

MÖSSBAUER AND INFRARED SPECTRAL STUDIES ON THE COMPLEXES OF SOME ALKALOIDS WITH FERRO- AND FERRICYANIC ACIDS

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ABSTRACT

The reactions of alkaloids like quinine, cinchonine, quinaldine and procaine with ferro- and ferricyanic acid have been reported. Procaine forms a 2 : 1 complex with ferricyanic acid and 1 : 1 complex with ferrocyanic acid while all other alkaloids give 1 : 1 complexes. Infrared studies show that the alkaloids undergoes protonation of the amine group during complex formation. The $C \equiv N$ stretching frequency appears as a doublet which may be explained on the basis of unsymmetrical hydrogen bonding. Mössbauer studies have shown that iron in hydroferro- and ferrisyanide complexes is present as Fe^{2+} and Fe^{3+} respectively. The isomer shift and quadrupole splitting shows the slight distortion in the symmetry hexacyanoferrate (II) and (III).

INTRODUCTION

REACTIONS of complex iron cyanides with organic bases and related compounds have been reported^{1,2}. However, very limited studies have been carried out with an important class of compounds, the alkaloids. Only recently Burkat³ reported the reaction of antipyrine in acidic medium with potassium hexacyanoferrate (II) while Kreshkov *et al.*^{4,5} reported the reaction of dimethylamino antipyrine with potassium hexacyanoferrate (III). Since, nothing much has been done in this direction, studies have been carried out on the reaction of some alkaloids with ferro- and ferricyanic acids.

EXPERIMENTAL

Reagents :

Ferro- and ferricyanic acids were prepared from potassium hexacyanoferrate (II) and (III) (AnalaR grade, BDH) by the method of Brauer^{6,7}. The alkaloids, quinine sulphate, cinchonine, quinaldine and procaine hydrochloride were of reagent grade and purified by crystallisation from ethanol or double distillation. All other reagents were AnalaR grade (BDH).

Conductometric titrations were performed on Toshniwal Conductivity Bridge CLO1/OIA (India) using a dip type conductivity cell. Infrared spectra of the complexes were recorded on a Beckmann IR-20 infrared spectrophotometer in KBr discs. Mössbauer studies were carried out on Mössbauer spectrometer MBS 35 (ECIL, Hyderabad) using a Co^{57} source in Rh matrix having an initial activity of 2 mCi. The spectrometer was calibrated against sodium nitroprusside.

Preparation of the Complexes :

The complexes were prepared by mixing in stoichiometric ratio, a 0.01 M solution of ferro- or ferricyanic acid with a 0.01 M solution of the

alkaloid in alcohol. The precipitate formed was filtered off at once and washed with alcohol until all the excess unreacted reactants are removed. The precipitate was then dried in vacuum over anhydrous calcium chloride.

Chemical Analysis :

Iron was estimated spectrophotometrically using 1, 10 phenanthroline after decomposing the complexes with aqua regia. Water of crystallisation was determined by desiccating the complexes at about 100° C. Carbon, hydrogen and nitrogen were estimated at I.I.P., Dehradun (India).

RESULTS AND DISCUSSION

The composition of the complexes was determined by conductometric titrations, which shows that procaine forms a 2 : 1 complex with ferricyanic acid and 1 : 1 complex with ferrocyanic acid. On the other hand, quinine, cinchonine and quinaldine form 1 : 1 complexes both with ferro- and ferricyanic acids. The composition of these complexes, as determined by chemical analysis are given in Table I.

Infrared Studies :

The infrared spectra (Table II) of those complexes show O-H symmetric and asymmetric stretching bands and H-O-H bands in the range 3360–3400 cm^{-1} and 1600–1650 cm^{-1} respectively, indicating the presence of water of crystallisation. The Fe-C stretching band in the hydroferro- and ferricyanide complexes appears in the range 520–600 cm^{-1} .

The $C \equiv N$ stretching frequency appears in the range 2000–2070 cm^{-1} for the hydroferrocyanide complexes and 2020–2140 cm^{-1} for the hydroferricyanide complexes. The appearance of a doublet for the $C \equiv N$ frequency is explained on the basis of protonation of alkaloid and subsequent hydrogen bonding^{9, 10} as proposed for ferro- and ferricyanic acids.

TABLE I
Elemental analysis of the complexes

Complex	H ₂ O%		Fe%		C%		N%		H%	
	Cal.	Found	Cal.	Found	Cal.	Found	Cal.	Found	Cal.	Found
1. H ₄ [Fe(CN) ₆] [C ₂₀ H ₂₁ N ₂ O ₂] 0.5 H ₂ O	1.63	2.00	10.20	10.16	56.83	57.95	20.40	21.01	4.91	4.75
2. H ₃ [Fe(CN) ₆] [C ₂₉ H ₂₁ N ₂ O ₂] 1.0 H ₂ O	3.23	3.15	10.05	10.27	56.01	57.32	20.10	21.35	5.20	5.45
3. H ₄ [Fe(CN) ₆] [C ₁₉ H ₂₂ N ₂ O] 1.0 H ₂ O	3.40	3.61	10.60	10.89	56.81	55.76	21.21	20.97	5.30	5.54
4. H ₃ [Fe(CN) ₆] [C ₁₉ H ₂₂ N ₂ O] 0.5 H ₂ O	1.73	2.01	10.81	10.99	57.91	57.02	21.62	20.98	5.01	5.39
5. H ₁₆ [Fe(CN)] [CH ₃ CH ₂ N] 0.5 H ₂ O	2.44	2.54	15.21	15.01	52.17	53.07	26.63	27.39	3.80	3.62
6. H ₃ [Fe(CN)] [CH ₃ C ₁ H ₁ N] 1.0 H ₂ O	4.78	4.98	14.89	14.57	51.06	51.89	26.06	26.79	3.72	3.94
7. H ₄ [Fe(CN) ₆] [C ₁₃ H ₂₆ N ₂ O ₂] 0.5 H ₂ O	1.95	2.27	12.14	11.96	49.45	50.75	24.29	25.15	5.42	5.71
8. H ₃ [Fe(CN)] [C ₉ H ₂₂ N ₂ O ₂] 0.5 H ₂ O	1.29	1.60	8.04	8.20	55.17	56.17	20.11	20.99	6.32	6.21

TABLE II
Infrared absorption bands of the complexes (Cm⁻¹)

Complex	ν (H ₂ O)	ν (NH), ν (NH ₃ ⁺)	ν (C \equiv N)	NH ⁺ , NH ₃ ⁺	ν (Fe — C)
Quinine hydroferrocyanide	3400 (b, st) 1620	2600 (b) ν (NH ⁺)	2000 (s, st) 2020 (s, st) 2040 (sh)	1390 (s) (NH ⁺)	570 (s, st)
Quinine hydroferricyanide	3400 (b, st) 1610	2600 (b) ν (NH ⁺)	2100 (s, st) 2140 (s, st)	1390 (s) (NH ⁺)	520 (st)
Cinchonine hydroferrocyanide	3360 (b) 1620 (m)	2650 (w) ν (NH ⁺)	2030 (s, st) 2060 (s, st)	1730 (s) (HN ⁺)	540 (b)
Cinchonine hydroferricyanide	3380 (m) 1625 (w)	2700 (w) ν (NH ⁺)	2080 (s, st) 2120 (sh)	1400 (w) (NH ⁺)	600 (w)
Quinaldine hydroferrocyanide	3400 (b) 1650 (m)	—	2010 (sh) 2070 (s, st)	1390 (s) (NH ⁺)	550 (st)
Quinaldine hydroferricyanide	3400 (b) 1630 (m)	2600 (w) ν (NH ⁺)	2080 (s) 2110 (s, st)	1395 (s) (NH ⁺)	590 (m)
Procaine hydroferrocyanide	3400 (b) 1610 (b)	2840 (w) ν (NH ₃ ⁺) sym	2050 (s, st)	1470 (w) (NH ₃ ⁺) sym	560 (s, st)
Procaine hydroferricyanide	3400 (b) 1605 (s)	2960 (w) ν (NH ₃ ⁺) asym	2020 (sh) 2100 (s, st)	1550 (w) (NH ₃ ⁺) asym	620 (w)

s = sharp, st = strong, sh = shoulder, b = broad, m = medium, w = weak.

The N—H symmetric and asymmetric stretching bands and N—H deformation bands of the alkaloids shifted to a lower frequency¹¹⁻¹³, on complex formation which indicate protonation of the alkaloids.

In the light of the above considerations it may be concluded that the interaction of the alkaloid with ferro- and ferricyanic acids is taking place through unsymmetrical hydrogen bonding between

TABLE III
Mössbauer parameters of hydroferro- and ferricyanide complexes

Sl. No.	Alkaloid	Hydroferrocyanides		Hydroferricyanides	
		Isomer shift δ (mm/sec) ± 0.02	Quadrupole splitting ΔE_q (mm/sec) ± 0.02	Isomer shift δ (mm/sec) ± 0.02	Quadrupole splitting ΔE_q (mm/sec) ± 0.02
1.	Quinine	-0.206	No	-0.268	0.845
2.	Chinchonine	-0.232	No	-0.263	0.834
3.	Quinaldine	-0.223	No	-0.227	1.133
4.	Procaine	-0.227	No	-0.278	0.824
	Hexacyano- ferrate (II)	-0.138
	Hexacyano- ferrate (III)			-0.186	0.132

the nitrogen of the cyanide group and proton of the amine group of the alkaloid.

Mössbauer Studies :

The Mössbauer spectra of the hydroferrocyanide complexes (Table III) show a small isomer shift and on quadrupole splitting. On the other hand small quadrupole splitting and small isomer shifts are obtained in the case of hydroferricyanide complexes.

The values of isomer shift and quadrupole splitting show that iron in hydroferro- and ferricyanide complexes is present as Fe^{2+} and Fe^{3+} respectively¹⁴. The low values of isomer shift also indicate that they are low spin complexes.

The values of isomer shift and quadrupole splitting in these complexes show a change from those of hexacyanoferrate (II) and (III). This change may be attributed to slight distortions in the symmetry of hexacyanoferrate (II) and (III) on interaction with the alkaloid due to unsymmetrical hydrogen bonding which supports the conclusions drawn on the basis of splitting of the $\text{C} \equiv \text{N}$ stretching frequency in the infrared spectra.

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ACS ELECTION OF CENTENNIAL FOREIGN FELLOWS

Dr. C. N. R. Rao, Professor of Chemistry, Indian Institute of Technology, Kanpur, has been elected as a Fellow from India.