REDUCTIVE NITROSYLATION OF TETRAOXOMETALLATES: SYNTHESIS, STRUCTURE AND REACTIVITY OF SOME TRANSITION METAL NITROSYL DERIVATIVES*

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The tetraoxometallates, $\text{MO}_n^{n-}$ ($M = \text{Cr, Mo when } n = 2; M = \text{Mn, Re, when } n = 1; M = \text{V when } n = 4$ and $M = \text{Os when } n = 0$) react with $\text{NH}_3\text{OH}$ in the presence of $\text{CN}^-$, $\text{NCS}^-$, $\text{N}_3^-$ or $\text{C}_2\text{O}_4^{2-}$ in alkaline, neutral or in slightly acidic medium affording a variety of mono- and dinitrosyl derivatives of the metal ions mentioned in their $+2$, $+1$, or $0$-oxidation states. The course of the reductive nitrosylation of $\text{MoO}_3^{3-}$ affording mono- or different dinitrosyl molybdenum moieties, using $\text{NH}_3\text{OH}.\text{HCl}$ and $\text{NCS}^-$ is extremely pH sensitive. While the reductive mono-nitrosylation affording products such as $[\text{Mo(NO)}(\text{NH}_3\text{O})_2(\text{NCS})_2(\text{L} - \text{L})]_2$, $(\text{L} - \text{L} = \text{2, bipyridine, (bpy)}$ or 1, 10-phenanthroline (phen) gives a mixture of isomeric species, of which the trans is predominant, the reductive dinitrosylation leading to $[\text{Mo(NO)}_3(\text{NHO})_2(\text{NCS})_2(\text{L} - \text{L})]$ or $[\text{Mo(NO)}_3(\text{NCS})_2(\text{L} - \text{L})]$ is rather stereoselective, trans- and cis-NCS geometries respectively being favored.

$\text{KReO}_4$ undergoes reductive nitrosylation in the presence of $\text{NH}_3\text{OH}.\text{HCl}$ and $\text{NCS}^-$ generating $[\text{Re(NO)}_2]^{3+}$ moiety, in an aqueous alkaline medium. The product molecule $[\text{Re(NO)}(\text{NCS})_3(\text{H}_2\text{O})]^{2-}$ and $[\text{Re(NO)}(\text{NCS})_2(\text{L} - \text{L})(\text{H}_2\text{O})]$, show interesting structural isomerism. The reaction mixture containing $[\text{Re(NO)}_3]^{2+}$ moiety if acidified and treated with $\text{NO}_2^-$ gives $[\text{Re(NO)}_3(\text{NCS})_2]^{3+}$ or $[\text{Re(NO)}_3(\text{NCS})_2(\text{L} - \text{L})]$, both of which, obviously, contain $[\text{Re(NO)}_3]^{2+}$ moiety.

The complexes, $[\text{Mo(NO)}(\text{NH}_3\text{O})(\text{NCS})_2]^{2-}$ or the corresponding $\text{L} - \text{L}$ derivatives are highly reactive, and it will be shown that the reactivity stems from the activated $\text{NH}_2\text{O}$ group.

**Key Words:** Reductive Nitrosylation; Tetraoxometallates; Metal Nitrosyl Derivatives; Hydroxylamine as a Reducing-cum-Nitrosylating Agent

**INTRODUCTION**

The reduction and subsequent nitrosylation (hence reductive nitrosylation) of a tetraoxometallate using $\text{NH}_3\text{OH}$ and $\text{CN}^-$ was discovered by Hieber et al. who reformulated the purple crystalline solid as $K_4[\text{Mo(NO)}(\text{CN})_3]$, originally obtained by Von Der Heide and Hofmann, but erroneously formulated as $\text{MoO}_2.4\text{KCN}$. $\text{NH}_3\text{OH}$ $\text{H}_2\text{O}$. After one decade, work in this area was pursued and complexes

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of the types [Cr(NO) (CN)₅]³⁻ and [V(NO) (CN)₅]³⁻ could be obtained³⁻⁵ from CrO₄²⁻ and VO₄³⁻ respectively. However, several other pentacyanoniitrosyl metallates of general formula [M(CN)₅ NO]⁻ (n = 2, 3 for M = Fe⁶⁺,⁷ and Mn⁸⁺⁹; n = 3 for M = Co¹⁰ and n = 2 for M = Ru¹¹) were prepared from the respective low valent cyanometallate substrates using NH₂OH,⁸⁻¹⁰ NO₃⁻⁷ or gaseous NO⁷ as the source of NO group. Since, in all the above nitrosylation reaction a highly alkaline medium was necessary, the probable mechanism suggested by Hieber et al.¹ was considered to be prevalent until it was shown¹² that reductive nitrosylation of tetraoxometallates can take place even in neutral or in slightly acidic medium. However, all the synthetic work mentioned above succeeded only in a partial conversion of the tetraoxometallate anions mentioned, to the respective lower-valent metal nitrosyl derivatives, since in each case rather an insufficient amount i.e. only 3–4 moles of NH₂OH.HCl per mole of the tetraoxometallate substrate was used. The present author has recently reported¹³ that an excess of NH₂OH.HCl is necessary for the nitrosylation reaction to occur smoothly and for the near quantitative conversion of the substrates to the metal nitrosyl products. We have shown that the tetraoxometallates, MO₄ⁿ⁻ (M = Cr, Mo when n = 2; M = Re, Mn when n = 1; M = V when n = 4 and M = Os when n = 0) react with excess of NH₂OH.HCl in the presence of an ample quantities of CN⁻¹⁴, NCS⁻¹³⁻¹⁵ N₃⁻¹⁶ or C₂O₄²⁻¹²⁷ in alkaline, neutral or in slightly acidic medium affording a varieties of mono- and di-nitrosyl complexes of the transition metal ions mentioned.

In this present report, attention is focussed on our work in the area of the reductive nitrosylation of MoO₄²⁻ and ReO₄⁻ in the presence of NCS⁻ or CN⁻, using NH₂OH as the source of NO group, and the synthesis, structural evidences and reactivity of mono- and dinitrosyl-thiocyanato or cyano complexes of formally Mo(II), Mo(I), Mo(O), Re(I) and Re(O).

Though, much of the account to be displayed here stems from our published results, an attempt will also be made to mention some interesting and unpublished observations.

**REDUCTIVE NITROSYLATION OF MOO₄²⁻ NH₂OH. HCl IN THE PRESENCE OF NCS⁻**

The intrinsic pH dependence of the reaction as entailed above is evident from Table I, where a general survey of our work with respect to the reaction condition on reductive nitrosylation reaction of different tetraoxometallates using NH₂OH. HCl in the presence of CN⁻, NCS⁻, N₃⁻ or C₂O₄²⁻ has been made.

**The Overall Reaction Pattern**

In the presence of an excess of NH₂OH.HCl and NCS⁻ the conversion of MoO₄²⁻ into the {Mo(NO)₃}⁺ moiety is complete within 5min, the pH being fixed in the range 4–4.5 (Scheme I). Even if the reactants are subjected to prolonged boiling (2–4h) the dinitrosylation is negligible and so this pH range is specific for the conversion of MoO₄²⁻ into {Mo(NO)₃}⁺. However, if the pH is adjusted to
<table>
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<tr>
<th>Substrate (a) and excess of reagent (b)</th>
<th>Reaction conditions in aqueous medium</th>
<th>Product moieties and compositions of the isolated complex</th>
<th>References</th>
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<tbody>
<tr>
<td>(a) CrO$_4^{2-}$ (b) NH$_2$OH</td>
<td>Neutral or slightly acid medium in the presence of NCS</td>
<td>{Cr(NO)$_3$}^{3+}; [Cr(NO)(NCS)$_2$]$^{3-}$</td>
<td>13</td>
</tr>
<tr>
<td>(a) CrO$_4^{2-}$ (b) NH$_3$OH</td>
<td>Strongly alkaline (first two products) or in slightly acidic medium, using KCN</td>
<td>[Cr(NO) (CN)$_2$]$_2^{-}$, [Cr(NO) (CN)$_2$ (L-L)] [Cr(NO) (NCS)$_2$ (L-L)]</td>
<td>14f</td>
</tr>
<tr>
<td>(a) MoO$_4^{2-}$ (b) NH$_2$OH</td>
<td>(1) pH 4-4.5 (5min)</td>
<td>(1) {Mo(NO)$_3$}^{3+}; [Mo(NO) (NH$_2$O) (NCS)$_2$]$_2^{-}$ [Mo(NO) (NH$_2$O) (NCS)$_2$ (L-L)] (isomeric)</td>
<td>14a</td>
</tr>
<tr>
<td></td>
<td>(2) pH 5.2-5.4 (4h)</td>
<td>(2) {Mo(NO)$_3$}^{4+}; [Mo(NO)$_3$ (NHO) (NCS)$_2$]$_2^{-}$ [Mo(NO)$_3$ (NHO) (NCS)$_2$ (L-L)]</td>
<td>15a</td>
</tr>
<tr>
<td></td>
<td>(3) pH 5.7-6 (1.5-2h) (See Scheme I)</td>
<td>(3) {Mo(NO)$_3$}^{3+}; [Mo(NO)$_3$ (NCS)$_2$]$_2^{-}$ [Mo(NO)$_3$ (NCS)$_2$ (L-L)]</td>
<td>15a</td>
</tr>
<tr>
<td>(a) MoO$_4^{2-}$ (b) NH$_2$OH</td>
<td>(1) NaOH solution and KCN; nitrosylation at pH 11 isolation at pH 8</td>
<td>(1) {Mo(NO)$_3$}^{3+}; [Mo(NO) (CN)$_2$]$_2^{-}$ [Mo(NO) (CN)$_2$ (L-L)]</td>
<td>14e</td>
</tr>
<tr>
<td></td>
<td>(2) KCN solution, initial pH 7.5, during isolation, pH 5.5</td>
<td>(2) {Mo(NO)$_3$}^{4+}; [Mo(NO)$_3$ (CN)$_2$]$_2^{-}$ [Mo(NO)$_3$ (CN)$_2$ (phen)$_2^{-}$]</td>
<td>14b</td>
</tr>
<tr>
<td>(a) ReO$_4^{-}$ (b) NH$_2$OH</td>
<td>(1) Preheating in acidic NCS$^-$ medium  See for instance, Scheme II</td>
<td>(1) {Re(NO)$_3$}$^{2+}$; [$\alpha$-[Re(NO) (NCS)$_2$ H$_2$O]$^{-}$. $\alpha$- and $b$-[Re(NO) (NCS)$_2$ (L-L)] and the corresponding azido products when $N_3$ is used</td>
<td>15b</td>
</tr>
<tr>
<td></td>
<td>(2) Alkaline solution of NCS$^-$ from the beginning. See also Scheme II</td>
<td>(2) Some moiety; $b$-[Re(NO) (NCS)$_2$ (H$_2$O)]$^{-}$ $c$-[Re(NO) (NCS)$_2$ (L-L)]</td>
<td>16a</td>
</tr>
<tr>
<td>(a) ReO$_4^{-}$ (b) NH$_3$OH</td>
<td>heated in alkaline medium with NCS$^-$ and then acidified with HCl and treated with NaNO$_3$</td>
<td>{Re(NO)$_3$}$_2^{3+}$; [Re(NO)$_2$ (NCS)$_2$]$^{-}$</td>
<td>15c</td>
</tr>
<tr>
<td>(a) ReO$_4^{-}$ (b) NH$_2$OH</td>
<td>alkaline KCN solution</td>
<td>{Re(NO) (CN)$_2$}$_2^{-}$</td>
<td>14c</td>
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<th>1</th>
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<th>4</th>
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</table>
| (a) VO$_4^{3-}$ (b) NH$_3$OH | alkaline KCN solution | \[
\text{\{V(NO)$_6$\}$_3^{3+}$; [V(NO)$_3$ (CN)$_6$]$_3^{3-}$}
\]
| | | \[
\text{[V(NO)$_3$ (CN)$_6$ (L-L)]}
\] | 14d |
| (a) OsO$_4$ (b) NH$_3$OH | neutral and then slightly acidic | \[
\text{\{Os(NO)$_3$\}$_3^{3+}$; [Os(NO)$_3$X$_3$]$_3^{3-}$}
\]
| | | \[
\text{[Os(NO) X$_3$ (L-L)] (X = NCS$^-$, N$_3^-$)}
\] | 15d |
| (a) MnO$_4^{-}$ (b) NH$_3$OH | alkaline condition containing CN$^-$ | \[
\text{\{Mn(NO)$_3$\}$_3^{3+}$; [Mn(NO)$_3$]$_3^{3+}$; (Mn(NO)$_3$)$_3^{3+}$;}
\]
| | | \[
\text{[Mn(NO)$_2$ (CN)$_4$]$_3^{3-}$, [Mn(NO) (CN)$_6$]$_3^{3-}$}
\] | To be published |
| (a) ReO$_4^{-}$ (b) NH$_3$OH | alkaline solution | \[
\text{\{Re(NO)$_3$\}$_3^{3+}$; [Re(NO) (OH)$_3$]$_3^{3-}$}
\]
| | | \[
\text{[Re(NO) (OH)$_3$ (L-L)] (isomeric)}
\] and KMn[Mn(NO) (CN)$_6$]$_3$ and many other products via their nucleophilic reactivity | To be published |
| (a) OsO$_4$ (b) NH$_3$OH | slightly acidic solution containing C$_2$O$_4^{2-}$ | \[
\text{\{Os(NO)$_3$\}$_3^{3+}$; [Os(NO) (OH)$_3$]$_3^{3-}$ and many other products}
\]
| | | \[
\text{via its nucleophilic reactivity}
\] | To be published |
Scheme I  
(i) Boil for 5 min; (ii) L-L solution; (iii) extract with CH₂CN; (iv) evaporate and extract solid with CH₂Cl₂; (v) evaporate; (vi) dissolve in CH₂NO₂, add Et₂O; (vii) S₂CNEt₂ solution; (viii) PPh₃Cl solution; (ix) adjust pH to 5.2, boil for 4 h, readjust pH to 5.2; (x) L-L solution, pH ca. 5.2; (xi) PPh₃Cl solution, pH 5.2; (xii) adjust pH to 5.7-6, boil for 2 h, readjust pH to 5.7-6; (xiii) L-L solution, pH 5.7-6; (xiv) stir with CH₂CN (xv) PPh₃Cl solution, pH 5.7-6; (xvi) evaporate, dissolve solid in acetone, add Et₂O.
5.2-5.4, the same reactants on prolonged boiling (4h) afford in ca 85 per cent yield the complexes (5)-(7) (cf. Table II) containing the \((\text{Mo(NO)}_2)_4^{14+}\) moiety. So, this pH range is specific for the conversion of \(\text{MoO}_2^{2-}\) into \(\{\text{Mo(NO)}\}_4^{14+}\). A very interesting reaction occurs when the reactants are boiled in an aqueous-aerobic medium in the range pH 5.7-6 (Scheme I). After an hour the colour of the solution changes from yellow to brown and within 2min suddenly becomes bluish green; at this stage the presence of a \(\text{Mo}_2\text{O}_5^{2+}\) species is detected. The formation of bluish green colour is complete (spectrophotometric probing) after boiling for another 1h and the \(\{\text{Mo(NO)}_2\}_2^{2+}\) and \(\text{Mo}_2\text{O}_5^{2+}\) species could be obtained in relative yield of 1:1 (i.e. 1:2, w.r.t. Mo). The \(\{\text{Mo(NO)}_2\}_2^{2+}\) species was always contaminated with the oxo-species. This fact, along with the relative yield of the dinitrosyl and oxo-products, indicates that in this pH range the \(\{\text{Mo(NO)}\}_3^{3+}\) species (formally, containing Mo(III) and NO\(^{20,21}\)) which is the initial product of nitrosylation in all the above pH ranges (confirmed by isolating the corresponding bpy complexes in each case after 5-10min) disproportionate presumably according to the equation (1). That \(\{\text{Mo(NO)(NH}_2\text{O)}\}_2^{2+}\) takes part in the disproportionation was proved by trapping and characterising the products at regular intervals using bpy, including that present a few seconds before the appearance of the blue-green colour.

Also, the mode of the disproportionation reaction was verified experimentally by repeating a relevant i.e., boiling an aqueous solution (pH = 6) of (NMe\(_4\))\(_2\) [\(\text{Mo(NO)(NH}_2\text{O)}\text{(NCS)}_4\)] in a vacuum line and analysing quantitatively (the gases generated were accumulated in evacuated vessels and the vapour pressure measured) the evolved N\(_2\)O (obtained as N\(_2\) + \(\frac{1}{2}\) O\(_2\) due to electron impact) and NH\(_3\) (after boiling the NH\(_4\) salt with KOH) mass spectrometrically.

Complexes containing \(\{\text{Mo(NO)}\}_3^{3+}\) Moiety

The product (PP\(_4\))\(_2\) [\(\text{Mo(NO)(NH}_2\text{O)}\text{(NCS)}_4\)] obtained in quantitative yield by us\(^{15a}\) was structurally characterised by Muller et al.\(^{22}\) as a seven coordinate pentagonal-bipyramidal species, the N, O-bonded hydroxylamido-ligand occupying two equatorial positions. The other complexes of this series may also possess a similar structure, stabilised by 18-electron configuration.

If the N, O-bonded NH\(_2\)O\(^-\) ligand is always cis to the axial\(^{22,23}\) nitrosyl group, three isomeric forms may be predicted for the compounds (1) and (2) as shown in structures (I)-(III). All three isomeric species have been isolated by us by taking advantage of their different solubilities in organic solvents. Their analytical, molecular weight and NMR data (Table II) are practically identical, but the species differ in the important IR band positions and in their electronic absorption spectra. The orange isomer of both the bpy and phen compounds possesses only one \(v_{\text{CN}}\) band at a good resolution (± 2 cm\(^{-1}\)) with a symmetrical contour, indicating that the NCS groups are trans to each other [structure (I)]. On the other hand yellow and rose (yellow in the case of phen) isomers both have split \(v_{\text{CN}}\) bands and so-
<table>
<thead>
<tr>
<th>Complex</th>
<th>Selected IR data (cm(^{-1}))</th>
<th>( v_{(\text{CN})} )</th>
<th>( v_{(\text{NO})} )</th>
<th>( ^1H \text{ NMR data}^b ) in ppm</th>
<th>( \nu_{\text{max}} (kK)^c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1a) [Mo(NO) (NH(_4)) (NCS)(_2) (bpy)]</td>
<td>2080s</td>
<td>1655s</td>
<td></td>
<td>3.2(^b), 4.2(^c)</td>
<td>26.6 (420), 31.1 (4000)</td>
</tr>
<tr>
<td>(1b) [Mo(NO) (NH(_4)) (NCS)(_2) (bpy)]</td>
<td>2070s</td>
<td>1657s</td>
<td></td>
<td>3.6(^d) (2H)</td>
<td>32.5 (2650), 34.2 (1800)</td>
</tr>
<tr>
<td>(1c) [Mo(NO) (NH(_4)) (NCS)(_2) (bpy)]</td>
<td>2100(sh)</td>
<td>1647s</td>
<td></td>
<td>2.8(^d) (2H)</td>
<td>26.6 (440), 31.7 (3000)</td>
</tr>
<tr>
<td>(2a) [Mo(NO) (NH(_4)) (NCS)(_2) (phen)]</td>
<td>2080s</td>
<td>1657s</td>
<td></td>
<td>3.2(^b), 4.2(^c)</td>
<td>33.8 (4150)</td>
</tr>
<tr>
<td>(2b) [Mo(NO) (NH(_4)) (NCS)(_2) (phen)]</td>
<td>2070s</td>
<td>1625m</td>
<td></td>
<td>(2H)</td>
<td>24.5 (50), 27.1 (450)</td>
</tr>
<tr>
<td>(2c) [Mo(NO) (MH(_2)) (NCS)(_2) (phen)]</td>
<td>2080s</td>
<td>1645s</td>
<td></td>
<td>2.9(^b) (2H)</td>
<td>26.5 (500), 30.9 (4250)</td>
</tr>
<tr>
<td>(3) [Mo(NO) (NH(_4)) (S(_2)CNEt(_2))(_2)]</td>
<td>2072s</td>
<td>1650s</td>
<td></td>
<td>3.9(^c) (2H)</td>
<td>32.5 (2850), 34.7 (2000)</td>
</tr>
<tr>
<td>(4) [PPh(_3)](_2) [Mo(NO) (NH(_4)) (NCS)(_2)]</td>
<td>2072s</td>
<td>1658s</td>
<td></td>
<td>2.5(^c) (2H)</td>
<td>26.5 (500), 31.6 (3250)</td>
</tr>
<tr>
<td>(5) [Mo(NO)(_2) (NHO) (NCS)(_2) (bpy)]</td>
<td>2080s</td>
<td>1780m</td>
<td></td>
<td>[5.0(^b) (1H)]</td>
<td>32.9 (4050)</td>
</tr>
<tr>
<td>(6) [Mo(NO)(_2) (NHO) (NCS)(_2) (phen)]</td>
<td>2080s</td>
<td>1780m</td>
<td></td>
<td>[5.48]</td>
<td>24.5 (40), 26.6 (500)</td>
</tr>
<tr>
<td>(7) [PPh(_3)](_2) [Mo(NO)(_2) (NHO) NCS](_2)]</td>
<td>2110(sh)</td>
<td>1777m</td>
<td></td>
<td>[5.2(^b) (1H)]</td>
<td>21.3 (30) (e \rightarrow b(_1))</td>
</tr>
<tr>
<td>(8) [Mo(NO)(_2) (NCS)(_2) (bpy)]</td>
<td>2087(sh)</td>
<td>1785s</td>
<td></td>
<td>13.9 (32), 16.7 (10)</td>
<td>13.9 (32), 16.7 (10)</td>
</tr>
<tr>
<td>(9) [Mo(NO)(_2) (NCS)(_2) (phen)]</td>
<td>2070s</td>
<td>1672s</td>
<td></td>
<td>21.5 (75)</td>
<td>21.5 (75)</td>
</tr>
<tr>
<td>(10) [PPh(_3)](_2) [Mo(NO)(_2) (NCS)(_2)]</td>
<td>2105(sh)</td>
<td>1780s</td>
<td></td>
<td>16.5 (16)</td>
<td>13.5 (25), 16.5 (16)</td>
</tr>
<tr>
<td></td>
<td>2072s</td>
<td>1658s</td>
<td></td>
<td>21.8 (70)</td>
<td></td>
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</table>

\(^a\)Values are for \( \delta(\text{NH}_4) \) except for those in square brackets [\( \delta(\text{NHO}) \)]. \(^b\)In (CD\(_3\))\(_2\) CO (cold). \(^c\)In CD\(_3\)CN. \(^d\)In (CD\(_3\))\(_2\)SO. \(^e\)Values of \( \nu_{\text{max}} \) (lit mole\(^{-1}\) cm\(^{-1}\)) are given in parentheses. \(^f\)Probable assignments.
they possess structure (II) or (III) in which the NCS groups are cis but the nature of the ligand trans to the nitrosyl group differs. However, bpy and phen being stronger ligands than NCS⁻, when trans to NO will cause a reduction of the N–O stretching frequency of the coordinated nitrosyl group. So, from Table II it is apparent that the yellow isomer possesses structure II and the rose (yellow for phen), structure III. It may be noted that the dithiocarbamato complex of only this series could be prepared. The dinitrosyl molybdenum moieties do not afford any isolable product with dithiocarbamate, under the described conditions.

Assuming that complex (4) MoN₆O chromophore) may be described by a similar MO picture to that applicable²⁰ to C₄₈ cases, the two observed electronic absorption bands of the anion [Mo(NO) (NH₂O) (NCS)₄]²⁻ could be assigned as in Table II. The four closely spaced absorption bands exhibited by (1a), (1b), (2a), and (2b) (Table II) are due possibly to the apparent lower symmetry of these molecules compared to (4).

Complexes containing \{Mo(NO)₂\}⁴⁺ Moiety

Before our report¹⁵ no complex containing the above moiety was known. We have shown that the isolated complexes containing the above species were always found to be associated with a coordinated NHO²⁻ group and can be generated only when the reactions are conducted within a very narrow pH range. The analytical and physicochemical data indicate that the compounds contain essentially a \{Mo(NO)₂\}⁴⁺ core; since a coordination no of 7 would conform to the 18-electron rule it may be presumed that the NHO²⁻ ligand is possibly unidentate coordinating as the hydroxylimido = N(OH)²⁻ form. The ¹H NMR signal for the NH₂O⁻ protons in compounds (1)–(4) disappears (the lability of these protons is evidenced by their sensitivity to different solvents) and a new signal appears at 6–5.4 ppm (1H). The slight change in the bpy resonances in going from complex (1a) to (5) may be due to the different coordination environments.²⁴ However an N, O–bonded hydroxylamido (2⁻) ligand²⁵ was assumed by previous workers to be present in the complex [Mo(NO) (NHO) (terpy) (CN)] (terpy = 2, 2' : 6', 2''-terpyridine), where a bidentate coordination of the NHO²⁻ group conforms to the 18-electron rule.
Of the two $v_{\text{NO}}$ bands observed here (Table II), one is markedly weaker than the other, possibly due to the reduction in N-O bond polarity via H-bonding interaction with the adjacent $=\text{N(OH)}$ group (structure IV).

The isolated L-$L$ complexes are fully soluble in acetonitrile and nitromethane and appear to represent a single substance; the crystallised products from these solvents exhibit only a single and symmetrical $v_{\text{CN}}$ band at good resolution. The acetonitrile solution of these crystals also show a single spot on a TLC plate. All these indicate that the substance represent a unique compound which contains trans thiocyanato groups. So, it may be argued that the generation of $\{\text{Mo(NO)}_2(\text{NHO})\}$ via the reductive nitrosylation of $\text{MoO}_4^{2-}$ by $\text{NH}_2\text{OH}$ and $\text{NCS}^-$ in the range $p\text{H}$ 5.2–5.4 is stereoselective.

In the cases of the $L$–$L$ derivatives i.e. compounds (5) and (6) three electronic absorption bands are observed (Table II) as predicted for a $C_3$ configuration. The appearance of only two bands for complex (7) may be due to its somewhat higher symmetry.

*Complexes Containing $[\text{Mo(NO)}_2]^2+$ Moiety*

To date, dinitrosymolybdenum (O) complexes have been generated by three general routes; (1) Oxidation by NO$^+$ (as NOCl, etc.) or substitution by NO of molybdenum carbonyl derivatives$^{25a,26}$ (2) reduction of MOCl$_3$ by NO$^{27}$; in both routes (1) and (2) the reactions were carried out in dry oxygen free atmospheres; and (3) reductive dinitrosylation of $\text{MoO}_4^{2-}$ with $\text{NH}_2\text{OH}$ in dimethylformamide or pyridine acetic acid where only a limited yield was obtained and the course of the reaction not being properly understood.$^{28}$

In the present work, the above species is generated via a disproportionation reaction as described earlier. These dinitrosyl compounds, $[\text{Mo(NO)}_2(\text{NCS})_2]^2-$ or $[\text{Mo(NO)}_2(\text{NCS})_2(\text{L}–\text{L})]$, are 6-coordinate and thereby conform to the 18-electron rule. The two strong $v_{\text{NO}}$ bands found for each complex is as expected for a cis-dinitrosyl structure. These compounds do not exhibit any $v_{\text{NH}}$ bands. The oxo-species shows two prominent absorptions, at 900 and 930cm$^{-1}$, due to $v_{\text{Mo=O}}$ vibrations, characteristic of a cis $\text{Mo}_2\text{O}_4^{2+}$ group.$^{29}$ The $v_{\text{MoO}_2\text{Mo}}$ bands are found between 700 and 800cm$^{-1}$.$^{30a,30b}$

If the two nitrosyl groups are placed cis to each other, the above species may be represented by the three isomeric forms (V)–(VII). The isolated complexes are soluble in acetone, acetonitrile, nitromethane and moderately so in dichloromethane, and the crystallised products from these solvents show identical IR spectra. The $v_{\text{CN}}$ band of all complexes is split and so it may be presumed that the structure is either (VI) or (VII), i.e., the molecules possess cis-NCS groups and the reaction is rather stereoselective. This stereoselectivity obtained via the reductive dinitrosylation of $\text{MoO}_4^{2-}$ in an aqueous aerobic medium is opposite to that obtained by Cotton and Johnson$^{25ab}$ in the case of $[\text{Mo(NO)}_2(\text{L})_2X_2]$ ($\text{L} = \text{PPh}_3$, $X = \text{Cl}^-$) achieved via oxidative nitrosylation ($[\text{Mo(CO)}_6] + \text{NOCl}$) but parallels that claimed by Sarkar et al.$^{28}$ for $[\text{Mo(NO)}_2(\text{py})_2\text{Cl}_2]$ (py = pyridine) obtained by reductive nitrosylation of $\text{MoO}_4^{2-}$ in pyridine-acetic acid.
In the \( \{\text{Mo(NO)}_2\}^6 \) species the nitrosyl groups in \textit{cis} configuration should deviate very slightly from linearity because of the nature of the \( a_1 \) and \( b_2 \) orbitals.\textsuperscript{20} However, their electronic configuration in a \( C_{2v} \) field may be\textsuperscript{20} \((a_2)^2 (a_1)^2 (b_2)^2\). Consequently, three electronic absorption bands are observed for complex (10), the assignments of which are shown in Table II, the first absorption is unusually intense. Complexes (8) and (9) possess a still lower symmetry and hence show a greater number of absorption bands.

That the NCS ligands in all the above cases are N-bonded\textsuperscript{32a} is apparent from their IR data (Table II). Obviously, the mononitrosyl compounds contain a single \( v_{\text{NO}} \) vibration while the dinitrosyls of both the series contain two such bands. The \( v_{\text{MO-S}} \) band in the dtc complex is found at 370cm\(^{-1}\).\textsuperscript{32b} All the compounds show a feeble temperature-independent paramagnetism (T.I.P.) which has been confirmed in complexes (1a), (5) and (10) by measurement of the susceptibility at liquid nitrogen temperature, where the room temperature values (\( \chi_\alpha \approx 150 \) cgs units mole\(^{-1}\) are seen to be retained. The \( \{\text{Mo(NO)}\}^4 \) systems should naturally exhibit T. I. P.\textsuperscript{33} but in the \( \{\text{Mo(NO)}_2\}^6 \) cases possibly a second order spin-orbit interaction occurs due to the low symmetry of the molecules and reasonably high spin-orbit coupling constant of molybdenum.\textsuperscript{34}

**Reductive Nitrosylation of MoO\(^{2-}\) by NH\(_2\)OH.HCl in the Presence of CN\(^{-}\)**

Though \( K_4[\text{Mo(NO)}(\text{CN})_3] \) containing \( \{\text{Mo(NO)}\}^+ \) moiety has been known for many years,\textsuperscript{12a} the conversion of \( \text{MoO}_4^{2-} \) to \( \{\text{Mo(NO)}_2(\text{CN})_3\}^{2-} \) was unknown until our recent report.\textsuperscript{14b} Again, paramagnetic \( \{\text{Mo(NO)}(\text{CN})_3\}^{3-} \) has recently been characterised\textsuperscript{12a} whilst the corresponding diamion, \( [\text{Mo(NO)}(\text{CN})_3]^{2-} \), which contains \( \{\text{Mo(NO)}\}^{3+} \) moiety and represents, a missing link in the series of isostructural anions, \( [\text{Mo(NO)}(\text{CN})_3]^{n-} \) \( (n = 4-2) \), has been reported by us in the current year.\textsuperscript{14e} It is quite interesting to note that, in the presence of an excess of NH\(_2\)OH.HCl and CN\(^{-}\), it is the \( p\text{H} \) of the reaction medium which decides whether the reaction will be stopped at \( \{\text{Mo(NO)}\}^{3+} \) stage or can progress further furnishing \( \{\text{Mo(NO)}_2\}^{2+} \) moiety. While the facile conversion to the former proceeds at a relatively higher \( p\text{H} \) (8), the latter requires a slightly acedic medium (\( p\text{H} \) 5).

The lattice held water molecules in the mono-nitrosyl complexes can be removed at a lower temperature than the dinitrosyl complexes where the two water molecules are rather strongly held as evidenced from their TGA and DTA curves.
This fact indicates that in the dinitrosyl complexes the water molecules are possibly strongly hydrogen-bonded to the NO\(^+\) and CN\(^-\) ligands, as structurally characterised in the cases of some other cyanonitrosyl species\(^{5b,35}\).

The \(v_{\text{CN}}\) vibrations in the range 2100–2160cm\(^{-1}\) show two absorptions; the \(v_{\text{NO}}\) vibrations show, as usual, single bands (1650–1690cm\(^{-1}\)) in the mononitrosyl complexes and double bands (ca 1660 and ca 1790cm\(^{-1}\)) in the \(\text{cis}\)-dinitrosyl cases. The complexes are diamagnetic, as is expected for \{\text{Mo(NO)}\}\(^4\) and \{\text{Mo(NO)}\}\(^2\)\(^6\) systems. All the complexes grossly show only a single MLCT (\(d\rightarrow\pi^*\text{NO}\)) transition, the dinitrosyl species absorbing more intensely than their mononitrosyl analogues.

**Reductive Nitrosylation of ReO\(_4^-\) Using NH\(_2\)OH.HCl in the Presence of NCS**

While in the case of CrO\(_4^2^-\), MoO\(_4^2^-\) and OsO\(_4\) the reductive nitrosylation using NH\(_2\)OH and NCS\(^-\) occurs at a neutral or slightly acidic medium, a strong alkaline medium is necessary in the case of ReO\(_4^-\).

**Overall Reaction Pattern**

The analytical molecular weight and spectroscopic data (Table III) of the isolated Re complexes indicate that the 6-coordinate complexes are always obtained as an isomeric mixture if the reaction is routed through a preheating operation at a slightly acidic medium, before the reaction mixture is made alkaline, and the specific

**Table III**

*Some spectroscopic data of thiocyanato nitrosyl complexes of rhenium(I)*

<table>
<thead>
<tr>
<th>Compound</th>
<th>Selected IR Data (cm(^{-1}))</th>
<th>(v\text{CN})</th>
<th>(v\text{NO})</th>
<th>(v_{\text{max}}) (kK)(^{6b,d})</th>
</tr>
</thead>
<tbody>
<tr>
<td>((11a)) (Ph(_4)P) [Re(NO) (NCS)(_2)H(_2)O](^b)</td>
<td>2080(s)</td>
<td>1698(s)</td>
<td>17.7 (130)(^4); 24.4 (620); 28.7 (525)</td>
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<tr>
<td>((11b)) (Ph(_4)P) [Re(NO) (NCS)(_2)H(_2)O](^c)</td>
<td>2082(s)</td>
<td>1675(s)</td>
<td>15.8 (394); 23.2 (410); 25.0 (4,500)</td>
<td></td>
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<tr>
<td>((12a)) [Re(NO) (NCS)(_2) (bpy) H(_2)O](^b)</td>
<td>2080(s)</td>
<td>1695(s)</td>
<td>17.7 (530); 20.8 (235); 27.0 (440)</td>
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<tr>
<td>((12b)) [Re(NO) (NCS)(_2) (bpy) H(_2)O](^c)</td>
<td>2075(s)</td>
<td>1690(s)</td>
<td>20.8 (316); 24.4 (3,580); 28.4 (1,890)</td>
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<td>((12c)) [Re(NO) (NCS)(_2) (bpy) H(_2)O](^c)</td>
<td>2080(s)</td>
<td>1678(s)</td>
<td>16.0 (240); 25.0 (1,200); 28.4 (578)</td>
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<tr>
<td>((13a)) [Re(NO) (NCS)(_2) (phen) H(_2)O](^b)</td>
<td>2080(s)</td>
<td>1695(s)</td>
<td>17.7 (285); 21.3 (570); 24.4 (695)</td>
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<tr>
<td>((13b)) [Re(NO) (NCS)(_2) (phen) H(_2)O](^c)</td>
<td>2075(s)</td>
<td>1690(s)</td>
<td>20.6 (190); 24.2 (126); 27.1 (158)</td>
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<tr>
<td>((13c)) [Re(NO) (NCS)(_2) (phen) H(_2)O](^c)</td>
<td>2085(s)</td>
<td>1680(s)</td>
<td>15.9 (258); 21.5 (95); 24.4 (1,050)</td>
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</table>

\((a)\) For probable assignments see text, \((b)\) in acetonitrile, \((c)\) in DMF and \((d)\) figures in parentheses indicate molar absorptivity in litre mol\(^{-1}\) cm\(^{-1}\).
and kinetically stable stereoisomers (species having identical elemental analyses and molecular weight but differ in the νNO frequencies in IR, as well as in their electronic absorption spectra) could be separated by taking advantage of their solubility differences (Scheme II). It is also noted that maintenance of an alkaline condition right from the beginning affords exclusively the compound (12c) and (13c) as crude products and an attempt at crystallisation of these c-isomers lead to their conversion into the stable isomers. The former are insoluble in acetone and acetonitrile, and soluble only in DMF. Addition of ether to DMF solution precipitates a product which is a mixture of both a and b-isomers from which the former can be extracted by acetonitrile. The residue on being redissolved in DMF and precipitated with ether resembles b-isomers (12b) and (13b) respectively. However, the two isomeric forms of the 5-coordinate complexes hitherto isolated (11a) and (11b) are obtained uniquely by the two separate routes. Unlike the c-isomers of the 6-coordinate one, i.e., the product 11b (obtained by the same route as followed for the c-isomers) is found to be non-labile in the solution phase.

**Scheme II**

(i) NaOH added to the hot solution; (ii) stirred for 1.5h at 80 °C at pH-10; (iii) stirred at 80 °C for 1.5h and then pH increased to −10; (iv) Part I, PPh₃Cl (2-3mol); (v) Part II, bpy or phen (L-L), 2mol; (vi) extracted with acetone (vii) dissolved in DMF and precipitated with ether; (viii) concentrated and precipitated with pentane; (ix) pH reduced to 4.

**Five-Coordinate Complexes**

The analytical, conductance (1:1 electrolytes in CH₃CN)[31], thermoanalytical (H₂O is lost at 140°, the process being exothermic) and spectroscopic (IR and UV-vis).
data indicate that the anionic complexes \([\text{Re (NO) (NCS)}_3 (\text{H}_2\text{O})^{-}\) precipitated with \(\text{PPh}_3^+\) is 5-coordinate. Actually, \(\text{Ph}_4\text{A}^+ (A = \text{P, AS})\) has a special preference for 5-coordinate uninegative complex ions (compare also \(\text{Ph}_4\text{As}[\text{ReOCCl}_3]\) and \(\text{Ph}_4\text{P}[\text{Mo (NO) Cl}_4]\) as against \(\text{Cs}_2[\text{Re OCl}_3]\) and \(\text{Cs}_2 [\text{Mo(NO)Cl}_3]\)).

The appearance of \(\nu_{\text{CN}}\) as a sharp and symmetrical band in (11a) is indicative of the three NCS groups occurring at the equatorial plane and \(\text{H}_2\text{O}\) \textit{trans}-to the axial NO, thereby conforming to a TBP structure (VIII). In a TBP geometry the anions have two predicted isomeric structures (VIII) and (IX); a probable square pyramidal (SP) arrangement is the structure X. Since (11b) shows \(\nu_{\text{CN}}\) as a broad and unsymmetrical band, it should be represented by the structure IX or X. But the position of \(\nu_{\text{NO}}\) in (11b) at a lower frequency as compared to the respective \(\alpha\)-isomer indicate that the former compound should be represented by structure (IX), where NCS-ligand, situated \textit{trans} to NO can facilitate electron drainage from metal (d\(\pi\)) to NO(\(\pi^-\)) orbital, since the same (NCS\(^-\)) is a somewhat stronger ligand than \(\text{H}_2\text{O}\) and can transfer a little more electron density to the central rhenium atom. This proposition is also supported by the position of \(\nu_{\text{Re(NO)}}\) vibration,---the \(\beta\)-isomer is having a slightly stronger \(M-\text{N (NO)}\) bond than the \(\alpha\)-isomer.

\[
\text{NO} \\
\text{X} \\
\text{R\text{e} } \\
\text{X} \\
\text{H}_2\text{O} \\
\text{X} \\
\text{VIII} \\
\text{NO} \\
\text{X} \\
\text{R\text{e} } \\
\text{X} \\
\text{H}_2\text{O} \\
\text{X} \\
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Considering NO\(^+\) formalism,\(^{20\text{-}21}\) the formal oxidation state of rhenium should be +1 (5d\(^6\)). The magnetic susceptibility of all the complexes (\(\chi_A \approx +150 \times 10^{-6}\) cgs units mol\(^{-1}\)) at room temperature remains fairly constant down to 20 K. However, such temperature-independent paramagnetism of the isolated pentacoordinate anions is extremely difficult to explain on the basis of the perfect C\(_{3v}\) symmetry which requires (\(e_1\))\(^4\) (\(e_2\))\(^2\) MO configuration.\(^{20}\) Five coordinate systems are stereochemically non-rigid and, moreover, the electronic configuration of 5-coordinate 5d systems are very much dependent on the actual geometry of the molecule (on a rigorous basis) and the slightest distortion of the symmetry species from its ideal condition can cause a radical change of its magnetic behaviour.\(^{38}\) Consequently, no attempt is made to assign the electronic absorption bands for these complexes.

\textit{Six-Coordinate Complexes}

As shown in the Scheme II, if instead of precipitating the complex anion generated by the reductive nitrosylation of ReO\(_4\)^{-}, using a counter ion, neutral chelators
like bpy or phen are used, the 6-coordinate complexes [Re(NO) (X)2 (L-L) (H2O)] (X=NCS) are formed. That these are 6-coordinate species are proved by analytical molecular weight, conductance (non-electrolyte, thermoanalytical (the water molecule in each case is lost after heating at 130°C), IR and electronic spectral data (see Table III).

Four isomeric structures can be predicted (XI-XIV) for the [Re(NO) (X)2 (L-L) (H2O)] species, on the basis of octahedral geometry with axial NO. The c-isomers of this series possess a $\nu_{CN}$ vibrational mode which is of quite symmetrical contour and is unsplit at a good resolution, and, moreover, position of $\nu_{NO}$ mode in these cases appear in the lowest wave number region. Due to the very high trans-labilizing effect of the NO ligand, it is quite reasonable to assume that the L-L groups coordinated trans to the former do not exhibit $\pi$-acidity. On the other hand, these being stronger $\sigma$-donors also compared to H2O and NCS−, the c-isomers should be assigned structure XI on the basis of the same argument as put forth for the 5-coordinate species. No other species is hitherto isolated which contains $\nu_{NO}$ modes at such a low spectral region (15-20cm$^{-1}$ lower than the other isomers, see Table III) and so it may be presumed that any isomer possessing the structure XII is not isolable at all via the synthetic routes followed herein. Now, the isomers (a) and (b), viz., (12a), (12b), (13a) and (13b), all have broad and unsymmetrical $\nu_{CN}$ mode (implying the mutual cis-configuration of the NCS groups), but on the basis of the slight (but conspicuous) differences in $\nu_{SO}$ modes, the isomers of the (a)-series should be assigned structure XIII and that of the (b)-series the structure XIV. It may be pertinent to mention here that the similar trend in the shift of $\nu_{NO}$ modes depending on the nature of the ligand trans to NO was also observed by Feltham et al.39 in their Co-nitrosyl complexes of the type [Co(NO) (diars)$_2$X] X(X= Cl, NCS, diars = O-phenylene bis (dimethyl arsine).

![Diagram of isomeric structures XI-XIV](image)

Considering that the local symmetry of [Re NN$_4$O] chromophore is expected to generate the MO energy levels, not much different from that worked out for C$_4v$ symmetry, and also based on the fact that all the 6-coordinate complexes exhibit a feeble temperature-independent paramagnetism ($\chi_T \approx +150$ cgs units mole$^{-1}$) in the temperature range 300-20 K, the ground state MO configuration, here, may be ($e$)$^4$ ($b_2$)$^2$ (ref. 20). The occurrence of tip in these {Re(NO)}$^6$ system is again,
due to the conditional suitability of the second-order spin-orbit interaction due to the low symmetry of the molecules and a high spin-orbit coupling constant of rhenium.\textsuperscript{34} This observation also supports the $\pm 1$ formal oxidation state of rhenium in these complexes.

The five coordinate complexes hitherto reported are 16-electron and the six coordinate ones are 18-electron systems. Adams \textit{et al.}\textsuperscript{33} reported a paramagnetic and EPR sensitive 16-electron species, \textit{viz}, $[\text{Re(NO)} \ C\text{Cl}_2 \ (\text{PPh}_3)_2]$. However, recently Cameron \textit{et al.}\textsuperscript{40} have shown that the correct formula of the compound reported by Adams \textit{et al.} should be $[\text{Re(NO)} \ C\text{Cl}_2 \ (\text{OCH}_3)\ (\text{PPh}_3)_2]$—a 17 electron system containing $\{\text{ReNO}\}_5$ moiety.

However, our basic assumption is further supplemented by the electronic absorption spectral data (Table III) of the isolated complexes. All the complexes show three characteristic absorption bands, owing possibly\textsuperscript{20} to $b_2\rightarrow e$; $b_2\rightarrow b_1$ and $b_2\rightarrow a_1$ transitions; obviously the isomeric species, differing from one another both in positions and in intensities of the observed bands.

Since all the isolated rhenium nitrosyl complexes described above do possess $\{\text{MNO}\}_6$ moiety, thereby implying that the orbital antibonding with respect to $M-N$ and $O$ remains unoccupied, it may be reasonably presumed that the $M-N-O$ group in all the complexes is essentially linear.

**Reductive Nitrosylation of ReO$_4^-$ using NH$_2$OH·HCl and NaNO$_2$**

The overall reaction pattern is shown in equation (2). The observed facile conversion of $\{\text{Re(NO)}\}_2^{2+}$ to $\{\text{Re(NO)}\}_2^{2+}$ using NO$_2^-\cdot$H$^+$ indicates that the nitrosylating agent in the second step is NO rather than NO$^+$.

\[
\begin{align*}
\text{NH}_2\text{OH} / \text{OH}^- / \text{NCS}^- & \quad \text{ReO}_4^- – \text{[Re(NO) (NCS)H}_2\text{O}]^- \quad \text{NO}_2^- / \text{H}^+ \\
& \quad \text{[Re(NO) (NCS)H}_2\text{O}]^- \quad \text{[Re(NO) (NCS)H}_2\text{O}]^- \\
& \quad \{\text{Re(NO)}\}_2^{2+} \quad \{\text{Re(NO)}\}_2^{2+} \quad \{\text{Re(NO)}\}_2^{2+} \quad \{\text{Re(NO)}\}_2^{2+}
\end{align*}
\]

\textsuperscript{(2)}

This observation also parallels the process of nitrosylation of $\{\text{Cr(H}_2\text{O)}_6\}_2^{2+}$ to $[\text{Cr(NO)}]^{2+}$ using NO$_2^-/\text{H}^+$\textsuperscript{41} It is interesting to note that an attempt to introduce the second nitrosyl group in the compounds containing the $\{\text{Re(NO)}\}_2^{2+}$ moiety by the passage of pure NO gas, even in non-aqueous and non-aerobic media, met with no success. Instead of further nitrosylation the decomposition of the respective species \textit{via} an oxidation of the metal centre (Re = O band observed in the IR spectra) took place, which may be due to the thermodynamic instability of gaseous NO\textsuperscript{42}

It is also interesting to note that the thiocyanato dinitrosyl rhenate (O), as precipitated by using bulky cations, \textit{viz}, Ph$_4$P$^+$, Ph$_4$AS$^+$, Me$_4$N$^+$ or Et$_4$N$^+$ is always 5-coordinate (i.e., the composition of the species is independent of the type of cation used; also note the difference with the cyano-nitrosyl chromates\textsuperscript{14s}, whereas $L-L$ derivatives $[\text{Re(NO)}_2 \ (\text{NCS})_2 \ (L-L)]$ are always six-coordinate. However, although the composition of the complex anionic are independent of the cations
used, their structural features differ. While the Me₄N⁺ and Et₄N⁺ salts have similar magnetic moment values (0.8–0.9 B.M.) and electronic absorption spectra, the bulkier and more polarizable cations (Ph₄P⁺ and Ph₄As⁺) give complexes with high magnetic moment values (4.7 B.M.) and their electronic absorption spectral features are also different from those of Et₄N⁺ and Me₄N⁺ complexes.

Neutral 6-Coordinate Complexes

The analytical, molecular weight, electrolytic conductance (non electrolyte in CH₃CN), thermo-analytical and spectroscopic (IR, U.V.-vis and EPR) data all indicate that the neutral L-L derivatives are 6-coordinate complexes. The cis configuration of the two nitrosyl groups in the complexes is evident from the appearance of two well separated (~1860 and 1715 cm⁻¹; ~150 cm⁻¹) ν(NO) IR bands. Also, by comparing the relatively small separation (~50 cm⁻¹) between the two ν(NO) frequencies in the previously reported⁴³–⁴⁴ Re-dinitrosyl compounds, it seems that the arrangement of the two NO groups around the central metal ion in the present case may be quite different from that in the previous ones, and in the present case the two MNO angles may differ considerably.²⁰ Moreover, the broad and unsymmetrical nature of the ν(NO) IR band in both cases indicates that the two NCS group are in cis configuration with respect to each other. The L-L derivatives, [Re(NO)₂(NCS)₂(L-L)] exothermically loses one NO molecule at 160 and the mono-nitrosyl product [Re(NO)(NCS)₂(L-L)] exists in the temperature range ca 200–280 °C, under dinitrogen, as evidenced from TGA and DTA data.

Based on MO configuration²⁰ of six coordinate {M(NO)₃}ₖ system the ground state electronic configuration in C₄ᵥ field (one axial and other equatorial NO in mutually cis positions) should be (la⁺)² (la⁻)² (la⁻)² (lb⁻)¹ while in C₂ᵥ field (both equatorial NO) the configuration be (la²)² (la⁻)² (lb⁻)² (lb⁻)¹. On bulk magnetic susceptibility arrangement the compounds show a moment value of 1.5 BM at 298 K—a subnormal value so far as the μₑ₀ for magnetically dilute compounds containing one unpaired electron is concerned. As per NO⁺ formalism,²⁰ the formal oxidation state of Re in those compounds should be zero and hence they contain d⁷ Re. Since the compounds were found to be monomeric in solution, the subnormal magnetic moment values may be due to intermolecular magnetic exchange coupling.

The X-band EPR spectra of both the L-L derivatives in polycrystalline state at 298 and 80 K show signs of magnetic exchange (Fig. 1). Since a well-defined axial symmetry (g⊥ ≈ 2.1, g∥ ≈ 1.9, g₈ᵛ ≈ 2.0 with insignificant temperature-dependence) is exhibited, the effective symmetry of the molecules should be higher than the strict one. The profile of EPR curves in both the cases (Fig. 1) indicate that the nuclear hyperfine splitting is of a complicated nature; a sextet appears due to coupling with ¹⁸⁵Re and ¹⁸⁷Re (both have I = 5/2, see ref. 45) of which possibly two lines in perpendicular region are further split due to the interaction of the unpaired electron with ¹⁴N of NO.⁴⁶

Though in the EPR spectra an axially symmetric structure is indicated, the electronic spectra cannot distinguish between the C₄ or C₂ₓ structure. In both the
cases four electronic transition is predicted ($b_1 \rightarrow a'$, $b_1 \rightarrow a'$, $b_1 \rightarrow a''$ and $b_1 \rightarrow b_2$ for $C_s$ and $b_2 \rightarrow a_1$, $b_2 \rightarrow b_1$, $b_2 \rightarrow b_2$ and $b_2 \rightarrow a_2$ for $C_{2v}$) and four bands are actually observed at ca 640, 480, 400 and 315 nm regions in the complexes studied.

Five-Coordinate Complexes

The position of $v_{NO}$ vibrations in these mono-anionic complexes fall in two distinctly different regions. The complexes containing quaternary ammonium
salts absorb at a considerably higher wave number region (~1860, 1720) than their quaternary phosphonium and arsonium counterparts (~1840, 1720). This might imply that the $[\text{Re(NO)}_2(\text{NCS})_3]^-$ species precipitated as $\text{Ph}_4\text{A}(\text{A} = \text{P}, \text{As})$ salts have TBP geometry where the NCS group *trans* to NO facilities the Re–NO back π-bonding, while the isomeric species precipitated as quaternary ammonium salt possibly possess SP structure. The $\nu_{\text{CN}}$ vibration of the N-bonded thiocyanato ligands also differs in the two classes of compounds — in the phosphonium and arsenium salts it is at lower wavenumbers than their ammonium analogues. The σ-π synergic mechanism as prevails in the TBP complexes, also in turn facilitates the σ-electron transfer from NCS nitrogen to the metal ion which weakens the CN π-bonding and hence, lower the force constant of the said bond. Some components of the $\nu_{\text{CN}}$ bands, however, have comparable positions in both the TBP and SP series. This is quite realistic, insofar as in TBP geometry the both (assuming fluxionality via Berry mechanism in TBP) cases and in SP, one of the NO groups have NCS$^-$ as a *trans* ligand.

It is even more interesting to note that the magnetic moments of these two sets of complexes differ significantly. This $\{M(\text{NO})_2\}$ moiety in TBP configuration have comparatively closely spaced HOMO$^{20}$ and this may be the reason why the Ph$_4$A salts have magnetic moments as high as 4.7BM. On the contrary, the R$_4$N salts have their magnetic moment values almost half the spin-only value for one unpaired electron. In SP configuration one unpaired electron (residing at $d_{z^2}$ orbital) for a $\{\text{Re(NO)}_2\}$ moiety should be the expected situation and a drastic lowering in the moment values may be due to intermolecular exchange coupling interaction.

Another prominent difference that exists between these two series of complexes is that while the supposed TBP complexes show up only one UV-vis spectral band (800–280nm), the SP Species show four such bands. However, absence of any unequivocal working model in $\{M(\text{NO})_2\}^n$ system, in TBP and SP cases, does not permit the designation of the origin of the above electronic transitions.

**Reactivity of $\{\text{Mo(NO)} (\text{NH}_2\text{O})\}$ Fragment**

Recently, there has been a considerable upsurge in the study on the reactivity of coordinated NO. This is partly because it provides understanding regarding the mode of bondings of NO to metals; another stimulus to investigating NO reactivity is the catalytic application of metal nitrosyls in organic syntheses and in pollution control.$^{48}$ The main types of reactivity of NO centre of the metal nitrosyl systems can be classed as 1) Nucleophilic attack; 2) Electrophilic attack; 3) Redox reactions; and 4) Homogeneous disproportionation reaction.

It has been marked *vide supra* that [Mo(NO) (NH$_2$O) (NCS)$_4$]$^{2-}$ or its $L$-$L$ derivatives (1) undergo an interesting disproportionation reaction producing $\{\text{Mo(NO)}_2\}^{2+}$ and $\{\text{MoO}_4\}^{2+}$ moieties. Müller *et al.$^{23a}$ have shown that [Mo(NO) (NH$_2$O) (NCS)$_4$]$^{2-}$ can be refluxed with acetone to yield [Mo(NO) (ONCMe$_2$) (NCS)$_4$]$^{2-}$ i.e., the N, O-bonded hydroxylamido ligand being converted to a N, O-bonded acetoximato ligand. It has been found by us that this type of oximation
with acetone of the coordinated ONH₂ group occurs only in the nitrosyl complexes and in the present case both 1(a) and 2(a) (Table II) on being refluxed with acetone also form complexes containing the analogous oximate group (analytical, IR, and ¹H NMR data; the singlet disappears and a quintet appears at 3.7ppm). Also, DMF reacts with coordinated NH₂O group in those complexes yielding a C, O bonded reactive carbamido moiety presumably via C-H bond cleavage (equation (3)).

$$\text{DMF} \quad [\text{Mo(NO)} (\text{NH}_2\text{O}) (\text{NCS})_2 (L-L)] \rightarrow [\text{Mo(NO)} \text{OCN(CH}_3)_2 (\text{NCS})_2 \times (L-L)] + \text{NH}_2\text{OH} \quad \ldots \ (3)$$

However, if the diamagnetic complex (2a) is refluxed for 3–4h in acetonaphone (another ketone), a formally Mo(I) species [Mo(NO) (NCS)₂ (phen)] (15b) is produced which is paramagnetic and ESR sensitive (Table IV, Fig. 1). On the other hand, if acetonaphone solutions of (1a) and (2a) are photolysed using a tungsten filament (100 W) at 80 °C it is also converted to the paramagnetic and ESR sensitive compounds (14) and (15a). From the analytical data, IR and electronic spectra (Table IV) it is quite clear that (15a) and (15b) are isomeric and differ in the position of both $\nu_{\text{NO}}$ (rather drastically) and $\nu_{\text{CN}}$ (broad and unsymmetrical in all the nitrosyl complexes studied here) vibrations as well as in the position and intensity of their electronic spectral bands. All the complexes are non-electrolytes $\Delta_M$ (measurements) and monomeric in CH₃CN. The IR data suggest that the NCS–

| Table IV |
| Magnetic and spectral data for the molybdenum(I) complexes |

<table>
<thead>
<tr>
<th>Compound</th>
<th>Selected IR Data (cm⁻¹)ᵃ</th>
<th>Electronic absorption</th>
<th>$\mu_{\text{eff}}$ (BM)ᵇ</th>
<th>$\langle g_{\text{av}} \rangle$ ᵜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>(14) [Mo(NO) (NCS)₂ (bpy)]</td>
<td>$\nu_{\text{CN}}$ 2065s, $\nu_{\text{NO}}$ 1678s, $\nu_{\text{M-NO}}$ 585w</td>
<td>21.3 (120ᵇ)</td>
<td>2.1 1.99</td>
<td></td>
</tr>
<tr>
<td>(15a) [Mo(NO) (NCS)₂ (phen)]</td>
<td>$\nu_{\text{CN}}$ 2065s, $\nu_{\text{NO}}$ 1665s, $\nu_{\text{M-NO}}$ 610w</td>
<td>21.7 (150)</td>
<td>1.8 1.99</td>
<td></td>
</tr>
<tr>
<td>(15b) [Mo(NO) (NCS)₂ (phen)]</td>
<td>$\nu_{\text{CN}}$ 2055s, $\nu_{\text{NO}}$ 1600s, $\nu_{\text{M-NO}}$ 585w</td>
<td>25.6 (250)</td>
<td>1.9 1.97</td>
<td></td>
</tr>
<tr>
<td>(16) [Mo₄ (NCS)₄ (bpy)₄]</td>
<td>$\nu_{\text{CN}}$ 2055s, $\nu_{\text{NO}}$ 1600s, $\nu_{\text{M-NO}}$ 585w</td>
<td>30.7 (1510)</td>
<td>e —</td>
<td></td>
</tr>
<tr>
<td>[Mo₄(NCS)₄ (bpy)₄]ᶠ</td>
<td>$\nu_{\text{CN}}$ 2090s, $\nu_{\text{NO}}$ 2060s,</td>
<td>15.3</td>
<td>e —</td>
<td></td>
</tr>
</tbody>
</table>

ᵃ$\nu_{\text{CN}}$ and $\delta$(NCS) vibrations for all complexes at ca. 750 and 480 cm⁻¹ respectively. See ref. 12 for assignments of IR bands. ᵅValues in litre mol⁻¹ cm⁻¹ are given in praenesthesis. ᵜAt 298 K; ᶜFrom the ESR spectra of the polycrystalline samples. ᵇDiamagnetic. ᵈSee ref. 52.
ligands are N-bonded in all complexes. Since, for the thermally obtained complex (15b) \( \nu_{NO} \) occurs at a substantially lower wave number than for the photolysis products (14) and (15a), probably it has a TBP geometry with (14) and (15a) having a square pyramidal (SP) configuration with the trans-position of NO ligand vacant. It is worth mentioning here that (14) and (15a) could not be obtained simply by heating (1) at any suitable temperature and photolysis was essential. Two non-nitrosyl Mo(I) complexes, trans-[MoX(N\(_2\)](dppe)\(_2\)] (\( X = Cl \) or Br; dppe = 1, 2 bis (diphenyl phosphino) ethane) have been obtained from the zero valent trans-[Mo(N\(_2\)](dppe)\(_2\)] by photooxidation in the presence of CH\(_3\)X\(^49\) and Johnson \textit{et al.}\(^50\) reported a photooxidation reaction of a \{Mo(NO)\(_2\)]\(^2+\) to \{Mo(NO)\]^\(^3\) by UV irradiation; however no report is available of the formation of Mo(I) species by the photoreduction of a suitable higher valent molybdenum compound. It is interesting to note that in the present case the seven-co-ordinate species (1) containing a N, O-bonded hydroxylamido-ligand in the equatorial plane (i.e. the molecule possesses a pentagonal equatorial plane)\(^23\) eliminates this ligand possibly via a transient oximation stage in refluxing acetophenone and produces a TBP species, i.e. \textit{via} a retention of configuration of the residual fragments: two of the equational coordination positions simply became free resulting in a trigonal equatorial plane. However, the thermally assisted photochemical process affording a SP product possibly proceeds \textit{via} a migration of a thiocyanato or L-L nitrogen atom from the apical to a basal plane during the elimination of the hydroxylamino-acetophenone ligand (Scheme III).

The transition around 21,500 cm\(^{-1}\) in (14) and (15a) could be \( b_2 \rightarrow e(\pi^*NO) \) for an SP species\(^20\) and a band at this position is absent in the supposed TBP product (15b). The EPR spectra (Fig. 1) are extremely illuminating. The X-band spectrum (88 K) of the photochemically obtained SP complexes (14) and (15a) (Table IV) show molybdenum hyperfine splitting without any \(^{14}\)N (of NO) hyperfine coupling, the single line in both the cases being superimposed on a sextet arising from coupling to the spin active nuclei \(^{95}\)Mo (15.7 per cent) and \(^{97}\)Mo (9.5 per cent); both having \( I = 5/2 \) \( \langle A \rangle_{MO} \) in (14) is \( Ca \) 40–50 G, but that in (15a) is \( ca \) 20 G;

\[
\begin{align*}
\text{Scheme III} & \quad \text{See text for the structure of isomers of (1) (i) photolyzed in acetophenone at 80}^\circ C, \\
& \text{(ii) heated in acetophenone under reflux; (iii) elimination of Ph–C(Me) = NOH} \\
& \text{(water molecules formed during oximation may be used); (O) bpy or phen nitrogen;} \\
& \text{(●) thiocyanate nitrogen; and (●) oxygen.}
\end{align*}
\]
see ref. 51]. The thermally obtained TBP product (15b) shows a typical orthorhombic (trigonal) type of splitting with $g_{xx} = 1.99$, $g_{yy} = 1.97$ and $g_{zz} = 1.93$ with no molybdenum or ligand hyperfine structure.

Another interesting feature is that the compound [Mo(NO) (NH$_2$O) (NCS)$_2$ bpy] on refluxing in acetophenone gave a deep greenish brown product, which is crystallisable from acetonitrile-diethylether (1:3) and contains no nitrosyl group. Its analytical and molecular weight data suggest it to be [Mo$_2$(NCS)$_3$ (bpy)$_2$] (16) which is diamagnetic and therefore may contain quadruple Mo-Mo band. Its novel feature (compared to the nitrosyl complexes described above) is a responsibly intense band at 15,300 cm$^{-1}$ (Table IV) a region where $\sigma \rightarrow \sigma^*$ transitions do occur.$^{52}$

The solubility, spectral characteristics, and colour of the compound of identical composition reported by Nimry and Walton$^{52}$ are different from those of (16), however (Table IV). While (16) contains a single and symmetrical $\nu_{CN}$ band, the product of Nimry and Walton has a double absorption in this region. We suggest that compound (16) has structure XVI or XVII; Nimry et al.'s compound may possess structure XV.

\[ \text{(XV)} \]
\[ \text{(XVI)} \]
\[ \text{(XVII)} \]

(O) bipy nitrogen
(O) thiocyanate nitrogen

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