

TRICYANOBIS (γ -PICOLINE) NITROSYLIRON (II)

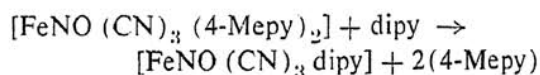
Hexa-coordinated, substituted cyano nitrosyl iron (II) has been prepared using γ -picoline as a substituent. Infra-red spectrum of this compound indicates that the complex is of *cis* variety having C_{3v} symmetry and there is stronger F-NO back bonding than in nitroprusside ion.

In continuation of our interest to prepare same hexa-coordinated iron (II) nitrosyl complexes¹, which are rare², 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 CO₂ for about five hours when the dehydrocyanogenation reaction ceased and a pale greyish-brown mass was obtained. It was cooled under CO₂ atmosphere and then washed with methanol and dried in vacuum.

Found : Fe, 16.30 ; N, 23.8% ; [FeNO(CN)₃(4-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 AgNO₃ does not give any immediate precipitation but on standing, precipitation of AgCN occurs slowly. In aqueous or alcoholic medium, dipyriddy gives immediately a red colour which is presumed to be due to the reaction given below. The dipyriddy complex has been characterised recently using different synthetic routes¹.



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-Mepy)₂]

| 4-Mepy | [FeNO (CN) ₃ (4-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_{3v} . 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 substituents¹. 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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