Reductive Nitrosylation of Tetraoxometallates. Part 3.† Generation of $\{Mo(NO)\}^4$, $\{Mo(NO)_2\}^4$, and $\{Mo(NO)_2\}^6$ Moieties: ‡ Synthesis of 2,2′-Bipyridine, 1,10-Phenanthroline, Thiocyanato-, and Diethyldithiocarbamato-complexes of Mono- and Di-nitrosylmolybdenum directly from MoO_4^{2-} in Aqueous and Aerobic media

Ramgopal Bhattacharyya * and Gobinda Prashad Bhattacharjee
Department of Chemistry, Jadavpur University, Calcutta 700 032, India

In an aqueous aerobic medium MoO_4^{2-} can be reductively nitrosylated using excess of $NH_2OH{\cdot}HCl$ and SCN^- in the range pH 4—4.5, generating selectively the $\{Mo(NO)\}^4$ moiety. This has been confirmed by synthesising complexes of the types $[Mo(NO)(NH_2O)(NCS)_4]^{2-}$, $[Mo(NO)(NH_2O)(S_2CNEt_2)_2]$, and the isomeric $[Mo(NO)(NH_2O)(NCS)_2(L\text{-}L)]$ [L-L = 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen)] almost in quantitative yield. However, if the same reaction is conducted at pH 5.2—5.4 a selective generation of the $\{Mo(NO)_2\}^4$ moiety occurs leading to the stereoselective synthesis of $[Mo(NO)_2(NHO)(NCS)_4]^{2-}$ and $[Mo(NO)_2(NHO)(NCS)_2(L\text{-}L)]$. In the range pH 5.7—6 the initially formed $Mo(NO)^{3+}$ species undergoes disproportionation to a formally molybdenum(0) species, $\{Mo(NO)_2\}^6$, *viz.* $[Mo(NO)_2(NCS)_4]^{2-}$ or $[Mo(NO)_2(NCS)_2(L\text{-}L)]$ along with an oxomolybdenum(v) species, *viz.* $[Mo_2O_4(NCS)_6]^{4-}$ or $[Mo_2O_4(NCS)_2(L\text{-}L)_2]$. Here also, the dinitrosylmolybdenum moiety is formed stereoselectively.

The reductive nitrosylation of tetraoxometallates using hydroxylamine in strongly alkaline media is well known [1-3] but has been little exploited.[3] Subsequently it was shown that this type of reaction can occur in neutral as well as in slightly acidic media.[4] However, the lack of general applicability of the reaction and the reason for the rather low extent of conversion of tetraoxometallates in metal nitrosyl derivatives had not been appreciated until recently.[5] We have described [5,6] the reductive nitrosylation of CrO_4^{2-} and ReO_4^- using NH_2OH and NCS^- and reported the synthesis of thiocyanato-nitrosyl derivatives formally containing Cr^I and Re^I. For the generation of the former, a slightly acidic medium, and for the latter, an alkaline medium, is necessary. In the case of MoO_4^{2-} the reaction was found [4] to occur in a slightly acidic medium, furnishing $[Mo(NO)(NH_2O)(NCS)_4]^{2-}$ which also contains an N,O-bonded hydroxylamido-ligand; [7] in an aqueous medium only the mononitrosyl complex was formed (see also ref. 8 where $C_2O_4^{2-}$ was used instead of NCS^-).

To date, dinitrosylmolybdenum(0) complexes have been generated by three general routes: (1) oxidation by NO^+ (as NOCl, *etc.*) or substitution by NO of molybdenum carbonyl derivatives; [9,10] (2) reduction of $MoCl_5$ by NO [11] [in both routes (1) and (2) the reactions were carried out in dry oxygen-free atmospheres]; and (3) reductive dinitrosylation of MoO_4^{2-} with NH_2OH in dimethylformamide or pyridine–acetic acid where only a limited yield was obtained. [The 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) derivatives could not be isolated pure.] The nature of the last reaction is rather strange since a mixture of nitrosyl- and oxo-molybdenum products was obtained.[12]

The present work describes for the first time the extreme pH sensitivity of the reaction of MoO_4^{2-} with an excess of $NH_2OH{\cdot}HCl$ and NCS^- (all previous workers employed 3 or 4 mol of $NH_2OH{\cdot}HCl$ per mol of MoO_4^{2-}) in an aqueous aerobic medium, and shows that under carefully controlled pH conditions an almost quantitative synthesis of complexes containing either the $\{Mo(NO)\}^4$, $\{Mo(NO)_2\}^6$, or even the hitherto unknown $\{Mo(NO)_2\}^4$ moiety can be achieved from MoO_4^{2-} in a single-step process.

Results and Discussion

(*a*) *The Overall Reaction Pattern.*—The course of the reductive nitrosylation of MoO_4^{2-} and its intrinsic pH dependence is shown in the Scheme. In the presence of an excess of $NH_2OH{\cdot}HCl$ and NCS^- the conversion of MoO_4^{2-} into the $Mo(NO)^{3+}$ moiety is complete within 5 min, the pH being fixed in the range 4—4.5. Even if the reactants are subjected to prolonged boiling (2—4 h) the dinitrosylation is negligible and so this pH range is specific for the conversion of MoO_4^{2-} into $Mo(NO)^{3+}$. However, if the pH is adjusted to 5.2—5.4, the same reactants on prolonged boiling (4 h) afford in *ca.* 85% yield the complexes (5)—(7) containing the $Mo(NO)_2^{4+}$ moiety. So, this pH range is specific for the conversion of MoO_4^{2-} into $Mo(NO)_2^{4+}$. A very interesting reaction occurs when the reactants are boiled in an aqueous aerobic medium in the range pH 5.7—6. After 1 h the colour of the solution changes from yellow to brown and within 2 min suddenly becomes bluish green; at this stage the presence of a $Mo_2O_4^{2+}$ species is detected. The formation of the bluish green colour is complete (by spectrophotometry) after boiling for another 1 h and the $Mo(NO)_2^{2+}$ and the $Mo_2O_4^{2+}$ species could be obtained in relative yield of 1 : 2. The $Mo(NO)_2^{2+}$ 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 $Mo(NO)^{3+}$ species (formally containing Mo^{II} and NO^+ [13,14]) which is the initial product of nitrosylation in all the above pH ranges (confirmed by isolating the corresponding bipy complexes in each case after 5—10 min) disproportionates presumably according to equation (i). That $Mo(NO)(NH_2O)^{2+}$ takes part in the

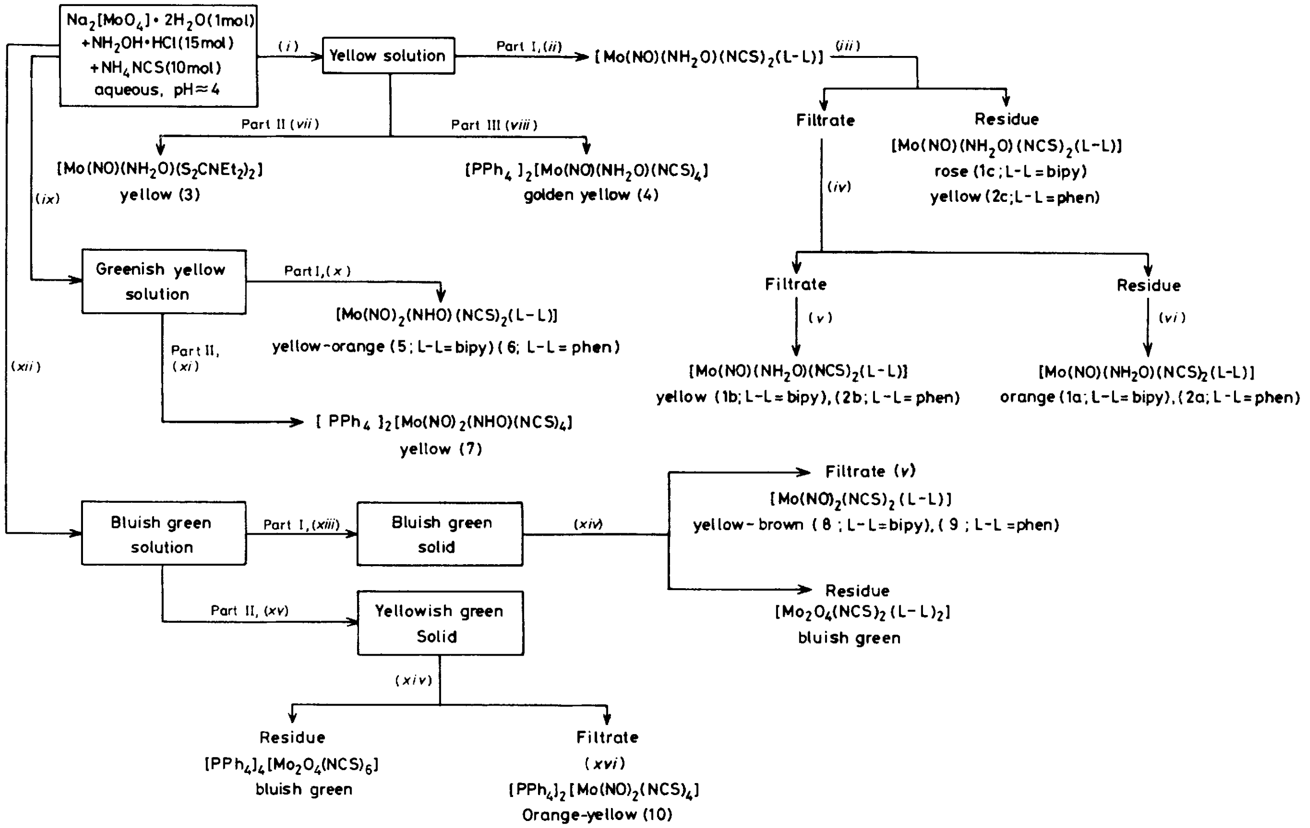
$$3Mo(NO)(NH_2O)^{2+} + H_2O \longrightarrow Mo(NO)_2^{2+} + Mo_2O_4^{2+} + N_2O + 2NH_3 + 2H^+ \quad \text{(i)}$$

disproportionation was proved by trapping and characterising the products at regular intervals using bipy, including that present a few seconds before the appearance of the blue-green

---

† Part 2 is ref. 6*b*.

‡ The numerical superscripts indicate the total number of valence electrons in the metal and NO orbitals (see, for example, refs. 4 and 14).

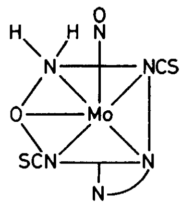


Scheme. (*i*) Boil for 5 min; (*ii*) L–L solution; (*iii*) extract with CH_3CN; (*iv*) evaporate and extract solid with CH_2Cl_2; (*v*) evaporate; (*vi*) dissolve in CH_3NO_2, add Et_2O; (*vii*) $S_2CNEt_2^-$ solution; (*viii*) PPh_4Cl solution; (*ix*) adjust pH to 5.2, boil for 4 h, readjust pH to 5.2; (*x*) L–L solution, pH *ca.* 5.2; (*xi*) PPh_4Cl solution, pH *ca.* 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 CH_3CN; (*xv*) PPh_4Cl solution, pH 5.7–6; (*xvi*) evaporate, dissolve solid in acetone, add Et_2O

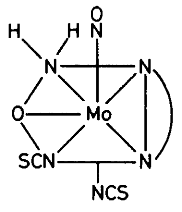
colour. Also, the mode of the disproportionation reaction was verified experimentally by repeating a relevant experiment {*i.e.* boiling an aqueous solution (pH 6) of $[NMe_4]_2[Mo(NO)(NH_2O)(NCS)_4]$} in a vacuum line and analysing quantitatively (the gases generated were accumulated in evacuated vessels and the vapour pressure measured) the evolved N_2O (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. It should be pointed out that the compound claimed[15] to be $[MoO_2(NO)_2(bipy)X_2]$ (an extremely improbable species indeed!) is a mixture of $[Mo(NO)_2(bipy)X_2]$ and $[Mo_2O_4(bipy)_2X_2(H_2O)_2]$ formed simultaneously according to reaction (i).

(*b*) *Complexes containing* $\{Mo(NO)\}^4$.—The product $[PPh_4]_2[Mo(NO)(NH_2O)(NCS)_4]$, now obtained in quantitative yield, was structurally characterised by Müller *et al.*[7] as a seven-co-ordinated 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 the 18-electron configuration.

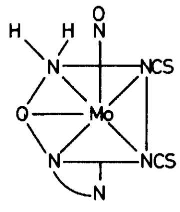
Isomerism in the $[Mo(NO)(NH_2O)(NCS)_2(L{-}L)]$ *species.* If the N,O-bonded NH_2O^- ligand is always *cis* to the axial[7,16,17] nitrosyl group, three isomeric forms may be predicted for the compounds (1) and (2) as shown in structures (I)—(III). All three isomeric species have been isolated by taking advantage of their different solubilities in organic solvents. Their analytical, molecular-weight, and n.m.r. data (Table 1) are practically identical but the species differ in the important i.r. band positions and in their electronic absorption spectra. The orange isomer of both the bipy and phen compounds possesses only one ν(CN) band at 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, the yellow and rose (yellow in the case of phen) isomers both have split ν(CN) bands and so 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, bipy or phen, being stronger ligands than NCS^-, when *trans* to NO will cause a reduction of the N–O stretching frequency of the co-ordinated nitrosyl group. So, from Table 1, it is apparent that the yellow isomer possesses structure (II) and the rose (yellow in the case of phen) structure (III).



(I)



(II)



(III)

The CH_2Cl_2-soluble isomers, (1b) and (2b), could not be isolated very pure (analyses and i.r. spectra), but the spectral features still suggest that the product has in all probability the structure assigned. Unfortunately, no other solvent selectively removed (1b) and (2b) from their respective isomeric mixtures and a chromatographic separation was impossible owing to reaction of the complexes with the column materials. Following the same experimental procedure, only the dithiocarbamato-

Table 1. Analytical, physicochemical, and spectroscopic data of the complexes

Complex	Colour	M.p. (°C) (decomp.)	*M* [a]	Analysis [a] (%)					Selected i.r. data (cm^{-1})			^{1}H N.m.r. data [b] (p.p.m.)
				C	H	N	S	Mo	ν(CN)	ν(NO)	ν(M–N)(NO)	
(1a) $[Mo(NO)(NH_2O)(NCS)_2(bipy)]$	Orange	118—122	418 (430.5)	33.6 (33.5)	2.0 (2.3)	19.2 (19.5)	14.5 (14.9)	22.7 (22.3)	2 080s	1 655s	600w	3.2,[c] 4.2[d] 3.6[e] (2 H)
(1b) $[Mo(NO)(NH_2O)(NCS)_2(bipy)]$	Yellow	120—125	390 (430.5)	34.3 (33.5)	3.1 (2.3)	18.9 (19.5)	14.2 (14.9)	22.2 (22.3)	2 090 (sh), 2 070s	1 657s	590w	[f]
(1c) $[Mo(NO)(NH_2O)(NCS)_2(bipy)]$	Rose	292—295	404 (430.5) [g]	33.0 (33.5)	2.0 (2.3)	19.1 (19.5)	14.2 (14.9)	22.6 (22.3)	2 080s, 2 100 (sh)	1 647s	610w	2.8[e] (2 H)
(2a) $[Mo(NO)(NH_2O)(NCS)_2(phen)]$	Orange	110—114	417 (454.5)	37.3 (37.0)	2.0 (2.2)	18.1 (18.5)	13.7 (14.1)	21.5 (21.1)	2 080s	1 657s	600w	3.2,[c] 4.2[d] (2 H)
(2b) $[Mo(NO)(NH_2O)(NCS)_2(phen)]$	Yellow	106—110	400 (454.5)	32.1 (37.0)	3.2 (2.2)	18.0 (18.5)	13.3 (14.1)	20.7 (21.1)	2 080 (sh), 2 052s	1 652m	610w	[f]
(2c) $[Mo(NO)(NH_2O)(NCS)_2(phen)]$	Yellow	300—305	435 (454.5) [g]	36.6 (37.0)	1.8 (2.2)	18.3 (18.5)	13.4 (14.1)	21.8 (21.1)	2 105 (sh), 2 080s, 2 050 (sh)	1 645s	610w	2.9[e] (2 H)
(3) $[Mo(NO)(NH_2O)(S_2CNEt_2)_2]$	Yellow	110—112	417 (454.5)	26.4 (26.4)	4.6 (4.8)	12.1 (12.1)	27.7 (28.2)	21.4 (21.1)		1 650s	590w	3.9[d] (2 H)
(4) $[PPh_4]_2[Mo(NO)(NH_2O)(NCS)_4]$ [h]	Golden yellow	223—225		57.6 (58.4)	3.6 (3.9)	7.0 (7.9)	11.8 (12.0)	9.4 (9.0)	2 072s	1 658s	620w	2.5[d] (2 H)
(5) $[Mo(NO)_2(NHO)(NCS)_2(bipy)]$	Yellow-orange	115—117	440 (459.5)	31.1 (31.4)	1.8 (2.0)	20.8 (21.4)	13.6 (14.0)	21.3 (20.9)	2 080s	1 780m, 1 658s	618w, 583w	[5.0[c] (1 H)] [5.4[d]]
(6) $[Mo(NO)_2(NHO)(NCS)_2(phen)]$	Yellow-orange	128—132	447 (483.5)	35.0 (34.8)	1.5 (1.7)	19.8 (20.3)	12.9 (13.3)	20.3 (19.9)	2 080s	1 780m, 1 660s	620w, 580w	[5.2[c] (1 H)]
(7) $[PPh_4]_2[Mo(NO)_2(NHO)(NCS)_4]$ [i]	Yellow	210—212		56.4 (56.9)	4.0 (3.7)	8.0 (8.9)	10.9 (11.7)	9.0 (8.7)	2 110 (sh), 2 077s	1 777m, 1 655s	618w, 618w	[5.2[c] (1 H)]
(8) $[Mo(NO)_2(NCS)_2(bipy)]$	Yellow-brown	123—126	402 (428.5)	34.1 (33.7)	2.2 (1.9)	19.5 (19.6)	14.7 (14.9)	22.7 (22.4)	2 087 (sh), 2 070s	1 785s, 1 672s	583w, 570w	
(9) $[Mo(NO)_2(NCS)_2(phen)]$	Yellow-brown	118—122	421 (452.5)	36.9 (37.2)	1.7 (1.8)	18.8 (18.6)	13.6 (14.2)	21.7 (21.2)	2 105 (sh), 2 070s,	1 780s, 1 665s	620w, 580w,	
(10) $[PPh_4]_2[Mo(NO)_2(NCS)_4]$ [j]	Orange-yellow	200—202		57.1 (56.9)	3.4 (3.7)	8.0 (8.9)	10.9 (11.7)	9.5 (9.0)	2 105 (sh), 2 072s	1 786s, 1 658s	615vw	

[a] Calculated values are shown in parentheses. [b] Values are for δ(NH_2O) except for those in square brackets [δ(NHO)]. [c] In $(CD_3)_2CO$ (cold). [d] In CD_3CN. [e] In $(CD_3)_2SO$. [f] Inconclusive. [g] In dmf, all others are in CH_3CN. [h] P 5.5 (5.8%). [i] P 5.3 (5.7%). [j] P 5.6 (5.8%).

Table 2. Electronic absorption, magnetic susceptibility and electrolytic conductance data of the complexes

Complex	Electronic absorption ($10^{-3}\tilde{\nu}/cm^{-1}$) [a]	$10^{-6}\chi_A$ [b]/ $cm^3\ mol^{-1}$	Λ_M [c]/$ohm^{-1}\ cm^2\ mol^{-1}$
(1a) [d]	26.6 (420), 31.1 (4 000), 32.5 (2 650), 34.2 (1 800)	140	*e*
(1b) [d]	26.6 (440), 31.7 (3 000), 33.8 (4 150), 35.5 (2 300)	130	*e*
(1c) [f]	24.5 (50), 27.1 (450)	140	*e*
(2a) [d]	26.5 (500), 30.9 (4 250), 32.5 (2 850), 34.7 (2 000)	150	*e*
(2b) [d]	26.5 (500), 31.6 (3 250), 32.9 (4 050)	130	*e*
(2c) [f]	24.5 (40), 26.6 (500)	130	*e*
(3) [d]	23.8 (25), 35.7 (4 750)	160	*e*
(4) [d]	21.3 (30) $(e\rightarrow b_2)$, [g] 30.1 (90) $(e\rightarrow e)$ [g]	130	235
(5) [d]	13.9 (32), 16.7 (10), 21.5 (75)	190	*e*
(6) [d]	13.5 (25), 16.5 (16), 21.8 (70)	180	*e*
(7) [d]	21.6 (1 100), 31.3 (370)	150	240
(8) [d]	13.5 (90), 16.4 (20), 21.9 (315), 32.1 (2 200)	170	*e*
(9) [d]	13.9 (70), 16.6 (15), 22.0 (340), 31.8 (2 300)	150	*e*
(10) [d]	20.6 (4 200) $(b_2\rightarrow a_1)$, [g] 27.6 (440) $(b_2\rightarrow b_1)$, [g] 31.3 (330) $(b_2\rightarrow b_2)$ [g]	140	250

[a] Values of $\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ are given in parentheses. Intraligand transitions are not listed. [b] Corrected molar susceptibilities of the solid. [c] Solvents used as for electronic spectra. [d] In acetonitrile. [e] Non-electrolyte. [f] In dmf. [g] Probable assignment.

complexes of the $\{Mo(NO)\}^4$ series are isolable. The dinitrosylmolybdenum moieties do not afford isolable products with dithiocarbamate under the described conditions.

Electronic absorption spectra. Assuming that complex (4) (MoN_6O chromophore) may be described by a similar molecular-orbital (m.o.) picture to that applicable [14] to C_{4v} cases, the two observed electronic absorption bands of the anion $[Mo(NO)(NH_2O)(NCS)_4]^{2-}$ could be assigned as in Table 2. The four closely spaced absorption bands exhibited by (1a), (1b), (2a), and (2b) (Table 2) are due possibly to the apparent lower symmetry of these molecules [18] compared to (4).

Reaction of co-ordinated NH_2O. The co-ordinated NH_2O^- ligand in complexes (1)—(4) reacts with acetone under previously described experimental conditions [7] to furnish a co-ordinated (side-on bonded [7]) acetoximato-ligand, $-\underset{|}{N}=CMe_2$. The products have been characterised by analytical, i.r. [ν(NH) disappeared], and ^1H n.m.r. data. The singlet at δ 4.3 p.p.m. in CD_3CN solution due to the NH_2O^- protons disappears and a new quintet (6 H) appears at *ca.* 3.7 p.p.m. ($J = 6$ Hz); in $(CD_3)_2SO$, a singlet (6 H) occurs at 3.6 p.p.m. The said NH_2O^- group does not react with CH_3CN *at room temperature* and the products can be crystallised unchanged from this solvent, without heating; but crystals obtained from *boiling* acetonitrile solution do not exhibit the ν(NH) band found in the parent complexes.

Dimethylformamide (dmf) reacts with the co-ordinated NH_2O^- group in these complexes yielding possibly a C,O-bonded reactive carbamido-moiety [19] presumably *via* C−H bond cleavage in the dmf [equation (ii)]. All the above

$$[Mo(NO)(NH_2O)(NCS)_2(L{-}L)] \xrightarrow{dmf} [Mo(NO)\{OCN(CH_3)_2\}(NCS)_2(L{-}L)] + NH_2OH \quad (ii)$$

reaction products were characterised by ^1H n.m.r. spectroscopy.[19]

Interestingly, complexes (1a)—(1c) react with acetophenone under reflux to furnish a compound of composition $[Mo_2(NCS)_4(bipy)_2]$ (analytical, i.r., and molecular-weight data). It may be presumed that this contains a quadruple Mo−Mo bond since the complex is diamagnetic. Under the same conditions, the conversion of compounds (2)—(4) into the corresponding dimeric species is slow, the reason for this not being obvious at present.

(*c*) *Complexes containing* $\{Mo(NO)_2\}^4$.—To date, no complex containing the above moiety is known. In the present study, the isolated complexes containing the above species were always found to be associated with a co-ordinated NHO^{2-} 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 co-ordination number of 7 would conform to the 18-electron rule it may be presumed that the NHO^{2-} ligand is possibly unidentate co-ordinating as the hydroxylimido $[=N(OH)^{2-}]$ form. The ^1H n.m.r. signal for the NH_2O^- 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 δ 5.4 p.p.m. (1 H). A representative spectrum in CD_3CN is shown in the Figure. The slight change in the bipy resonances in going from complex (1a) to (5) may be due to the different co-ordination environments.[20] However, an N,O-bonded hydroxylamido(2−)-ligand was assumed [17] by previous workers to be present in the complex [Mo(NO)(NHO)(terpy)(CN)] (terpy = 2,2′: 6′,2″-terpyridine), where a bidentate co-ordination of the NHO group conforms to the 18-electron rule.

Of the two ν(NO) bands observed here (Table 1), one is markedly weaker than the other, possibly due to the reduction in N−O bond polarity *via* a hydrogen-bonding interaction with the adjacent =N(OH) group.

Isomerism in $[Mo(NO)_2(NHO)(NCS)_2(L{-}L)]$. 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 ν(CN) band at good resolution. This indicates that the complexes contain *trans* thiocyanato-groups. So it may be argued that the generation of $\{Mo(NO)_2(NHO)\}^4$

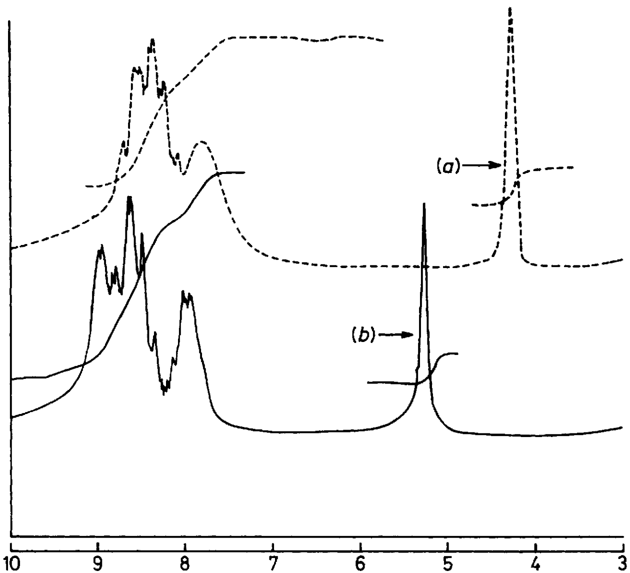


Figure. Proton n.m.r. spectra of compounds (1a) (*a*) and (5) (*b*)

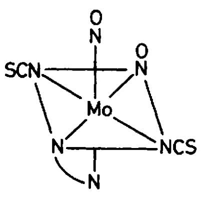
via the reductive nitrosylation of MoO_4^{2-} by NH_2OH and NCS^- in the range pH 5.2—5.4 is stereoselective.

Electronic absorption spectra. For the $[Mo(NO)_2(NHO)(NCS)_2(L{-}L)]$ species three electronic absorption bands are observed (Table 2) as predicted for a C_s configuration. The appearance of only two bands for complex (7) may be due to its somewhat higher symmetry.

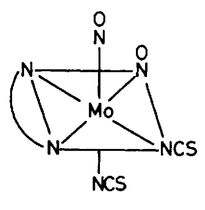
Reactivity of $\{Mo(NO)_2(NHO)\}^4$. Although these complexes may be crystallised unchanged from acetonitrile and acetone, they react with CH_2Cl_2. Preliminary studies indicate the introduction of a third nitrosyl group (*ca.* 1 850 cm^{-1}) and the disappearance of the $=N(OH)^{2-}$ ligand.

(*d*) *Complexes containing* $\{Mo(NO)_2\}^6$.—This species is generated *via* a disproportionation reaction as described in section (*a*). Interestingly, although the pH of the blue-green solution was adjusted to 5.7 after completion of the nitrosylation, and the pH of the added bipy or phen solution was also adjusted to *ca.* 5.5, the phen compounds, *viz.* $[Mo(NO)_2(NCS)_2(phen)]$ and $[Mo_2O_4(NCS)_2(phen)_2]$, were precipitated together in a 1 : 2 mol ratio and the pH of the colourless filtrate was found to be *ca.* 3.5, whereas with bipy almost pure (5—10% contamination by the oxo-product) $[Mo(NO)_2(NCS)_2(bipy)]$ was precipitated leaving a deep blue-green filtrate (pH 5.6) which when adjusted to pH 3.0 by adding a few drops of 6 mol dm^{-3} HCl quantitatively precipitated the oxo-product $[Mo_2O_4(NCS)_2(bipy)_2]$ leaving a colourless solution. The ultimate yield of the nitrosyl and oxo-products was in the ratio of 1 : 2 as per equation (i). Alternatively, the pH of the reaction medium could be brought down to 3.0 after the bipy had been added to the reaction mixture, when both the dinitrosyl and the oxo-product were co-precipitated in the same mol ratio and then separated as described in the Experimental section. These dinitrosyl compounds are all six-co-ordinated and thereby conform to the 18-electron rule. The two strong ν(NO) bands found for each complex is as expected for a *cis*-dinitrosyl structure. These compounds exhibit no ν(NH) bands. The oxo-species showed two prominent absorptions, at 900 and 930 cm^{-1}, due to Mo–O vibrations, characteristic of a *cis*-$Mo_2O_4^{2+}$ group.[21] The $\nu(MoO_2Mo)$ bands are found between 700 and 800 cm^{-1}.[21,22]

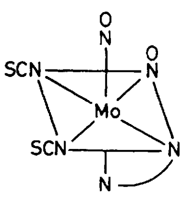
Isomerism in $[Mo(NO)_2(NCS)_2(L{-}L)]$. If the two nitrosyl



(IV)



(V)



(VI)

groups are placed *cis* to each other, the above species may be represented by the three isomeric forms (IV)—(VI). The isolated complexes are soluble in acetone, acetonitrile, nitromethane, and moderately so in dichloromethane, and the crystallised products from these solvents show identical i.r. spectra. The ν(CN) band of all the complexes is split and so it may be presumed that the structure is either (V) or (VI), *i.e.* the molecules possess *cis*-NCS groups and the reaction is rather stereoselective. This stereoselectivity obtained *via* the reductive dinitrosylation of MoO_4^{2-} in an aqueous aerobic medium is opposite to that obtained by Cotton and Johnson [9a,b] in the case of $[Mo(NO)_2L_2X_2]$ ($L = PPh_3$, $X = Cl^-$) achieved *via* oxidative nitrosylation $\{[Mo(CO)_6] + NOCl\}$, but parallels that claimed by Sarkar and Subramanian [12] for $[Mo(NO)_2(py)_2Cl_2]$ (py = pyridine) obtained by reductive nitrosylation of MoO_4^{2-} in pyridine–acetic acid.

Electronic absorption spectra. In the $\{Mo(NO_2\}^6$ species the nitrosyl groups in *cis* configuration should deviate very slightly from linearity because of the nature of the a_1 and b_2 orbitals.[14] However, their electronic configurations in a C_{2v} field may be [14] $(a_2)^2(a_1)^2(b_2)^2$. Consequently, three electronic absorption bands are observed for complex (10), the assignments of which are shown in Table 2; the first absorption is unusually intense. Complexes (8) and (9) possess a still lower symmetry and hence show a greater number of absorption bands.

(*e*) *General Characterisation.*—The anionic complexes are 2 : 1 electrolytes in acetonitrile,[23] the others are non-electrolytes. The i.r. data (Table 1) show that the thiocyanate groups are N-bonded.[24a] Obviously, the mononitrosyl complexes are characterised by one ν(NO) band, the dinitrosyls of both $\{Mo(NO)_2\}^4$ and $\{Mo(NO)_2\}^6$ by two bands. Complex (3) also has a Mo–S(dithiocarbamate) vibration at 370 cm^{-1}.[24b] All the compounds show a feeble temperature-independent paramagnetism (t.i.p) (Table 2) which has been confirmed in complexes (1a), (5), and (10) by measurement of the susceptibility at liquid-nitrogen temperature, where the room-temperature values are seen to be retained. The $\{Mo(NO)\}^4$ systems should naturally exhibit t.i.p.[25] but in the $\{Mo(NO)_2\}^6$ cases possibly a second-order spin–orbit interaction occurs due to the low symmetry of the molecules and a reasonably high spin–orbit coupling constant of molybdenum.[26]

Conclusions

The course of the reductive nitrosylation reaction of MoO_4^{2-} using NH_2OH and NCS^- ion is extremely pH sensitive. While reductive mononitrosylation, affording products such as $[Mo(NO)(NH_2O)(NCS)_2(L{-}L)]$, gives a mixture of isomeric species, of which the *trans* is predominant, the reductive dinitrosylation leading to $[Mo(NO)_2(NHO)(NCS)_2(L{-}L)]$ or $[Mo(NO)_2(NCS)_2(L{-}L)]$ is rather stereoselective, *trans*- and *cis*-NCS geometries respectively being favoured. The reactivity of the complexes is due to the activated NH_2O^- or $=N(OH)^{2-}$ groups; the $\{Mo(NO)_2\}^6$ species is the least reactive.

Experimental

Materials and Methods.—All reagents required for compound preparation were of analytical grade. The analytical grade solvents used for physicochemical studies were further purified by literature methods [27] before use. Infrared spectra were recorded for KBr pellets (or hexachlorobutadiene mulls in the range 4 000—2 800 cm^{-1}) on a Perkin-Elmer 597 spectrophotometer and were calibrated with polystyrene. The ^{1}H n.m.r. spectra were obtained on a Varian EM-390 (90 MHz) spectrometer, electronic spectra on a Pye-Unicam SP8-150 UV-VIS spectrophotometer (800—200 nm). All the pH measurements were made with an E.C. (India) digital pH meter (model 5651). A Knauer vapour-pressure osmometer was used for the molecular-weight determination and the solution conductances were measured with a Wayne Kerr B331 Autobalance Precision Bridge. The magnetic susceptibilities were obtained by the Faraday method with the help of a Bruker BSU 10 instrument equipped with BE 10 electromagnets and a Sartorius 4411 electronic microbalance. The melting points (decomposition) reported are all uncorrected and were measured using a Sunvic apparatus. The elements C, H, and N were analysed microanalytically and Mo, S, and P by standard methods.[28] Unless otherwise stated, all the complexes were dried *in vacuo* over fused $CaCl_2$.

Preparation of the Complexes.—[Mo(NO)(NH_2O)$(NCS)_2$(L–L)] (1a)—(1c) *and* (2a)—(2c). To an aqueous solution (25 cm^3) of $Na_2[MoO_4]\cdot 2H_2O$ (1 g, 4 mmol) were added NH_4NCS (3 g, 40 mmol) and $NH_2OH\cdot HCl$ (4.2 g, 60 mmol) and the resulting solution (pH *ca.* 4) was boiled for 5 min. The yellow-orange precipitate formed initially dissolved to give a yellow solution. The solution was filtered whilst hot to remove precipitated sulphur (if any) and to this (solution A) was added a hot aqueous solution (40 cm^3) of L–L (0.935 g, 6 mmol for bipy; 1.2 g, 6 mmol for phen) giving an orange-yellow precipitate. The mixture was cooled to room temperature (*ca.* 25 °C) and stirred for 45 min. The orange-yellow solid was filtered off, washed with water, ethanol, and diethyl ether and dried *in vacuo*. The dried mass was extracted with acetonitrile when a rose-red residue (yellow in the case of phen) was obtained [compounds (1c) and (2c)] which was washed with ethanol and ether and dried *in vacuo*. The acetonitrile extract was evaporated and the orange residue obtained was again extracted with CH_2Cl_2. The CH_2Cl_2-soluble part was evaporated to a yellow solid [compounds (1b) and (2b)]. The CH_2Cl_2-insoluble part was dissolved in CH_3NO_2 and then precipitated with ether, filtered off, washed with ether, and dried *in vacuo* [compounds (1a) and (2a)]. Yields: (1a), 1.1 g (62%); (1b), 0.35 g (20%); (1c), 0.035 g (2%); (2a), 1.2 g (63%); (2b), 0.36 g (19%); and (2c), 0.038 g (2%).

[Mo(NO)(NH_2O)$(S_2CNEt_2)_2$] (3). Solution A was cooled to *ca.* 20 °C and an aqueous solution (75 cm^3) of $Na[S_2CNEt_2]\cdot 3H_2O$ (2.3 g, 10 mmol) was added dropwise with constant stirring for 30 min. A yellow precipitate was filtered off, washed thoroughly with water, and dried *in vacuo* over P_4O_{10}. The crude product was crystallised from acetonitrile. Yield 1.5 g (80%).

$[PPh_4]_2[Mo(NO)(NH_2O)(NCS)_4]$ (4). Solution A was cooled to room temperature and an aqueous solution (75 cm^3) of PPh_4Cl (3.8 g, 10 mmol) was added dropwise with stirring giving a yellow precipitate. The mixture was stirred for *ca.* 2.5 h at 50 °C and then the solid was filtered off, washed with 80% ethanol (to remove PPh_4SCN) and ether, and dried. The dry product was crystallised from acetonitrile–diethyl ether (1 : 3) to give a golden yellow solid. Yield 3.8 g (86%).

[Mo$(NO)_2$(NHO)$(NCS)_2$(L–L)] (5) *and* (6). To an aqueous solution (25 cm^3) of $Na_2[MoO_4]\cdot 2H_2O$ (1 g, 4 mmol) were added NH_4NCS (3 g, 40 mmol) and $NH_2OH\cdot HCl$ (4.2 g, 60 mmol) and the resulting mixture was warmed to 50 °C when a clear orange solution was obtained (pH *ca.* 4). The solution was cooled to room temperature, the pH raised to 5.2—5.4 using 5% NaOH solution, then boiled for 4 h with the addition of water from time to time so as to keep the total volume *ca.* 25 cm^3. The greenish yellow solution was cooled to room temperature, filtered, and the pH readjusted to 5.2—5.4. This solution (solution B) was added to a L–L solution (0.935 g, 6 mmol for bipy; 1.2 g, 6 mmol for phen; in 50 cm^3 hot water, pH being adjusted to 5.2—5.4) and then stirred for 1 h. The yellow-orange precipitate formed was filtered off, washed with water, ethanol, and ether, and dried. The crude product was crystallised from acetonitrile–diethyl ether (1 : 3). Yields: compound (5), 1.6 g (83%); (6), 1.6 g (82%).

$[PPh_4]_2[Mo(NO)_2(NHO)(NCS)_4]$ (7). To solution B was added dropwise an aqueous solution (75 cm^3) of PPh_4Cl (pH 5—5.2; 3.8 g, 10 mmol) and the yellow precipitate formed was stirred for 2.5 h at 50 °C. It was then filtered off, washed with water, ethanol, and ether, and recrystallised from acetonitrile–diethyl ether (1 : 3). Yield 3.6 g (80%).

[Mo$(NO)_2(NCS)_2$(L–L)] (8) *and* (9). To an aqueous solution (25 cm^3) of $Na_2[MoO_4]\cdot 2\ H_2O$ (1 g, 4 mmol) were added NH_4NCS (3 g, 40 mmol) and $NH_2OH\cdot HCl$ (4.2 g, 60 mmol) and the resulting mixture was warmed to 50 °C to give a clear orange solution (pH *ca.* 4). This was cooled to room temperature, the pH raised to 5.7—6 with 5% NaOH solution, and then boiled for 2 h when a bluish green solution was obtained. The solution was cooled to room temperature and the pH readjusted to 5.7—6 using 5% NaOH solution. This solution (solution C) was added to a solution of phen (1.2 g, 6 mmol; in 50 cm^3 hot water, pH adjusted to 5.7—6 using 2 mol dm^{-3} HCl) when a blue-green precipitate appeared. The mixture was stirred for 30 min, filtered (pH of the filtrate *ca.* 3.5), and the solid washed with water, ethanol, and ether and dried *in vacuo*. The product (greenish brown) was stirred with acetonitrile and the acetonitrile solution then filtered. The yellowish brown filtrate was evaporated to yellow-brown crystals of compound (9), yield 0.56 g (30%). The bluish green residue was washed with methanol and ether and dried. Yield 1.8 g (60%) (Found: Mo, 26.8; N, 11.2; S, 8.5. $C_{26}H_{16}Mo_2N_6O_4S_2$ requires Mo, 26.3; N, 11.5; S, 8.7%); for spectroscopic characterisation see Results and Discussion section. Compound (8) (the bipy complex) was precipitated as a yellow-brown solid which was stirred for 30 min and then filtered off. It was extracted with acetonitrile and the extract on evaporation gave yellow-brown crystals, yield 0.55 g (31%), leaving a very small amount of the bluish green product. The filtrate was dark bluish green (pH *ca.* 5.6). The pH of the filtrate was reduced to 3 when immediately a bluish green precipitate appeared which was filtered off, washed with methanol and ether, and dried *in vacuo*. Both the bluish green products were identical (i.r. spectra). Combined yield 1.7 g (61%) (Found: Mo, 28.7; N, 12.0; S, 8.9. $C_{22}H_{16}Mo_2N_6O_4S_2$ requires Mo, 28.1; N, 12.3; S, 9.3%).

$[PPh_4]_2[Mo(NO)_2(NCS)_4]$ (10). To solution C was added dropwise a solution of PPh_4Cl (3.8 g, 10 mmol; in 75 cm^3 of water, pH adjusted to 5.7—6). An yellowish green precipitate appeared and the mixture was then stirred for 2.5 h. The solid was filtered off, washed with water, ethanol, and ether, and dried. The product was stirred with acetonitrile and the acetonitrile solution filtered. The yellow filtrate was evaporated and the solid thus obtained was redissolved in acetone and precipitated with ether as an orange-yellow solid. This was filtered off, washed with ethanol and ether, and dried. Yield 1.3 g (30%). The residue left after the acetonitrile extraction was blue-green in colour, yield 4.9 g (60%) (Found: Mo, 10.3; N, 4.0; P, 6.7; S, 9.6. $C_{102}H_{80}Mo_2N_6O_4P_4S_6$ requires Mo, 9.8; N, 4.3; P, 6.3; S, 9.8%).

Acknowledgements

We convey our grateful thanks to the Alexander von Humboldt Foundation for donating (to R. G. B.) the infrared spectrophotometer used, and to the U.G.C. (New Delhi) for financial support. We also thank Drs. A. A. Bhattacharyya and J. C. Bricker of Ohio State University, Columbus, Ohio, for carrying out the mass spectrometric experiment.

References

1 W. Hieber, R. Nast, and G. Gehring, *Z. Anorg. Allg. Chem.*, 1948, **169**, 256.

2 R. Colton, R. D. Peacock, and G. Wilkinson, *J. Chem. Soc.*, 1960, 1374.

3 K. G. Caulton, *Coord. Chem. Rev.*, 1975, **14**, 317.

4 S. Sarkar and A. Müller, *Z. Naturforsch., Teil B*, 1978, **33**, 1053.

5 R. G. Bhattacharyya, G. P. Bhattacharjee, and P. S. Roy, *Inorg. Chim. Acta*, 1981, **54**, L263.

6 (*a*) R. G. Bhattacharyya and P. S. Roy, *J. Coord. Chem.*, 1982, **12**, 129; (*b*) *Transition Met. Chem.*, 1982, **7**, 285.

7 A. Müller, N. Mohan, S. Sarkar, and W. Eltzner, *Inorg. Chim. Acta*, 1981, **55**, L33 and refs. therein.

8 A. Müller, S. Sarkar, N. Mohan, and R. G. Bhattacharyya, *Inorg. Chim. Acta*, 1980, **45**, L245.

9 (*a*) F. A. Cotton and B. F. G. Johnson, *Inorg. Chem.*, 1964, **3**, 1609; (*b*) B. F. G. Johnson, *J. Chem. Soc. A*, 1967, 475; (*c*) B. F. G. Johnson, K. H. Al-obaidi, and J. A. McCleverty, *ibid.*, 1969, 1688; (*d*) M. Green and S. H. Taylor, *J. Chem. Soc., Dalton Trans.*, 1972, 2629.

10 F. Canziani, U. Sartorella, and F. Cariati, *Ann. Chim. (Rome)*, 1964, **54**, 1354; M. W. Anker, R. Colton, and I. B. Tomkins, *Aust. J. Chem.*, 1968, **21**, 1149.

11 L. Bencze, J. Kohan, B. Mohai, and L. Marko, *J. Organomet. Chem.*, 1974, **70**, 421.

12 S. Sarkar and P. Subramanian, *Inorg. Chim. Acta*, 1979, **35**, L357.

13 A. G. Sharpe, 'The Chemistry of Cyano Complexes of the Transition Metals,' Academic Press, London, 1976; F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Wiley-Interscience, New York, 1972.

14 J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, 1974, **13**, 339.

15 S. Sarkar, R. Sabharwal, and R. C. Maurya, *Acta Ciencia Indica*, 1978, **4**, 111.

16 K. Weighardt, W. Holzbach, J. Weiss, B. Nuber, and B. Prinker, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 548.

17 K. Weighardt and W. Holzbach, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 549.

18 B. N. Figgis, 'Introduction to Ligand Fields,' Wiley, New York, 1966.

19 A. Müller, U. Seyer, and W. Eltzner, *Inorg. Chim. Acta*, 1979, **32**, L65.

20 J. D. Birchall, T. D. O'Donoghue, and J. R. Wood, *Inorg. Chim. Acta*, 1979, **37**, L461.

21 W. E. Newton, J. L. Corbin, and J. W. McDonald, *J. Chem. Soc., Dalton Trans.*, 1974, 1044.

22 R. M. Wing and K. P. Callahan, *Inorg. Chem.*, 1969, **8**, 2303.

23 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.

24 (*a*) K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds,' Wiley-Interscience, New York, 1978; (*b*) A. Müller, R. G. Bhattacharyya, N. Mohan, and B. Pfefferkorn, *Z. Anorg. Allg. Chem.*, 1979, **454**, 118.

25 R. W. Adams, J. Chatt, N. E. Hooper, and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1974, 1074.

26 E. A. Boudreaux and L. N. Mulay, 'Theory and Applications of Molecular Paramagnetism,' Wiley-Interscience, New York, 1976.

27 D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, 'Purification of Laboratory Chemicals,' Pergamon, New York, 1966.

28 A. I. Vogel, 'A Text Book of Quantitative Inorganic Analysis,' The English Language Book Society and Longmans, London, 1968.

Received 14*th May* 1982; *Paper* 2/794