Thermal and Thermally assisted Photochemical Conversion of $[Mo(NO)]^{3+}$ to $[Mo(NO)]^{2+}$ in a Ketonic Solvent: Single-step Synthesis of Nitrosyl(thiocyanato)molybdenum(I) Derivatives from $[Mo(NO)(NH_2O)(NCS)_2(L\text{-}L)]$ (L–L = 2,2′-Bipyridine or 1,10-Phenanthroline)

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$[Mo(NO)(NH_2O)(NCS)_2(phen)]$ (phen = 1,10-phenanthroline) on refluxing in acetophenone or on photolysis at 80 °C affords five-co-ordinated paramagnetic and e.s.r. sensitive $[Mo(NO)]^{2+}$ species, $[Mo(NO)(NCS)_2(phen)]$, the products obtained by the two different routes being isomeric. The i.r. and u.v.–visible spectral data suggest that while the former route affords a trigonal bipyramidal geometry, the latter affords a square pyramidal product. The 2,2′-bipyridine (bipy) analogue on identical photolysis reaction gives the corresponding square pyramidal product like the phen complex, but on reflux with acetophenone it probably forms $[Mo_2(NCS)_4(bipy)_2]$.

Direct conversion of $[MoO_4]^{2-}$ to the nitrosyl derivatives containing the species $[Mo(NO)]^{2+}$ is still unknown although in the case of $[CrO_4]^{2-}$ the analogous conversion is quite facile.[1] We have shown [2,3] that the products of reductive nitrosylation of $[MoO_4]^{2-}$ using NH_2OH and NCS^- are extremely pH dependent; $[Mo(NO)]^{3+}$, $[Mo(NO)_2]^{4+}$, or $[Mo(NO)_2]^{2+}$ species are produced but the process never yields $[Mo(NO)]^{2+}$. Complexes containing formally Mo^{I} species are relatively few,[4] still fewer being the nitrosyl complexes.[4–7] Examples are $[Mo(NO)Cl_4(H_2O)]^{2-}$ and $[Mo(NO)(CN)_5]^{3-}$ (ref. 5), $[Mo(NCO)L(S_2CNEt_2)(NO)]$ (L = Me_2SO, NH_3, or pyridine),[6] and $[Mo(NO)(MeCN)_5]^{2+}$ and $[MoCl(NO)(dppe)_2]^+$ [dppe = 1,2-bis(diphenylphosphino)ethane],[7] which have been shown to contain the discrete $[Mo(NO)]^{2+}$ moiety. These are prepared either by oxidation of the zerovalent carbonyl or nitrosyl derivatives or by chemical reduction of formally Mo^{II} complexes. Herein we describe the photolysis (80 °C) of acetophenone solutions of the diamagnetic compounds $[Mo(NO)(NH_2O)(NCS)_2(L\text{-}L)]$ † [L–L = 2,2-bipyridyl, bipy (1a) or 1,10-phenanthroline, phen (1b)] containing the $[Mo(NO)]^{3+}$ moiety [3] to yield $[Mo(NO)]^{2+}$ species, namely the hitherto unknown paramagnetic products $[Mo(NO)(NCS)_2(L\text{-}L)]$ (2a) and (2b). When (1b) is heated under reflux in the same solvent, an isomer of (2b), compound (3), is produced; (1a) gives under identical conditions a dimeric product, $[Mo_2(NCS)_4(bipy)_2]$, originally reported by Nimry and Walton,[8] being obtained essentially from $[Mo_2Cl_8]^{4-}$.

Results and Discussion

Müller *et al.*[9] have shown that $[Mo(NO)(NH_2O)(NCS)_4]^{2-}$ 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 [10] that this type of oximation with acetone of the co-ordinated $^-ONH_2$ group is a general reaction and the L–L derivatives, namely compound (1) on being refluxed with acetone also form complexes containing the analogous oximato-group (analytical, i.r., and ^1H n.m.r. data).[2,10] However, if the diamagnetic complex (1b) is refluxed for 3—4 h in acetophenone, a formally Mo^{I} species (assuming NO^+ formalism [11]), $[Mo(NO)(NCS)_2(phen)]$ (3), is produced which is paramagnetic and e.s.r. sensitive (Table). On the other hand if acetophenone solutions of (1a) and (1b) are photolysed using a tungsten lamp (100 W) without eliminating its heating effect it is also converted to the paramagnetic and e.s.r.-sensitive compounds (2a) and (2b). From the analytical data, and i.r. and electronic spectra (Table) it is quite clear that (2b) and (3) are isomeric and differ in the position of both ν(NO) (rather drastically) and ν(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 compounds are non-electrolytes (Λ_M measurement) and monomeric in MeCN. The i.r. data suggest that the NCS^- ligands are *N*-bonded in all complexes.[12] Since for the thermally obtained complex (3) ν(NO) occurs at a substantially lower wavenumber than that for the photolysis products (2a) and (2b) probably it has a trigonal bipyramidal (t.b.p.) geometry with (2a) and (2b) having a square pyramidal (s.p.) configuration with the *trans* position of the NO ligand vacant. It is worth mentioning here that (2a) and (2b) 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) have been obtained from the zerovalent *trans*-$[Mo(N_2)(dppe)_2]$ by photo-oxidation in the presence of CH_3X [4b] and Johnson *et al.*[13] reported a photo-oxidation reaction of a $[Mo(NO)_2]^{2+}$ to $[Mo(NO)]^{3+}$ by u.v. 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-ordinated species (1) containing a *N*,*O*-bonded hydroxylamido-ligand in the equatorial plane (*i.e.* the molecule possesses a pentagonal equatorial plane) [9] eliminates this ligand possibly *via* a transient oximation stage in refluxing acetophenone and produces a t.b.p. species, *i.e. via* a retention of configuration of the residual fragments: two of the equatorial co-ordination positions simply became free resulting in a trigonal equatorial

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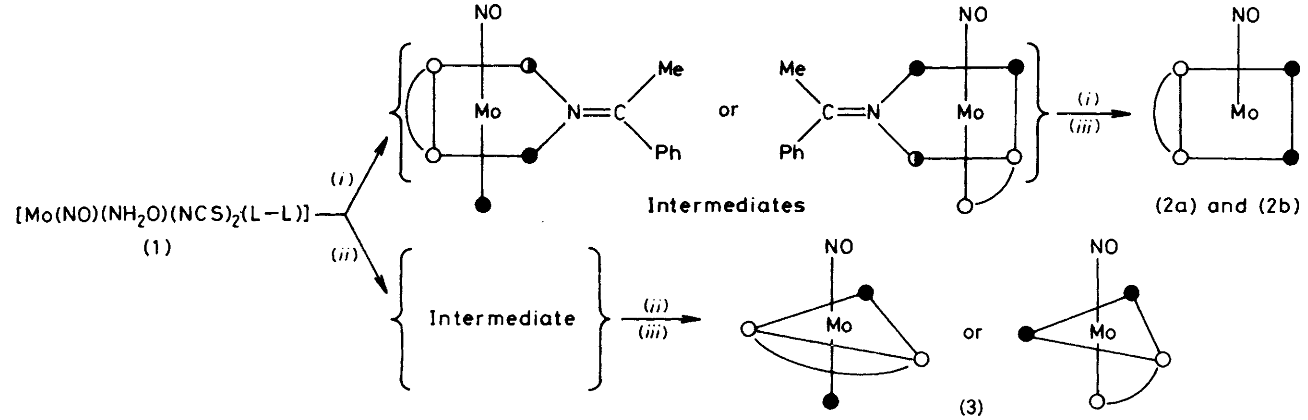
† Either the isomeric mixture or the pure orange isomer (see ref. 2) can be used without any change in the nature and amount of the products obtained.

Table. Magnetic and spectral data for the complexes

Complex	Selected i.r. data (cm^{-1})[a]			Electronic absorption ($10^{-3}\nu/cm^{-1}$)[b]	$\mu_{eff.}$ (B.M.)[c]	$\langle g_{av.} \rangle$[d]
	ν(CN)	ν(NO)	ν(M–NO)			
(2a) $[Mo(NO)(NCS)_2(bipy)]$	2 065s	1 678s	585w	21.3 (120) 26.0 (270)	2.1	1.99
(2b) $[Mo(NO)(NCS)_2(phen)]$	2 065s	1 665s	610w	21.7 (150) 25.6 (245) 31.3 (950)	1.8	1.99
(3) $[Mo(NO)(NCS)_2(phen)]$	2 055s	1 600s	585w	25.6 (250) 30.7 (1 510)	1.9	1.97
(4) $[Mo_2(NCS)_4(bipy)_2]$	2 055s	—	—	16.1 (540) 20.9 (sh) 26.7 (sh)	*e*	—
$[Mo_2(NCS)_4(bipy)_2]$[f]	2 090s 2 060s	—	—	15.3 17.7 (sh) 23.5 (sh)	*e*	—

[a] ν(CS) and δ(NCS) vibrations for all complexes at *ca.* 750 and 480 cm^{-1} respectively. See ref. 12 for assignments of i.r. bands. [b] Values of $\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ are given in parentheses. Intraligand transitions are not listed. [c] At 298 K; 1 B.M. = 9.274×10^{-24} J T^{-1}. [d] From the e.s.r. spectra of the polycrystalline samples. [e] Diamagnetic. [f] See ref. 8.



Scheme. See ref. 2 for structure of isomers of (1). (*i*) Photolysed in acetophenone at 80 °C; (*ii*) heated in acetophenone under reflux; (*iii*) elimination of Ph–C(Me)=NOH (water molecules formed during oximation may be used). (○) bipy or phen nitrogen; (●) thiocyanate nitrogen; (◑) oxygen

plane. However, the thermally assisted photochemical process affording an s.p. product possibly proceeds *via* a migration of a thiocyanato or L–L nitrogen atom from the apical to a basal plane during the elimination of the hydroxyliminoacetophenone ligand (Scheme).

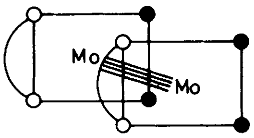
The transition around 21 500 cm^{-1} in (2a) and (2b) could be $b_2 \longrightarrow e$ (π^* NO) for an s.p. species[5] and a band at this position is absent in the supposed t.b.p. product (3). The e.s.r. spectra (88 K) of the photochemically obtained s.p. complexes (2a) and (2b) (Table) show molybdenum hyperfine splitting without any ligand 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%) and ^{97}Mo (9.5%, $I = \frac{5}{2}$) [$\langle A_{Mo} \rangle$ in (2a) is *ca.* 40—50 G, but that in (2b), is *ca.* 20 G; see ref. 7]. The thermally reduced t.b.p. product (3) shows a typical orthorhombic type of splitting with $g_{xx} = 1.99$, $g_{yy} = 1.97$ (intense line), and $g_{zz} = 1.93$, with no molybdenum or ligand hyperfine structure.

Another interesting feature is that the compound (1a) on refluxing in acetophenone gave a deep greenish brown product, which is crystallisable from acetonitrile–diethyl ether (1 : 3) and contains no nitrosyl group. Its analytical and molecular-weight data suggest it to be $[Mo_2(NCS)_4(bipy)_2]$ (4) which is diamagnetic and therefore may contain a quadruple Mo–Mo bond. Its novel feature (compared to the nitrosyl complexes described above) is a reasonably intense band at 16 100 cm^{-1} (Table), a region where δ–δ* transitions do occur.[8]

The solubility, spectral characteristics, and colour of the compound of identical composition reported by Nimry and Walton[8] are different from those of (4), however (Table). While (4) contains a single and symmetrical ν(CN) band the product of Nimry and Walton[8] has a double absorption in this region. We suggest that compound (4) has structure II or III; Nimry and Walton's compound[8] may possess structure I. [The i.r. data (Table) indicate that in this complex also the NCS^- ligands are *N*-bonded.[12]] Crystals of (4) suitable for *X*-ray diffraction have not been prepared as yet.

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[14] before use. Infrared spectra were recorded for KBr pellets on a Perkin-Elmer 597 spectrophotometer and were calibrated with polystyrene. Electronic



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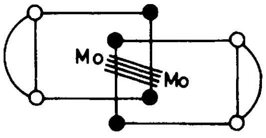

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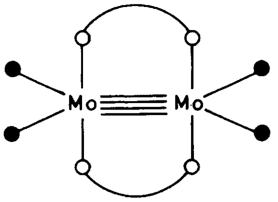

III

(O) bipy nitrogen

(●) thiocyanate nitrogen

spectra were obtained on a Pye-Unicam SP8-150 spectrophotometer (800—200 nm). A Knauer vapour-pressure osmometer was used for the molecular weight determination. The magnetic susceptibilities were obtained by the Faraday method using a vibrating-sample Magnetometer model 155. A Varian E-112 EPR spectrometer in the *X*-band at 9.3 GHz was used for recording the e.s.r. spectra. 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 and S by standard methods.[15] All the complexes were dried *in vacuo* over fused $CaCl_2$.

Preparation of the Complexes.—$[Mo(NO)(NCS)_2(L^-L)]$ (2a) *and* (2b). $[Mo(NO)(NH_2O)(NCS)_2(L^-L)]$ [1 g, 2.3 mmol for (2a) and 2.2 mmol for (2b)] was dissolved in acetophenone (50 cm^3). The resulting orange-yellow solution was photolysed using a 100-W tungsten filament lamp for 6 h when the temperature of the solution rose to 80 °C. The green solution so obtained was cooled to room temperature, filtered from any undissolved particles and then to this clear filtrate diethyl ether (60—70 cm^3) was added and the resulting slightly turbid solution was kept at 0 °C for 15 h. Compound (2a) separates as a red-brown solid and (2b) as green crystals. Each of the products was extracted in MeCN and crystallised by adding ether (MeCN : Et_2O = 1 : 3). These were filtered off, washed thoroughly with ethanol and ether and dried *in vacuo*. Yields, (2a) 0.28 g (30%), (2b) 0.35 g (38%); m.p. 170—175 °C (decomp.) for (2a) and 162—166 °C (decomp.) for (2b) [Found: C, 36.6; H, 1.8; Mo, 24.4; N, 17.2; S, 15.8%; *M*, 450. $C_{12}H_8MoN_5OS_2$ (2a) requires C, 36.2; H, 2.0; Mo, 24.1; N, 17.6; S, 16.1%; *M*, 398] [Found: C, 40.1; H, 1.7; Mo, 23; N, 16.3; S, 14.7%; *M*, 460. $C_{14}H_8MoN_5OS_2$ (2b) requires C, 39.8; H, 1.9; Mo, 22.7; N, 16.6; S, 15.2%; *M*, 422].

$[Mo(NO)(NCS)_2(phen)]$ (3). $[Mo(NO)(NH_2O)(NCS)_2(phen)]$ (1 g, 2.2 mmol) was dissolved in acetophenone (40 cm^3) and the yellow-orange solution was refluxed for 4 h when the solution became deep green. The solution was then cooled to room temperature, filtered from any undissolved solid and to the filtrate ether (70 cm^3) was added and the slightly turbid solution kept at 0 °C for 15 h. The separated solid was filtered off, washed with ethanol and then ether, and dried *in vacuo*. The compound was further crystallised from acetonitrile–ether (1 : 3) giving deep brown-black crystals. Yield 0.6 g (64%), m.p. 275—280 °C (decomp.) (Found: C, 40.0; H, 2.1; Mo, 23.2; N, 16.2; S, 14.6%; *M*, 424. $C_{14}H_8MoN_5OS_2$ requires C, 39.8; H, 1.9; Mo, 22.7; N, 16.6; S, 15.2%; *M*, 422).

$[Mo_2(NCS)_4(bipy)_2]$ (4). A method similar to that above was followed using the bipy analogue. The compound was crystallised from acetonitrile–ether (1 : 3). Yield 0.7 g (41%) (Found: Mo, 26.9; N, 14.4; S, 16.8%; *M*, 725. $C_{24}H_{16}Mo_2N_8S_4$ requires Mo, 26.1; N, 15.2; S, 17.4%; *M*, 736). The compound is soluble in acetone, acetonitrile, nitromethane and tetrahydrofuran and very moderately in chloroform but insoluble in benzene, diethyl ether, pentane, and light petroleum.

Acknowledgements

We thank the Alexander von Humboldt Foundation for donating the i.r. spectrophotometer used in this work. Our sincere thanks are due to Professor F. A. Cotton (Texas A and M University) for his interest and suggestions, and to Dr. M. Chavan of Ohio State University for the e.s.r. spectra. We also thank U.G.C. (New Delhi) for financial assistance.

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Received 21*st June* 1983; *Paper* 3/1052