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Metal Cyanonitrosyl Complexes: Synthesis, Magnetic, Thermal and Spectral Studies of Some Novel Mixed-Ligand Cyanonitrosyl {MnNO} Complexes of Manganese(I) with Potentially Mono. and Bidentate Aniline Derivatives

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METAL CYANONITROSYL COMPLEXES: SYNTHESIS, MAGNETIC, THERMAL AND SPECTRAL STUDIES OF SOME NOVEL MIXED-LIGAND CYANONITROSYL $\{MnNO\}^6$ COMPLEXES OF MANGANESE(I) WITH POTENTIALLY MONO- AND BIDENTATE ANILINE DERIVATIVES

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ABSTRACT

Novel mixed-ligand cyanonitrosyl $\{MnNO\}^6$ complexes of manganese(I), formed by the interaction of pentacyanonitrosylmanganate(I) anion, $[Mn(NO)(CN)_5]^{3-}$, with potentially bidentate aniline derivatives, viz., o-phenylenediamine (o-PDA, I), m-phenylenediamine (m-PDA, II), and potentially monodentate aniline derivatives, o-anisidine (o-ANS, III), m-anisidine (m-ANS, IV), p-anisidine (p-ANS, V), o-phenetidine (o-PD, VI) and m-phenetidine (m-PD, VII), are described. The resulting mixed-ligand complexes, which have been characterized by analytical data, electrical conductances, magnetic measurements, electronic spectra, thermogravimetric analyses and infrared spectral studies, have the compositions $[Mn(NO)(CN)_2(o\text{-PDA})(H_2O)]$, $[Mn(NO)(CN)_2(m\text{-PDA})(H_2O)_2]$ or $[Mn(NO)(CN)_2(L)_2(H_2O)]$ (where L = III, IV, V, VI or VII). Suitable octahedral structures have been proposed for the complexes. Manganese(I) has a low-spin $\{MnNO\}^6$ electron configuration in these complexes.

INTRODUCTION

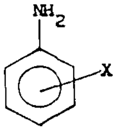
Aniline and substituted anilines possess a lone pair of electrons on the nitrogen of the NH_2 group and have an appreciable tendency to coordinate with metal ions. The donor ability of aniline and its derivatives has been known since long[1-3].

Maurya et al.[4] have reported the synthesis, structure and bonding of some mixed-ligand cyanonitrosyl complexes of the $\{CrNO\}^5$ electron configuration with aniline and substituted anilines. The synthesis and physico-chemical investigation of some mixed-ligand cyanonitrosyl $\{Mo(NO)_2\}^6$ complexes of Mo(O) with some substituted anilines, viz., o-anisidine, m-anisidine, p-anisidine, o-phenetidine, m-phenetidine, p-phenetidine, N-methylaniline and N,N'-dimethylaniline have been reported recently by Maurya and his co-workers[5]. Although in recent years there has been a great interest in the synthesis, structure and bonding of mixed-ligand cyanonitrosyl complexes of manganese with heterocyclic nitrogen donors[6], there is no report on cyanonitrosyl $\{MnNO\}^6$ complexes of manganese(I) with some substituted anilines. Moreover, the academic importance of $\{MnNO\}^6$ complexes provides an additional incentive for investigations of such complexes. It was, therefore, thought worthwhile to synthesise and characterize some mixed-ligand cyanonitrosyl $\{MnNO\}^6$ complexes of manganese(I) with aniline derivatives, viz., o-phenylenediamine (o-PDA, I), m-phenylenediamine (m-PDA, II), o-anisidine (o-ANS, III), m-anisidine (m-ANS, IV), p-anisidine (p-ANS, V), o-phenetidine (o-PD, VI), and m-phenetidine (m-PD, VII). The ligands are shown in Fig. 1.

EXPERIMENTAL

Materials

Potassium cyanide (May and Baker Co., India), hydroxylammoniumchloride (Robert Johnson, India), potassium hydroxide



(*o*-PDA, I) : X = NH_2(*o*)
(*m*-PDA, II) : X = NH_2(*m*)
(*o*-ANS, III) : X = OCH_3(*o*)
(*m*-ANS, IV) : X = OCH_3(*m*)
(*p*-ANS, V) : X = OCH_3(*p*)
(*o*-PD, VI) : X = OC_2H_5(*o*)
(*m*-PD, VII) : X = OC_2H_5(*m*)

Fig. 1. Structures of the Ligands.

(Central Drug House Priv. Ltd., Bombay), $KMnO_4$ (B. D. H. Chemical, Bombay), *o*-phenylenediamine and *m*-phenylenediamine (E. Merck, India Ltd., Worli, Bombay), *o*-anisidine, and *p*-anisidine (Fluka Chemie A. G., Switzerland), *m*-anisidine, *o*-phenetidine, *m*-phenetidine (Koch-Light Lab. Ltd., England), were used as supplied The parent compound, pentacyanonitrosylmanganate(I) anion, $[Mn(NO)(CN)_5]^{3-}$, was prepared by following the procedure of Bhattacharya *et al.*[7].

Synthesis of the Complexes

To a red-purple solutions of the parent anion, $[Mn(NO)(CN)_5]^{3-}$ (0.688 g, 3.2 mmol) an aqueous acetic acid solution (5-6 ml, 1:1) of *o*-PDA/*m*-PDA (0.345 g, 3.2 mmol), *o*-ANS/*m*-ANS/*p*-ANS (0.787 g, 6.4 mmol) or *o*-PD/*m*-PD (0.876 g, 6.4 mmol) was added with shaking. A coloured solid was precipitated on heating the resulting mixture for 40-60 minutes over a hot plate at 80°C. It was filtered by suction, washed several times with 5% dilute acetic acid, finally with water and dried *in vacuo* at room temperature to a constant weight. The analytical data of the resulting complexes are given in Table I.

Table I. Analytical Data and Some Physical Properties of the Complexes.

Sr. No.	Compound Empirical Formula (Formula Weight)	Found (Calc.),% C	H	N	Mn	Λ_M (ohm^{-1} cm^2- mol^{-1})	Yield	Decomp. Temp. ^oC	Colour
1.	$[Mn(NO)(CN)_2(\underline{o}\text{-PDA})(H_2O)]$ $MnC_8H_{10}N_5O_2$(262.94)	36.75 (36.50)	3.90 (3.80)	27.10 (26.62)	21.40 (20.89)	46.5(DMF)	53	>300	Blackish brown
2.	$[Mn(NO)(CN)_2(\underline{m}\text{-PDA})(H_2O)_2]$ $MnC_8H_{12}N_5O_3$(280.94)	34.52 (34.17)	4.40 (4.27)	25.04 (24.92)	19.26 (19.55)	8.5(Ethanol)	55	>250	Light brown
3.	$[Mn(NO)(CN)_2(\underline{o}\text{-ANS})_2(H_2O)]$ $MnC_{16}H_{20}N_5O_4$(400.94)	48.01 (47.88)	5.07 (4.99)	17.63 (17.46)	13.94 (13.72)	4.0(Ethanol)	55	>300	Brown
4.	$[Mn(NO)(CN)_2(\underline{m}\text{-ANS})_2(H_2O)]$ $MnC_{16}H_{20}N_5O_4$(400.94)	47.93 (47.88)	5.09 (4.99)	17.62 (17.46)	13.90 (13.72)	4.0(DMF)	52	>200	Brown
5.	$[Mn(NO)(CN)_2(\underline{p}\text{-ANS})_2(H_2O)]$ $MnC_{16}H_{20}N_5O_4$(400.94)	47.97 (47.88)	5.11 (4.99)	17.55 (17.46)	13.88 (13.72)	5.0(Ethanol)	50	>300	Light brown
6.	$[Mn(NO)(CN)_2(\underline{o}\text{-PD})_2(H_2O)]$ $MnC_{18}H_{24}N_5O_4$(428.94)	50.62 (50.35)	5.63 (5.59)	16.75 (16.32)	13.17 (12.81)	8.0(Ethanol)	42	>290	Brown
7.	$[Mn(NO)(CN)_2(\underline{m}\text{-PD})_2(H_2O)]$ $MnC_{18}H_{24}N_5O_4$(428.94)	50.55 (50.35)	5.70 (5.59)	16.56 (16.32)	13.03 (12.81)	5.0(Ethanol)	45	>250	Blackish brown

Analyses

Carbon, hydrogen and nitrogen were determined by microanalysis at C. D. R. I., Lucknow. Manganese was determined as ammonium manganese phosphate monohydrate, $MnNH_4PO_4.H_2O$, using the standard procedure[8].

Physical Methods

Conductance measurements were performed at room temperature in ethanol and dimethylformamide using a Toshniwal conductivity bridge and dip-type cell with a smooth platinum electrode. Solid state infrared spectra of the ligands and complexes were recorded on a FT-IR spectrophotometer in Nujol mulls in the range 4000-500 cm^{-1}. Electronic spectra of the complexes were recorded in 10^{-3} M solution in DMF on a Shimadzu, model UV-160, spectrophotometer. Thermogravimetric curves were recorded on a Perkin-Elmer instrument at a heating rate of $12^oC\ min^{-1}$ in the temperature range $40-740^oC$, at Regional Sophisticated Instrumentation Centre, Nagpur. The magnetic susceptibility was measured at room temperature on a Gouy balance using $Hg[Co(NCS)_4]$ as calibrant, at Central Salt and Marine Chemical Research Institute, Bhavnagar. Decomposition temperatures of compounds were determined using on electrothermal apparatus having capacity to record temperatures upto 360^oC.

RESULTS AND DISCUSSION

The mixed-ligand complexes, $[Mn(NO)(CN)_2(L)_2(H_2O)]$, $[Mn(NO)(CN)_2(\underline{o}\text{-PDA})(H_2O)]$ and $[Mn(NO)(CN)_2(\underline{m}\text{-PDA})(H_2O)_2]$, were prepared according to the following equations:

$$[Mn(NO)(CN)_5]^{3-} + 2L \xrightarrow[H_2O]{CH_3COOH} [Mn(NO)(CN)_2(L)_2(H_2O)] + 3HCN + H_2O + CH_3COO^-$$

where L = <u>o</u>-ANS, <u>m</u>-ANS, <u>p</u>-ANS, <u>o</u>-PD, or <u>m</u>-PD,

$$[Mn(NO)(CN)_5]^{3-} + \underline{o}\text{-PDA} \xrightarrow[H_2O]{CH_3COOH} [Mn(NO)(CN)_2(\underline{o}\text{-PDA})(H_2O)] + 3HCN + CH_3COO^- + H_2O$$

and

$$[Mn(NO)(CN)_5]^{3-} + \underline{m}\text{-PDA} \xrightarrow[H_2O]{CH_3COOH} [Mn(NO)(CN)_2(\underline{m}\text{-PDA})(H_2O)_2] + 3HCN + CH_3COO^- + H_2O$$

The partial replacement of the cyano groups in the parent anion, $[Mn(NO)(CN)_5]^{3-}$, by two molecules of o-ANS/m-ANS/p-ANS/ o-PD/m-PD or one molecule of o-PDA/m-PDA is facilitated due to the trans-directing effect of the nitrosyl group, as observed by Maurya et al.[9] in the interaction of pentacyanonitrosylchromate(I) anion with different biologically active organic donors.

The resulting compounds synthesised in this investigation are non-hygroscopic and air-stable coloured solids (see Table I for colour). They are thermally stable and their thermal decomposition temperatures are recorded in Table I. The solubility of these complexes in different solvents is given in Table III. All compounds, after decomposition with KOH followed by acidifying with acetic acid, give a pink colour with a few drops of Griess reagent[10]. This test shows the presence of the NO^+ grouping[9] in these complexes. The resulting complexes were characterized on the basis of the following physical studies.

Conductance Measurements

The molar conductances of all the complexes in 10^{-3} M ethanol solutions (except complexes, 1 and 4, for which 10^{-3} M DMF solutions were used) are given in Table I. These values are indicative of the non-electrolytic nature[11] of these complexes.

Magnetic Measurements

The magnetic susceptibility measurements of these complexes indicate that they are diamagnetic and, hence, they should have a ground state with a molecular orbital configuration[12] $(2e)^4(1b_2)^2$. This result is consistent with a low-spin $\{MnNO\}^6$ electron configuration of manganese(I) in all these complexes. The diamagnetic and non-electrolytic nature of these complexes also support the presence of the NO^+ grouping in the complexes.

Electronic Spectra

The electronic spectrum of one of the representative compounds, $[Mn(NO)(CN)_2(\underline{o}\text{-ANS})_2(H_2O)]$, was recorded in DMF. It shows three characteristic absorption peaks at 388, 576 and 705 nm. The electronic transitions responsible for these characteristic UV-Vis peaks in the compound are likely to be $1b_2 \rightarrow 4a_1$, $1b_2 \rightarrow 1b_1$ and $1b_2 \rightarrow 3e$, respectively, considering an M. O. picture[12] applicable to hexa-coordinated mononitrosyl complexes of C_{4v} symmetry. These observations are comparable to the results reported elsewhere[7].

Infrared Spectra

The important infrared spectral bands for the synthesized complexes are presented in Table II. The very strong to strong band at 1771-1800 cm^{-1}, a strong band at 2125-2144 cm^{-1} with a shoulder at 2107-2120 cm^{-1} and a weak band at 568-649 cm^{-1} are assigned to $\nu(NO)^+$, $\nu(CN)$ and $\nu(MnNO)$, respectively, in agreement with results reported elsewhere[7,13,14].

The ligands o-PAD and m-PAD used in the present studies possess two amino groups as two potential donor sites, while the remaining ligands o-ANS, m-ANS, p-ANS, o-PD and m-PD possess only

Table II. Important Infrared Spectral Bands (cm^{-1}) of the Complexes

Sr. No.	Compound	$\nu(NO)^{\ddagger}$	$\nu(CN)$	$\nu(MnNO)$	$\nu(NH)$	$\nu(OH)$
1.	$[Mn(NO)(CN)_2(\underline{o}\text{-PDA})(H_2O)]$	1793	2144 2107	601	3366 3183	3550–3360(b)
2.	$[Mn(NO)(CN)_2(\underline{m}\text{-PDA})(H_2O)_2]$	1771	2133 2100	646	3450* 3233	3433(s)
3.	$[Mn(NO)(CN)_2(\underline{o}\text{-ANS})_2(H_2O)]$	1800	2130 2100	591	3251 -	3530–3439(b)
4.	$[Mn(NO)(CN)_2(\underline{m}\text{-ANS})_2(H_2O)]$	1800	2132 2120	588	3242 -	3530(s)
5.	$[Mn(NO)(CN)_2(\underline{p}\text{-ANS})_2(H_2O)]$	1784	2132 -	649	3325 3292	3565(s)
6.	$[Mn(NO)(CN)_2(\underline{o}\text{-PD})_2(H_2O)]$	1800	2125 2106	568	3242 -	3600–3400(b)
7.	$[Mn(NO)(CN)_2(\underline{m}\text{-PD})_2(H_2O)]$	1790	2130 2110	598	3260 -	3550–3400(b)

Abbreviations: b = broad and s = sharp.

* $\nu(NH)$ of an uncoordinated NH_2 group.

one amino group as the donor site. The ν(NH) bands which occur at around 3450 and 3350 cm^{-1} in all the aniline derivatives undergo a low-energy shift (see Table II) after complexation. This suggests the coordination of the amino nitrogen(s)[4] to manganes in all the complexes. An additional band observed at 3450 cm^{-1} for the free ν(NH) indicates that one of the NH_2 groups of m-PDA is reluctant towards coordination in the compound 2. This is further substantiated by the appearance of two SP^2 ν(C–N) bands[15], one around the same frequency as that of free ligand (1300 cm^{-1}) and other at a lower frequency (1270 cm^{-1}) in this compound. These observations suggest the unidentate coordination of m-PDA to manganese. Such a result is expected because of the rigidity of the aromatic ligand and the presence of two amino groups far apart in m-PDA. This is consistent with the T. G. A. data (vide infra) of compound 2, indicating its mononuclear composition. All the complexes exhibit a broad/sharp ν(OH) stretching band (see Table III) for coordinated water.

Thermogravimetrical Analysis

Thermogravimetric curves of two representative compounds, 2 and 4, are given in Figures 2a and 2b, respectively. These curves indicate that these compounds are stable up to 250°C. The weight loss observed for compound 2 at a temperature around 338°C corresponds to the elimination of two molecules of water along with two cyano groups, per molecule of the complex of the comppsition $[Mn(NO)(CN)_2(m\text{-}PDA)(H_2O)_2]$. In the case of compound 4, the weight loss at a temperature of 231°C corresponds to the elimination of only one molecule of water and two cyano groups, per molecule of the complex $[Mn(NO)(CN)_2(m\text{-}ANS)_2(H_2O)]$. Further weight loss of this compound observed at a temperature of 270°C suggests the elimination of half a molecule of m-ANS. Both compounds decompose further and, ultimately, change to stable forms at 440 and 400°C, respectively. These results suggest the monomeric nature of both the complexes.

Table III. Solubility Data of the Synthesized Complexes in Different Solvents

Sr. No.	Compound	Ethanol	Methanol	1,4-dioxan	Acetone	DMF
1.	$[\mathrm{Mn(NO)(CN)_2}(\underline{o}\text{-PDA})(\mathrm{H_2O})]$	S	SS	IS	IS	PS
2.	$[\mathrm{Mn(NO)(CN)_2}(\underline{m}\text{-PDA})(\mathrm{H_2O})_2]$	S	SS	SS	SS	PS
3.	$[\mathrm{Mn(NO)(CN)_2}(\underline{o}\text{-ANS})_2(\mathrm{H_2O})]$	S	SS	IS	IS	PS
4.	$[\mathrm{Mn(NO)(CN)_2}(\underline{m}\text{-ANS})_2(\mathrm{H_2O})]$	SS	SS	PS	SS	S
5.	$[\mathrm{Mn(NO)(CN)_2}(\underline{p}\text{-ANS})_2(\mathrm{H_2O})]$	S	SS	IS	PS	IS
6.	$[\mathrm{Mn(NO)(CN)_2}(\underline{o}\text{-PD})_2(\mathrm{H_2O})]$	S	SS	SS	PS	S
7.	$[\mathrm{Mn(NO)(CN)_2}(\underline{m}\text{-PD})_2(\mathrm{H_2O})]$	S	PS	PS	SS	PS

Abbreviations: IS = Insoluble, S = Soluble, PS = Partially soluble (50–70%), SS = Sparingly soluble (20–40%). Solubility was tested taking 20 mg of each compound/1 mL of solvent.

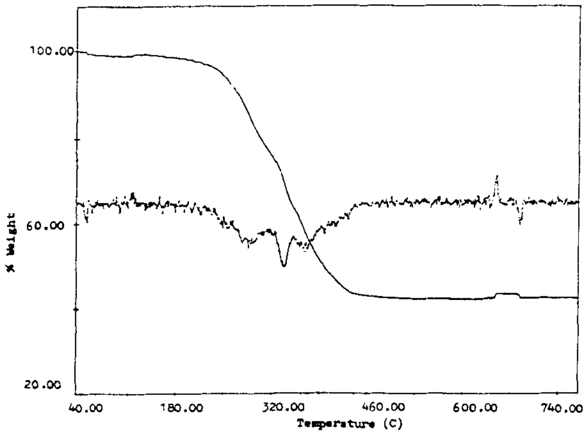


Fig. 2a. TG Curve of $[Mn(NO)(CN)_2(\underline{m}\text{-PDA})(H_2O)]$

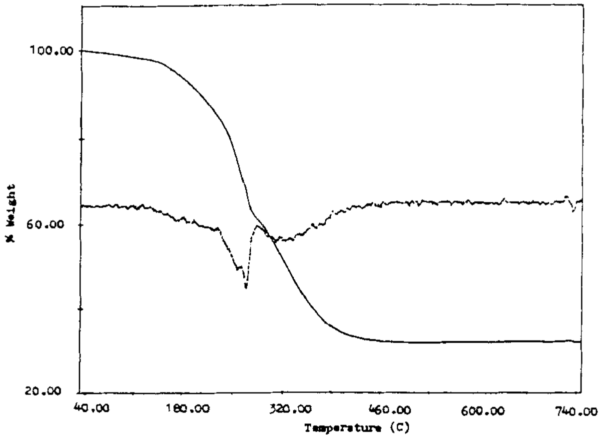


Fig. 2b. TG Curve of $[Mn(NO)(CN)_2(\underline{m}\text{-ANS})_2(H_2O)]$

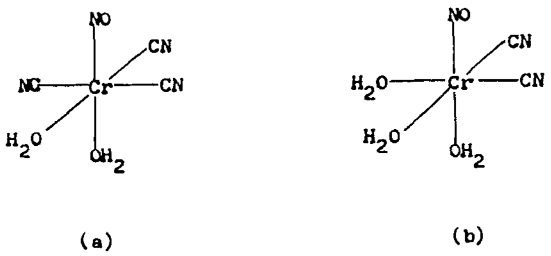
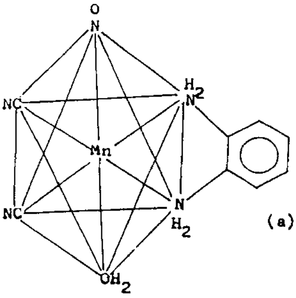
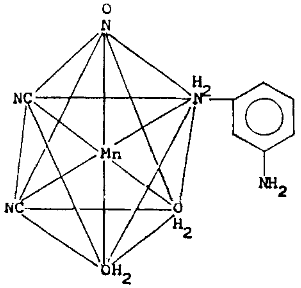


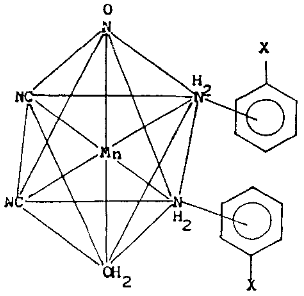
Fig. 3. The First and Third Aquated Species of $[Cr(NO)(CN)_5]^{3-}$.



(a) $[Mn(NO)(CN)_2(o\text{-}PDA)(H_2O)]$



(b) Structure of $[Mn(NO)(CN)_2(m\text{-}PDA(H_2O)_2]$



(c) Structure of $[Mn(NO)(CN)_2(L)_2$-
$(H_2O)]$
where L= o,m,p-ANS, o-PD or m-PD, and
X= OCH_3(o-,m,p-ANS)
= OC_2H_5(o,m-PD)

Fig.4. Proposed Octahedral Structure of Manganese(I) Complexes.

Conclusions

The satisfactory analytical data and physical studies presented above suggest that the complexes are of the compositions $[Mn(NO)(CN)_2(o\text{-}PDA)(H_2O)]$, $[Mn(NO)(CN)_2(m\text{-}PDA)(H_2O)_2]$ or $[Mn(NO)(CN)_2(L)_2(H_2O)]$ (where L = III, IV, V, VI or VII). Considering the structures (i) and (ii) shown in Fig. 3 of the first and third aquated species of $[Cr(NO)(CN)_5]^{3-}$ (similar to $[Mn(NO)(CN)_5]^{3-}$) reported by Raynor and co-workers[16], it is reasonable to propose for the analogous Mn complexes, the octahedral structures shown in Fig. 4.

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