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Mössbauer Spectroscopy of Iron(III) Species with Pyridine and Other Nitrogen Donor Ligands

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Introduction

A large number of spectroscopic techniques have been widely used in the study of complexes in solution. Mössbauer spectroscopy seems promising as it gives information on the electronic structure of the Mössbauer atoms, provided the solutions are frozen.

In this study we have compared the Mössbauer data obtained for frozen solutions of iron(III) in pyridine with those obtained for solid complexes of iron(III) with nitrogen donor ligands already characterized by other methods.

Experimental

Reagents and Iron(III) Species

All solvents were purified and dried by standard methods. The anhydrous $FeCl_3$ was used without further purification. The anhydrous solutions of $FeCl_3$ and $Fe(SCN)_3$ [1] in pyridine were prepared in an inert-atmosphere glove box with a water content lower than 10 p.p.m.

The preparation of the compounds $FeCl_3py_4$ (py = pyridine), $FeCl_3pz_3$ (pz = pyrazole), $FeCl_3(Mepz)_3$ (Mepz = methylpyrazole) and $Fe(SCN)_3py_3$ is described elsewhere [2–4].

Mössbauer Spectra

The Mössbauer samples were mounted in a copper sample holder with PVC windows. The liquid samples were frozen by immersion in liquid nitrogen. All the experiments were run with the absorber at liquid nitrogen temperature and the source (^{57}Co in a Pd matrix) at 298 K. The Mössbauer equipment is described elsewhere [5]. The spectrometer calibration was made with a natural iron foil.

Infrared Spectra

The infrared spectra in the range 4000–200 cm^{-1} were recorded on a Perkin Elmer 577 spectrometer. The samples were mounted between CsI plates.

Results and Discussion

A typical spectrum of a frozen solution containing iron trichloride in pyridine is given in Fig. 1.

The spectral parameters for the anhydrous solutions and for the solid complexes with nitrogen donor ligands are shown in Table I.

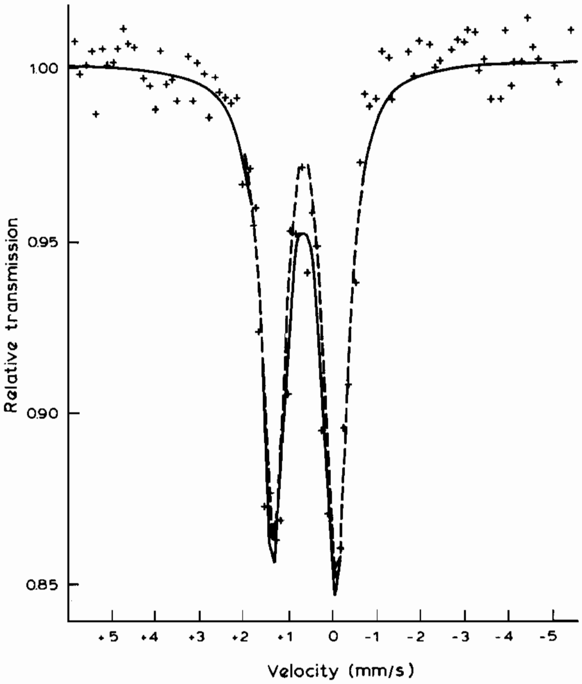

Fig. 1. Mössbauer spectra of a frozen solution of $FeCl_3$ in pyridine.

TABLE I. Mössbauer Parameters for Iron(III) Species with Nitrogen Donor Ligands.

Sample	δ (mm/s)^a	Δ (mm/s)	Γ_a, Γ_b (mm/s)
$FeCl_3$ in pyridine^b	0.56	1.45	0.66; 0.62
$FeCl_3py_4$	0.57	0.39	0.34; 0.32
$FeCl_3pz_3$	0.58	–	0.90
$FeCl_3(Mepz)_3$	0.55	0.94	0.35; 0.60
$Fe(SCN)_3py_3$	0.54	0.75	0.56; 0.56
$Fe(SCN)_3$ in pyridine^b	0.56	0.79	0.60; 0.56

$^a\delta$ stands for the centre shift referred to stainless steel; Δ for the quadrupole splitting and Γ_a and Γ_b for the linewidths for the lines of higher and lower velocity respectively. The error is estimated at ±0.02 mm/s. ^{b}The conc. of $FeCl_3$ and $Fe(SCN)_3$ in pyridine was ~0.2 *M*.

The isomer shift for $FeCl_3$ in pyridine solution probably indicates a six coordinated species [6] although the quadrupole splitting is larger than the

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one usually found for an iron(III) species of high spin. An I.R. spectrum obtained for this solution indicates the presence of coordinated pyridine (ring vibrations at 630 cm^{-1} and 432 cm^{-1} compared with 604 cm^{-1} and 405 cm^{-1} respectively, in free pyridine). A conductivity measurement of the same solution shows evidence of a molecular species. The conductivity measurement of a $FeCl_3$ solution in pyridine shows a negligible ionization compared with a solution of tetraethylammonium perchlorate, which is known to be a 1:1 electrolyte in pyridine [7]. From these observations the solution of $FeCl_3$ in pyridine can be formulated as a polymeric or monomeric species of the type MA_3B_3.

If the point charge model is applied to complexes of type MA_3B_3, a zero quadrupole splitting is expected for a facial configuration and a non-zero quadrupole splitting for a meridional one [6]. In fact the $FeCl_3pz_3$ and the $FeCl_3py_4$ species that have been formulated elsewhere as being of a facial type [3] have no quadrupole splitting in the former case and only 0.39 mm/s in the latter, this small value probably being caused by a slight distortion from the octahedral geometry due to the presence in the lattice of the fourth pyridine molecule that is not coordinated (as shown by the I.R. spectra). On the other hand, the $FeCl_3(Mepz)_3$ with a meridional structure [3] shows an appreciable quadrupole splitting, although much smaller than the one found in $FeCl_3$ in pyridine. Moreover, the $Fe(SCN)_3py_3$ compound and a solution of $Fe(SCN)_3$ in pyridine have similar Mössbauer parameters, as shown in Table I, indicating that the species present in the solid and in the solution are probably identical and they must have a meridional configuration as shown by the quadrupole splitting values. Nevertheless, the quadrupole splittings are also smaller than in the case of the solution of $FeCl_3$ in pyridine.

The abnormally high value for the quadrupole splitting of the iron chloride in pyridine solution may be explained by the formation of a polymeric species. In fact, in previous studies of some Schiff-base iron(III) compounds, Bancroft *et al.* [8] found that the dimeric species gave larger q.s. values thant the monomeric species. Moreover, the values that these authors obtained for the difference between the q.s. values for the dimeric and monomeric compounds are about the same as those we found between the q.s. value for $FeCl_3$ in pyridine solution and the q.s. values for $FeCl_3(MePz)_3$ and $Fe(SCN)_3py_3$.

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References

1 J. C. Bailar, H. J. Emeleus, R. Nyholm and A. F. Trotman-Dickenson, 'Comprehensive Inorganic Chemistry', 3, 1040.

2 G. Spacu, *Ann. Sci. Univ. Jassy, 8*, 30 (1914).

3 S. A. Cotton and J. F. Gibson, *J. Chem. Soc. (A)*, 1696 (1971).

4 C. D. Burbridge, M. J. Cleare and M. L. Goodgame, *J. Chem. Soc. (A)*, 1698 (1966).

5 Noémia Marques, *M.Sc. Thesis (U.N.L.)* (1978).

6 G. M. Bancroft and R. H. Platt, 'Mössbauer Spectra of Inorganic Compounds: Bonding and Structure' in *Advances in Inorganic Chemistry and Radiochemistry, 15*, 59 (1972).

7 H. Peterson, Jr. and R. S. Drago, *Inorg. Chim. Acta, 3*, 155 (1969).

8 G. M. Bancroft, A. G. Maddock and R. P. Randl, *J. Chem. Soc. (A)*, 2939 (1968).