

SHORT COMMUNICATIONS

THE INFRARED SPECTRA OF SOME IRON(II) PYRIDINE COMPLEXES*

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Iron forms a series of high-spin pyridine complexes of the type $\text{Fe}^{\text{II}}\text{X}_2\text{py}_4$ where py is pyridine and X is any anionic ligand (e.g. Cl, Br, I, SCN, OCN, and HCOO). The preparative description of these complexes is well known¹ but the investigation of their other properties has been limited only to a recent study of the infrared spectrum of the thiocyanate.² In this note we report the infrared spectra of seven such compounds, two of which ($\text{FeI}_2\text{py}_4\cdot 2\text{py}$ and $\text{Fe}(\text{OCN})_2\text{py}_4$) have not been prepared before. The conclusions obtained from this work support those from investigations of the Mössbauer spectra, the u.v. spectra, and the magnetic properties of these complexes which are reported elsewhere.³

The infrared spectra of the complexes in the 270–4000 cm^{-1} region have been investigated but only the bands between 270 and 800 cm^{-1} are given in Table 1. In the 400–4000 cm^{-1} region the main features of the spectra are the strong and sharp absorption bands of the coordinated pyridine molecule. These are identical with those of the free pyridine molecule with the exception of three bands at 403, 601, and 1578 cm^{-1} in the free pyridine molecule which shift to 420, 625, and 1600 cm^{-1} respectively in the coordinated molecule. This observation is consistent with that by Gill *et al.*² who investigated the thiocyanate only from 400 to 2000 cm^{-1} . A band at 745 cm^{-1} in the free base also shifted to just above 750 cm^{-1} in the compounds we investigated. The compounds with empirical formulae FeI_2py_6 and $\text{Fe}(\text{OCN})_2\text{py}_6$ showed bands characteristic of both coordinated and free pyridine (see Table 1). Therefore they are more appropriately represented as, respectively, $[\text{FeI}_2\text{py}_4]\cdot 2\text{py}$ and $[\text{Fe}(\text{OCN})_2\text{py}_4]\cdot 2\text{py}$. Five of the pyridine molecule absorption bands in FeI_2py_4 are split. The splittings probably result from the weak iron–pyridine bonding since FeI_2py_4 is the least stable of all the pyridine complexes studied here and it decomposes even in an atmosphere of dry pyridine.

The thiocyanate ion can coordinate to the metal through either the nitrogen or the sulphur.⁴ These two different modes of coordination are easily distinguishable by the infrared absorption frequencies of the thiocyanate radical. The free thiocyanate ion absorbs at about 750 and 2055 cm^{-1} (C–S and C–N stretching vibrations respectively); these peaks are shifted to 780–860 and 2080–2095 cm^{-1} respectively in the

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¹ Weinland, R., Effinger, K., and Beck, V., *Arch. Pharm.*, 1927, **265**, 352.

² Gill, N. S., Nuttall, R. H., Scaife, D. E., and Sharp, D. W. A., *J. Inorg. Nucl. Chem.*, 1961, **18**, 79.

³ Golding, R. M., Mok, K. F., and Duncan, J. F., *Inorg. Chem.*, in press.

⁴ Ebsworth, E. A. V., "Infra-red Spectroscopy and Molecular Structure." Ch. IX. (Elsevier: New York 1963.)

SCN-metal complex and 690–720 and 2100–2125 cm^{-1} respectively in the NCS-metal complex.⁴ The thiocyanate group in the complex $\text{Fe}(\text{SCN})_2 \text{py}_4$ absorbed at 480, 804, and 2070 cm^{-1} , as would be expected if coordination occurred through the nitrogen atom. This is in accordance with the observation established by X-ray methods that a metal (M) of the first transition series normally forms M–N bonds with the thiocyanate group.⁵

TABLE I

INFRARED SPECTRA OF SEVEN FERROUS PYRIDINE COMPLEXES IN THE 800–270 cm^{-1} REGION
(The assignments of the pyridine molecule vibration bands are those of Gill *et al.*³)

$\text{FeCl}_2 \text{py}_4$	$\text{FeBr}_2 \text{py}_4$	$\text{FeI}_2 \text{py}_4$	$[\text{FeI}_2 \text{py}_4]_2 \text{py}$	$\text{Fe}(\text{SCN})_2 \text{py}_4$	$\text{Fe}(\text{OCN})_2 \text{py}_4$	$[\text{Fe}(\text{OCN})_2 \text{py}_4]_2 \text{py}$	Assignments
752s	765s 754s	750s	765s 755s 744s	764s 752s	762s 755s	765s 755s 745s	4
690s	695s	702s 694s	702s 695s	707s 696s	700s	706s 700s	11
668w (sh)	668w (sh)	670w (sh)	668w (sh)	668w (sh)	667m	670w (sh)	6b
652w (sh)	650w (sh)	650w	650w (sh)	649w (sh)	645w	652w	
622s	622s	622s	627s 622s 603m	622s	612s	623s 618s 604m	6a
485w (b)				480s			
418s	424s	420s	422s 402s	427s 420s	425s 418m	427s 423s 403s	16b
388w	387w	387w	387w	395m	397w	396w	
282w	282w	281w	281w	277s (b)	313s (b)	314s (b)	

The cyanate ion is expected to behave similarly, i.e. it could coordinate through either one of the two terminal atoms. The C–N stretching, C–O stretching, and the skeletal deformation vibrations of the free cyanate ion occur at 2130–2200, 1200–1210, and 625–630 cm^{-1} respectively.⁶ By similar argument to that for the thiocyanate complex, the presence of strong bands at 1330 and 2200 cm^{-1} in the two cyanate complexes suggests a coordination through the nitrogen atom.

In the region from 400 to 250 cm^{-1} all the complexes studied have a relatively weak band at about 390 cm^{-1} . In addition the thiocyanate complex has a strong and broad band at 278 cm^{-1} while the two cyanate complexes have a similar band at 313 cm^{-1} . Such a band is likely to be due to iron–nitrogen vibration where the nitrogen atom is part of the thiocyanate or the cyanate ligand. This is consistent with the

⁵ Nakamoto, K., "Infra-red Spectra of Inorganic and Coordination Compounds," (John Wiley: New York 1963.)

⁶ Maki, A., and Decius, J. C., *J. Chem. Phys.*, 1959, **31**, 772.

fact that the ratio of these two frequencies, $278/313 = 0.89$, is approximately equal to the expected value calculated on the assumption that the force constant is approximately the same for the two Fe-N bonds. Thus:

$$\frac{\nu(\text{Fe-NCS})}{\nu(\text{Fe-NCO})} = \left\{ \frac{\mu(\text{Fe-NCO})}{\mu(\text{Fe-NCS})} \right\}^{\frac{1}{2}} = \left\{ \frac{97.87}{113.93} \right\}^{\frac{1}{2}} = 0.93$$

which is in as good agreement with the observed value as can be expected on the assumptions made.