Synthesis, magnetic and spectral studies of some mixed-ligand nitrosyl complexes of \{MoNO\}^4^4 electron configuration involving potentially mono-, bi- and tri-dentate heterocyclic donors

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Mixed-ligand cyanonitrosyl complexes of Mo(II) of the type [Mo(NO)(CN)J(L)2], formed by the interaction of pentacyanonitrosomolybdate(II) anion with some pyridine derivatives (L), viz., nicotinamide, nicotinic acid hydrazide, isonicotinic acid hydrazide, 2-benzoylpyridine, nicotine and 2-hydroxy methylpyridine have been prepared, and the products characterized by elemental analyses, molar conductances, magnetic measurements, electronic and infrared spectral studies. The IR spectral studies suggest that all the heterocyclic compounds behave as monodentate ligands coordinating through the ring nitrogen. Molybdenum(II) has a low-spin \{MoNO\}^4 electron configuration in these diamagnetic complexes which behave as non-electrolytes. Suitable octahedral structures have been proposed for these complexes.

A perusal of the literature of mixed-ligand cyanonitrosyl complexes of molybdenum(II) of \{MoNO\}^4^4 electron configuration reveals only one report by Bhattacharyya et al.\(^1\) In this report, the investigators have reported the synthesis of [Mo(NO)(CN)J3^3 anion in solution by the interaction of Na2MoO4.2H2O, KCN and NH2OH.HCl in aqueous medium at pH 8. They were able to isolate only two compounds, [Mo(NO)(CN)J3(bipy)]H2O and [Mo(NO)(CN)J3(phen)]H2O, when hot aqueous solution of bipyridyl (bipy) or o-phenanthrolin (phen) was reacted with the resulting solution of [Mo(NO)(CN)J3^3 anion.

In continuation of our interest in the synthesis and characterization some novel mixed-ligand cyanonitrosyl complexes of transition metals in unusual oxidation states, and following the earlier reports\(^3\) of partial replacement of the cyano groups in appropriate cyanonitrosyl complexes by heterocyclic donors in aqueous-acetic acid medium, the present investigation is an extension to the report of Bhattacharyya et al.\(^1\) to the synthesis of mixed-ligand \{MoNO\}^4 cyanonitrosyl complexes of molybdenum(II) with water insoluble heterocyclic donors.

In the present investigation [Mo(NO)(CN)J3^3 anion has been prepared and reacted with some potentially mono-, bi- and tri-dentate heterocyclic donors, viz., nicotinamide (NICA), nicotinic acid hydrazide (NICA H), nicotine (NICO), 2-benzoylpyridine (BZP), isonicotinic acid hydrazide (INICA H) and 2-hydroxymethylpyridine (2-HMP) (I).

**Experimental**

Nicotinamide (Sisco Chem. Industries, Bombay), nicotinic acid hydrazide and isonicotinic acid hydrazide (Aldrich Chemicals, U.S.A), nicotine (B.D.H Chemicals, Bombay), 2-benzoylpyridine (obtained as a gift sample
from Raschig GmbH, Germany). 2-hydroxymethylpyridine (obtained as gift samples from Kawaken Fine Chemicals Co. Ltd., Japan), sodium molybdate (B.D.H. Chemicals Bombay), potassium cyanide (B.D.H. Chemicals, Bombay) and hydroxylamine hydrochloride (Wilson Lab., Bombay) were used as supplied. All other chemicals used were of AR grade. The parent anion, pentacyanonitrosylmolybdate(II) anion, [Mo(NO)(CN)₅]²⁻, was prepared by the method reported by Bhattacharyya et al.¹.

**Synthesis of mixed-ligand complexes**

To the solution of the parent anion¹, [Mo(NO)(CN)₅]²⁻, an aqueous-acetic acid solution (8 mL, 1:1) of NICA (0.505 g), NICAH (0.566 g), INICAH (0.566 g), BZP (0.757 g), NICO (0.670 g, 0.66 mL) or 2-HMP (0.451 g, 0.40 mL) was added with stirring. The resulting solution was refluxed [NICA/NICAH/BZP: 2 hr; NICO: 7 hr; INICAH: 4 hr; 2-HMP: 3 hr] when a coloured solid was precipitated. The coloured solid obtained was filtered by suction, washed with dilute acetic acid and finally with water and dried in vacuo at room temperature to a constant weight. The analytical data of the synthesized complexes are given in Table 1.

Microanalysis for carbon, hydrogen and nitrogen in the complexes was carried at C D R I, Lucknow. The molybdenum content in the synthesized complexes was determined gravimetrically as MoO₃(C₉H₇NO₃) by the standard method⁶.

### Table 1 - Analytical data, important IR spectral bands (cm⁻¹) and electronic spectral peaks of the synthesized complexes

<table>
<thead>
<tr>
<th>Sr No</th>
<th>Compound (Empirical Formula)</th>
<th>Found (calc.),%</th>
<th>v(NO) (cm⁻¹)</th>
<th>v(CN)</th>
<th>v(MoNO)</th>
<th>v(C≡N)</th>
<th>Pyridine breathing mode</th>
<th>v_CCN (cm⁻¹)</th>
<th>Band Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Mo(NO)(CN)₅(NICA₂)]</td>
<td>40.38 (40.12)</td>
<td>2.50 (2.67)</td>
<td>24.57 (24.99)</td>
<td>21.78 (21.80)</td>
<td>1651</td>
<td>2110 (2156)</td>
<td>648 (656)</td>
<td>* 1030 (1028)</td>
</tr>
<tr>
<td>2</td>
<td>[Mo(NO)(CN)₅(NICAH)₁]</td>
<td>37.28 (37.66)</td>
<td>2.53 (2.93)</td>
<td>20.65 (29.29)</td>
<td>20.52 (29.08)</td>
<td>1652</td>
<td>2156 (2164)</td>
<td>600 (610)</td>
<td>* 1035 (1028)</td>
</tr>
<tr>
<td>3</td>
<td>[Mo(NO)(CN)₅(INICAH)₁]</td>
<td>37.39 (37.66)</td>
<td>2.52 (2.93)</td>
<td>20.62 (29.29)</td>
<td>20.54 (29.08)</td>
<td>1646</td>
<td>2164 (2166)</td>
<td>610 (608)</td>
<td>* 1028 (1020)</td>
</tr>
<tr>
<td>4</td>
<td>[Mo(NO)(CN)₅(BZP)₂]</td>
<td>56.45 (56.40)</td>
<td>3.39 (3.15)</td>
<td>14.50 (14.73)</td>
<td>14.62 (14.83)</td>
<td>1640</td>
<td>2166 (2166)</td>
<td>608 (605)</td>
<td>1605 (1601)</td>
</tr>
<tr>
<td>5</td>
<td>[Mo(NO)(CN)₅(NICO)₂]</td>
<td>52.62 (52.22)</td>
<td>6.02 (5.30)</td>
<td>21.35 (21.19)</td>
<td>18.70 (18.16)</td>
<td>1652</td>
<td>2155 (2156)</td>
<td>620 (625)</td>
<td>1605 (1601)</td>
</tr>
<tr>
<td>6</td>
<td>[Mo(NO)(CN)₅(2-HMP)₁]</td>
<td>42.50 (42.63)</td>
<td>3.15 (3.31)</td>
<td>19.51 (19.89)</td>
<td>22.30 (22.73)</td>
<td>1650</td>
<td>2140 (2140)</td>
<td>649 (650)</td>
<td>1601 (1590)</td>
</tr>
</tbody>
</table>

* Merged with v(NO)¹

### Table 2 - Some physical properties of the complexes

<table>
<thead>
<tr>
<th>Sr No</th>
<th>Compound</th>
<th>yield (%)</th>
<th>Colour</th>
<th>Decom. Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Mo(NO)(CN)₅(NICA₂)]</td>
<td>58</td>
<td>Yellowish</td>
<td>&gt;260</td>
</tr>
<tr>
<td>2</td>
<td>[Mo(NO)(CN)₅(NICAH)₁]</td>
<td>59</td>
<td>Green</td>
<td>&gt;260</td>
</tr>
<tr>
<td>3</td>
<td>[Mo(NO)(CN)₅(INICAH)₁]</td>
<td>58</td>
<td>Brown</td>
<td>220</td>
</tr>
<tr>
<td>4</td>
<td>[Mo(NO)(CN)₅(BZP)₂]</td>
<td>59</td>
<td>Yellow</td>
<td>150</td>
</tr>
<tr>
<td>5</td>
<td>[Mo(NO)(CN)₅(NICO)₂]</td>
<td>55</td>
<td>Yellow</td>
<td>180</td>
</tr>
<tr>
<td>6</td>
<td>[Mo(NO)(CN)₅(2-HMP)₁]</td>
<td>60</td>
<td>Yellow</td>
<td>220</td>
</tr>
</tbody>
</table>

Conductance measurements were performed at room temperature in DMF using a Toshniwal conductivity bridge and a dip-type cell with a smooth platinum electrode. Electronic spectra of the complexes were recorded in 10⁻³ M solution in DMF on a Shimadzu model, UV-160 spectrophotometer. FT-IR spectra of the complexes were recorded in nujol mulls in the range 4000 - 400 cm⁻¹ at the University of Poona, Pune. The magnetic susceptibilities of the complexes were measured at room temperature on a Gouy balance using Hg[Co(NCS)₄]₂ as the calibrant. Decomposition temperatures of complexes were determined using an electrothermal apparatus having capacity to record temperatures up to 360°C.

### Results and discussion

The mixed-ligand complexes reported here were prepared according to the following equation
strong alkali. The resulting $\text{NO}_2^-$ then gives a pink colouration with the Griess reagent.\(^{13}\)

The molar conductances measured in $10^{-3}\text{ M DMF}$ solutions of these complexes were found to be in the range $20-25 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ indicating their non-electrolytic nature\(^{14}\).

The magnetic susceptibility measurements of these complexes indicated their diamagnetic nature and, hence, they should have a ground state with a molecular orbital configuration\(^{15}\) $(2e)^4 (1b)^9$. This result is consistent with a low-spin $[\text{MoNO}]^4$ electron configuration of molybdenum(II). The diamagnetic and non-electrolytic nature of these complexes also support the presence of $\text{NO}^-$ grouping in these complexes.

The electronic spectra of these compounds were recorded in DMF. They show three absorption peaks at 345 - 365 nm (28,985 - 27,397 cm\(^{-1}\)), 450 - 490 nm (22,222 - 20,408 cm\(^{-1}\)) and 520 - 580 nm (19,230 - 17,241 cm\(^{-1}\)) which are assigned as $2e \rightarrow b_\pi , 2e \rightarrow 3e$ and $2e \rightarrow 1b_\pi$ transitions, respectively, considering an M.O. picture applicable to hexacoordinated mononitrosyl complexes of $C_{av}$ symmetry. These assignments are comparable to the results reported elsewhere\(^{16}\). The electronic spectrum of compound 2 is given in Fig. 1.

In the IR spectra (Table 1) of these complexes, a very strong band observed at 1640-1652 cm\(^{-1}\), a strong band observed at 2110-2166 cm\(^{-1}\), and a weak band observed at 600-649 cm\(^{-1}\) are assigned to $v(\text{NO})^+$, $v(\text{CN})$ and $v(\text{MoNO})$, respectively. These assignments are in accordance with the reported results of Bhattacharyya\(^1\) and Maurya et al.\(^3\). The ligands NICA, NICAH and INICAH used in the present study contain three potential donor sites: (i) the pyridine ring nitrogen, (ii) the amide oxygen and (iii) the hydrazine nitrogen in case of NICA and INICAH or amide nitrogen in case of NICA.

The ligands BZP has two potential donor sites: (i) the pyridine ring nitrogen, (ii) the carbonyl group oxygen, while the remaining ligands NICO and 2-HMP contain only the ring nitrogen as the donor site.

**Complexes of NICAH and INICAH**

These ligands show amide-I band, $v(\text{CO})$, around 1660 cm\(^{-1}\) and $v(\text{N-H})$ symmetric and asymmetric modes at 3200-3250 cm\(^{-1}\) and 3300-3350 cm\(^{-1}\), respectively. These remain almost unchanged after complexation, thus indicating that neither the amide oxygen nor the hydrazine nitrogen participate in coordination. The pyridine ring $v(\text{C}=\text{N})$ appearing around 1580 cm\(^{-1}\) in the free ligands, undergoes a significant shift to higher
wave numbers in their complexes. However, they seem to be merged with the broad \( v(\text{NO})^+ \) peaks in the respective complexes. Another characteristic mode, for ring nitrogen coordination, the pyridine ring breathing mode, appears at 1028-1030 cm\(^{-1}\) in these complexes\(^{17}\).

**NICA complex**

The significant IR absorption modes of the amide group, namely, \( v(\text{NH}) \), \( v(\text{C}=\text{O}) \) and \( v(\text{C}-\text{N}) \), remain almost unchanged in its complex, suggesting that the amide oxygen is not bonded to molybdenum. However, the pyridine ring breathing mode occurring at 995 cm\(^{-1}\) in free ligand undergoes a significant shift to higher wave number in its complex (see Table 1). The other characteristic band, \( v(\text{C}=\text{N}) \) for ring nitrogen coordination, which should appear above 1600 cm\(^{-1}\), seems to be merged with the broad \( v(\text{NO})^+ \) peak\(^{18,19}\).

**Complex of BZP**

The \( v(\text{C}=\text{O}) \) mode in BZP appears at 1654 cm\(^{-1}\) which remains almost unchanged in the spectrum of the complex, and seems to be merged with the broad \( v(\text{NO})^+ \) peak. This excluded any possibility of carbonyl group oxygen coordination to molybdenum. The coordination of ring nitrogen of this ligand towards molybdenum was inferred from the appearance of one band at 1605 cm\(^{-1}\) due to \( v(\text{C}=\text{N}) \) and other at 1030 cm\(^{-1}\), due to pyridine ring breathing mode\(^{18,19}\).

**Complexes of NICO and 2-HMP**

The two characteristic bands, the pyridine ring \( v(\text{C}=\text{N}) \) and the ring breathing mode appearing at 1603-1605 and 1030-1045 cm\(^{-1}\), respectively, in the complexes of these ligands, suggest the coordination of the pyridine ring nitrogen to molybdenum\(^{18,19}\).

The experimental results presented above suggest that the complexes are of the type \([\text{Mo(NO)(CN)}]_2(\text{L}_2)\), where \( \text{L} = \text{NICA, NICAH, INICAH, BZP, NICO or 2-HMP} \). An octahedral structure (II), is proposed for these complexes.

**References**