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Inorganic Chemistry Article

Unusual Reduction of Ammonium Heptamolybdate to Novel Molybdenum(IV)-Stabilized Azo Anion Radical Complexes

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In an unusual reaction of the polyacid, ammoniumheptamolybdate tetrahydrate ($(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$), and the ligand, 2-[(arylamino)phenylazo]pyridine (general abbreviation HL), in the presence of PPh_3 afforded the brown oxo free molybdenum complexes of type $[Mo(L)_2]$ in high yields (ca. 80%). The reaction occurs smoothly in ethanol. It is slow on a steam bath (25 h) but is complete in about an hour in a microwave oven. X-ray structures of two representatives are reported. In these complexes the ligand acted as a tridentate ligand using its pyridyl(N), azo(N), and the deprotonated amine(N), respectively. The geometry is meridional, and the relative orientations within the coordinated pairs of nitrogens are *cis*, *trans*, and *cis,* respectively. Bond length data of the coordinated ligands are consistent with a $Mo^{IV}[L^{\bullet}]_2$ ($[L^{\bullet}]^{2-}$ = azo dianion radical formed by one electron reduction of the deprotonated anionic ligand, $[L]^-$) description. For example, the N–N lengths (1.349(5)–1.357(2) Å) in these complexes are appreciably longer than that (1.246(3) Å) in the uncoordinated and protonated salt of a representative ligand, $[H_2L^d]ClO_4$. The N–N lengths, however, correspond well with metal complexes of the ligand containing azo ion radical. The complexes are diamagnetic and showed highly resolved ^1H NMR and ^{13}C NMR spectra. The two coordinated ligands in these are magnetically equivalent, and resonances for only one ligand were observed in their spectra. Diamagnetism in the present molybdenum complexes is attributed to strong antiferromagnetic coupling between $Mo^{IV}(4d^2)$ and the two planar radical $[L^{\bullet}]^{2-}$ ligands. The complexes display multiple redox responses. The ESR spectrum of electrogenerated $[\mathbf{1a}]^-$ showed a characteristic spectrum for Mo(III) with weak hyperfine lines due to the presence of molybdenum isotopes having nonzero nuclear spin. Visible range multiple charge transfer transitions in these complexes are ascribed to ligand-to-metal transitions.

Introduction

There has been considerable interest in the chemistry of polyoxomolybdates[1] (molybdenum−oxygen cluster anions) for several reasons including their structural diversity[2] and catalytic action.[3] These compounds contain oxygen atoms that are multiply bonded to molybdenum in the highest oxidation state and, in principle, are capable of transferring oxygen atom(s) to reductants such as phosphines, sulfides, and alkenes, etc., as these occur in several monometallic oxo−molybdenum(VI) complexes.[4,5] The above reactions are important in the context of industrial processes and biological processes such as enzyme catalysis. Our literature survey has revealed that examples of the chemical reduction

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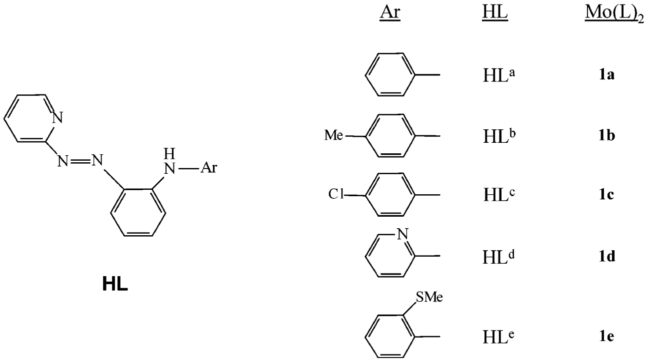
Chart 1



involving oxygen atom transfer from molybdenum(VI) oxides or their salts, polyoxomolybdates, are uncommon.[6] Recently, reduction of K_2MoO_4 to its lower valent oxides by the use of KBH_4 as a reductant was reported.[7] Multiple step electrochemical reductions of polyoxomolybdates are known; however, the original polymeric structure can be restored upon reoxidation.[8]

Herein we wish to disclose our results on the chemical reduction as well as degradation of the hydrated ammonium heptamolybdate salt, $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ by PPh_3 in the presence of a series of N_3-donors[9] of general abbreviation HL [HL = 2-[(arylamino)phenylazo]pyridine], $NH_4C_5N{=}N\text{-}C_6H_4N(H)Ar$ (Chart 1). The reaction resulted in the formation of oxo-free molybdenum complexes in high yields. It may be relevant to note here that coordination chemistry of the reference ligand system has been studied[10] in our laboratory over the past few years. Usually, it dissociates the secondary amine proton (pK_a ca. 8.5) and binds as a monoanionic bis chelate. Moreover, the ligand contains a reducible azo function, and one electron reduction of the azo chromophore (eq 1) is known to generate an azo anion radical in solutions.

$$—N{=}N— + e^- \longrightarrow [—N\overset{\cdot}{—}N—]^- \qquad (1)$$

Hence, azo anion radical metal complexes of this redox noninnocent ligand system may be anticipated. Interestingly, the structural parameters of the reference molybdenum complexes point to reduced azo radical descriptions of the coordinated ligands. It may be noted here that isolable metal ion stabilized azo radical complexes are scanty and are reported[11,12] only in the recent past. To the best of our knowledge, only three examples of such complexes are reported involving the bivalent metal ions ruthenium and osmium, and monovalent copper. However, molybdenum-stabilized azo radical complexes are not known in the literature.

Results and Discussion

A. Synthetic Studies. The relevant ligands, complexes, and their abbreviations are collected in Chart 1.

The reaction of the salt, $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$, with HL in boiling ethanol in the presence of PPh_3 produced a brown mixture. A new brown crystalline compound, $[Mo(L)_2]$ (**1**), was separated from crude mass on a preparative TLC plate using toluene as an eluent. The reaction is slow (25 h) on a steam bath but is complete in less than an hour in a microwave oven. The optimum concentration of PPh_3 to each mole of the polyacid is 1:24. At a lower concentration of PPh_3, a portion of the ligand (HL) remains unreacted, which causes the lower yield of the final product. As far as we are aware, such a reductive substitution reaction with complete oxo transfer from polyoxomolybdates is uncommon in the literature. We have come across with one such example where the oxo free molybdenum complex, $Mo(SS)_3$ (SS = 4-methyl-1, 2-dimercaptobenzene) was synthesized[6] starting directly from ammoniumheptamolybdate. Notably, the polyacids of molybdenum are otherwise robust[13] and do not undergo decomposition easily. Oxygen-free molybdenum complexes are reported generally in low valent states (≤ 2) and are mostly synthesized[14] starting from $Mo(CO)_6$ and related non-oxo molybdenum starting materials.[15] The yields of the compounds **1a**−**1e** are high, (ca. 80%) and these compounds are soluble in almost all common solvents. The FAB mass spectra of these indicated monometallic bis chelated compound. For example, the complex $[Mo(L^a)_2]$ showed an intense peak due to the parent molecular ion at m/z 642 amu, while that for $[Mo(L^d)_2]$ appeared at m/z 646 amu.

B. Crystal Structure. Single crystal X-ray structures of two representative molybdenum complexes, viz. **1a** and **1e**, are solved. ORTEP and atom numbering schemes of these are shown in Figures 1 and 2, respectively. Selected bond lengths are collected in Table 1. The two deprotonated

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(15) Following the suggestion of a reviewer, we performed a similar reaction starting from $MoO_2(acac)_2$ (acac = acetylacetonate), which also produced the reference molybdenum complex, **1**, in a high yield ca. 90%.

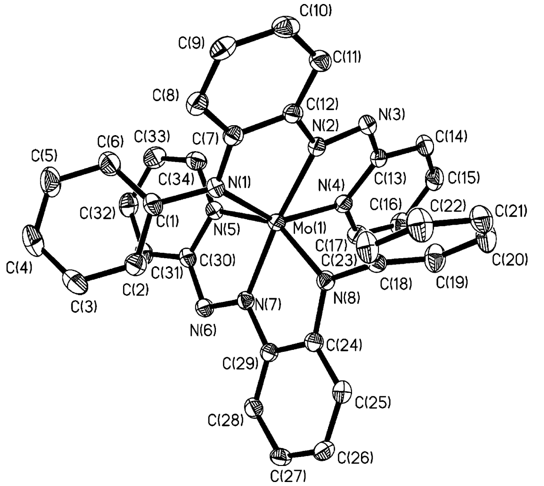


Figure 1. Molecular structure and atom numbering scheme for Mo[L^a]$_2$.

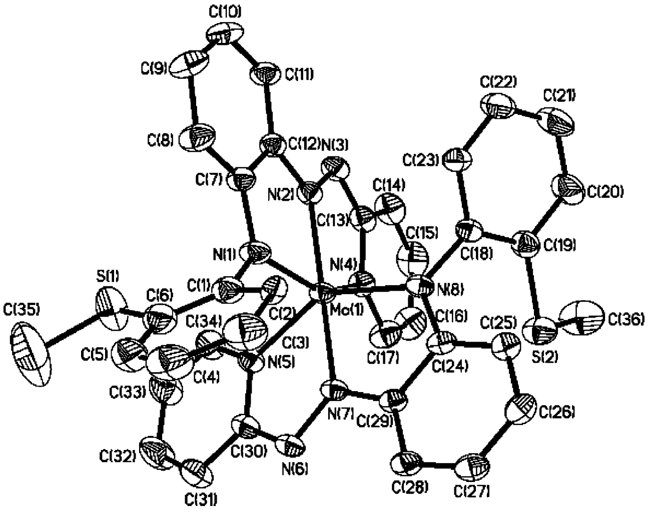
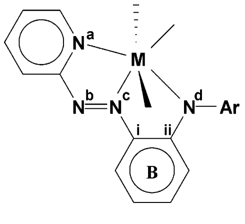


Figure 2. Molecular structure and atom numbering scheme for Mo[L^e]$_2$.

Scheme 1



ligands in **1a** coordinate the metal ion in N$_6$-fashion using pairs of pyridyl-N, azo-N, and amido-N(deprotonated secondary amine) atoms. The geometry of its meridional and relative orientations within the aforesaid pairs are *cis*, *trans*, and *cis*, respectively. The average of the chelate bite angles of N(pyridyl)−Mo−N(azo) (71.78(7)°) is smaller than that of N(azo)−Mo−N(amide) (76.47(7)°). A similar trend was noted[10] before in related [M(L)$_2$]$^{n+}$ type complexes. The structure of the compound **1e** has also revealed a similar coordination and geometry, but the additional thioether site of the ligand remains pendent and unused.

The most notable part of these two structures is the unusual elongation of N−N lengths of azo chromophores. For example, the average of two N−N lengths in **1a** is 1.357(2) Å, while that in **1e** is 1.349(5) Å. Notably, this length in the uncoordinated ligand[16] salt, [H$_2$L^d]ClO$_4$, is 1.246(3) Å. Usually, coordination of the anionic ligand [L]$^-$ to a metal ion is associated with delocalization of anionic charge along the ligand backbone resulting in contraction of C−N lengths on either side of the middle phenyl (B) ring (Scheme 1) and elongation of N−N length as compared to those in uncoordinated ligand. Bond length data of some known examples are collected in Table 2 for comparison. Thus, the N−N length in the known complexes of [L]$^-$ never exceeded[10a] 1.308(3) Å. In contrast, these are notably longer (≥1.349 Å) in the present molybdenum compounds. Moreover, the C−N lengths on either sides of the middle phenyl (B) ring in the reported examples are much shorter than the corresponding average C−N lengths of the molybdenum compounds. In fact, these lengths in the molybdenum complexes indicate single bonds and are nearly identical to those observed in the protonated ligand salts, [H$_2$L^d](ClO$_4$), where no charge delocalization is anticipated. Furthermore, we wish to note that the N−N lengths in uncoordinated azo (−N=N−)[17] and hydrazine (>N−N<)[18] are 1.25 and 1.45 Å, respectively. Thus, in an azo ion radical

$$[\text{-N} \dot{-} \text{N-}]^{-}$$

formed by addition of an electron to the π^* orbital, the bond order is 1.5, and its length may be estimated to be 1.35 Å. The bond parameters of **1a** and **1e** thus indicate the radical description of the coordinated ligands. The effect of elongation of N−N lengths in these complexes is also reflected in the lowering of vibration frequencies of $\nu_{\text{N=N}}$ as compared to that of uncoordinated HL and the known examples of [M(L)$_2$]$^{n+}$ complexes (Table 3). Examples of metal-ion-stabilized azo anion radical complexes are rare in the literature. The first two simultaneous reports on such examples were on copper(I) and ruthenium(II) systems involving two related 2-(arylazo)pyridine ligands. The reported N−N lengths are 1.345(7) Å in [(μ-abpy$^{\bullet}$){Cu(PPh$_3$)$_2$}$_2$](PF$_6$)$_2$[12] (abpy = 2,2′- azobispyridine) and 1.341(17) Å in [Ru(pap$^{\bullet}$)(Cl)(CO)(PPh$_3$)$_2$][11] (pap = 2-(phenylazo)pyridine). Evidently, the N−N lengths in the present molybdenum complexes are even longer than the reported complexes that contain anionic azo radical ligands. The Mo−N lengths in these complexes are more or less unexceptional with two Mo−N(py) bonds longer than the other four Mo−N bonds. This not surprising since out of the three available coordination sites of the reduced ligand, [L$^{\bullet}$]$^{2-}$, only the N(py) is neutral and other two nitrogens are anionic in character.

C. Charge Distribution. Two charge distributions I and II between ligand and metal in the molybdenum complex, [Mo(L)$_2$], are presented in Scheme 2.

Spectroscopic properties provide little information on metal charge, but structural features of the coordinated ligands (vide

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Table 1. Selected Bond Distances (Å) and Angles (deg) of **1a** and **1e**

			1a		
Mo(1)−N(8)	2.0035(17)	N(2)−N(3)	1.368(2)	N(8)−C(18)	1.438(3)
Mo(1)−N(1)	2.0263(17)	N(6)−N(7)	1.347(2)	C(12)−C(7)	1.412(3)
Mo(1)−N(2)	2.0252(17)	N(7)−C(29)	1.408(3)	C(24)−C(29)	1.406(3)
Mo(1)−N(4)	2.1027(17)	N(2)−C(12)	1.398(3)	N(1)−C(1)	1.431(2)
Mo(1)−N(5)	2.1222(17)	N(1)−C(7)	1.397(3)	N(8)−C(24)	1.401(2)
Mo(1)−N(7)	2.0379(16)				
N(1)−Mo(1)−N(2)	76.48(7)	N(2)−Mo(1)−N(4)	72.36(7)		
N(8)−Mo(1)−N(7)	76.47(7)	N(7)−Mo(1)−N(5)	71.21(7)		
			1e		
Mo(1)−N(8)	2.015(4)	N(2)−N(3)	1.345(5)	N(8)−C(18)	1.434(5)
Mo(1)−N(1)	2.002(4)	N(6)−N(7)	1.353(5)	C(12)−C(7)	1.408(6)
Mo(1)−N(2)	2.029(3)	N(7)−C(29)	1.405(6)	C(24)−C(29)	1.397(6)
Mo(1)−N(4)	2.103(3)	N(2)−C(12)	1.397(6)	N(1)−C(1)	1.448(6)
Mo(1)−N(5)	2.091(4)	N(1)−C(7)	1.394(6)	N(8)−C(24)	1.406(5)
Mo(1)−N(7)	2.019(3)				
N(1)−Mo(1)−N(2)	77.08(14)	N(2)−Mo(1)−N(4)	71.86(14)		
N(8)−Mo(1)−N(7)	77.33(14)	N(7)−Mo(1)−N(5)	71.97(14)		

Table 2. Selected Bond Distances[a] of Some Known Complexes of $[L]^-$

compd	N^b-N^c (av) (Å)	N^c-C^i (av) (Å)	N^d-C^{ii} (av) (Å)	ref
$[H_2L^d]ClO_4$	1.246(3)	1.413(4)	1.406(4)	16
$[Co(L^a)_2]ClO_4$	1.294(5)	1.362(6)	1.354(6)	9
$[Fe(L^a)_2]ClO_4$	1.299(3)	1.373(3)	1.353(3)	10f
$[Cr(L^a)_2]ClO_4$	1.296(7)	1.386(8)	1.371(8)	10c
$[Rh(L^d)_2]ClO_4$	1.290(5)	1.357(6)	1.340(6)	10a
$[RuCl(L^a)(HL^a)]$	1.308(3)	1.378(3)	1.355(3)	10a
$[Mo(L^a)_2]$	1.357(2)	1.408(3)	1.401(2)	*b*
$[Mo(L^e)_2]$	1.349(5)	1.404(6)	1.406(5)	*b*

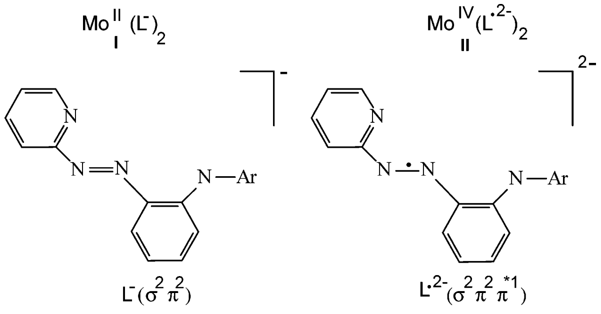
[a] Atom numbers are as shown in Scheme 1. [b] This work.

Table 3. Characterization Data

compd	UV−vis abs[a] [λ_{max}, nm(ϵ/M^{-1} cm^{-1})]	IR[c] (ν, cm^{-1})		electrochemical data[d]	
		ν(C═N)	ν(N═N)	oxidn E_p, V	redn $E_{1/2}$,V (ΔE_p, mV)
1a	680(2510), 460[b](19940), 380(23730), 300(40600), 235[b](28780)	1595, 1610	1250, 1290	0.65[e]	0.85(105), 1.80(90)
1b	680(2300), 460[b](16115), 375(19515), 295(34200), 235[b](25020)	1575, 1610	1235, 1280	0.65[e]	0.90(135), 1.85(115)
1c	680(1995), 455[b](16790), 385(20310), 295(37990), 240[b](24325)	1585, 1610	1240, 1275	0.70[e]	0.80(80), 1.75(95)
1d	675(1375), 455[b](14540), 385(17630), 295(32165), 230[b](21715)	1580,1615	1245, 1280	0.60[e]	0.75(115), 1.70(145)
1e	685(1685), 450[b](16270), 395(19050), 300(32000),245[b](28480)	1580, 1610	1255, 1285	0.65[e]	0.95(70), 1.85(110)

[a] Solvent, acetonitrile. [b] Shoulder. [c] In KBr disk. [d] Versus SCE. [e] Anodic peak potential; the irreversible response without cathodic counterpart.

Scheme 2



supra) are more consistent with the Mo(IV)−$[L^\bullet]^{2-}$ (**II**) form. Though observable in solution, such examples of coordinated radical $[L^\bullet]^{2-}$ in its complexes have so far eluded isolation in pure form. The molybdenum complexes are diamagnetic at a room temperature (300 K). Diamagnetism in these molybdenum compounds may be ascribed to strong antiferromagnetic coupling between the two unpaired spins of Mo(IV)(4d^2) and the two radical ligands. This is not unreasonable because the crystal structures of the reference complexes indicate that the coordinated ligands are planar, which is one of the requisites for strong intramolecular interactions. We note here that spin pairing[19] in the complexes of paramagnetic metal ions and paramagnetic radical ligand(s) is common in the literature. These, however, imply a high degree of covalency as a result of strong mixing of metal d(π) and ligand p(π) frontier orbitals. Thus, there has been an intrinsic difficulty and ambiguity in the assignment of conventional oxidation states in these systems. The molybdenum complexes displayed highly resolved ^{1}H NMR spectra. A representative spectrum of $[Mo(L^a)_2]$ is submitted as Supporting Information, Figure S1. All the complexes showed resonances due to only one coordinated ligand. This confirms that the two coordinated ligands in these are magnetically equivalent, which is in complete agreement with the X-ray crystal structures of the two representative complexes, (vide infra). The ^{13}C NMR spectrum of a representative complex, **1a**, is also submitted as Supporting Information (Figure S2).

The overall chemical reaction, described herein, is a

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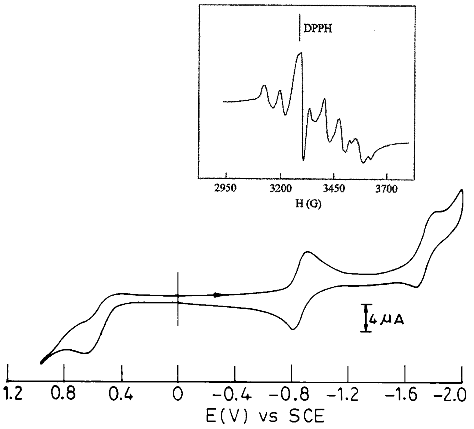

Figure 3. Cyclic voltammogram of Mo[L^a]$_2$ in acetonitrile (supporting electrolyte: TEAP). Inset: ESR spectrum of electrogenarated [**1a**]$^-$ at 77 K.

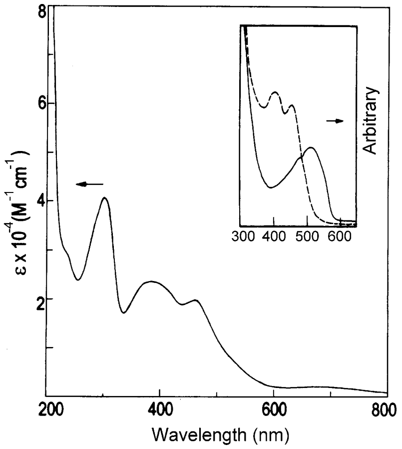

Figure 4. UV−vis spectrum of Mo[L^a]$_2$ in acetonitrile. Inset: visible range spectra of (i) Mo[L^a]$_2$ (- - -), and (ii) electrogenerated Mo[L^a]$_2$$^-$ (—).

multiple electron reduction process. Each molybdenum(VI) ion of the polyacid underwent two electron reduction

$$\mathrm{Mo(VI)} \xrightarrow{2e} \mathrm{Mo(IV)}$$

and is associated with one electron reduction of each L$^-$.

$$2[\mathrm{L}]^- \xrightarrow{2e} 2[\mathrm{L}^\bullet]^{2-}$$

It is reasonable that PPh$_3$ has mediated reductive oxo transfer[20] from the starting polyoxomolybdate, which is followed by internal electron transfer from low valent molybdenum intermediate(s) to the coordinated [L]$^-$. It may be relevant to note that the reports on deoxygenation plus 2e$^-$ reduction of oxo−molybdenum compounds are many, but a single step 4e$^-$ reduction of oxo−molybdenum compounds (2e$^-$ at metal center and 2e$^-$ at the coordinated ligands) by oxo abstraction is uncommon.[4a,6]

D. UV−Vis Spectra and Redox. The redox properties of the molybdenum complexes were studied by cyclic voltammetry (CV) with a platinum disk working electrode. Voltammetric data are collected in Table 3, and a representative voltammogram is displayed in Figure 3. In acetonitrile, the complexes uniformly showed three responses in the range 1.5 to −2.0 V. Of these, two at ca. −0.9 and −1.8 V are cathodic and quasireversible. To have insight into the nature of the electronic level associated with the reversible redox processes, we generated [**1a**]$^-$ in dichloromethane solution[21] by controlled potential bulk electrolysis (applied potential −1.3 V) of [**1a**]. It became pink upon electrolysis but was not stable and reverted to the parent brown complex rapidly. We could, however, manage to record the ESR spectrum of the electrogenerated pink complex [**1a**]$^-$ by quickly freezing the electrolyzed solution at 77 K. It showed an axial spectrum, which is displayed as an inset in Figure 3. The two g components ($g_\perp$ and $g_\parallel$) of the spectrum appeared at 2.00 and 1.85, respectively. These are associated with weak hyperfine lines (A = ca. 65 G) due to the presence of molybdenum isotopes (ca. 25%) that have nonzero nuclear spin ($I_{\mathrm{Mo}} = {}^5/_2$). The ESR spectral nature[22] of [**1a**]$^-$ matches well with those observed in monomeric molybdenum(III) complexes. Thus, the cathodic responses[23] in Mo-complexes [**1**] may be attributed to Mo(IV)/Mo(III) and Mo(III)/Mo(II) couples, respectively. The irreversible anodic response near 0.6 V may be attributed to oxidation of the radical ligand.

The solution electronic spectra of the molybdenum complexes consisted of multiple transitions in the visible range (850−350 nm). In addition, there are two transitions in the UV region, which are due to intraligand charge transfer.[10] Semiempercal EHMO calculations on the compounds **1a** and **1e** using the CACAO program[24] by Mealli and Proserpio indicated that the vacant orbitals, viz. LUMO, LUMO + 1, and LUMO + 2, are all predominantly metal orbitals with small contributions from the ligand orbitals. The occupied orbitals, on the other hand, HOMO, HOMO − 1, are ligand orbitals. Hence, the visible range transitions in these complexes may be ascribed as ligand-to-metal charge transfer. The visible range spectrum of electrogenerated [**1a**]$^-$ is shown as an inset of Figure 4. Diagrams of some selected molecular orbitals are submitted as Supporting Information (Figure S3). Electronic spectral analysis is thus consistent with the ESR spectrum of the reduced [**1a**]$^-$, which has indicated that electrons are added essentially to the metal orbitals during the electrochemical reduction (Table 3, Figure 4) of the present molybdenum complexes.

Conclusion

Herein we have presented an unusual reductive degradation of an otherwise robust and chemically inert molybdenum polyacid using PPh$_3$ as a reducing agent in the presence of a N$_3$-donor, 2-[(arylamino)phenylazo]pyridine. The reaction resulted in a monometallic molybdenum complex with complete removal of oxides. The reduced metal ion is trapped by the ligand. In the present molybdenum complexes, there has been strong delocalization leading to ambiguities in

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(20) OPPh$_3$ was isolated from the reaction mixture. It showed characteristic $\nu_{\mathrm{P=O}}$ in its IR spectrum.

(21) In dichloromethane solution, only one cathodic response was observable. The second response falls outside the accessible range.

(22) Jacobsen, C. J. H.; Pedersen, E. *Inorg. Chem.* **1991**, *30*, 4477.

(23) ESR spectrum of electrogenerated [**1a**]$^-$ could not be recorded due to its instability in solution ($E_{1/2} > -1.8$ V, see text).

(24) Mealli, C.; Proserpio, D. M. *J. Chem. Educ.* **1990**, *67*, 399.

oxidation state assignment, though the X-ray sructural parameters of the present complexes point to a $Mo^{IV}(L^{\bullet})_2$ description. We note here that authentic examples of metal-stabilized azo radical complexes are rare. The work described in this paper indeed suggests the new application of the polymetalates in synthetic and catalytic chemistry may be anticipated. Investigation of these and related chemical reductions of metal−oxo cluster anions are being explored in our laboratory.

Experimental Section

Materials. The starting metal salt, $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$, and triphenylphosphine were obtained from Emerck and Spectrochem India, respectively. 2-Methylthioaniline was an Aldrich reagent. Tetraethylammoniumperchlorate (TEAP) was prepared and recrystallized as reported earlier. All other chemicals and solvents were of reagent grade and used as received.

Physical Measurements. A JASCO V-570 spectrophotometer was used to record electronic spectra. The IR spectra were obtained with a Perkin-Elmer 783 spectrophotometer. ^1H NMR spectra were recorded in $CDCl_3$ with a Brucker Avance DPX 300 spectrometer, and $SiMe_4$ was used as the internal standard. Electrochemical measurements were performed at 298 K under a dry nitrogen atmosphere on a PC-controlled PAR model 273A electrochemistry system. A platinum disk (working) electrode, a platinum wire (auxiliary) electrode, and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. The $E_{1/2}$ for the ferrocenium−ferrocene couple under our experimental condition was 0.39 V. A Perkin-Elmer 240C elemental analyzer was used to collect microanalytical data (C, H, N). FAB mass spectra were recorded on a JEOL SX 102/DA 6000 model mass spectrometer/data system using argon/xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV, and the spectra were recorded at room temperature. NBA (*m*-nitrobenzyl alcohol) was used as matrix.

Reactions of $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ with HL. The reactions of $(NH_4)_6$ $[Mo_7O_{24}].4H_2O$ with different substituted ligands (HL) were performed in the presence of PPh_3 in ethanol as a solvent. A detail of a representative reaction with HL^a is elaborated below.

Isolation of $[Mo(L^a)_2]$ (1a). The ligand HL^a (100 mg, 0.365 mmol) was dissolved in 30 mL of ethanol. To this solution were added $(NH_4)_6[Mo_7O_{24}]$ (65 mg, 0.052 mmol) and PPh_3 (0.35 gm, 1.33 mmol), and the mixture was refluxed continuously for 25 h on a steam bath. During this period, the color of solution changed from red to brown. The resultant solution was cooled and filtered. On evaporation of the brown filtrate, a dark mass was obtained, which was then loaded on a preparative silica gel TLC plate for purification. Toluene was used as the eluent. A brown band moved just ahead of the red ligand band. The brown band was collected and evaporated. Finally, it was recrystallized by slow diffusion of a dichloromethane solution of the compound into hexane. Yield: 80%. Anal. Calcd for $C_{34}H_{26}MoN_8$: C, 63.5; H, 4.0; N, 17.4. Found: C, 63.4; H, 3.9; N, 17.5.

^1H NMR data (chemical shift in ppm): 7.39(d), 7.27(d), 7.07(m), 6.80(s), 6.67(m), 6.38(d), 6.20(t). ^{13}C NMR data (chemical shift in ppm): 162.54, 155.47, 150.56, 146.67, 143.34, 133.53, 129.14, 125.53, 123.09, 121.17, 114.76, 114.58, 112.87. FAB mass: *m*/*z* 642 amu.

A minor second brown band was also eluted with toluene which moved after the red ligand band. Upon evaporation, it was found that the second brown band is a mixture of $OPPh_3$ and a brown compound whose identity is uncertain. By repeated fractional crystallization we could, however, isolate $OPPh_3$ as a white crystalline product from the mixture but in a poor yield (ca. 25%). Most of it remains contaminated with the brown product.

Table 4. Crystallographic Data of **1a** and **1e**

	1a	**1e**
empirical formula	$C_{34}H_{26}N_8Mo$	$C_{36}H_{30}N_8S_2Mo$
molecular mass	642.57	734.74
T (K)	150(2)	295(2)
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a (Å)	10.4545(6)	10.5691(4)
b (Å)	17.1635(9)	13.9169(6)
c (Å)	16.2844(9)	14.5209(6)
α (deg)	90	107.781(1)
β (deg)	104.585(10)	105.807(1)
γ (deg)	90	98.666(1)
V (Å^3)	2827.8(3)	1892.11(13)
Z	4	2
D_{calcd} (mg/m^3)	1.509	1.290
cryst dimens (mm^3)	0.37 × 0.17 × 0.14	0.22 × 0.15 × 0.1
θ range for data collection (deg)	1.75−27.51	1.78−27.50
GOF	0.997	1.127
wavelength (Å)	0.71073	0.71073
reflns collected	17708	25196
unique reflns	6435	8664
largest diff between peak and hole (e Å^{-3})	0.782, −0.575	1.208, −0.454
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0295 wR2 = 0.0597	R1 = 0.0601 wR2 = 0.1775

Similarly, other substituted complexes were prepared by using the appropriate ligand, HL^b−HL^e. The yields and their characterization data are as follows.

1b. Yield: 78%. Anal. Calcd for $C_{36}H_{30}N_8Mo$: C, 64.3; H, 4.4; N, 16.9. Found: C, 64.3; H, 4.4; N, 16.8. ^1H NMR data (chemical shift in ppm): 7.38(d), 7.26(t), 7.09(m), 6.87(d), 6.65(m), 6.38(d), 6.19(t), 2.24(s).

1c. Yield: 82%. Anal. Calcd for $C_{34}H_{24}N_8Cl_2Mo$: C, 57.1; H, 3.9; N, 15.6. Found: C, 57.1; H, 3.9; N, 15.5. ^1H NMR data (chemical shift in ppm): 7.44(d), 7.25(t), 7.13(m), 7.04(d), 6.7-(m), 6.34(d), 6.23(t).

1d. Yield: 75%. Anal. Calcd for $C_{32}H_{24}N_{10}Mo$: C, 59.6; H, 3.7; N, 21.7. Found: C, 59.7; H, 3.8; N, 21.7. ^1H NMR data (chemical shift in ppm): 8.13(d), 7.46(d), 7.42(t), 7.19(d), 7.14(t), 6.91(t), 6.75(m), 6.62(q), 6.18(t). FAB mass: *m*/*z* 646 amu.

1e. Yield: 71%. Anal. Calcd for $C_{36}H_{30}N_8S_2Mo$: C, 58.9; H, 4.1; N, 15.2. Found: C, 58.9; H, 4.1; N, 15.3. ^1H NMR data (chemical shift in ppm): 7.42(d), 6.91(t), 6.78(d), 6.68(m), 6.29(t), 6.16(t), 6.05(d), 2.03(s).

The above reaction occurs much faster in a microwave oven. A commercial domestic microwave oven (BPL) was used[25] by making a suitable hole on the top wall for inserting a reflux condenser (B24 size). The reaction mixture was irradiated for about 1 h at 700 W in a 1-L round-bottom flask. During the irradiation, a cold water−glycerin solution (temp −15 °C) was circulated through the condenser to avoid evaporation of solvents.

X-ray Structure Determination. Crystallographic data for the compounds **1a** and **1e** are collected in Table 4. The suitable X-ray quality crystals were obtained by slow diffusion of dichloromethane solution of compounds **1a** and **1e** into hexane.

1a. The data were collected on a Brucker SMART diffractometer, equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å), and were corrected for Lorentz-polarization effects. A total of 17708 reflections were collected out of which 6435 were

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(25) Narasimhan, S.; Velmathi, S. *Molecules* **2003**, *8*, 256.

unique ($R_{\text{int}} = 0.0306$), satisfying the ($I > 2\sigma(I)$) criterion, and were used in subsequent analysis.

1e. The data were collected on a Brucker SMART diffractometer, equipped with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$Å), and were corrected for Lorentz-polarization effects. A total of 25196 reflections were collected out of which 8664 were unique ($R_{\text{int}} = 0.0395$), satisfying the ($I > 2\sigma(I)$) criterion, and were used in subsequent analysis.

Both the structures were solved by employing the SHELXS-97[26] program package and refined by full-matrix least-squares based on F^2 (SHELXL-97).[27] All the hydrogen atoms were added in calculated positions.

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Supporting Information Available: NMR spectra of a representative, **1a**. Molecular orbital diagrams of **1a**: (i) HOMO − 1, (ii) HOMO, (iii) LUMO, (iv) LUMO + 1, and (v) LUMO + 2. X-ray crystallographic details of the two compounds (**1a** and **1e**) in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(27) Sheldrick, G. M. *SHELXL 97. Program for the refinement of crystal structures*; University of Göttingen: Göttingen, Germany, 1997.