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Contribution from the Department of Inorganic Chemistry,
Indian Association for the Cultivation of Science, Calcutta 700 032, India

Chemistry of Molybdenum. 3. Synthesis, Characterization, and Electrochemical Studies of Monomeric Oxodihalogenomolybdenum(VI), Molybdenum(V), and Molybdenum(IV) Complexes of 2-Aminocyclopent-1-ene-1-dithiocarboxylic Acid

MUKTIMOY CHAUDHURY

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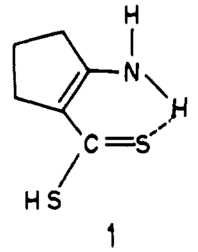
The chemistry of molybdenum in the oxidation states VI, V, and IV with a potential bidentate $(S,S)^-$ donor ligand, 2-aminocyclopent-1-ene-1-dithiocarboxylic acid (Hacda), is described. The molybdenum(VI) compounds, $MoOX_2(acda)_2$ (X = F, Cl, Br, I), have been synthesized by the reaction of $MoO_2(acda)_2$ with the corresponding acids, HX. A systematic shift of the LMCT band (S (π) $\rightarrow$ Mo (dπ)) to higher energy occurs as the ligand field strength of the group X increases. The Mo(VI)-Mo(V) couple of these compounds ($E_{1/2} \sim -0.76$ to -0.27 V) is quasi-reversible, and the reduction of Mo(V) species occurs irreversibly ($E_{irrev} \sim -1.28$ V). The potentials of these couples show a good correlation with the LMCT band energy. Reduction of $MoOCl_2(acda)_2$ with thiols (HL) produces monomeric molybdenum(V) compounds of the type $MoOL(acda)_2$. These compounds exhibit nearly reversible voltammograms ($E_{1/2} \sim -0.25$ V) due to oxidation of Mo(V) to the Mo(VI) state. Reduction of $MoOCl_2(acda)_2$ with excess Hacda (1:4 mole ratio) produces $Mo(acda)_4$, a non-oxo molybdenum(IV) compound that displays a unique voltammogram consisting of two reversible couples, viz. Mo(V)-Mo(IV) ($E_{1/2} = -0.22$ V) and Mo(IV)-Mo(III) ($E_{1/2} = -0.42$ V).

Introduction

The design and synthesis of complex compounds containing molybdenum-sulfur bonds have currently become a fascinating field for research in coordination chemistry. This is partly due of the fact that in biological systems molybdenum is found in a number of redox-active enzymes, where a high degree of sulfur coordination around molybdenum provides a unique center that carries out the redox reactions.[1] Work in this field has acquired further momentum due to the recent application of EXAFS technique, which has revealed[2,3] the coordination environment of molybdoenzymes to near-atomic resolution.

As a part of our ongoing research in this area[4,5] we have recently reported[5] that 2-aminocyclopent-1-ene-1-dithiocarboxylic acid (Hacda) (**1**) binds molybdenum through disulfur chelation, forming a *cis*-dioxomolybdenum(VI) compound, $MoO_2(acda)_2$. We now report that treatment of $Mo^{VI}O_2(acda)_2$ with hydrohalogenic acids affords compounds of composition $Mo^{VI}OX_2(acda)_2$ (X = F, Cl, Br, I). The compounds $MoOX_2(acda)_2$ are highly reactive toward amino thiol, aminothiophenol or thiophenol (HL), and undergo one-electron reduction, leading to the formation of monomeric oxomolybdenum(V) compounds, $MoOL(acda)_2$. The reagent Hacda itself causes two-electron reduction of $MoOX_2(acda)_2$ and affords a novel tetravalent molybdenum compound $Mo(acda)_4$. The present paper deals with synthesis, characterization, and electrochemical studies of these compounds.



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Experimental Section

Synthesis. All manipulations involving molybdenum(V) and -(IV) compounds were carried out under an atmosphere of purified dinitrogen. Analytical reagent grade solvents were dried and distilled before use. *o*-Aminobenzenethiol (Habt), 2-aminoethanethiol hydrochloride (Haet·HCl) and thiophenol (Htp) were obtained commercially. Habt and Htp were dried over molecular sieves (3 Å, Merck) and distilled before use. $MoO_2(acda)_2$ was prepared as described earlier.[5] Hacda was prepared by using a published procedure.[6]

$MoOF_2(acda)_2$ (2a).[7] A suspension of $MoO_2(acda)_2$ (0.45 g, 1.0 mmol) in methylene chloride (50 mL) was allowed to react with 0.5 mL of aqueous HF (ca. 50%) added dropwise over a period of 15 min. The suspension was stirred at room temperature for 1 h, when the color of the reaction mixture darkened from its original maroon color. The dark brown product was collected by filtration, washed with CH_2Cl_2 and diethyl ether, and finally dried over $CaCl_2$; yield 0.42 g (90%).

$MoOCl_2(acda)_2$ (2b). To a stirred suspension of $MoO_2(acda)_2$ (0.45 g, 1.0 mmol) in MeCN (20 mL) was added 0.6 mL of concentrated HCl (11.3 M) dropwise over a period of 30 min. Stirring at room temperature was continued for 30 h, and the brick red microcrystalline product was filtered, washed with methanol, and dried over $CaCl_2$; yield 0.43 g (85%).

$MoOBr_2(acda)_2$ (2c). To a stirred suspension of $MoO_2(acda)_2$ (0.45 g, 1.0 mmol) in methanol (25 mL) was added dropwise 0.5 mL of concentrated HBr (ca. 50%) over a period of 30 min. The maroon color of the suspension was discharged, and the solid material dissolved in 2h to give a dark red solution. Stirring was further continued for 48 h when a saffron-colored microcrystalline compound separated. The compound was filtered off, washed with methanol and ether, and dried over $CaCl_2$; yield 0.4 g (70%).

$MoOI_2(acda)_2$ (2d). A stirred suspension of $MoO_2(acda)_2$ (0.45 g, 1.0 mmol) in CH_2Cl_2 was cooled to 0 °C, and to this was added dropwise 0.5 mL of freshly distilled HI (ca. 57%). Within 2 h, the solid went into solution and a deep red solution resulted. The solution was kept stirred for a period of 30 h at 0 °C. The purple product deposited was collected by filtration, washed with methanol, and dried over $CaCl_2$; yield 0.5 g (70%).

MoO(tp)(acda)$_2$ (3a). A methanol solution (20 mL) of thiophenol (Htp) (0.22 g, 2.0 mmol) was added dropwise in approximately 0.5 h to a vigorously stirred suspension of $MoOCl_2(acda)_2$ (0.25 g, 0.5 mmol) in 20 mL of methanol. The reaction mixture was warmed at 40 °C, and the stirring was continued for a period of 6 h. The solution was then cooled to room temperature, and the dark brown product formed was filtered, washed with methanol and chloroform, and finally dried under vacuum; yield 0.13 g (50%).

MoO(abt)(acda)$_2$ (3b). To a suspension of $MoOCl_2(acda)_2$ (0.25 g, 0.5 mmol) in methanol (20 mL) was added dropwise *o*-aminobenzenethiol (Habt) (0.25 g, 2.0 mmol) dissolved in methanol (20 mL). The stirred solution was then heated gently at 40 °C for 4 h

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(5) Part 2: Chaudhury, M. *J. Chem. Soc., Dalton Trans.* **1984**, 115.

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(7) This preparation was carried out in all-polyethylene apparatus.

Table I. Analytical Data for the Complexes

	% Mo		% C		% H		% N		% X	
complex	calcd	found	calcd	found	calcd	found	calcd	found	calcd	found
$MoOF_2(acda)_2$	20.60	20.38	30.90	30.72	3.43	3.27	6.01	5.88		
$MoOCl_2(acda)_2$	19.24	19.27	28.86	28.71	3.21	3.05	5.61	5.89	14.23	14.16
$MoOBr_2(acda)_2$	16.33	16.29	24.49	24.63	2.72	2.51	4.76	4.59	27.21	27.42
$MoOI_2(acda)_2$	14.08	14.35	21.11	20.87	2.35	2.48	4.10	3.98	37.25	37.41
$MoO(tp)(acda)_2$	17.88	18.17	40.22	39.98	3.91	3.95	5.21	5.37		
$MoO(abt)(acda)_2$	17.39	17.19	39.13	39.10	3.98	3.56	7.61	7.49		
$MoO(aet)(acda)_2$	19.05	19.32	33.33	33.61	4.36	4.28	8.33	8.36		
$Mo(acda)_4$	13.19	13.05	39.56	39.64	4.39	4.44	7.69	7.87		

Table II. Infrared Data (cm^{-1}) and Tentative Band Assignments for the Complexes

complex	$\nu(NH)^a$	$\nu(Mo{=}O)$	$\nu_{asym}(CSS)$	$\nu(Mo-S)$	$\nu(Mo-X)$
$MoOF_2(acda)_2$	3390 3210	960 (s)	815 (s)	360 (m)	530 (s)
$MoOCl_2(acda)_2$	3360 3130	955 (s)	810 (s)	355 (m)	315 (m)
$MoOBr_2(acda)_2$	3360 3100	950 (s)	810 (s)	355 (m)	310 (m)
$MoOI_2(acda)_2$	3365 3100	950 (s)	810 (s)	355 (m)	310 (m)
$MoO(tp)(acda)_2$	3355 3130	955 (s)	810 (s)	350 (m)	
$MoO(abt)(acda)_2$	3360 3100 2930	940 (s)	800 (s)	340 (m)	
$MoO(aet)(acda)_2$	3380 3100 2920	940 (s)	790 (s)	340 (m)	
$Mo(acda)_4$	3380 3120		815 (s)	350 (m) 325 (w)	

[a] Indicated peaks from broad band.

when a deep red solution resulted. Addition of diethyl ether (30 mL) caused precipitation of the deep brown microcrystalline product. This was collected by filtration, washed with chloroform, and dried in vacuo; yield 0.17 g (60%).

$MoO(aet)(acda)_2$ (3c). Et_3N (0.4 mL, 3 mmol) and 2-aminoethanethiol hydrochloride (Haet·HCl) (0.34 g, 3 mmol) were dissolved in methanol (20 mL), and the solution was added dropwise to a stirred suspension in methanol (20 mL) of $MoOCl_2(acda)_2$ (0.25 g, 0.5 mmol). The dark brown product was then isolated as described in **3b**, yield 0.13 g (50%).

$Mo(acda)_4$ (4). A suspension of $MoOCl_2(acda)_2$ (0.25 g, 0.5 mmol) in methanol (20 mL) was allowed to react with a methanol solution (30 mL) of Hacda (0.32 g, 2 mmol) under stirred conditions. The reaction was continued as in **3a**. The product is a black-violet solid, yield 0.33 g (90%).

Recrystallizations of the above compounds were not attempted because of their insolubility in common organic solvents. However, all of the compounds prepared are sufficiently pure and gave satisfactory analytical results (Table I).

Physical Measurements. Infrared spectra (4000–200 cm^{-1}) were recorded as KBr disks with a Perkin-Elmer 783 infrared spectrophotometer. Solution conductivity was measured with a Philips PR9500 bridge. Electronic spectra covering the 280–900-nm range were measured with a Pye-Unicam SP8-150 recording spectrophotometer. EPR spectra were obtained at X-band frequency on a Varian E-109 spectrometer equipped with a 100-kHz field modulation unit. Bulk magnetic susceptibility measurements were carried out at room temperature with use of a PAR Model 155 vibrating-sample magnetometer. Cyclic voltammetry, differential-pulse voltammetry, and coulometric measurements were made on a PAR Model 370-4 electrochemistry system. Cyclic voltammetry and differential-pulse voltammetric measurements were made with a PAR 174A polarographic analyzer, a PAR175 Universal Programmer, and a PAR RE0074 X-Y recorder. The three electrode measurements were carried out with a Metrohm E410 hanging-mercury-drop electrode (HMDE) as the working electrode, a platinum-wire auxiliary electrode, and a saturated calomel reference electrode (SCE). For coulometry, a mercury-pool working electrode was used. All measurements were performed in DMF solutions at 298 K under an atmosphere of purified dinitrogen. The potentials reported here are uncorrected for junction potentials. Electrochemically pure DMF was obtained from analytically pure solvent by using a procedure as described in literature.[8] Tetraethylammonium perchlorate (TEAP) was obtained according to literature method[9] and employed as supporting electrolyte (0.1 M).

Results and Discussion

A. $MoOX_2(acda)_2$ Complexes (2a–d). These are obtained in high yields by reacting a suspension of $MoO_2(acda)_2$[5] in aprotic solvent with the corresponding hydrohalogenic acid. Efficient cooling of the solution (0 °C) is essential for the preparation of the iodo compound (**2d**) in order to avoid some unidentified reactions. Their elemental analyses (Table I) are in good agreement with the assigned formulations. The compounds are sparingly soluble in common organic solvents except DMF and Me_2SO. Conductivity measurements in DMF indicate that the complexes are uncharged; upon standing, however, the conductivity slowly increases, probably owing to some halide ion dissociation as reported in literature.[10] Attempts to isolate the solvolysis products yielded dark oils that could not be induced to crystallize.

A few characteristic infrared frequencies are considered in Table II for the sake of identification of these compounds. The two $acda^-$ ligands are bound to the metal ion in the S,S mode as described previously.[5,11] The compounds, $MoOX_2(acda)_2$, also show a sharp band at ~955 cm^{-1} due to $\nu(Mo{=}O)$ stretching[12,13] together with another $\nu(Mo-X)$ vibration in the range 530–310 cm^{-1}. The order of $\nu(Mo-X)$ frequencies is I ~ Br < Cl < F. It may be mentioned that very few

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Table III. Summary of Electronic Spectral[a] and Electrochemical Data[b] for $MoOX_2(acda)_2$ Complexes

complex	λ_{max}/nm	Mo(VI)/Mo(V) $(E_{1/2})_1{}^c$/V	$\Delta E_p{}^d$/mV	i_{pc}/i_{pa}	n^e	Mo(V)/Mo(IV) $(E_{irrev})_2{}^f$	$n_{irrev}{}^g$
$MoOF_2(acda)_2$	420	−0.76	110	1.37	1.20	−1.30	0.93
$MoOCl_2(acda)_2$	475	−0.29	200	1.40	0.97	−1.28	0.96
$MoOBr_2(acda)_2$	495	−0.27	220	1.15	1.1	−1.24	1.08
$MoOI_2(acda)_2$	500						

[a] Nujol mull. [b] Solvent DMF; supporting electrolyte TEAP (0.1 M); solute concentration $\sim 10^{-3}$ M. [c] From CV using a scan rate of 50 mV s^{-1}; $(E_{1/2})_1 = 0.5(E_{pc} + E_{pa})$. [d] $\Delta E_p = E_{pc} - E_{pa}$. [e] Number of electrons/molecule determined by controlled-potential coulometry. [f] Calculated from DPV data. Scan rate 10 mV s^{-1}; modulation amplitude (ΔE) 25 mV; $(E_{irrev})_2 = E_p + 0.5(\Delta E)$ where E_p is DPV peak potential. [g] Number of electrons/molecule determined by comparison of voltammetric peak current parameters (see text).

halomolybdenum compounds are known in which the halogen atom has been systematically varied from F to I.

The electronic spectra (Nujol mull) of these compounds have several absorption maxima in the range 300–600 nm. The absorption bands appearing below 400 nm are due to internal ligand transitions.[11] Of particular interest to us is the energy of ligand-to-metal charge-transfer (LMCT) transition S (π) → Mo (dπ), which varies throughout the series **2a** > **2b** > **2c** > **2d** (Table III). The decreased order of energy on going from fluoro (**2a**) to iodo (**2d**) complexes is understandable because the heavier halides being softer in nature will be more efficient in stabilizing the dπ orbital of metal due to more effective X → Mo π bonding.

The electron-transfer behavior of the $MoOX_2(acda)_2$ complexes in DMF solution was examined by cyclic voltammetry (CV) and differential-pulse voltammetry (DPV) at a hanging-mercury-drop electrode (HMDE) (Table III). Hacda is electrode inactive in the potential range studied (+0.5 to −1.8 V). All of the four complexes exhibit a quasi-reversible redox process (Figure 1)[14] with the $(E_{1/2})_1$ values ranging from −0.76 to −0.27 V (couple 1) and an irreversible reduction at a much negative potential (~−1.28 V) (couple 2). On the basis of results obtained from cyclic voltammetric measurements and from controlled-potential coulometric (CPC) experiments, the couple in (1) is judged to be a quasi-reversible metal-centered one-electron transfer comprising the Mo(VI) and Mo(V) oxidation states:

$$Mo^{VI}OX_2(acda)_2 + e^- \overset{(E_{1/2})_1}{\rightleftharpoons} Mo^{V}OX_2(acda)_2^- \quad (1)$$

$$Mo^{V}OX_2(acda)_2^- + e^- \xrightarrow{(E_{irrev})_2} Mo^{IV}OX_2(acda)_2^{2-} \quad (2)$$

Determination of electron stoichiometry for the redox couple in (2) by coulometry was vitiated by the continuous electrolysis that occurred at a potential more negative to the cathodic peak potential (E_{pc}). However, the one-electron nature of each couple is established by comparing the observed current height at E_{pc} to those of the corresponding authentic one-electron reversible reactions by using the relationship[15,16]

$$n_{irrev} = \frac{0.90(i_{pc})_{irrev}}{(i_{pc})_{rev}} \frac{(n_{rev})^{3/2}}{[(n_a\alpha)_{irrev}]^{1/2}}$$

where $(n_a\alpha) = 0.0477/(E_{pc} - E_{pc/2})$ (in V) and both $(i_{pc})_{rev}$ and $(i_{pc})_{irrev}$ were measured under identical experimental conditions. The n_{irrev} values estimated in this manner are listed in Table III. The lack of anodic response for the couple in (2) (Figure 1) even at a high scan rate (0.5 V s^{-1}) is evidently due to rapid decomposition of the reduced Mo(IV) species.[10] The potentials for the Mo(VI)–Mo(V) ($(E_{1/2})_1$) and Mo(V)–Mo(IV) ($(E_{irrev})_2$) couples are also given in Table III. It may be noted that the variation of the halide ions has caused a shift in the value of $(E_{1/2})_1$ by almost 500 mV and a change in the value of $(E_{irrev})_2$ by about 60 mV. The results show that the complexes in which X has relatively weaker ligand field strength are reduced at relatively more positive potentials. This can be rationalized by taking into consideration the LMCT band energy (ν_{CT}) discussed earlier. If the ligand π levels are left more or less unaffected, ν_{CT} should decrease as the stability of the metal dπ level increases; consequently, a parallel shift of E to more positive potentials is anticipated as electron transfer involves the dπ orbital of the metal. Indeed the data shown in Table III[17] reveal a good correlation between ν_{CT}, $(E_{1/2})_1$, and $(E_{irrev})_2$.

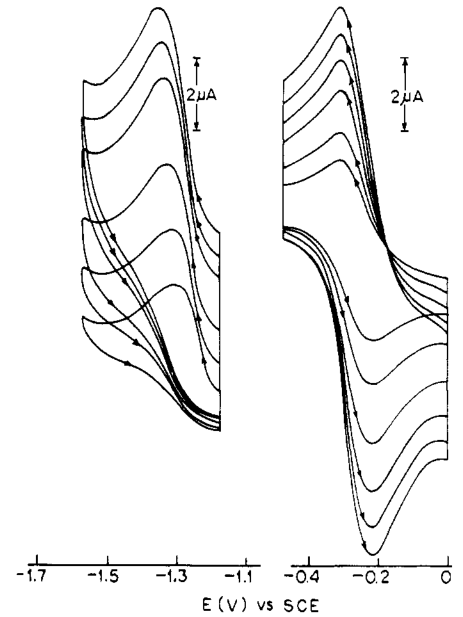

Figure 1. Cyclic voltammetric traces for 0.93 × 10^{-3} M $MoOBr_2(acda)_2$ in 0.1 M TEAP/DMF. Scan rates (mV s^{-1}): 50, 100, 200, 300, 400, 500.

B. MoOL(acda)$_2$ Complexes (L = tp (3a), abt (3b), aet (3c)). The compound $MoOCl_2(acda)_2$ has turned out to be a remarkably useful precursor for the generation of the compounds $MoOL(acda)_2$ (**3a–c**). In these preparations the thiolato ligands function both as reductants and as incoming ligands. The solid compounds are stable and remain unchanged for several months when stored in a desiccator. IR spectra (Table II) show the presence of a strong Mo═O stretching frequency (955–940 cm^{-1}) in the range expected for monooxomolybdenum(V) complexes[18,19] but lack Mo—O—Mo bridge absorption.[18,19] The appearance of a medi-

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(14) A typical voltammogram for $MoOBr_2(acda)_2$ is shown in Figure 1. Similar voltammograms are also observed for the remaining other three compounds.

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(17) $MoOI_2(acda)_2$ undergoes solvolysis slowly in DMF solution and has the following electrochemical features: $(E_{1/2})_1 = -0.33$ V; $\Delta E_p = 135$ mV; $(E_{irrev})_2 = -1.24$ V.

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Table IV. Electronic Spectral, Magnetic, and EPR Data for the MoOL(acda)_2 and Mo(acda)_4 Complexes

complex	λ_{max}/nm (ϵ/mol^{-1} cm^2)	μ_B	$\langle g \rangle$
MoO(tp)(acda)_2	800 (760), 625 (2525), 535 (sh), 390 (33 760)	1.53	1.999
MoO(abt)(acda)_2	795 (860), 648 (2260), 535 (sh), 395 (30 860)	1.51	1.998
MoO(aet)(acda)_2	810 (820), 660 (2710), 540 (sh), 395 (22 210)	1.59	1.998
Mo(acda)_4	800 (2695), 730 (sh), 660 (6370), 536 (13 390), 495 (11 225), 395 (51 020)	2.09	

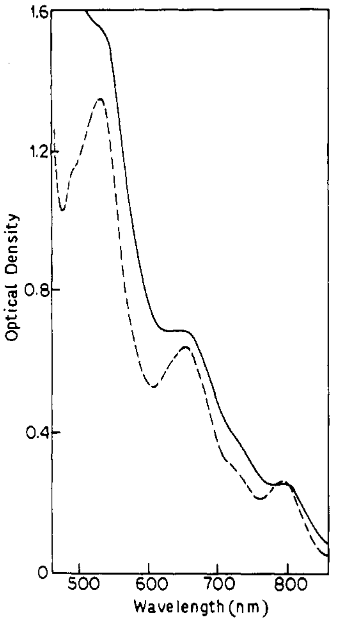

Figure 2. Electronic spectra of MoO(abt)(acda)_2 (3×10^{-4} M) (—) and Mo(acda)_4 (0.98×10^{-4} M) (---) in DMF solution.

um-intensity band in **3b** and **3c** at ~2900 cm^{-1} (assignable to ν(NH) stretching) suggests that both abt and aet anions are ligated to the metal center by N,S mode.

An important feature of all these monomeric Mo(V) complexes is their intense red color in DMF solution owing to electronic transition, in the region 850–300 nm (Table IV; Figure 2).[20] The band occurring below 400 nm is due to an intraligand transition.[11] The results are consistent with the $(4d_{xy})^1$ electronic ground state ($^2B_2$) for Mo(V), and the bands at ~800 and ~540 nm may be interpreted as due to $^2B_2 \rightarrow {}^2E$ ($O_{2p_\pi} \rightarrow Mo_{4d_{xy}}$) and $^2B_2 \rightarrow {}^2E$ ($Mo_{4d_{xy}} \rightarrow Mo_{4d_{xz,yz}}$) transitions, respectively, which are characteristic for the MoO^{3+} moiety of monomeric Mo(V) complexes.[21,22] The remaining band appearing at ~650 nm is probably due to a ligand-to-metal (S → Mo) charge transfer.[23]

The magnetic moment and EPR data for the complexes are listed in Table IV. The room-temperature magnetic moments of these compounds (1.51–1.59 μ_B) are similar to those observed in various other mononuclear oxomolybdenum(V) complexes.[23,24] The values are quite close to the spin-only value for a d^1 system. Unfortunately, the room-temperature EPR spectra of the polycrystalline samples offer little information since the spectra of magnetically nondilute solids consist of a single line. The $\langle g \rangle$ values presented in Table IV are the same for all three compounds, showing that the unpaired electron being located in a metal-centered orbital has almost similar composition for the entire series of compounds.

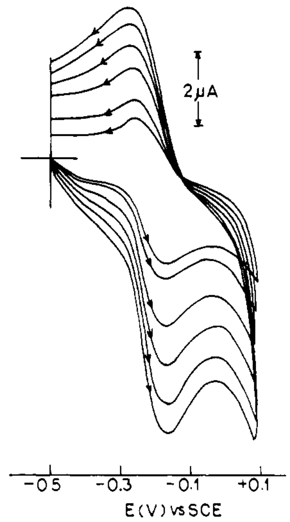

Figure 3. Cyclic voltammetric traces for 0.98×10^{-3} M MoO(aet)(acda)_2 in 0.1 M TEAP/DMF. Scan rates (mV s^{-1}): 50,100, 200, 300, 400, 500.

The cyclic voltammograms[25] and electrochemical data for the oxidation of Mo(V) complexes (**3a–c**) in DMF are shown in Figure 3 and Table V. All of the complexes show a well-defined cyclic response in the potential range +0.5 to −1.8 V. On the basis of the results from constant-potential coulometric experiments and cyclic voltammetric data ($i_{pc}/i_{pa} \sim 1.0$, $\Delta E_p \sim 100$ mV at scan rates 50–500 mV s^{-1}), this response is judged to be a nearly reversible one-electron transfer involving the Mo(V)/Mo(VI) oxidation states. In stirred solution, electrolysis occurred smoothly when the working potential was set above E_{pa}; below E_{pc} little electrolysis occurred. The electrode reaction can then be represented by the couple in (3). The $(E_{1/2})_3$ values of this couple (Table V)

$$\text{Mo}^{V}\text{OL(acda)}_2 \overset{(E_{1/2})_3}{\rightleftharpoons} \text{Mo}^{VI}\text{OL(acda)}_2^{+} + e^- \qquad (3)$$

change by about 70 mV on going from **3a** to **3c**. Constant-potential coulometry performed at −0.1 V (**3a–c**) confirms one-electron involvement. For **3a** and **3b** another cathodic response with a peak potential (E_{pc}) of ~−1.3V is observed, which, however, lacks anodic peak on scan reversal. Coulometry at potentials more negative to −1.3 V did not give meaningful results due to continuous accumulation of coulombs, presumably owing to some unidentified reactions. However, comparison of the cathodic peak current at E_{pc} to those of the corresponding authentic one-electron redox processes as described previously for the couple in (2) lead us to conjecture a metal-centered one-electron transfer comprising the Mo(V) and Mo(IV) oxidation states as in the couple in (4). Evidently the reduced Mo(IV) species is unstable in the

$$\text{Mo}^{V}\text{OL(acda)}_2 + e^- \xrightarrow{(E_{irrev})_4} \text{Mo}^{IV}\text{OL(acda)}_2^{-} \qquad (4)$$

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[20] Electronic spectrum for MoO(abt)(acda)_2 is shown as a typical one. The gross features of the electronic spectra of the remaining compounds (**3a** and **3c**) are similar.

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[25] A typical voltammogram for MoO(aet)(acda)_2 is shown in Figure 3. Similar voltammograms are observed with **3a** and **3b** in this region. However, for the later two compounds another cathodic response of irreversible nature appears at a much negative potential ($E_{irrev} \sim -1.25$ V).

Table V. Electrochemical Data[a] for the MoOL(acda)$_2$ Complexes

complex	Mo(VI)/Mo(V) $(E_{1/2})_3$[b]/V	Mo(VI)/Mo(V) ΔE_p[c]/mV	Mo(VI)/Mo(V) i_{pa}/i_{pc}	Mo(VI)/Mo(V) n[d]	Mo(V)/Mo(IV) $(E_{irrev})_4$[e]/V	Mo(V)/Mo(IV) n_{irrev}[f]
MoO(tp)(acda)$_2$	−0.28	110	1.03	1.20	−1.26	1.11
MoO(abt)(acda)$_2$	−0.25	100	1.14	0.98	−1.25	0.95
MoO(aet)(acda)$_2$	−0.21	80	1.14	0.95		

[a] Solvent DMF; supporting electrolyte TEAP (0.1 M); solute concentration ~10^{-3} M. [b] From CV using a scan rate of 50 mV s^{-1}; $(E_{1/2})_3 = 0.5(E_{pc} + E_{pa})$. [c] $\Delta E_p = E_{pa} - E_{pc}$. [d] Number of electrons/molecule determined by controlled-potential coulometry. [e] Calculated from DPV data. Scan rate 10 mV s^{-1}; modulation amplitude (ΔE) 25 mV; $(E_{irrev})_4 = E_p + 0.5(\Delta E)$ where E_p is DPV peak potential. [f] Number of electrons/molecule determined by comparison of voltammetric peak current parameters (see text).

voltammetric time scale even at a high scan speed (0.5 V s^{-1}) and no longer survives to undergo oxidation.[10] $(E_{irrev})_4$ values for **3a** and **3b** as obtained from differential-pulse polarographic measurements together with the n_{irrev} values are given in Table V.

C. The Mo(acda)$_4$ Complex (4). The black-violet Mo(IV) compound has been synthesized by the direct reaction of MoOCl$_2$(acda)$_2$ with excess Hacda (1:4 mole ratio) in methanol. The vibrational spectrum (Table II) of the Mo(IV) complex is typical of completely chelated dithiocarboxylato complexes.[5,11,26] The absence of the oxo group is indicated by the lack of characteristic ν(Mo═O) in the IR spectrum. Similar neutral eight-coordinated nonoxo Mo(IV) compounds with a MoS$_8$ core have also been synthesized with some dithiocarbamato[27–29] and dithiocarboxylato[26] ligands. These are obtained through (1) insertion of CS$_2$ into molybdenum(IV) dialkylamides,[27] (2) reaction of sodium *N*,*N*-dialkyldithiocarbamates with molybdenum(IV) chloride,[28] (3) oxidative decarbonylation of Mo(CO)$_6$ with tetraalkylthiuram disulfide,[29] and (4) reaction between hexachloromolybdate(III) of suitable organic cations and the appropriate dithiocarboxylic acids.[26] In all these preparative methods, the source of molybdenum is a non-oxo species and the oxidation state of molybdenum is either increased due to oxidation or remains invariant during the course of reaction. Our method is quite unique in the sense that it involves reduction of and oxygen abstraction from the substrate, viz. MoOCl$_2$(acda)$_2$.

The electronic spectrum of this compound in DMF (Figure 2; Table IV) is complex in nature. In addition to the high-energy internal ligand π-π^* bands,[5,11] five more bands are observed for this compound, between 450 and 800 nm. Most of them should be assigned to charge-transfer transitions[26] (possibly of the L → M type) because of their high extinction values (ϵ = 2700–13 400 M^{-1} cm^{-1}). Mo(acda)$_4$ has a magnetic moment (2.09 μ_B) much smaller than the spin-only value of 2.83 μ_B, which probably is due to the large spin–orbit coupling constants of this element.[28]

The cyclic voltammogram of Mo(acda)$_4$ in DMF at a HMDE is shown in Figure 4. In the potential range +0.1 to −0.9 V identical voltammograms comprising two redox couples were obtained irrespective of the direction of scanning. In either case the scan was initiated from −0.3 V. The observed redox potentials are $(E_{1/2})_5 = -0.42$ V (couple 5) and $(E_{1/2})_6$

$$[\mathrm{Mo^{III}(acda)_4}]^- \underset{(E_{1/2})_5}{\overset{e^-}{\rightleftharpoons}} [\mathrm{Mo^{IV}(acda)_4}]^0 \quad (5)$$

$$[\mathrm{Mo^{IV}(acda)_4}]^0 \underset{(E_{1/2})_6}{\overset{e^-}{\rightleftharpoons}} [\mathrm{Mo^{V}(acda)_4}]^+ \quad (6)$$

= −0.22 V (couple 6). Both electron-transfer processes are reversible with the use of the criteria of scan rate (50–500 mV s^{-1}) dependence of the cathodic peak current and width and equivalence of the cathodic and anodic peak heights. The separations of peak potentials (ΔE_p) for the cathodic and anodic sweeps are 60 and 90 mV for the couples in (5) and (6), respectively. Moreover, $E_{1/2}$ values remain practically invariant (±4%) for both couples on varying of the scan rate in the range 50–500 mV s^{-1}. These show that the couple in (5) is fully reversible and the couple in (6) is almost reversible.[30] The involvement of one-electron transfer for each of the electrode processes has been confirmed from coulometric experiments. In stirred solution, for the couple in (5), brisk electrolytic reduction occurred only at working potentials more negative than E_{pc} (n = 1.1); while for the couple in (6), electrolytic oxidation occurred smoothly when the working potential was set above E_{pa} (n = 0.96). The overall redox reactions can be illustrated in a manner as shown in (5) and (6). Grossly similar voltammetric features, both of which include two redox couples—one for Mo(IV)/Mo(V) oxidation ($E_{1/2}$ ~ −0.5 V) and the other for Mo(IV)/Mo(III) reduction ($E_{1/2}$ ~ −1.2 V)—were reported for Mo(Et$_2$dtc)$_4$ complex.[29,31] Relatively easier oxidation of Mo(Et$_2$dtc)$_4$ compared to Mo(acda)$_4$ could be interpreted in terms of a greater electron-releasing character of dithiocarbamato ligands.[32,33] This tendency contributes high charge density on the central metal ion, thereby causing a larger decrease in the formal charge on molybdenum, and thus favors a lower oxidation potential for Mo(Et$_2$dtc)$_4$. A similar conclusion was also reached from molecular orbital calculations of some eight-coordinated mo-

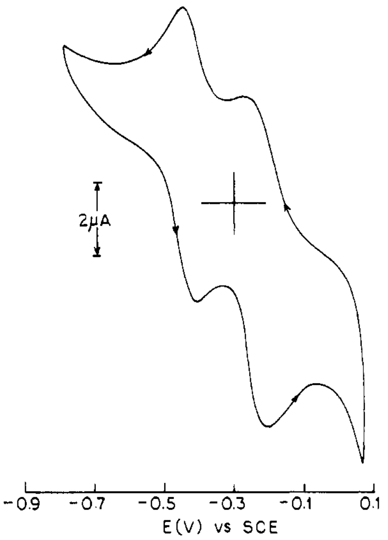

Figure 4. Cyclic voltammogram for 1.15 × 10^{-3} M Mo(acda)$_4$ in 0.1 M TEAP/DMF. Scan rate (mV s^{-1}): 50.

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lybdenum compounds containing the MoS_8 core.[34]

Concluding Remarks. The reaction between halogenic acids and $MoO_2(acda)_2$ produced seven-coordinated[12] dihalogeno compounds, $MoOX_2(acda)_2$. The function of acid here is to protonate and hence to labilize one of the oxo groups[35,36] of $MoO_2(acda)_2$. Similar oxo group abstraction due to protonation by ATP is thought to be operative in the functioning of nitrogenase.[37,38] The compound $MoOCl_2(acda)_2$ has a redox potential, $(E_{1/2})_1 = -0.29$V, that is about 650 mV more positive to that of $MoO_2(acda)_2$[5] because of the stabilization of the electron-transfer orbital of the metal ion by more effective π bonding due to chloride ion. To our knowledge, among all molybdenum(VI) complexes reported so far $MoOBr_2(acda)_2$ is undergoing reduction at the least negative potential. The less negative value of the formal potential of $MoOCl_2(acda)_2$ and the relative ease of its preparation have made it a remarkably useful starting material for the preparation of lower valent molybdenum compounds.

Electrochemical features of $MoOX_2(acda)_2$ and MoOL-$(acda)_2$ compounds are grossly similar and can be represented by the following generalized scheme (B = X_2, L):[39]

$$[\mathrm{Mo^{VI}OB(acda)_2}] \xrightleftharpoons[E_{1/2} \sim -0.3\ \mathrm{V}]{e^-}$$

$$[\mathrm{Mo^{V}OB(acda)_2}] \xrightarrow[E_{\mathrm{irrev}} \sim -1.25\ \mathrm{V}]{e^-} [\mathrm{Mo^{IV}OB(acda)_2}]$$

In both cases, the electrochemically generated Mo(IV) species are unstable and undergo post chemical reaction. One interesting observation is the quasi-reversible nature of the reduction of $MoOX_2(acda)_2$, unlike many other Mo(VI) compounds of *cis*-dioxo type where irreversible behavior generally is observed.[40-42]

The voltammetric features of $Mo(acda)_4$ are noteworthy in the sense that it can be used as a possible starting material for the generation of various non-oxo Mo(V) and Mo(III) compounds. Work is now in progress to stabilize these oxidation states by using suitable redox-active reagents.

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Registry No. **2a**, 92985-00-7; **2b**, 92985-01-8; **2c**, 92985-02-9; **2d**, 92985-03-0; **3a**, 92985-04-1; **3b**, 92985-05-2; **3c**, 92985-06-3; **4**, 89172-34-9; $MoO_2(acda)_2$, 89742-18-7.

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Contribution from the Department of Chemistry,
North-Eastern Hill University, Shillong 793003, India

Hydrazinium, Alkali-Metal, and Ammonium Trifluorooxovanadates(IV). Synthesis and Spectroscopic Studies of a New Oxofluorovanadate(IV) Complex, VOF_3^-

MIHIR K. CHAUDHURI,* SOUMITRA K. GHOSH, and JAPYESAN SUBRAMANIAN*

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Blue crystalline $N_2H_5VOF_3$ has been synthesized from the reaction of V_2O_5 with 99% hydrazine hydrate in the presence of 40% HF. The alkali-metal and ammonium salts of the complex anion, $AVOF_3$ (A = Na, K, or NH_4), have been prepared by metathesis between $N_2H_5VOF_3$ and alkali-metal or ammonium fluoride, AF, in an aqueous medium. Characterization and assessment of structure were made from the results of chemical analyses, chemical determination of the oxidation state of vanadium, molar conductance and magnetic susceptibility measurements, and infrared, electronic, and ESR spectroscopic studies. The molar conductances of $N_2H_5VOF_3$ and $AVOF_3$ lying between 130 and 135 Ω^{-1} cm^2 mol^{-1} provide evidence for their 1:1 electrolytic nature; their infrared spectra show the multiple nature of the V–O bond and the absence of water. The magnetic moments of the compounds were observed to fall between 1.51 and 1.53 μ_B and the chemically estimated oxidation states of vanadium were found to lie between +3.9 and +4.1. The electronic spectra of the compounds show absorptions at ca. 11 900 and ca. 16 000 cm^{-1} owing to the two d–d transitions characteristic of an oxovanadium(IV) species. The ESR spectrum of $N_2H_5VOF_3$ in a frozen aqueous solution at 100 K indicates that the complex species, VOF_3^-, has a distorted octahedral structure. In the solid state, the complex species VOF_3^- may have a polymeric structure through weak V–O···V and V–F···V interactions.

Although several oxofluorovanadate(IV) complexes are known,[1] the species of the formula VOF_3^- does not seem to have any reported evidence in the literature. The corresponding trichlorooxovanadate(IV), $VOCl_3^-$, has, however, been reported.[2] The salts of the $VOCl_3^-$ anion were synthesized by the reduction of V^{5+}, in the presence of an excess of Cl^- ions, with ethanol followed by precipitation of the salts from aqueous ethanolic media.[2] Similar reactions of V^{5+} in the presence of an excess of F^- ions, however, did not lead to the synthesis of the VOF_3^- complex.[3] As an extension of our studies of oxo fluoro[3] and heteroligand peroxo[4] compounds of

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