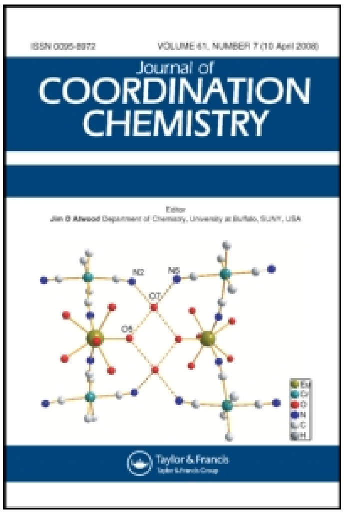

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Synthesis, chemical and electrochemical studies of complexes of a tridentate ONS chelating ligand built around the elusive $[Mo^{VI}OS]^{2+}$ core

Arindam Rana[a]; Manas Sutradhar[b]; Sudhanshu Sekhar Mandal[b]; Saktiprosad Ghosh[ab]
[a] Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Kolkata 700 032, India [b] Department of Chemistry, University College of Science, University of Calcutta, Kolkata 700 009, India

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Synthesis, chemical and electrochemical studies of complexes of a tridentate ONS chelating ligand built around the elusive $[Mo^{VI}OS]^{2+}$ core

ARINDAM RANA†, MANAS SUTRADHAR‡, SUDHANSHU SEKHAR MANDAL‡ and SAKTIPROSAD GHOSH*†‡

†Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India
‡Department of Chemistry, University College of Science, University of Calcutta, 92, Acharya Prafulla Chandra Road, Kolkata 700 009, India

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Synthesis and characterization of four Mo(VI) complexes of a diprotic tridentate ONS chelating ligand (H_2L) containing the rather elusive $[Mo^{VI}OS]^{2+}$ core is reported. These $[Mo^{VI}OSL]$ complexes are obtained from their corresponding $[Mo^{VI}O_2L]$ precursors using a combination of PPh_3 and PPh_3S. This process of oxo-abstraction and sulfido-inclusion affected by PPh_3–PPh_3S is reported for the first time and may be considered as a general method of converting $[Mo^{VI}O_2L]$ complexes to the corresponding $[Mo^{VI}OSL]$ complexes. Direct structural characterization of these complexes could not be done due to the ease of solvolysis of these oxosulfidomolybdenum(VI) complexes to the corresponding dioxomolybdenum(VI) analogues. However, the structure of these $[Mo^{VI}OSL]$ complexes could be reasonably surmised from the corresponding structurally characterized $[Mo^{VI}O_2L]$ complexes. Points of attachment of the potentially pentadentate but functionally tridentate ONS chelating ligands to $[Mo^{VI}OS]^{2+}$ are located mainly through analysis of IR and UV-Vis spectral data and comparison with corresponding $[Mo^{VI}O_2L]$ complexes of known structure. Conditions under which solvolysis of $[Mo^{VI}OS]^{2+}$ to the $[Mo^{VI}O_2]^{2+}$ core is significantly retarded have been identified and make us hopeful of obtaining single crystals of $[Mo^{VI}OSL]$.

Keywords: Oxosulfido Mo(VI) complexes; Functionally tridentate ONS ligands; PPh_3–PPh_3S combination; Facile SAT in solution; Cyanolysis of the Mo=S bond

1. Introduction

Molybdenum is an essential trace element and is present at the active sites of more than fifty redox enzymes belonging to three well-recognized classes [1–6]. Most members of the molybdenum hydroxylase family such as xanthane oxidase are involved in several vitally important biological functions. Insufficiency/shortage or dysfunction of xanthane oxidase in humans has been related to numerous disorders like xanthineurea, hyperuricemia, gout, arthritis, atherosclerosis as well as to Alzheimer's and Parkinson's diseases [1–7]. The oxo-sulfido function *cis*-$[Mo^{VI}OS]^{2+}$ is known to be present in the

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*Corresponding author. Email: ghosh_sakti@vsnl.net

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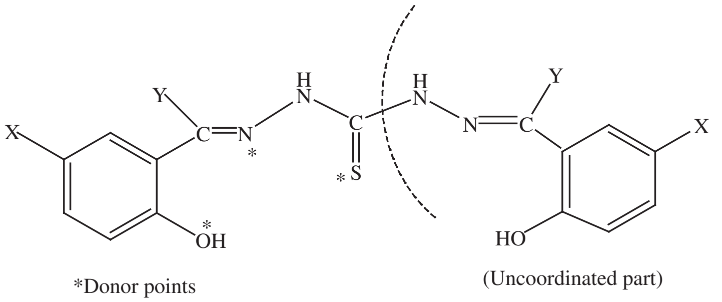


Ligand	Formula	X	Y
H_2L^1	$C_{15}H_{14}N_4O_2S$	H	H
H_2L^2	$C_{15}H_{12}N_4O_2SBr_2$	Br	H
H_2L^3	$C_{15}H_{12}N_6O_6S$	NO_2	H
H_2L^4	$C_{17}H_{18}N_4O_2S$	H	CH_3

Scheme 1. General structural formulation of ligands H_2L^{1-4}.

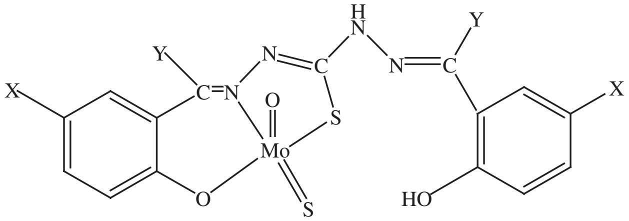
fully oxidized form of xanthine oxidase [2, 8–12] and is recognized as essential for proper functioning of the enzyme. The desulfo form of the enzyme is inactive [13–15], which underscores essentiality of the presence of the $[Mo^{VI}OS]^{2+}$ center in xanthine oxidase. Recent studies [1, 16, 17] have revealed that the Mo-site of xanthine oxidase contains an apical oxo and an equatorial sulfide [1]. This vitally important $[Mo^{VI}OS]^{2+}$ moiety is an ‘‘elusive’’ synthetic target in five or six coordinate complexes as models of xanthine oxidase [13, 18–23]. The main difficulties encountered in synthesis of complexes with $[Mo^{VI}OS]^{2+}$ are: (i) ease of reduction of Mo(VI) by sulfide; (ii) facile formation of polymeric μ-sulfido complexes, and (iii) high reactivity of the sulfide itself [7, 13, 16, 24]. Fundamental chemical and electronic properties of $[Mo^{VI}OS]^{2+}$ are rather poorly explored and understood primarily because of the paucity of authentic oxo-sulfido Mo(VI) and Mo(V) complexes [1, 13, 25, 26].

Synthesis and adequate characterization of five or six coordinate stable model complexes containing the rather elusive $[Mo^{VI}OS]^{2+}$ core is challenging. The present work reports the synthesis and study of a few $[Mo^{VI}OS]^{2+}$ complexes of a previously reported [27] potentially pentadentate but functionally tridentate ONS donor from condensation of thiocarbodihydrazide and substituted salicylaldehydes (scheme 1). A noteworthy feature of this work is the use of triphenylphosphine and triphenylphosphine sulphide combination for generation of the $[Mo^{VI}OS]^{2+}$ core from its precursor complex containing $[Mo^{VI}O_2]^{2+}$. Possibly, triphenylphosphine produces $[Mo^{IV}O]^{2+}$ by oxo-abstraction followed by oxidative addition of sulphur from the triphenylphosphine sulphide.

2. Experimental

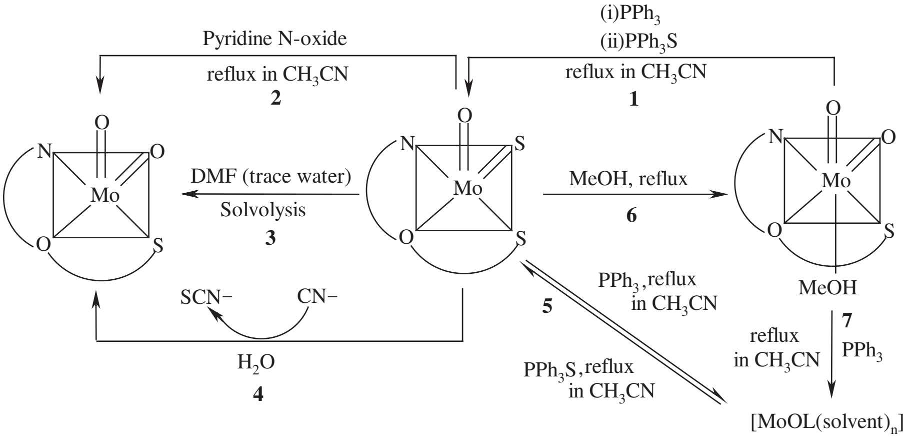
2.1. *Syntheses of H_2L^1 to H_2L^4*

The Schiff bases (H_2L^1), (H_2L^2), (H_2L^3), and (H_2L^4) were prepared by a previously reported procedure [27] by refluxing thiocarbodihydrazide with salicylaldehyde or its *para* substituted derivatives (bromo or nitro) in ethanol (scheme 1).



Compound	Formula	X	Y
1	$C_{15}H_{12}N_4O_3S_2Mo$	H	H
2	$C_{15}H_{10}N_4O_3S_2Br_2Mo$	Br	H
3	$C_{15}H_{10}N_6O_7S_2Mo$	NO_2	H
4	$C_{17}H_{16}N_4O_3S_2Mo$	H	CH_3

Scheme 2. General structural formulation of **1**–**4**.



Scheme 3. Synthesis and reactivity of $[Mo^{VI}OSL]$.

2.2. *Synthesis of dioxomolybdenum(VI) complexes, $[Mo^{VI}O_2L^{1-4}(MeOH)]$*

All four dioxomolybdenum(VI) complexes (scheme 2) used as starting materials were prepared using a previously reported [27] procedure by refluxing $MoO_2(acac)_2$ with H_2L in 1 : 1 molar ratio in methanol (yield: 80–85%).

2.3. *Synthesis of oxosulfidomolybdenum(VI) complexes, $[Mo^{VI}OSL]$*

All four complexes were synthesized using $[Mo^{VI}O_2L(MeOH)]$ (scheme 3, reaction 5). $[Mo^{VI}O_2L^1(MeOH)]$ [27] (0.44 g, 1 mM) was suspended in dry, degassed CH_3CN and refluxed under dry N_2. A solution of PPh_3 (0.33 g) (in 1 : 1.25 molar ratio) in CH_3CN was added and the mixture was refluxed for 2 h. A solution of 3.0 g (10 mM) PPh_3S in CH_3CN was then added and refluxing continued for another hour. The dark reddish brown microcrystalline solid formed was filtered off, washed thrice with degassed warm CH_3CN and dried in a vacuum desiccator over fused $CaCl_2$.

[Mo^{VI}OSL^1] (1). (Yield 70%). Anal. Calcd for $C_{15}H_{12}N_4O_3S_2Mo$ (%): C, 39.47; H, 2.63; N, 12.28; S, 14.04; Mo, 21.05. Found: C, 39.45; H, 2.60; N, 12.25; S, 13.78; Mo, 20.81. λ_{max}(DMF) nm^{-1} 320 (ε dm–$^{-3}$ M^{-1} cm^{-1} 18157), 362 (32299), 366 (28011), 423 (7391), Solid (powder): 309, 373, 426, 482, 541, and 659 (sh).

[Mo^{VI}OSL^2] (2). (Yield 78%). Found: C, 29.24; H, 1.59; N, 9.04; S, 9.93; Mo, 15.45. Calcd for $C_{15}H_{10}N_4O_3S_2Br_2Mo$: C, 29.32; H, 1.63; N, 9.12; S, 10.42; Mo, 15.64. λ_{max}(DMF)nm^{-1} 270 (ε dm^{-3} M^{-1} cm^{-1} 12423), 318 (10392), 362 (14313), and 432 (5527).

[Mo^{VI}OSL^3] (3). (Yield 75%). Found: C, 32.90; H, 1.75; N, 15.23; S, 11.35; Mo, 17.39. Calcd for $C_{15}H_{10}N_6O_7S_2Mo$: C, 32.97; H, 1.83; N, 15.38; S, 11.72; Mo, 17.58. λ_{max}(DMF) nm^{-1} 283 (ε dm^{-3} mol^{-1} cm^{-1} 15449), 325 (14557), 358 (10972), and 410 (9419).

[Mo^{VI}OSL^4] (4). (Yield 72%). Found: C, 41.97; H, 3.09; N, 11.36; S, 12.82; Mo, 19.50. Calcd for $C_{17}H_{16}N_4O_3S_2Mo$: C, 42.15; H, 3.31; N, 11.57; S, 13.22; Mo, 19.83. λ_{max}(DMF) nm^{-1} 301 (ε dm^{-3} mol^{-1} cm^{-1} 16901), 340 (17342), 366 (19586), and 467 (7350).

2.4. *Physical measurements*

Elemental analyses (C, H, N, and S) were done with a Perkin-Elmer 2400 CHNS/O analyzer and molybdenum contents (%) of the complexes were determined gravimetrically [27] as $[MoO_2(oxin)_2]$. Bromine was determined by the standard gravimetric method as AgBr. Electronic spectra of the complexes in DMF were recorded on a Hitachi U-3501 spectrophotometer. Spectrum of **1** was also recorded in the solid state (powder form). IR spectra (as KBr pellets) were taken with a Perkin-Elmer RXI FT-IR spectrophotometer. Electrochemical measurements were performed with a PAR model 362 scanning potentiostat and cyclic voltammograms were recorded at 25°C in the designated solvents under dry dintrogen with the electroactive complex at *ca* 10^{-3} M. Tetraethyl ammonium perchlorate (NEt_4ClO_4, 0.1 M) was used as the supporting electrolyte. A three-electrode configuration was employed with platinum working electrode, a calomel reference electrode, and a platinum auxiliary electrode. The ferrocene/ferrocenium (Fc/Fc^+) couple was used as the internal standard [28]. Room temperature magnetic susceptibilities were measured in the polycrystalline state on a PAR 155 vibrating magnetometer using $Hg[Co(SCN)_4]$ as the calibrant. Molar conductance values of the complexes in DMF were measured with a Systronics 304 digital conductivity meter.

2.5. *Materials*

$[MoO_2(acac)_2]$ was prepared as described in the literature [29] and is used as the source of molybdenum. PPh_3 and PPh_3S were purchased from Aldrich and used as received. Solvents were dried and distilled before use. All other chemicals were reagent grade, obtained from commercial sources and used without purification. Spectroscopic grade solvents were used for spectral measurement.

3. Results and discussion

Synthesis of $[\mathrm{Mo^{VI}OS}]^{2+}$ from $[\mathrm{Mo^{VI}O_2L \cdot CH_3OH}]$ is difficult [13, 16, 17, 24]. On reaction with tertiary phosphines oxosulfido complexes containing the $[\mathrm{Mo^{VI}OS}]^{2+}$ core undergo sulfur transfer (SAT) in preference to oxygen transfer (OAT) [1a]. This is why the strategy adopted for preparation of $[\mathrm{Mo^{VI}OSL}]$ is to use OAT from $[\mathrm{Mo^{VI}O_2L}]$ generating the corresponding $[\mathrm{Mo^{IV}OL}]$ species and then to react it *in situ* with an excess of $\mathrm{PPh_3S}$ to effect sulfido insertion to $[\mathrm{Mo^{IV}OL}]^{2+}$. Thus, an *in situ* "oxo removal-sulfido addition" process is employed here. SAT dominating over OAT is corroborated by formation of $[\mathrm{Mo^{IV}OL}]$ on treatment of the $[\mathrm{Mo^{VI}OSL}]$ with $\mathrm{PPh_3}$. Elemental analyses suggested that unlike $[\mathrm{Mo^{VI}O_2L \cdot CH_3OH}]$, these $[\mathrm{Mo^{VI}OSL}]$ complexes do not have solvent (methanol) coordinated to the metal. The larger volume of sulfur and a Mo=S bond tilted below the ONS meridian of the Schiff base may be responsible for rendering the sixth coordination site inaccessible and also precludes polymerization.

We have also obtained $[\mathrm{Mo^{VI}OSL}]$ complexes by the following experiment. A $[\mathrm{Mo^{VI}O_2L \cdot CH_3OH}]$ complex was refluxed in dry degassed $\mathrm{CH_3CN}$ with $\mathrm{PPh_3}$ in 1 : 1.25 molar ratio and the brown solid isolated corresponded to $[\mathrm{Mo^{IV}OL}]$ [27]. Presence of only one strong band at $\sim 965\,\mathrm{cm^{-1}}$ indicated the monooxo nature of these complexes. When such a $[\mathrm{Mo^{IV}OL}]$ complex is refluxed in $\mathrm{CH_3CN}$ with a large excess of $\mathrm{PPh_3S}$, the corresponding $[\mathrm{Mo^{VI}OSL}]$ complex was isolated and found to be identical with $[\mathrm{Mo^{VI}OSL}]$ obtained *in situ* by the reaction of $[\mathrm{Mo^{VI}O_2L \cdot CH_3OH}]$ first with $\mathrm{PPh_3}$ followed by a 10-fold excess of $\mathrm{PPh_3S}$ (scheme 3, reaction 5). Identity was checked by elemental (C, H, N, S, and Mo) analysis, electronic, and IR spectra.

$[\mathrm{Mo^{VI}OSL^1}]$ (**1**) reacts quantitatively with KCN and the Mo=S bond forms $\mathrm{SCN^-}$, which is detected in the filtrate by the characteristic blood-red color in reaction with $\mathrm{Fe^{3+}}$ (scheme 3, reaction 4). This reaction is reminiscent of deactivation of xanthine oxidase upon cyanolysis [2, 30–32]. Moreover, the $[\mathrm{Mo^{VI}OSL}]$ complexes are unstable in solution and gradually converted to the corresponding dioxo. The labile nature of the $[\mathrm{Mo^{VI}OS}]^{2+}$-core is further substantiated by the rapid conversion of **1**–**4** to their precursor $[\mathrm{Mo^{VI}O_2L}]$ by reacting with pyridine-N-oxide (scheme 3, reaction 2). All the complexes behave as non-electrolytes in DMF. Diamagnetic character of the complexes is consistent with the presence of Mo(VI). In DMF solution $[\mathrm{Mo^{VI}OSL}]$ complexes are slowly but spontaneously converted to the corresponding $[\mathrm{Mo^{VI}O_2L}]$ complexes. Such an observation was reported previously [18, 30]. Electronic spectra of the complexes were recorded in DMF at 5 min intervals. In each complex characteristic features of the spectra (optical density at $\lambda_{\max}$ and ε value) stayed identical up to 45 min. Optical density at $\lambda_{\max}$ began to change slowly along with the shift in $\lambda_{\max}$ and finally the spectrum became identical with the spectrum of its precursor $[\mathrm{Mo^{VI}O_2L}]$. Thus, all solution studies are completed within 45 min during which the complex exists as $[\mathrm{Mo^{VI}OSL}]$. Solvolysis is significantly retarded in the presence of excess $\mathrm{PPh_3S}$; $[\mathrm{Mo^{VI}OSL}]$ remained unchanged up to 2 h.

3.1. *IR spectra*

Important IR bands of the complexes are presented in table 1. IR spectra show clearly resolved bands due to ν(NH) [33] at $\sim 3200\,\mathrm{cm^{-1}}$. Spectra of the $[\mathrm{Mo^{VI}OSL}]$ complexes exhibit characteristics similar to the corresponding $[\mathrm{Mo^{VI}O_2L}]$ complexes [27] in this

Table 1. Selected IR[a] bands (cm^{-1}).

Compound	ν_{OH} (m, sh)	ν_{NH} (m, br)	$\nu_{C=N}$ (vs)	$\nu_{C–O}$ (vs)	$\nu_{Mo=O}$ (vs)	$\nu_{Mo–O}$ (w)	$\nu_{Mo=S}$ (m)	$\nu_{Mo–S}$ (s)	$\nu_{Mo–N}$ (s)	$\nu_{C=S} + \nu_{C=C}$ (m)
$[Mo^{VI}OSL^1]$ (**1**)	3300	3200	1610,1595	1230	965	525	488	350	590	760
$[Mo^{VI}OSL^1]$ (**2**)	3325	3290	1610,1590	1240	965	540	483	340	595	760
$[Mo^{VI}OSL^1]$ (**3**)	3400	3290	1605,1595	1260	960	550	480	345	600	755
$[Mo^{VI}OSL^1]$ (**4**)	3380	3280	1610,1590	1230	970	560	490	320	585	775

[a] In KBr disc, vs – very strong, m – medium, br – broad, w – weak, vw – very weak, sh – sharp, s – strong.

region, showing that substitution of one oxo by a sulfide does not effect the IR spectra of the ligand.

Coordination from the deprotonated phenolic hydroxyl oxygen is reflected in the appearance of the ν(C–O) at a position [34] similar to that in $[Mo^{VI}O_2L]$ complexes reported previously [27]. At ~965 cm^{-1} only a single band due to ν(Mo=O) is observed as opposed to the symmetric and asymmetric stretching twin bands for the $[Mo^{VI}O_2]^{2+}$ moiety in $[Mo^{VI}O_2L]$ complexes. The presence of Mo=S and Mo=O at the same metal center may also have a role in modifying the Mo=O stretching frequency, leading to optimum use of metal d-orbitals [31, 35]. The ν(C = S + C=C) bands of the free ligand around 765 cm^{-1} are profoundly modified in spectra of the complexes [27]. These $[Mo^{VI}OSL]$ complexes have ligands coordinated in the deprotonated thioenolate form. Such thioenolate sulphur coordination is corroborated by appearance of the weak but distinct ν(Mo–S) band in the 350–320 cm^{-1} region [34, 36a, 37]. Bands at ~595 cm^{-1} and 525–560 cm^{-1} are assigned to ν(Mo–N) and ν(Mo–O), respectively [33, 37–40]. The complexes exhibit a new band around 488 cm^{-1} (medium) characteristic of ν(Mo=S) [1, 30, 41–46]. Thus, analysis of the IR spectra of these $[Mo^{VI}OSL]$ complexes indicate ligand coordination through phenolate O, azomethine N and thioenolate S with one oxo of $[Mo^{VI}O_2L]$ replaced by S. The molecular structures of $[Mo^{VI}O_2L]$ complexes from X-ray diffraction have been helpful in proposing structures of the $[Mo^{VI}OSL]$ complexes.

3.2. *Electronic spectra*

Electronic spectra of oxosulfidomolybdenum(VI) complexes were taken in pure dry degassed DMF immediately after the solution was prepared. The spectral data are presented in the experimental section. The lowest energy absorption maximum is observed in the 510–400 nm range and may be assigned to thiolato–S→Mo(dπ) LMCT transition due to promotion of an electron from the filled HOMO of the ligand of primarily sulphur-pπ character to the empty LUMO of molybdenum-dπ character [1a, 26]. Other LMCT bands are observed in the region 400–300 nm [37a, 47, 48]. Bands at 350 and 310 nm may be assigned to nitrogen to molybdenum and oxygen to molybdenum charge transfer transitions [47, 49]. Bands below 300 nm are due to intra-ligand transitions. An interesting feature of the spectra of **1** is the shift of S(pπ)→Mo(dπ) charge transfer by about 60 nm towards higher energy in going from the solid state (482 nm) to solution (423 nm), attributed to change in conformation in the Mo-site symmetry in going from solid to solution [37b, c, 50]. Solution spectra of $[Mo^{VI}OSL]$ complexes recorded more than 45 min after solution preparation exhibit

Table 2. Cyclic voltammetric peak potential data[a] (V *vs.* SCE).

Compound	Cathodic peak potential Ec_{I} (V)	Cathodic peak potential Ec_{II} (V)
1	–0.95 (–1.20)	–1.55
2	–0.80 (–1.025)	–1.38
3	–0.70 (–0.913)	–1.30
4	–0.85 (–1.113)	–1.50

[a]In DMF (dry, degassed); supporting electrolyte 0.1 M TEAP; solution strength 10^{-3} M; scan rate: 200 mV s^{-1}. Data of Ec_{I} in parenthesis denotes the values of the corresponding precursor [$MoO_2L(MeOH)$].

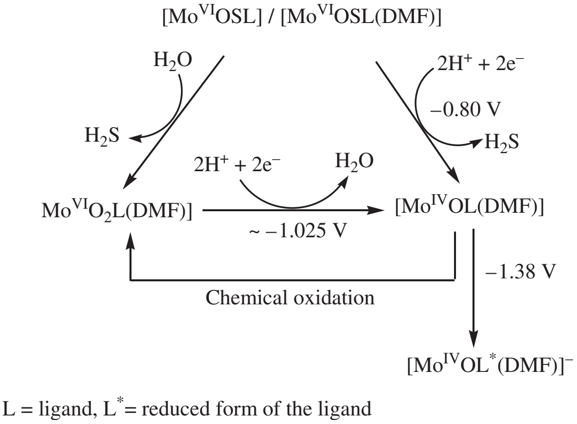
characteristics similar to those of the corresponding [$Mo^{VI}O_2L$] complexes [27], while the solid state spectrum of powdered **1** exhibits bands at ~540 nm with a shoulder at 659 nm, characteristic LMCT bands for Mo=S [45]. Recording spectra of **1**–**4** in presence of excess PPh_3S and at lower temperature (~0°C) significantly slowed solvolysis of [$Mo^{VI}OS$]$^{2+}$ to [$Mo^{VI}O_2$]$^{2+}$.

3.3. *Electrochemistry*

Cyclic voltammetry at a platinum electrode has been used to study the redox behavior of [$Mo^{VI}OSL$]. All experiments were performed within 10 min of preparation of a ~10^{-3} M solution in dry degassed DMF containing 0.1 M TEAP as supporting electrolyte. A SCE was used as reference electrode and 0.0 V to −1.9 V was the potential window examined. The results, uncorrected for junction potential, are presented in table 2.

All the complexes exhibit two successive reductive responses in the given potential range. Comparing with the I/E profile of the free ligand, the second cathodic response in the −1.30 to −1.55 V range is assigned to the ligand [27, 37a, 47c]. The first, irreversible, is a metal centered $2e^-$ process [27, 37a] as shown from comparison with authentic $1e^-$ systems [37a, 51]. A more striking observation was that, compared to the initial scan value, the first metal centered reduction peak due to Mo^{VI} to Mo^{IV} reduction shifted more negative on taking the reading after 75 min; the final reduction peak potential after 45 min of solution preparation was very similar to those of the corresponding [$Mo^{VI}O_2L$] complexes [27], confirming that [$Mo^{VI}OSL$] undergoes solvolysis with formation of [$Mo^{VI}O_2L(DMF)$] in solution. Similar observations have been previously reported by other workers [30, 51, 52]. Reduction of these oxosulfidomolybdenum(VI) and solvolytically generated dioxomolybdenum(VI) complexes in an aprotic solvent is irreversible [28, 51, 53–55]. Thus, the electrogenerated reduction product probably undergoes a subsequent chemical change [47b]. As our complexes undergo one step $2e^-$ reduction, proton assisted loss of the sulfido group to form [$Mo^{IV}O$]$^{2+}$ core is probable. This [$Mo^{IV}O$]$^{2+}$ center can undergo chemical oxidation to [$Mo^{VI}O_2$]$^{2+}$ [47b] in presence of trace water present in DMF. A representative example of the whole process is represented in scheme 4.

In the first scan, when [$Mo^{VI}OSL$] or [$Mo^{VI}OSL(DMF)$] is active at the electrode, reduction of Mo^{VI} is easier due to availability of a low energy vacant orbital on Mo=S. Reduction of [$Mo^{VI}OSL$] occurs from −0.95 to −0.70 V, while reduction of [$Mo^{VI}O_2L$] [27] occurs at ~−1.025 V. This is supported by the low energy LMCT band in the visible



Scheme 4. Electrochemical and chemical transformations of $[Mo^{VI}OSL]/[Mo^{VI}OSL(DMF)]$.

range of spectra of **1**. In general, substitution of O by S in the coordination sphere of Mo induces a more facile reduction at the metal center [37a, 56]. Since the reduction potential depends on the energy of the lowest unoccupied molecular orbital [57], it appears that energy of the pπ–pπ antibonding orbital of Mo=S is less than that of the corresponding Mo=O. Effect of substitution on the phenyl ring and/or on azomethine C of the ligand frame is negligible, identical to that of the corresponding $[Mo^{VI}O_2L]$ complexes [27]. Synthesis and reactivity of the $[Mo^{VI}OSL]$ complexes are presented in scheme 3.

4. Conclusion

The $[Mo^{VI}OS]^{2+}$ core present in the active site of xanthine oxidase is quite unstable in five/six coordinated Mo(VI) complexes and is generally considered an "elusive" synthetic target. In this work, four $[Mo^{VI}OSL]$ complexes of four tridentate $^{-}ONS^{-}$ chelating ligands are isolated in the solid state. All are characterized by elemental analysis, various spectroscopic techniques and by cyclic voltammetry. Single crystals could not be isolated presumably because of the propensity to undergo solvolysis in solution. The $[Mo^{VI}OSL]$ complexes are formed and isolated in the solid state by reacting the corresponding $[Mo^{VI}O_2L]$ complexes first with PPh_3 and then with excess PPh_3S, a combination of oxo-abstraction and sulfido-inclusion. To our knowledge, this is the first example of using PPh_3–PPh_3S combination for generating the $[Mo^{VI}OS]^{2+}$ core from $[Mo^{VI}O_2]^{2+}$. This reaction may be pertinent to reactivation of the inactive desulfo xanthine oxidase and may also be considered as a general procedure for converting $[Mo^{VI}O_2L]$ complexes to their $[Mo^{VI}OSL]$ analogues. Cyanolysis of all the complexes with KCN leading to the formation of CNS^{-} establishes the presence of Mo=S. This is also corroborated by existence of an IR band in the 480–490 cm^{-1} range originating from ν(Mo=S). Simultaneous presence of ν(Mo=O) at 960–970 cm^{-1} points to the general formula $[Mo^{VI}OSL]$ for all the complexes. Thus, even in the absence of crystallographic data, the presence of the $[Mo^{VI}OS]^{2+}$ core is confirmed.

The observation that solvolysis of [Mo^{VI}OSL] to [Mo^{VI}O$_2$L] is considerably retarded in presence of large excess of PPh$_3$S and at low temperature makes us hopeful of making further attempts to get single crystals of one or more of our [Mo^{VI}OSL] complexes.

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