

STUDIES ON THE COMPLEXES OF PENTACYANOAMMINEFERRATE (II) AND  
SOME ORGANIC BASES

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## ABSTRACT

Sodium pentacyanoammineferrate (II) reacts with *p*-phenylenediamine, *p*-anisidine, *m*-toluidine and *N*-methylaniline to give greenish blue complexes. The composition is 2:1 with *p*-phenylenediamine and 1:1 with the other three bases, confirmed by chemical analysis. Infrared spectra of the complexes show that the base is coordinated to iron through the amino group. Magnetic measurements show that iron is in the +2 oxidation state.

## INTRODUCTION

THE color reaction between pentacyanoammineferrate (II) and (III) and some organic compounds like aromatic amines, aldehydes, thioaldehydes and hydrazines has been used for spot test analysis of these organic reagents<sup>1-4</sup>. While Herington<sup>3</sup> has carried out detailed studies on the reaction of pentacyanoammineferrate (III) with aromatic amines, very little has been done towards this end for pentacyanoammineferrate (II). Studies have thus been carried out on the reaction of pentacyanoammineferrate (II) with *p*-phenylenediamine, *p*-anisidine, *m*-toluidine and *N*-methylaniline.

## EXPERIMENTAL

*N*-methylaniline, *p*-phenylenediamine, *p*-anisidine and *m*-toluidine were BDH products and were purified before use by distillation or crystallisation from ethanol. Sodium pentacyanoammineferrate (II) was prepared from sodium nitroprusside (AnalaR, BDH) by the method described by Brauer<sup>5</sup>.

Bausch and Lomb Spectronic 20 Spectrophotometer and Elico (India) pH meter, LI-10, were used.

Infrared spectra were recorded in KBr discs using Beckman IR '20' spectrophotometer. Magnetic measurements were carried out by Guoy's method at room temperature ( $30 \pm 1^\circ \text{C}$ ).

*Preparation of the Complexes:*

*N*-methylaniline, *p*-phenylenediamine, *p*-anisidine and *m*-toluidine were converted into their respective hydrochlorides. To 50 ml of a solution of 0.01 *M* base hydrochloride (0.005 *M* in the case of *p*-phenylenediamine) was added 50 ml of 0.01 *M* pentacyanoammineferrate (II). After allowing to stand for 1 hour, a solution of zinc acetate (about 4 g) in dilute acetic acid (20 ml of glacial acetic acid in 100 ml of water) was added to precipitate the green gelatinous product. This was filtered off immediately and washed with water till free from acid and  $\text{Zn}^{++}$ . The product was further

washed with alcohol, then ether and finally dried in vacuum over anhydrous calcium chloride.

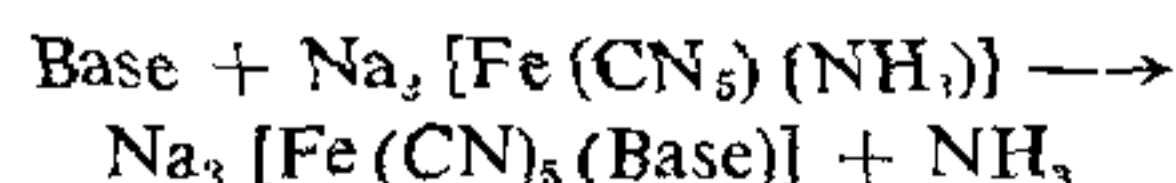
The complexes were chemically analysed<sup>6</sup> for iron and zinc after decomposing by boiling with *aqua regia*. Carbon, hydrogen and nitrogen were estimated at I.I.P., Dehra Dun.

## RESULTS AND DISCUSSION

The organic bases give bluish green complexes with pentacyanoammineferrate (II) in about 1 hour and the reaction decreased in the following order: *p*-phenylenediamine > *p*-anisidine > *m*-toluidine > *N*-methylaniline.

Vosburg and Cooper's method showed the formation of only one complex species. The  $\lambda_{\text{max}}$  of these complexes were observed at 715, 750, 730 and 740 nm for *p*-phenylenediamine, *p*-anisidine, *m*-toluidine and *N*-methylaniline respectively. Job's method and molar ratio method showed the stoichiometric ratio of *p*-phenylenediamine and  $\text{Na}_3[\text{Fe}(\text{CN})_5(\text{NH}_3)]$  is 1:2 and of *p*-anisidine, *m*-toluidine and *N*-methylaniline is 1:1, which is confirmed by chemical analysis (Table I).

The pH of 0.01 *M* pentacyanoammineferrate (II) was 9.7 and that of *p*-phenylenediamine hydrochloride, *p*-anisidine hydrochloride, *m*-toluidine hydrochloride and *N*-methylaniline hydrochloride of the same concentration was 2.9, 4.5, 4.0 and 4.3 respectively. After mixing, the pH rises almost immediately (within 30 seconds) to 6.5 in all the cases and becomes constant within one hour at a pH of 8.0, 7.8, 7.3 and 7.2 respectively. The rise in pH is obviously due to the release of ammonia according to the following scheme:



Magnetic measurements reveal their diamagnetic character, showing that iron is present as  $\text{Fe}^{2+}$  in all the complexes. The infrared bands together with their assignments are given in Table II. The band appearing at  $3300 \text{ cm}^{-1}$  is due to the amine group of the base<sup>7</sup> (absence of a band around  $1600 \text{ cm}^{-1}$  rules out water of crystallisation or  $\text{NH}_3$ ). The C-N band appearing around  $1250 \text{ cm}^{-1}$  also shows shifts indicating coordination through the amine group<sup>8</sup>. The  $\text{C} \equiv \text{N}$  stretching frequency

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TABLE I  
Chemical analysis of the complexes

Complex		% Zn	% Fe	% C	% N	% H
$\text{Zn}_3[\text{Fe}(\text{CN})_5\text{NH}_2\text{C}_6\text{H}_4\text{NH}_2\text{Fe}(\text{CN})_5]$	Found	27.52	16.30	29.10	23.39	1.00
	Calc.	28.93	16.51	28.31	24.77	1.18
$\text{Zn}_3[\text{Fe}(\text{CN})_5\text{NH}_2\text{C}_6\text{H}_4\text{OCH}_3]_2$	Found	24.80	13.53	36.13	19.94	1.00
	Calc.	24.06	13.76	35.38	20.64	1.10
$\text{Zn}_3[\text{Fe}(\text{CN})_5\text{NH}_2\text{C}_6\text{H}_4\text{CH}_3]_2$	Found	26.03	14.43	37.59	21.99	1.00
	Calc.	25.05	14.32	36.83	21.48	1.15
$\text{Zn}_3[\text{Fe}(\text{CN})_5\text{NHCH}_3\text{C}_6\text{H}_5]_2$	Found	25.75	14.41	35.97	22.32	1.00
	Calc.	25.05	14.32	36.83	21.48	1.15

TABLE II  
Infrared absorption bands ( $\text{cm}^{-1}$ )

Complex	$\nu(\text{NH}_3)^*$ or stretching frequency due to amine	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{C}-\text{N})$	$\nu(\text{Fe}-\text{C})$	$\nu(\text{Fe}-\text{N})$
$\text{Na}_3[\text{Fe}(\text{CN})_5(\text{NH}_3)] \cdot 3\text{H}_2\text{O}$	3400* b, st	2040 s, st	..	570 s, st	490 s, m
Complex of pentacyanoammine ferrate (II) with					
<i>p</i> -phenylenediamine	3300 b, st	2060 s, st	1320 sh	565 s, st	470 b, st
<i>p</i> -anisidine	3300 b, st	2090 s, st	1250 s, st	570 m	500 w
<i>m</i> -toluidine	3300 b, st	2080 s, st	1255 m	580 m	500 w
N-methylaniline	3300 b, st	2070 s, st	1260 m	575 m	500 w

s-sharp; st-strong; b-broad; m-medium; w-weak.

appears around  $2080\text{ cm}^{-1}$ . The band around  $600\text{ cm}^{-1}$  and  $500\text{ cm}^{-1}$  may be assigned to Fe-O and Fe-N respectively. It is thus evident that iron in these complexes is coordinated to cyano groups and to the organic base through nitrogen of the amine group.

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