TRICYANOBIS (γ-PICOLINE) NITROSYLIRON (II)

Hexa-coordinated, substituted cyano nitrosyl iron (II) has been prepared using γ-picoline as a substituent. Infra-red spectrum of this compound indicates that tht complex is of *cis* variety having C_{3v} symmetry and there is stronger F-NO back bonding than in nitroprusside ion.

In continuation of our interest to prepare same hexa-coordinated iron (II) nitrosyl complexes[1], which are rare[2], we now report the study of tricyanobis (γ-picoline) nitrosyl iron (II).

γ-PICOLINIUM salt of nitroprusside was prepared by the reaction of stoichiometric amounts of γ-picolinium hydrachloride and sodium nitroprusside dihydrate in methanol, digesting the mixture to precipitate NaCl, and evaporating the solution to a minimum volume followed by drying in vacuum, after removing NaCl by filtration. About 10·0 g of the brown salt was taken in a boat and heated at 145° in an atmosphere of CO_2 for about five hours when the dehydrocyanogenation reaction ceased and a pale greyish-brown mass was obtained. It was cooled under CO_2 atmosphere and then washed with methanol and dried in vacuum.

Found : Fe, 16·30 ; N, 23·8% ; $[FeNO(CN)_3(4\text{-Mepy})_2]$ requires Fe, 15·95 ; N, 24·0%.

The complex is sparingly soluble in alcohols and water and insoluble in other common solvents. Alcoholic solution of $AgNO_3$ does not give any immediate precipitation but on standing, precipitation of AgCN occurs slowly. In aqueous or alcoholic medium, dipyridyl gives immediately a red colour which is presumed to be due to the reaction given below. The dipyridyl complex has been characterised recently using different synthetic routes[1].

$$[FeNO(CN)_3(4\text{-Mepy})_2] + \text{dipy} \rightarrow [FeNO(CN)_3\,\text{dipy}] + 2(4\text{-Mepy})$$

Infra-red spectrum of the γ-pic. substituted complex shows two bands due to CN^- stretching modes and one very strong band due to NO stretching in addition to the bands of coordinated γ-picoline (Table I).

TABLE I

Infra-red spectra of 4-Mepy and [*FeNo*$(CN)_3$ $(4\text{-}Mepy)_2$]

4-Mepy	[FeNO $(CN)_3(4\text{-}Mepy)_2$]	assignments
742 s	722 m	co-ordinated
823 vs	802 s	4-Mepy bands
1015 vs	1022 s	,,
1060 m	1235 m	,,
1235 s	..	..
1430 w	1508 s	,,
1460 w	1625 vs	,,
1610 vs	1640 s	,,
	1907 vs	ν (NO)
	2148 m	ν (CN)
	2187 vs	ν (CN)

vs=very strong, s=strong, m=medium, w=weak. The spectra were recorded in Nujol.

The point group of the molecule should be C_g. The number of i.r. bands expected on this basis due to ν (CN) is three. However, the appearance of only two CN bands suggest that there is not much 'difference' between the nitrogen atoms of NO and γ-picoline and the local symmetry C_{3v} could be assigned for the molecule as observed for some substituted tricarbonyl compounds, where N-donor ligands are the substituents[4]. The appreciable reduction in ν (NO) indicates that Fe-NO back bonding is greater in this complex than that in the starting nitroprusside complex.

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1. Sarkar, S., Singh, R. and Mishra, R. C., Unpublished results.
2. Johnson, B. F. G. and McCleverty, J. A., *Progress in Inorganic Chemistry*, edited by Cotton, F. A., Interscience Publishers, 1966, Vol. 7, p. 339.
3. Cotton, F. A., Monchimp, R. R., Henry, R. J. and Young, R. C., *J. Inorg. Nucl. Chem.*, 1959, 10, 28.
4. Haines, L. M. and Stiddard, M. H. B., *Inorganic Chemistry and Radio Chemistry*, Edited by Emeléus, H. J. and Sharpe, A. G., Academic Press, 1969, Vol. 12, p. 55.