Synthesis of some manganese(0) cyanonitrosyl derivatives containing heterocyclic nitrogen donors

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Novel mixed-ligand cyanonitrosyl complexes of Mn(0), obtained from the interaction of tetracyanonitrosylmanganate(0) anion, \([\text{Mn(NO)}_2(CN)_4]^2-\) with 2-hydroxymethylpyridine (2-HMP), 3-hydroxymethylpyridine (3-HMP), 2-aminopyridine (2-AP), 2-(2'-aminoethyl)pyridine (2-AEP), quinaldic acid (QD) and methylnicotinate (MNIC) are described. The products have the general formula \([\text{Mn(NO)}_2(CN)_4(L)]^2-\) (where \(L=\text{H}_{2}O\) or \(\text{HCl}\)). Octahedral structures have been suggested for these complexes. Mn(0) has a low-spin \([\text{Mn(NO)}_2]^2-\) electron configuration in these complexes.

Reductive nitrolylation of tetraoxometallates using hydroxylamine hydrochloride in presence of \(\text{CN}^-\) in an aqueous-alkaline medium and synthesis of the corresponding pentacyanonitrosylmanganese(II) complexes are reported in literature. Pentacyanonitrosyl manganese(II), \([\text{Mn(NO)}_2(CN)_4]^2-\), containing the \([\text{Mn(NO)}_2]^2-\) core had been reported\(^9\) to be synthesized from \(\text{K}_2[\text{Mn(CN)}_4]\) using \(\text{HNO}_2\text{HCl}\), and shown to undergo oxidation by nitric acid\(^9\) or electrochemical oxidation\(^9\), forming \([\text{Mn(NO)}_2(CN)_4]^2-\) containing the \([\text{Mn(NO)}_2]^2-\) moiety. Bhattacharya et al.\(^10\) have recently reported a single step facile conversion of manganate(VII) into \([\text{Mn(NO)}_2(CN)_4]^2-\), containing \([\text{Mn(NO)}_2]^2-\) moiety, through reaction with an excess of \(\text{NH}_2\text{OH.HCl}\) and \(\text{KCN}\) in aqueous-alkaline medium, maintaining the \(\text{pH}\) at 5.

Following our observation of partial replacement of the cyano groups from an appropriate cyanonitrosyl complex by heterocyclic nitrogen donors\(^11\) in aqueous-acetic acid medium, we have examined the ligational behaviour of some potentially mono- and bidentate heterocyclic nitrogen donors using their aqueous-acetic acid solution towards \([\text{Mn(NO)}_2(CN)_4]^2-\) obtained by Bhattacharya et al. as indicated above. The heterocyclic nitrogen donors (I) selected by us in the present investigation are: 2-hydroxymethylpyridine (2-HMP), 3-hydroxymethylpyridine (3-HMP), 2-(2'-aminoethyl)pyridine (2-AEP), quinaldic acid (QD), nicotinic acid (NA), methyl nicotinate (MNIC) and 2-aminopyridine (2-AP).

Experimental

2-and 3-Hydroxymethylpyridine (Kawaken Fine Chemicals Co. Ltd., Japan), 2-(2'-aminoethyl)pyridine (Fluka Chemie, AG), 2-aminopyridine, quinaldic acid, nicotinic acid and methyl nicotinate (Aldrich Chemical Co., U.S.A.), potassium permanganate (B.D.H. Chemicals, England), potassium cyanide (B.D.H. chemicals, Mumbai) and hydroxylamine hydrochloride (Wilson Lab., Bombay) were used as supplied.

Synthesis of the parent anion, \([\text{Mn(NO)}_2(CN)_4]^2-\).

The parent anion, tetracyanonitrosylmanganate(0) was prepared by the method reported by Bhattacharya et al.\(^10\).

In a solution of KOH (2 g in 20 mL \(\text{H}_2\text{O}\)), \(\text{K MnO}_4\) (0.5 g, 3.2 mmol) was dissolved. The resulting solution was heated at 80°C and to the stirred solution, \(\text{KCN}\) (3.1 g, 48 mmol) was added. Heating and stirring was continued for another few minutes and then \(\text{NH}_2\text{OH.HCl}\) (3.3 g, 48 mmol) was added in small portions. The mixture was again heated with stirring for 30 min, when its colour became red-purple and the \(\text{pH}\) was 10.5. The solution was treated dropwise with dilute (1:4) \(\text{HCl}\) solution till \(\text{pH}\) was 5.
Synthesis of mixed-ligand complex

To a solution of the parent anion, \([\text{Mn(NO}_2\text{(CN)}_4]^2-\)

obtained as above, an aqueous-acetic acid solution (8 mL, 1:1) of 2-HMP (0.690g, 0.61 mL), 3-HMP (0.690, 0.61 mL), 2-AEP (0.388, 0.38 mL), QD (0.547g), NA (0.389g), MNIC (0.433g) or 2-AP (0.297g) was added with stirring. A pink coloured solid was precipitated on refluxing the resulting mixture at 80°C for the duration given below in each case.

The coloured precipitate was filtered by suction, washed several times with dilute acetic acid, 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. Carbon, hydrogen and nitrogen were determined microanalytically at CDRI, Lucknow. Manganese was determined as ammonium manganese phosphate monohydrate, MnNH_4PO_4•H_2O using the standard method.

Conductance measurements were performed at room temperature in acetonitrile using a Toshiba conductivity bridge and a dip-type cell with a smooth platinum electrode. Electronic spectra of the complexes were recorded in 10^{-3}M DMF solutions 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 at the National Chemical Laboratory, Pune. Thermogravimetric analysis of the samples were done in the temperature range 50-800°C using a thermal analyser at the University of Poona, Pune. Magnetic susceptibilities of the complexes were measured at room temperature on a Gouy balance using Hg[Co(NCS)₄] as calibrant. E.S.R. spectra of the complexes were recorded on a Bruker ESR X-band EPR spectrometer at room temperature using powdered samples. Decomposition temperatures of the complexes were determined using an electrothermal apparatus.

Results and discussion

The mixed-ligand complexes under the present investigation were prepared according to the following equations:

\[
\text{Mn(NO}_2\text{(CN)}_4]^2-+2\text{LCH}_2\text{COOH}\text{H}_2\text{O} \rightarrow \text{Mn(NO}_2\text{(CN)}_4\text{(L)}_2]+\text{HCN(g)}+\text{CH}_2\text{COO}^-+\text{H}_2\text{O}
\]

where \(L=2\text{-HMP or 3-HMP}\) and

\[
\text{Mn(NO}_2\text{(CN)}_4]^2-+\text{LCH}_2\text{COOH}\text{H}_2\text{O} \rightarrow \text{Mn(NO}_2\text{(CN)}_4\text{(L)}_2]+\text{HCN(g)}+\text{CH}_2\text{COO}^-+\text{H}_2\text{O}
\]

where \(L=2\text{-AP, 2-AEP, QD, NA or MNIC}\)

The partial replacement of the cyano groups in
by one molecule of the ligand \( \text{L-L} \)
or two molecules of the ligand \( \text{L} \), is in agreement with
the results reported by Maurya et al.\(^1\)

All the compounds synthesized during this
investigation are non-hygroscopic and air-stable,
coloured solids (Table 2). They are thermally stable
and their decomposition temperatures are recorded
in Table 2. All the complexes after decomposition with
\( \text{KOH} \), followed by acidification with acetic acid give
a pink colour with a few drops of Griess reagent.\(^2\)
The appearance of a pink colour is probably due to
\( \text{NO}^+ \) group of the compounds, which after
decomposition with \( \text{KOH} \) changes to \( \text{NO}_2^- \) and forms
a pink dye with the Griess reagent. The resulting
complexes are characterized on the basis of various
physicochemical studies.

The molar conductances of the \( 10^{-3} \) \( M \) acetonitrile
solutions of the complexes were found to be in the
range 10-15 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\) indicating that they are
non-electrolytes.\(^3\)

**Infrared spectra**

In the IR spectra, two strong bands in the region
1765-1842 cm\(^{-1}\) and 1650-1788 cm\(^{-1}\), a very strong band in the region 2103-2123 cm\(^{-1}\) with a shoulder at
2140-2159 cm\(^{-1}\) and a weak band at 637-666 cm\(^{-1}\) are
observed which are assigned to \( v(\text{NO})^+, v(\text{CN}) \) and
\( v(\text{MnNO}) \), respectively. These results are in
agreement with the data reported elsewhere.\(^4,5\)
The appearance of two \( v(\text{NO})^+ \) bands in the spectra of all
the synthesized complexes suggests the presence of a
cis [Mn(\text{NO})\text{CN}]\(^2+\) moiety\(^6\) in them.

The heterocyclic donors 2-HMP and 3-HMP
possess only the pyridine ring nitrogen as a donor site.
The other ligands, viz., 2-AP, 2-AEP, MNIC, QD and
NA have two potential donor sites: (i) pyridine ring
nitrogen and (ii) carboxyloxygen of the ester group in
case of MNIC, or carboxyl oxygen of acid group in
QD and NA, or amino group in case of 2-AP and 2-AEP.

The \( v(\text{C}=\text{O}) \) in uncoordinated QD, NA and MNIC
occurring at approximately 1675 cm\(^{-1}\) undergoes a
significant negative shift\(^7\) and appears at 1600, 1608
and 1602 cm\(^{-1}\), respectively, in the spectra of their
respective complexes. This indicates coordination of
carboxyl oxygen of the acid group in these ligands to
manganese. The appearance of a broad band centered
at 3166 cm\(^{-1}\) may be assigned to \( v(\text{NH}) \) of
coordinated 2-AEP.\(^8\) The coordination of amino
nitrogen in 2-AP is inferred by the shift of \( v_{\text{as}}(\text{NH}) \)
and \( v_{\text{s}}(\text{NH}) \) to lower wavenumbers which appear at
3350 and 3240 cm\(^{-1}\), respectively, in the complex. A
weak band at 1050-1078 cm\(^{-1}\) in 2-HMP, 3-HMP,
QD, NA and MNIC, 2-AEP complexes, assignable to
pyridine ring breathing mode suggests the
coordination of ring nitrogen to manganese in these
complexes. The appearance of a prominent band for
ring \( v(\text{C}=\text{N}) \) at 1607-1615 cm\(^{-1}\) in the complexes
1, 2, 3 and 7 may also be considered as diagnostic of
the coordinated pyridine nitrogen. The \( v(\text{C}=\text{N}) \) mode
of coordinated ring nitrogen of the ligands, QD, NA
and MNIC seems to be merged with \( v(\text{C}=\text{O}) \) band of
these ligands.

**Thermogravimetric analyses**

Thermogravimetric curves of three representative
compounds 1, 3 and 5, were recorded from room
temperature to 800°C. First stage of mass loss in all
these compounds, occurring 310, 275 and 220°C,
respectively, corresponds to the elimination of two
cyano groups from these complexes. The second mass
loss in complexes 1 and 5, occurring at 375°C and
330°C, respectively, corresponds to decomposition of
two NO groups from each compound. In compound 3,
the second mass loss recorded at 325°C corresponds to
the elimination of one NO group only. It shows
further mass loss with removal of another NO group
at 370°C. Further mass losses, however, could not
be interpreted in all the three complexes. These results
corroborate the analytical and IR data of the
complexes along with monodentate coordination of 2-
HMP and bidentate coordination of 2-AEP and NA.

**Magnetic measurements**

The observed magnetic moments (\( \mu_{\text{eff}}=1.89-1.92 \))
BM, see Table 2) of these derivatives suggest that
they are paramagnetic with one unpaired electron.
Hence they should have a ground state with a
molecular orbital configuration \((1\alpha)^2(1\alpha)^2(1\beta)^2\) \((2\alpha)^1\) based on the M.O. diagram reported elsewhere\(^{22}\). This result is consistent with low-spin \(\{\text{Mn(NO)}_2\}^+\) electron configuration\(^{22}\) of Mn(0) in all these complexes.

**Electronic spectra**

Electronic spectra of two representative compounds 2 and 5 (recorded in DMF) exhibited three characteristic absorption peaks at 365, 425-430 and 510-540 nm, assignable\(^{22}\) to \(2\alpha_1\to 3\alpha_1\), \(2\alpha_1\to 2\beta_2\) and \(2\alpha_1\to 1\beta_1\), respectively. These results are comparable to the electronic spectral data reported by Bhattacharya et al.\(^{10}\)

**ESR spectra**

The X-band room temperature ESR spectrum of one of the compound \([\text{Mn(NO)}_2(\text{CN})_2(\text{NA})]\) was recorded using powdered sample, both parallel and perpendicular features of \(^{55}\text{Mn}\) have been resolved. Nuclear hyperfine coupling is observed in the \(g_\parallel\) region with four components clearly resolved. It appears, therefore, that two other components are obscured by the \(g_\perp\) component\(^{23}\). The hyperfine coupling in the present case seems to arise from coupling of the unpaired electron to \(^{55}\text{Mn}\) \((I=5/2)\). This complex has \(g_\parallel=2.021, g_\perp=2.094\) and \(g_\perp=2.045\). The \(g_\parallel\) and \(g_\perp\) values in the complex deviate considerably from the free ion value of 2.0023, and this positive deviation indicates that the resulting complexes are appreciably covalent\(^{23}\).

The analytical data and the physicochemical results presented above indicate that these complexes are of the compositions \([\text{Mn(NO)}_2(\text{CN})_2(L)_2]\), where \(L=2\)-HMP or 3-HMP and \([\text{Mn(NO)}_2(\text{CN})_2(L-1)]_2\), where \(L-L=2\)-AEP, 2-AP QD, NA or MNIC. Since all the complexes exhibit two \(v(\text{NO})\) and two \(v(\text{CN})\) values, it is reasonable to propose octahedral structures for these complexes, wherein both the nitrosyl and cyano groups are \(cis\) to each other\(^{10}\) (II).

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**References**