:1.

Other Reagents. Sodium thiocyanate was recrystallized from 95% ethanol and converted to the anhydrous form by vacuum desiccation over P_4O_{10}. Solutions were determined by the standard procedure using silver nitrate. Perchloric acid and other reagents were of AnalaR grade and were used without further purification.

Thermodynamic Parameters for Complex Formation. The parameters ΔH and ΔS and the equilibrium constant K for the 1:1 formation reaction, eq 1, were determined by studying the temperature

$$[Mo_2S_2O_2(C_2O_4)_2(H_2O)_2]^{2-} + NCS^- \rightleftharpoons [Mo_2S_2O_2(C_2O_4)_2(H_2O)NCS]^{3-} + H_2O \qquad (1)$$

dependence (10–35 °C) of the absorbance (A) of solutions of $[Mo_2S_2O_2(C_2O_4)_2(H_2O)_2]^{2-}$ and NCS^-. Four soluutions were made up at pH 3.0, $I = 1.0$ M ($NaClO_4$), with $[Mo^V{}_2] = 4.1 \times 10^{-5}$ M, and $[NCS^-] = 0$, 0.050, 0.100, and 0.150 M, respectively. The temperature (T) of solutions in optical cells was recorded immediately before each absorbance (1-cm cell; λ 330 nm) reading, using a Comark Type 1604 electronic thermometer with a Cr/Al thermocouple protected by a Teflon sheath. The cell was initially cooled to 10 °C and then allowed to warm slowly in steps of ca. 2 °C. A computer fit of A and T to eq 2 was carried out, where ϵ_1 (3600 M^{-1} cm^{-1}) and

$$A = [Mo^V{}_2]\{\epsilon_2 + (\epsilon_1 - \epsilon_2)(1 + e^{-\Delta H/RT}e^{\Delta S/R}[NCS^-])^{-1}\} \qquad (2)$$

ϵ_2 (9200 M^{-1} cm^{-1}) are absorption coefficients at 330 nm for $[Mo_2S_2O_2(C_2O_4)_2(H_2O)_2]^{2-}$ and $[Mo_2S_2O_2(C_2O_4)_2(H_2O)(NCS)]^{3-}$, respectively, to obtain ΔH and ΔS. A procedure as described in ref 3 was also used to evaluate K at one fixed temperature.

Kinetic Measurements. These were obtained using temperature-jump apparatus from the Messanlagen-Studiengesellschaft, Göttingen, West Germany. Temperature rises in the range 1.6–2.5 °C were achieved by applying voltages of 25–35 kV across the cell. Temperatures before the jump were measured using the Comark electronic thermometer. As a precaution against cavitational effects, solutions were filtered through a Millipore filter. Also, to reduce the amount of dissolved gases, the cell and solution were placed in a desiccator which was evacuated until much of the dissolved gas had been removed (ca. 5 min). Cavitation effects resulting from decomposition of the complex or NCS^- during discharge (H_2S smell) as well as small relaxation times made measurement difficult at temperatures above 12 °C. Output from the photomultiplier was stored on a Tektronix 564 B storage oscilloscope and photographed on 35-mm film. The relaxation time (τ) was obtained by curve matching using an exponential generator.[7]

Acid Dissociation Constant. Attempts were made to determine the acid dissociation constant (H_2O ligand) of $[Mo_2S_2O_2(C_2O_4)_2(H_2O)_2]^{2-}$ by titration with OH^-. It was found that nonreversible processes were effective and measurements were critically dependent on the method of mixing. A procedure involving the measurement of pH of a solution of crystalline solid was also tested. It was concluded that the pK_a was >4.0, but we were unable to determine a precise value.

Treatment of Data. A nonlinear least-squares program[8] with weighting ($1/k$) was used for fitting of kinetic data. A weighting of ($1/K^2$) was used for thermodynamic studies.

Results and Discussion

Thermodynamic parameters for 1:1 complexing of $[Mo_2S_2O_2(C_2O_4)_2(H_2O)_2]^{2-}$ with NCS^- (eq 1) were obtained using eq 2 and gave $\Delta H = -2.6 \pm 0.1$ kcal mol^{-1} and $\Delta S = -5.1 \pm 0.3$ cal K^{-1} mol^{-1}. From these parameters $K = 7.3 \pm 1.3$ M^{-1} at 12 °C, to be compared with a value of 6.9 ± 0.5 M^{-1} determined independently from absorbance readings at 12 °C, $I = 1.00$ M ($NaClO_4$). At 25 °C, K is 6.0 M^{-1}. The value previously obtained for the 1:1 complexing of $[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2-}$ with NCS^- is 4.3 M^{-1} at 25 °C.[3]

Relaxation times, Table I, are independent of $[Mo^V{}_2]$, $(4.1–16.4) \times 10^{-5}$ M, and pH, 2.8–3.3. The kinetic data give a good fit to eq 3, where k_f and k_b are the forward and back

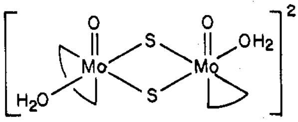
$$\tau^{-1} = k_f[NCS^-] + k_b \qquad (3)$$

rate constants in eq 1. Equation 3 can be expressed as eq 4,

$$\tau^{-1} = k_f([NCS^-] + 1/K) \qquad (4)$$

where a computational procedure was used in which ΔH and ΔS (hence K) were fixed at the measured values. This gave $k_f = 1.1 \times 10^5$ M^{-1} s^{-1} (12 °C), $\Delta H_f{}^\ddagger = 7.5 \pm 0.7$ kcal mol^{-1}, and $\Delta S_f{}^\ddagger = -9.2 \pm 3.0$ cal K^{-1} mol^{-1}. For the back-reaction $k_b = 1.5 \times 10^4$ s^{-1} (12 °C), $\Delta H_b{}^\ddagger = 10.1 \pm 1.8$ kcal mol^{-1}, and $\Delta S_b{}^\ddagger = -4.1 \pm 3.3$ cal K^{-1} mol^{-1} were obtained from thermodynamic parameters and activation parameters for the forward reaction. Rate constants extrapolated to 25 °C are $k_f = 2.1 \times 10^5$ M^{-1} s^{-1} and $k_b = 3.5$ 10^4 s^{-1}.

An x-ray crystallographic study of the cesium salt of the di-μ-sulfido complex has been made and the structure is as illustrated.[9] This is similar to that previously determined for $[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2-}$.[10] Each oxalate ligand occupies coordination sites cis and trans to the terminal oxo ligand, and the Mo–O(oxalate) bond lengths are all identical. Assuming the same structure is retained in solution, complex formation involves replacement of an equatorial H_2O ligand by NCS^-. The possibility of intramolecular rearrangement of the Mo coordination spheres in solution has been noted following ^{13}C NMR experiments (see note, ref 3). There is no evidence as yet for such changes affecting interpretation of kinetic data, e.g., ref 3. Substitution of H_2Os cis to the terminal oxo ligands (probably by an I_d mechanism) has been suggested for the aquo ions VO^{2+}, $Mo_2O_4^{2+}$, and TiO^{2+} [11] and would seem to provide a self-consistent interpretation with that for $[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2-}$ if the H_2O's of the latter also occupy cis positions. In other words small amounts of the trans form *may* be present in solution but do not obviously contribute to the kinetics. Extreme caution is required here, however.



Although equilibrium constants for 1:1 complexing to both the di-μ-sulfido and di-μ-oxo complexes are of similar magnitude (see above), rate constants k_f and k_b are more rapid, both by a factor of ca. 40, in the case of the di-μ-sulfido complex. These differences originate largely in the enthalpies of activation which are more favorable by 3.7 kcal mol^{-1} (k_f) and 5.0 kcal mol^{-1} (k_b) for the di-μ-sulfido complex, Table II. The labilizing effect of S as compared to O bridges can be accounted for in terms of different bonding characteristics of these ligands. Spivack and Dori[2] have observed that the sulfido bridges in the di-μ-sulfido aquo ion $Mo_2S_2O_2^{2+}$ are extremely inert to cleavage even in concentrated acid. The di-μ-oxo $Mo_2O_4^{2+}$ aquo ion on the other hand undergoes bridge cleavage in HCl > 7 M to yield mononuclear complexes. This different behavior is attributable to strong Mo–S bonding which reduces the availability of electron pairs on the sulfur for protonation as a preliminary to bridge cleavage. The same Mo–S bonding is presumably responsible for the labilizing effect identified in this study. The Mo(V) atoms cannot donate π electrons to the S ligands since metal–metal bond formation[4] has already accounted for the single d electron on each metal. The strong Mo–S bonding must therefore originate from σ and possibly π ligand to metal donations. The former would be expected to give a trans labilizing effect which is possibly enhanced (i.e., atoms drawn closer together) by the π bonding. Since the H_2O's in each Mo coordination sphere of $[Mo_2S_2O_2(C_2O_4)_2(H_2O)_2]^{2-}$ are trans to one bridging sulfide and cis to the other, it is not possible to specify the position being labilized.

Acknowledgment. F.A.A. and T.S. are grateful to the U.K. Science Research Council for postgraduate and postdoctoral support.

Registry No. NCS^-, 302-04-5; $[Mo_2S_2O_2(C_2O_4)_2(H_2O)_2]^{2-}$, 64130-27-4; $Na_2[Mo_2O_4(L\text{-cyst})_2]$, 64091-82-3; $Na_2[Mo_2O_2S_2(L\text{-cyst})_2]$, 30917-53-4; $Cs_2[Mo_2S_2O_2(C_2O_4)_2(H_2O)_2]$, 64091-81-2.

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Metal Complexes of Sulfur–Nitrogen Chelating Agents. 7. *N,N′*-Ethylenebis(methyl 2-amino-1-cyclopentenedithiocarboxylate) Complexes of Ni(II), Pd(II), Co(II), and Cu(II)

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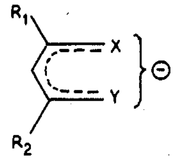
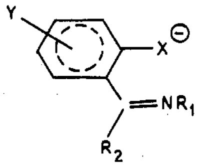
Received December 13, 1976

Investigations on stereochemical nonrigidity in tetracoordinated metal(II) chelates from the β-difunctional ligand systems I and II in terms of planar ⇌ tetrahedral equilibrium in noncoordinating solvents have been the subject matter of great interest.[1] A comparative study with bis(β-aminothione) and bis(β-ketoamine) complexes revealed[2] that sulfur exerts a relatively greater stabilization of planar stereochemistry than does oxygen. In connection with our studies on NiN_2S_2 complexes from 2-amino-1-cyclopentenedithiocarboxylic acid, its *N*-ethyl derivative, and its *S*-alkyl ester we have observed[3-5] that only the spin-paired species exist both in the solid state and in solution.



I

X = Y = NR, O, S, Se
X = O; Y = NR, S
X = S; Y = NR



II

X = O, S; Y = noncoordinating ring substituents

It is interesting to note that although extensive studies have been made on metal complexes derived from the related tetradentate N_2O_2 donors,[6] similar studies with corresponding N_2S_2 donor sets are scanty. The fact that *N,N′*-ethylenebis(salicylideniminato)cobalt(II) and *N,N′*-ethylenebis(acetylacetoniminato)cobalt(II) chelates in the presence of DMF, DMSO, and some other Lewis bases reversibly add molecular oxygen[7,8] provided much stimulus for their investigation as model oxygen carriers.[9] It is expected that the thio analogues may also have similar interesting features. Indeed quite recently metal(II) chelates of *N,N′*-ethylenebis(monothioacetylacetonimine)[10] and *N,N′*-ethylenebis(*o*-mercaptobenzaldiimine)[11,12] have been investigated. We wish to report