A single step synthesis of some cyanonitrosyl \([\text{CrNO}]^5\) complexes of chromium(I) involving multi-functional ligands directly from chromate(VI) in aqueous-aerobic medium

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Received 22 December 1998; revised 30 November 1999

Novel mixed-ligand cyanonitrosyl complexes of chromium(I), formed by interaction of tetracyanonitrosylchromate(I) anion, \([\text{Cr(NO)}(\text{CN})_4]^2^-\) with 8-hydroxyquinoline (8-HQ), benzothiazole (BZT), imidazole(IDL), methyl benzothiazole (MBZT) and pheniramine maleate (PHM) are described. The resulting mixed-ligand complexes, which have been characterized by elemental analyses, molar conductances, magnetic measurements, electron spin resonance, infrared and electronic spectral studies, have the compositions \([\text{Cr(NO)}(\text{CN})_2(L-\text{L})(\text{H}_2\text{O})_n]\), where \(L=\text{BZT}, \text{MBZT}\) or IDL and \([\text{Cr(NO)}(\text{CN})_4(L-\text{L})(\text{H}_2\text{O})_2]\) where \(L=L=\text{8-HQ}\) or PHM. A cis-octahedral structure has been proposed for these complexes.

Bhattacharya et al.\(^1\) have reported a single pot and virtually a single step synthesis of two mixed-ligand cyanonitrosyl complexes of composition, \([\text{Cr(NO)}(\text{CN})_2(L-\text{L})(\text{H}_2\text{O})_n]\) (where \(L=\text{dipyridyl and 1,10-phenanthroline}\)) directly from \(\text{CrO}_4^{2-}\) using hydroxylamine hydrochloride, \(\text{OH}\) and \(\text{CN}\) and the appropriate ligand. In this synthesis, they first prepared a solution of \([\text{Cr(NO)}(\text{CN})_4]^2^-\) by reductive nitrosylation of \(\text{CrO}_4^{2-}\) using \(\text{NH}_2\text{OH}\cdot\text{HCl}\) in alkaline medium in presence of potassium cyanide. The resulting solution when added to a hot aqueous solution of 2,2'-dipyridyl or 1,10-phenanthroline, gave the desired products.

Maurya et al.\(^2\) have recently reported the synthesis and characterization of several cyanonitrosyl derivatives of chromium(I), manganese(I), vanadium(I) and molybdenum(0) by the interaction of appropriate cyanonitrosyl complexes of the respective metal ion with heterocyclic nitrogen and oxygen donors, and the aromatic amines, in hot aqueous-acetic acid media. Their results show that the partial replacement of the cyan groups by the reacting ligands takes place. So, to make the process of Bhattacharya et al.\(^1\) of single pot and a single step synthesis of chromium(I) cyanonitrosyl derivatives effective for water insoluble heterocyclic bases, we have examined the ligational behaviour of some heterocyclic nitrogen donors using their 1:1 water-acetic acid solution towards tetracyanonitrosylchromate(I) obtained by Bhattacharya et al.\(^1\) as discussed above. The heterocyclic bases used in the present investigation are 8-hydroxyquinoline (8-HQ), benzothiazole (BZT), imidazole(IDL), methyl benzothiazole (MBZT) and pheniramine maleate (PHM).

Experimental

8-Hydroxyquinoline (BDH Chemicals, Bombay), pheniramine maleate(Bull Pharma Pvt. Ltd., Bombay), benzothiazole (E. Merck, India) or imidazole, 2-methylbenzothiazole (Sisco-Chem Industries, Bombay), hydroxylamine hydrochloride (Robert Johnson, Bombay), potassium cyanide (May and Baker, Bombay) and potassium chromate(BDH Co. Poole, England) were used as supplied. All other chemicals used were of analytical reagent grade.

Synthesis of the parent compound, \([\text{Cr(NO)}(\text{CN})_4]^2^-\)

The parent compound, tetracyanonitrosylchromate(I) anion, \([\text{Cr(NO)}(\text{CN})_4]^2^-\) was prepared by the method reported by Bhattacharya et al.\(^1\) as follows.

To a solution of KOH (3 g in 20 mL of H\(_2\)O) were added K\(_2\)CrO\(_4\) (0.5 g, 2.6 mol) and KCN (2.5 g, 38.6 mol) and the mixture was stirred for 5 min at \(-80^\circ\) C. To this solution, \(\text{NH}_2\text{OH}\cdot\text{HCl}\) (2.7 g, 38.6 mol) was added in small portions with constant stirring at \(-80^\circ\) C and the stirring was continued for another 45 min to get a yellowish green solution. This was cooled at room temperature and \(pH\) was adjusted to \(-5\) with 6\(M\) HCl. The resulting solution was the \([\text{Cr(NO)}(\text{CN})_4]^2^-\) (parent anion).

Synthesis of mixed-ligand complexes

To a solution of the parent anion, \([\text{Cr(NO)}(\text{CN})_4]^2^-\) obtained as above, an aqueous-acetic acid solution (5-6 mL, 1:1) of 8-HQ (0.373 g), BZT (0.695 g), MBZT (0.768 g), IDL (0.350 g) or PHM (0.917 g) was added with shaking. The resulting mixture was refluxed for 30-45 min over a hot plate at 80\(^\circ\) C. The
precipitate was filtered by suction, washed several times with dilute acetic acid, finally with water and dried in vacuo. The analytical data of the resulting complexes are given in Table 1.

The carbon, hydrogen and nitrogen contents of complexes were determined microanalytically. For the estimation of chromium as chromic oxide \( \text{Cr}_2\text{O}_3 \), the complexes were decomposed by heating with alkali followed by dissolving in nitric acid. Chromium was precipitated as chromic hydroxide by adding slight excess of dilute ammonium hydroxide solution. The chromic hydroxide \( \text{Cr(OH)}_3 \) on ignition gave \( \text{Cr}_2\text{O}_3 \). Repeated heating, cooling and weighing were continued till constant weight was obtained.

Conductance measurements were performed at room temperature in dimethylformamide 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 dimethylformamide on a Shimadzu model, UV-160 spectrophotometer. FT-IR spectra of the complexes were recorded in Nujol mulls in the range 4000-450 cm\(^{-1}\). EPR spectra of the complexes were measured at room temperature on a Bruker ESP-B-band EPR spectrometer using polycrystalline sample at the microwave frequency 9.00 GHz at R.S.I.C., L.T., Madras. The decomposition temperatures of the complexes were determined using an electrothermal apparatus.

**Results and discussion**

The complexes were prepared according to the equations

\[
\text{AcOH}, \text{H}_2\text{O} \quad [\text{Cr(NO)(CN}_4]^2+2L \xrightarrow{\text{Reflux}} \text{AcOH}, \text{H}_2\text{O}
\]

\[
[\text{Cr(NO)(CN}_2]^2+\text{L-L} \xrightarrow{\text{Reflux}} [\text{Cr(NO)(CN}_2]^2+\text{L-L}(\text{H}_2\text{O})]
\]

\[
+2\text{CH}_3\text{COO}^-+2\text{HCN}
\]

where \( L = \text{BZT, MBZT, or IDL} \).

The resulting compounds are air-stable, coloured solids (Table 2). They are thermally stable up to 250° C. They decompose in dilute acid or alkaline solutions only on heating. All the compounds are soluble in ethanol, methanol and partially soluble in hot dimethylformamide. The identification of coordinated nitrosyl group in the resulting complexes was made by a chemical method reported by Maurya.

The observed molar conductances of the resulting complexes \( 10^{-3} \) M ethanol solutions are in the range 3.5-7.2 Ohm\(^{-1}\)cm\(^2\) mol\(^{-1}\), and indicate that they are non-electrolytes. The observed magnetic moments in the range 1.77-1.82 B.M. suggest that these complexes are paramagnetic and have one unpaired electron. These values are similar to those of other reported chromium(I) complexes.

The X-band EPR spectra of compound 4 was recorded at room temperature in polycrystalline sample at the microwave frequency 9.00 GHz. Both parallel and perpendicular features of \( ^{52}\text{Cr} \) are resolved. Nuclear fine coupling is observed in \( g || \) region. The observed \( g || \) (2.08) and \( g \perp \) (2.01) values for this complex deviate considerably from the free ion value (2.0023). This positive deviation indicates that the present complex is covalent in nature. The

<table>
<thead>
<tr>
<th>S. No</th>
<th>Compounds</th>
<th>Found (Calc.) %</th>
<th>Pyridine Ring&lt;br&gt;breathing Mode/&lt;br&gt;n(C=O)</th>
<th>v(C=CrO)</th>
<th>v(CNO)</th>
<th>v(C=N)</th>
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<tbody>
<tr>
<td>1</td>
<td>[Cr(NO)(CN)_2(8-HQ)(H_2O)]</td>
<td>44.27, 3.20, 18.62, 17.65</td>
<td>v(NO) 1682, v(CN) 2158, v(C=CrO) 2115</td>
<td>641, 1111</td>
<td>Merge</td>
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</tr>
<tr>
<td>2</td>
<td>[Cr(NO)(CN)_2(BZT)(H_2O)]</td>
<td>45.32, 2.51, 16.72, 12.52</td>
<td>v(NO) 1721, v(CN) 2150, v(C=CrO) 2110</td>
<td>620, -</td>
<td>1585</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>[Cr(NO)(CN)_2(MBZT)(H_2O)]</td>
<td>48.29, 3.29, 15.68, 11.30</td>
<td>v(NO) 1710, v(CN) 2155, v(C=CrO) 2110</td>
<td>630, -</td>
<td>1590</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>[Cr(NO)(CN)_2(IDL)(H_2O)]</td>
<td>33.57, 3.20, 34.29, 18.52</td>
<td>v(NO) 1710, v(CN) 2155, v(C=CrO) 2110</td>
<td>620, -</td>
<td>1611</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>[Cr(NO)(CN)_2(8-HQ)(H_2O)]</td>
<td>51.59, 5.28, 13.62, 10.62</td>
<td>v(NO) 1700, v(CN) 2170, v(C=CrO) 2110</td>
<td>619, 1030</td>
<td></td>
<td>1660</td>
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Table 2—Some physical properties of the synthesized complexes

<table>
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<tr>
<th>S. No.</th>
<th>Compounds</th>
<th>Colour</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
<th>Yield %</th>
<th>Decomp. Temp. °C</th>
<th>$\Lambda_m$ (Ohm·cm$^2$/mol$^-$1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Cr(NO)(CN)$_2$(8-HQ)(H$_2$O)]</td>
<td>Yellow</td>
<td>1.79</td>
<td>50</td>
<td>200</td>
<td>4.2</td>
</tr>
<tr>
<td>2</td>
<td>[Cr(NO)(CN)$_2$(BZT)$_2$(H$_2$O)]</td>
<td>Brown</td>
<td>1.82</td>
<td>45</td>
<td>200</td>
<td>3.5</td>
</tr>
<tr>
<td>3</td>
<td>[Cr(NO)(CN)$_2$(MBZT)$_2$(H$_2$O)]</td>
<td>Brown</td>
<td>1.77</td>
<td>45</td>
<td>200</td>
<td>7.2</td>
</tr>
<tr>
<td>4</td>
<td>[Cr(NO)(CN)$_2$(IDL)$_2$(H$_2$O)]</td>
<td>Greenish yellow</td>
<td>1.78</td>
<td>40</td>
<td>200</td>
<td>4.1</td>
</tr>
<tr>
<td>5</td>
<td>[Cr(NO)(CN)$_2$(PHM)(H$_2$O)]</td>
<td>Yellowish brown</td>
<td>1.81</td>
<td>42</td>
<td>200</td>
<td>6.2</td>
</tr>
</tbody>
</table>

positive shifting of g values from 2.0023 in these complexes is due to mixing, via spin-orbit coupling, of the metal orbitals involved in molecular orbitals containing the unpaired electron with the filled ligand complexes.

The electronic spectrum of compound 2 was recorded in dimethylformamide. It exhibits three characteristic spectral peaks at 365, 430 and 660 nm comparable to the results reported elsewhere for chromium(I) cyanonitrosyl complexes.

The important infrared spectral bands and their probable assignments for the complexes under study are given in Table 1. The strong bands in the region 1682-1721 cm$^{-1}$ and 2150-2170 cm$^{-1}$ with a shoulder at 2110-2115 cm$^{-1}$ are assigned to v(C$=$N) and v(C-O) modes, respectively. The appearance of a weak band at 619-641 cm$^{-1}$ may be attributed to v(Cr-NO). These data are in agreement with the results reported elsewhere.

The ligand 8-HQ under study possesses two potential donor sites: (i) pyridine ring nitrogen and (ii) hydroxyl oxygen. A broad band occurring at 3350-3200 cm$^{-1}$ in 8-HQ has been assigned to v(O-H) mode. The appearance of this band in the complex suggests the non-deprotonation of the O-H group in the ligand after complexation. The significant absorption bands due to coordinated 8-HQ ligand are v(C$=$N) and v(C-O). The v(C$=$N) mode appears to be merged with v(NO) mode. However, the appearance of a strong band at 1111 cm$^{-1}$ due to v(C-O) in the spectrum of this complex suggests coordination of the ligand through hydroxyl oxygen. These results and also the nonelectrolytic nature of the complex (vide supra), which are in agreement with reported data, suggest the neutral bidentate coordination of the 8-HQ to chromium.

The ligands BZT and MBZT used in this investigation contain two potential donor sites: (i) benzothiazole-S and (ii) benzothiazole tertiary nitrogen. It is observed that (CSC) band of the two ligands occurring at approximately 700 cm$^{-1}$ is not affected appreciably in the respective complexes. This indicates that the benzothiazole-S is not taking part in coordination. However, the appearance of a band at 1585-1590 cm$^{-1}$ attributable to v(C$=$N), indicates the involvement of the benzothiazole nitrogen in bonding.$^{11}$ Further, a few bands appearing in the region 1300-1450 cm$^{-1}$ in the free ligands, were raised to higher frequencies and appeared in the region 1360-1460 cm$^{-1}$ in the complexes, which probably also suggest the involvement of tertiary nitrogen in bonding.

The ligand IDL has two potential donor sites: (i) the imidazole N-H nitrogen and (ii) the imidazole tertiary nitrogen. The v(N-H) band occurring at 3100 cm$^{-1}$ remains unchanged, in the complex, suggesting that the N-H nitrogen of the imidazole nitrogen is not taking part in coordination. However, a band appearing at 1611 cm$^{-1}$ in the present complex,
attributable to v(C=N), indicates the bonding of imidazole tertiary nitrogen to chromium in the complex.

The heterocyclic donor, PHM used in the present investigation has two potential donor sites: (i) the pyridine ring nitrogen and (ii) the amino nitrogen. The characteristic sp3 v(C-N)13 appearing at 1175 cm⁻¹ in this ligand undergoes a high-energy shift and appears at 1200 cm⁻¹ in the complex. This suggests coordination of the side chain amino nitrogen to chromium. Further, the presence ring v(C=N) and the pyridine ring breathing modes at 1660 and 1030 cm⁻¹, respectively, suggest coordination of the ring nitrogen to chromium. Thus the ligand PHM behaves as a bifunctional donor.

The satisfactory analytical data and the results of the physical studies discussed above suggest that the present complexes may be formulated as - [Cr(NO)(CN)₃(L)(H₂O)], where L= BZT, MBZT or IDL and [Cr(NO)(CN)₃(L-L')(H₂O)] where L-L' = 8-HQ or PHM. As these complexes exhibit two values of v(C=N), and one value of v(NO), cis-octahedral structures (I and II) have been proposed for these complexes.

Acknowledgement

One of the authors (RCM) is thankful to Prof. S. Sharma, Vice-Chancellor of this University, for encouragement and Prof. M. C. Agrawal, Head, Department of Chemistry, for providing laboratory facilities and helpful discussion.

References