

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 tetracyanodinitrosylmanganate(0) anion, $[\text{Mn}(\text{NO})_2(\text{CN})_4]^{2-}$ with 2-hydroxymethylpyridine (2-HMP), 3-hydroxymethylpyridine (3-HMP), 2-aminopyridine (2-AP), 2-(2'-aminoethyl)pyridine(2-AEP), quinaldic acid (QD), nicotinic acid (NA) and methyl nicotinate (MNIC) are described. The products have the general formula $[\text{Mn}(\text{NO})_2(\text{CN})_2(\text{L})_2]$ (where L=2-HMP or 3-HMP) and $[\text{Mn}(\text{NO})_2(\text{CN})_2(\text{L-L})]$ (where L-L=QD, NA, 2-AEP, 2-AP or MNIC). Octahedral structures have been suggested for these complexes. Mn(0) has a low-spin $[\text{Mn}(\text{NO})_2]^{7-}$ electron configuration¹ in these complexes.

Reductive nitrosylation of tetraoxometallates using hydroxylamine hydrochloride in presence of CN^- in an aqueous-alkaline medium²⁻⁷ and synthesis of the corresponding pentacyanonitrosylmetallates are reported in literature. Pentacyanonitrosylmanganate(I), $[\text{Mn}(\text{NO})(\text{CN})_5]^{3-}$, containing the $[\text{MnNO}]^{2+}$ core had been reported⁸ to be synthesized from $\text{K}_3[\text{Mn}(\text{CN})_6]$ using $\text{NH}_2\text{OH}\cdot\text{HCl}$, and shown to undergo oxidation by nitric acid⁸ or electrochemical oxidation⁹, forming $[\text{Mn}(\text{NO})(\text{CN})_5]^{2-}$ containing the $[\text{MnNO}]^{3+}$ moiety. Bhattacharya *et al.*¹⁰ have recently reported a single step facile conversion of manganate(VII) into $[\text{Mn}(\text{NO})_2(\text{CN})_4]^{2-}$, containing $[\text{Mn}(\text{NO})_2]^{2+}$ moiety, through reaction with an excess of $\text{NH}_2\text{OH}\cdot\text{HCl}$ and KCN in aqueous-alkaline medium, maintaining the pH at 5.

Following our observation of partial replacement of the cyano groups from an appropriate cyanonitrosyl complex by heterocyclic nitrogen donors¹¹ 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 $[\text{Mn}(\text{NO})_2(\text{CN})_4]^{2-}$ 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).

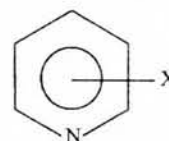
Experimental

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.

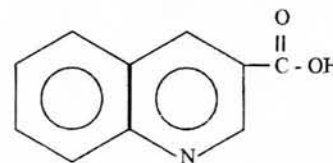
Synthesis of the parent anion, $[\text{Mn}(\text{NO})_2(\text{CN})_4]^{2-}$

The parent anion, tetracyanodinitrosylmanganate(0) was prepared by the method reported by Bhattacharya *et al.*¹⁰

In a solution of KOH (2g in 20 mL H_2O), KMnO_4 (0.5 g, 3.2 mmol) was dissolved. The resulting solution was heated at 80°C and to the stirred solution, KCN (3.1g, 48 mmol) was added. Heating and stirring was continued for another few minutes and then $\text{NH}_2\text{OH}\cdot\text{HCl}$ (3.3g, 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 pH was 10.5. The solution was treated dropwise with dilute (1:4) HCl solution till pH was 5.



X = *o*- CH_2OH (2-HMP), *m*- CH_2OH (3-HMP),
o- $\text{CH}_2\text{CH}_2\text{NH}_2$ (2-AEP), *o*- COOH (NA),
m- COOCH_3 (MNIC),



(QD)

I

Table 1 — Analytical data and important IR spectral bands (cm^{-1}) of the synthesized complexes

Comp. (Empirical formula)	Found (Calc.), %				$\nu(\text{NO})^+$	$\nu(\text{CN})$	$\nu(\text{MnNO})$	$\nu(\text{C}=\text{N})$	Pyridine ring breathing mode
	C	H	N	Mn					
$[\text{Mn}(\text{NO})_2(\text{CN})_2(2\text{-HMP})_2]$ ($\text{C}_{14}\text{H}_{14}\text{N}_6\text{O}_4\text{Mn}$)	43.27 (43.61)	3.52 (3.63)	21.57 (21.80)	14.05 (14.27)	1789 1711	2109 2140	660	1614	1050
$[\text{Mn}(\text{NO})_2(\text{CN})_2(3\text{-HMP})_2]$ ($\text{C}_{14}\text{H}_{14}\text{N}_6\text{O}_4\text{Mn}$)	43.42 (43.61)	3.32 (3.63)	21.48 (21.80)	14.48 (14.27)	1804 1710	2109 2141	660	1615	1054
$[\text{Mn}(\text{NO})_2(\text{CN})_2(2\text{-AEP})]$ ($\text{C}_9\text{H}_{10}\text{N}_6\text{O}_2\text{Mn}$)	37.54 (37.35)	3.28 (3.46)	29.45 (29.05)	19.35 (19.02)	1840 1766	2109 2143	666	1607	1078
$[\text{Mn}(\text{NO})_2(\text{CN})_2(\text{QD})]$ ($\text{C}_{12}\text{H}_7\text{N}_5\text{O}_4\text{Mn}$)	42.62 (42.35)	20.27 (20.06)	20.37 (20.59)	16.45 (16.18)	1765 1650	2123 2159	637	1600*	1078
$[\text{Mn}(\text{NO})_2(\text{CN})_2(\text{NA})]$ ($\text{C}_9\text{H}_5\text{N}_5\text{O}_4\text{Mn}$)	33.27 (33.10)	1.60 (1.72)	24.35 (24.14)	18.61 (18.96)	1842 1788	2108 2145	666	1608*	1075
$[\text{Mn}(\text{NO})_2(\text{CN})_2(\text{MNIC})]$ ($\text{C}_9\text{H}_7\text{N}_5\text{O}_4\text{Mn}$)	35.68 (35.51)	2.45 (2.30)	23.30 (23.02)	18.45 (18.08)	1800 1728	2103 2140	642	1602*	1047
$[\text{Mn}(\text{NO})_2(\text{CN})_2(2\text{-AP})]$ ($\text{C}_7\text{H}_8\text{N}_6\text{O}_3\text{Mn}$)	30.37 (30.11)	2.92 (2.87)	30.79 (30.11)	19.20 (19.71)	1786 1667	2143 2106	666	1610	—

* $\nu(\text{C}=\text{O})$ merged with $\nu(\text{C}=\text{N})$.*Synthesis of mixed-ligand complex*

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

*Heterocyclic donor**Refluxing period (min)*

2-HMP/3-HMP	60
2-AEP	15
QD	25
NA	20
MNIC	15

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, $\text{MnNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ using the standard¹² method.

Conductance measurements were performed at room temperature in acetonitrile 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 DMF solutions on a Shimadzu model, UV-160 spectrophotometer. FT-IR spectra of the complexes were recorded in Nujol mulls in the range $4000\text{--}450\text{ cm}^{-1}$ at the National Chemical Laboratory, Pune. Thermogravimetric

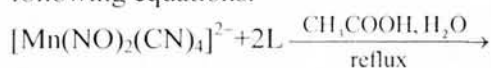
Table 2 — Some physical properties of the complexes

No.	Comp.	Decom., $^\circ\text{C}$	μ_{eff} BM
1.	$[\text{Mn}(\text{NO})_2(\text{CN})_2(2\text{-HMP})_2]$	230	1.89
2.	$[\text{Mn}(\text{NO})_2(\text{CN})_2(3\text{-HMP})_2]$	220	1.90
3.	$[\text{Mn}(\text{NO})_2(\text{CN})_2(2\text{-AEP})]$	290	1.89
4.	$[\text{Mn}(\text{NO})_2(\text{CN})_2(\text{QD})]$	300	1.90
5.	$[\text{Mn}(\text{NO})_2(\text{CN})_2(\text{NA})]$	240	1.92
6.	$[\text{Mn}(\text{NO})_2(\text{CN})_2(\text{MNIC})]$	260	1.92
7.	$[\text{Mn}(\text{NO})_2(\text{CN})_2(2\text{-AP})]$	220	1.79

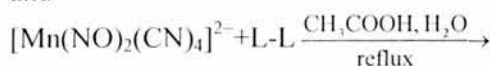
analysis of the samples were done in the temperature range $50\text{--}800^\circ\text{C}$ using a thermal analyser at the University of Poona, Pune. Magnetic susceptibilities of the complexes were measured at room temperature on a Gouy balance using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as calibrant. 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:



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



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

The partial replacement of the cyano groups in

$[\text{Mn}(\text{NO})_2(\text{CN})_4]^{2-}$ by one molecule of the ligand L-L or two molecules of the ligand L, is in agreement with the results reported by Maurya *et al.*¹³

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 KOH, followed by acidification with acetic acid give a pink colour with a few drops of Griess reagent¹⁴. The appearance of a pink colour is probably due to NO^+ group of the compounds, which after decomposition with KOH changes to NO_2^- and forms a pink dye with the Griess reagent. The resulting complexes are characterized on the basis of various physicochemical studies.

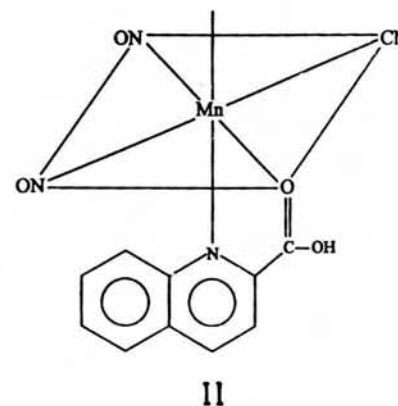
The molar conductances of the 10^{-3} M acetonitrile solutions of the complexes were found to be in the range $10\text{--}15 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ indicating that they are non-electrolytes¹⁵.

Infrared spectra

In the IR spectra, two strong bands in the region $1765\text{--}1842 \text{ cm}^{-1}$ and $1650\text{--}1788 \text{ cm}^{-1}$, a very strong band in the region $2103\text{--}2123 \text{ cm}^{-1}$ with a shoulder at $2140\text{--}2159 \text{ cm}^{-1}$ and a weak band at $637\text{--}666 \text{ cm}^{-1}$ are observed which are assigned to $\nu(\text{NO})^+$, $\nu(\text{CN})$ and $\nu(\text{MnNO})$, respectively. These results are in agreement with the data reported elsewhere^{10,16,17}. The appearance of two $\nu(\text{NO})^+$ bands in the spectra of all the synthesized complexes suggests the presence of a *cis* $[\text{Mn}(\text{NO})_2]^{2+}$ moiety^{10,18} 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) carbonyloxygen of the ester group in case of MNIC, or carbonyl oxygen of acid group in QD and NA, or amino group in case of 2-AP and 2-AEP.

The $\nu(\text{C}=\text{O})$ in uncoordinated QD, NA and MNIC occurring at approximately 1675 cm^{-1} undergoes a significant negative shift²⁰ and appears at 1600 , 1608 and 1602 cm^{-1} , respectively, in the spectra of their respective complexes. This indicates coordination of carbonyl 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 $\nu(\text{NH})$ of coordinated 2-AEP²¹. The coordination of amino nitrogen in 2-AP is inferred by the shift of $\nu_{\text{as}}(\text{NH})$



and $\nu_{\text{s}}(\text{NH})$ to lower wavenumbers which appear at 3350 and 3240 cm^{-1} , respectively, in the complex. A weak band at $1050\text{--}1078 \text{ cm}^{-1}$ 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 $\nu(\text{C}=\text{N})$ at $1607\text{--}1615 \text{ cm}^{-1}$ in the complexes **1,2,3** and **7** may also be considered as diagnostic of the coordinated pyridine nitrogen. The $\nu(\text{C}=\text{N})$ mode of coordinated ring nitrogen of the ligands, QD, NA and MNIC seems to be merged with $\nu(\text{C}=\text{O})$ 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 ($\mu_{\text{eff}}=1.89\text{--}1.92$ 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 $(1a_2)^2(1a_1)^2(1b_2)^2(2a_1)^1$ based on the M.O. diagram reported elsewhere²². This result is consistent with low-spin $\{\text{Mn}(\text{NO})_2\}^7$ electron configuration²² 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, assignable²² to $2a_1 \rightarrow 3a_1$, $2a_1 \rightarrow 2b_2$ and $2a_1 \rightarrow 1b_1$, 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 $[\text{Mn}(\text{NO})_2(\text{CN})_2(\text{NA})]$ was recorded using powdered sample, both parallel and perpendicular features of ^{55}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 $g_{\perp}$ component²³. The hyperfine coupling in the present case seems to arise from coupling of the unpaired electron to ^{55}Mn ($I=5/2$). This complex has $g_{\perp}=2.021$, $g_{\parallel}=2.094$ and $g_{\text{av}}=2.045$. 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 covalent²⁴.

The analytical data and the physicochemical results presented above indicate that these complexes are of the compositions $[\text{Mn}(\text{NO})_2(\text{CN})_2(\text{L})_2]$, where L=2-HMP or 3-HMP and $[\text{Mn}(\text{NO})_2(\text{CN})_2(\text{L-L})]$, where L-L=2-AEP, 2-AP QD, NA or MNIC. Since all the complexes exhibit two $\nu(\text{NO})^+$ and two $\nu(\text{CN})$ values, it is reasonable to propose octahedral structures for these complexes, wherein both the nitrosyl and cyano groups are *cis* to each other¹⁰ (II).

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