

Polarographic & Spectral Studies on the Reaction of Fe(III) with Pentacyanonitrosylmanganate

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Fe(III) reacts with $K_3[Mn(CN)_5NO]$ to give a green soluble complex in dilute solution ($\approx 0.001M$) and a solid complex in concentrated solutions ($\approx 0.1-0.01M$). Spectrophotometric and polarographic studies confirm 1:1 stoichiometry for the complex. The stability constant of the complex is 5.0×10^5 . The complex has the formula $Fe[Mn(CN)_5NO] \cdot 2H_2O$. That the iron in the complex is ionic and in +3 oxidation state is supported by magnetic, IR and Mössbauer spectroscopic data.

POTASSIUM pentacyanonitrosylmanganate, $K_3[Mn(CN)_5NO]$, is very stable and reacts^{1,2} with heavy metal ions, except Fe(III), to give colloidal precipitates³. However, Fe(III) reacts with it to give either a green-coloured soluble complex or a gelatinous precipitate depending upon the concentration of Fe(III) solution. Investigations on this complex in solution form as well as in the solid state have now been carried out employing techniques like polarography, IR and Mössbauer spectroscopy and magnetic measurements.

Potassium pentacyanonitrosylmanganate was prepared² from $K_3Mn(CN)_6$ and its solution standardized potentiometrically⁴ by titrating against $KMnO_4$. Ferric chloride (Analar grade, BDH) solution was standardized gravimetrically⁵.

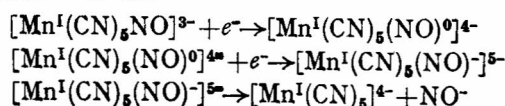
Absorption spectra were recorded on a Bausch and Lomb Spectronic 20 spectrophotometer. Polarographic waves were recorded on a Herovysky polarograph (LP 55A) which was operated manually in conjunction with a Pye scalamp galvanometer. The d.m.e. had the characteristics, $m^{2/3}i^{1/6} = 1.759$. IR spectra were recorded in KBr on a Beckmann IR 20 spectrophotometer. Magnetic measurements were carried out at room temperature ($30^\circ \pm 1^\circ$) employing Gouy's method. Mössbauer spectra were recorded on a spectrometer comprising a single channel analyser and an electronic constant velocity loud-speaker drive, using 3 m Ci Co^{57} in Pd matrix source. The spectrometer was calibrated against sodium nitroprusside and standard iron foil and the spectra were recorded at room temperature ($20^\circ \pm 1^\circ$).

The complex was isolated by mixing equal volumes of 0.1M solution of Fe(III) and $K_3[Mn(CN)_5NO]$ and adding acetone. The green precipitate was filtered, washed successively with water, acetone and ether and dried *in vacuo* over anhydrous calcium chloride. The complex was decomposed with HNO_3 and HCl to estimate Fe and Mn gravimetrically⁵. Water of crystallization was determined by desiccation at 110° for 3 hr {Found: Fe, 18.11; Mn, 17.82; C, 19.41; N, 22.65; H_2O , 11.87.

$Fe[Mn(CN)_5NO] \cdot 2H_2O$ requires Fe, 18.24; Mn, 17.91; C, 19.54; N, 22.80; H_2O , 11.72%.

The green-coloured soluble complex shows absorption maxima at 380 nm ($\epsilon = 700$) while the parent compound² shows λ_{max} at 220, 348 and 540 nm. Vosburg and Cooper's method reveals the formation of only one complex species. A 1:1 stoichiometry for the complex was established by the molar ratio and continuous variation methods. The stability constant of the complex as determined by the molar ratio method works out to be 5.60×10^5 . The value of $-\Delta G$ was found to be 5.105 kcal/mole.

$K_3[Mn(CN)_5NO]$ gives two reduction waves in $KClO_4$. The first wave is well defined and reversible with $E_{1/2} = -0.305$ V, while the second wave is irreversible and spread out with $E_{1/2} = -1.40$ V. The electrode process taking place at the d.m.e. has been suggested^{6,7} to be:



The formation of $[Mn^I(CN)_5]^{4-}$ has also been supported by the work of Jacob⁸.

However, on complexation with Fe(III), the second wave disappears and only one well-defined, diffusion-controlled wave is obtained with a definite shift in $E_{1/2}$ towards more negative potentials (Table 1). The wave is reversible, since the plots of $\log i/i_d - i$ versus $E_{d.e.}$ are linear. There is only one wave due to the reduction of Fe(III). After reaction with Fe(III), only the cationic part, i.e. Fe(III), gets reduced at d.m.e. while the cationic complex moiety has no role to play in the reduction. Lingane's method was used to determine the formula and stability constant of the complex⁹. The stability constant works out to be 5.0212×10^5 which is in agreement with the value obtained by the spectrophotometric method.

The IR spectra of the complex and the parent compound $K_3[Mn(CN)_5NO]$ were almost identical and showed characteristic bands for lattice water (3300 and 1600 cm^{-1}), ν , $C \equiv N$ (2100 cm^{-1}) and, ν , NO (1800 cm^{-1}), thus eliminating any fresh coordination with Fe(III) in the complex. The lowering of the frequency of lattice water suggests some bridging involving OH groups. However, the bridging OH group^{10,11} should show a band around 1100 cm^{-1} . Since no such band is observed, such a possibility is ruled out and the 3300 cm^{-1} band may be assigned to lattice water.

TABLE 1 — SHIFT IN $E_{1/2}$ IN INCREASING CONCENTRATION OF $K_3[Mn(CN)_5NO]$

{[Fe(III)] = $0.15 \times 10^{-2}M$ }	
$K_3[Mn(CN)_5NO] \times 10^3M$	$E_{1/2}$ V
1.5	-0.015
2.0	-0.04
4.0	-0.05
5.0	-0.06

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Magnetic susceptibility of 5.81 BM corresponded to 5 unpaired electrons in the complex indicating that iron in the complex is ionic and in the oxidation state $+3$. $K_3[Mn(CN)_5NO] \cdot 2H_2O$ is diamagnetic. IR spectra and magnetic data, therefore, provide clear evidence that the nitro and the cyano groups are not involved in the reaction with Fe(III).

The Mössbauer spectra of the complex shows isomer shift of 0.23 ± 0.02 mm/sec and a quadrupole splitting of 0.65 ± 0.02 mm/sec. The value of isomer shift and quadrupole splitting show¹² that iron is ionic and in the trivalent state. The narrow line shapes show that Fe is only in one valency state, i.e. $+3$. The unusually large value of quadrupole splitting may be due to lattice distortion^{13,14} around Fe ion as in the case of $FeCl_3 \cdot 6H_2O$.

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Schiff Base Formation from Coordinated Diamine in Mixed Complexes of Cu(II) & Ni(II)

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Template synthesis of Schiff base complexes has been attempted by the reaction of salicylaldehyde with the mixed ligand complexes of the type $[(L-L^2)M \cdot 1,3\text{-diaminopropane}]$, where $L-LH_2$ = catechol or 2,3-dihydroxynaphthalene. The resulting mixed complexes retain $(L-L^2)$ moiety in their structure and the $-OH$ groups of the Schiff base N,N' -propylenebis(salicylaldehyde) remain uncoordinated.

IN a recent communication¹ we have used the template method to react salicylaldehyde with ethylenediamine and propylenediamine in mixed

ligand complexes of the type MAL where $M = Cu(II)$ or $Ni(II)$, $A =$ catechol or 2,3-dihydroxynaphthalene and $L =$ ethylene- or propylene-diamine. Two salicylaldehyde molecules undergo condensation with the two $-NH_2$ groups of the coordinated diamines and because of steric reasons the resultant complexes have a square-planar geometry where coordination occurs through the azomethine nitrogens and ligand A . It has been suggested earlier^{2,3} that the Schiff base may occupy two equatorial and two axial positions if the length of the chain R in the diamine NH_2-R-NH_2 is more. As such the compounds of the type MAL where $M = Cu(II)$ or $Ni(II)$, $A =$ catechol or 2,3-dihydroxynaphthalene and $L =$ 1,3-diaminopropane have been prepared and their reactions with salicylaldehyde studied.

Methods of preparation — (i) Bis- or tris-(1,3-diaminopropane)nickel(II) chloride (0.5 g) was dissolved in the minimum quantity of water and aqueous solution of catechol (1M) added to it. The pH of the resultant solution was ~ 6 . On trituration and leaving the solution aside for 30 min, a bluish green compound was obtained. It was washed with water, dried and analysed. (ii) To a mixture of equimolar (1M) aqueous solutions of nickel chloride and catechol in 1:2 ratio, an aqueous solution of 1,3-diaminopropane (1M) was added till pH was ~ 6 . On trituration and leaving the solution aside for 30 min, a bluish green solid was obtained. It was washed with water, dried and analysed. The analysis of the compounds prepared by methods (i) and (ii) corresponds to the composition $[Ni(cat)-(1,3-pn)] \cdot 2H_2O$. The same method was used for the preparation of $[Cu(cat)(1,3-pn)] \cdot 2H_2O$. Similar mixed ligand complexes were also obtained when 2,3-dihydroxynaphthalene was used instead of catechol. The analytical results are shown in Table 1.

0.5 g of the diamine complex obtained above was reacted with 10 ml of salicylaldehyde. The mixture was refluxed on a water-bath for an hour. The solution was concentrated and excess of ether was added when a solid separated out. The compound in each case was washed with ether to remove excess of salicylaldehyde and recrystallized from chloroform. The compounds were found to be TLC pure (single spot). Co-TLC with Ni-SB indicated that the present complex is a mixed ligand complex of the type [MASB].

The magnetic susceptibilities of the isolated complexes were determined by Gouy's method.

The absorption spectra of the compounds I-IV (Table 1) have been studied in water and of the compounds V to VIII (Table 2) in chloroform. The spectra of the compounds were taken on a DU2 Beckman spectrophotometer at room temperature (30°), using 1 cm quartz cell in the range of 300-1000 nm.

The analysis of compounds I-IV shows them to be mixed ligand complexes. The water molecules are lost at 120° . These may be coordinated or may be water of crystallization.

The visible spectra of the Cu(II) complexes exhibit a broad band at ~ 650 nm. The Cu(II) complexes may have a square-planar structure. In