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Mössbauer Spectroscopy Studies of Tris(2-Pyridinalimine) and Tris(2-Pyridilketoimine)iron(II) Complexes

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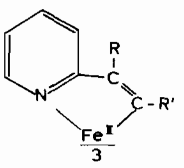
Introduction

In a recent review, Krumholz [1] pointed out the importance of back-donation in explaining the properties of iron(II)–diimine complexes. According to him and to most authors [2–4], the exceptional stability, the diamagnetism, the intense ET bands, and other properties of these spin-paired complexes are due to the extent of back-donation, *i.e.* the extent to which electrons in filled *d* orbitals localized essentially on the metal atom are delocalized into vacant π^* ligand orbitals. The degree of covalent bonding between the iron atom orbitals and those of the ligands will depend on the σ and π donor, and π acceptor abilities of the ligands.

The Mössbauer spectra of iron transition metal complexes provide information abou the iron configuration and have been progressively utilized in elucidating the structure and bonding in a large number of complexes [5, 6]. In particular, the isomer shift (δ) measures the electron density at the iron nucleus and the quadrupole interaction reflects the asymmetry of the iron electronic wavefunction. These two pieces of information cannot be used to define the several molecular orbitals important in chemical bonding, but they may prove useful in deciding between various models of a given molecule. The Mössbauer hyperfine parameters can be very useful when one studies a series of compounds in which a single group is varied systematically. Recent studies on a series of tris(diimine)–iron(II) complexes evidenced that the iron electronic structure is influenced by steric rather than electronic effects induced by the substituents [7].

In the present report we discuss some Mössbauer spectroscopy studies on the series of tris(2-pyridinalimine)- and tris(2-pyridilketoimine)iron(II) complexes shown in Figure 1. Some of these complexes have been already reported [8–12]. More drastic modifications are expected in the Mössbauer spectra for these complexes than in the tris(diimine)iron(II) complexes due to the greater proximity of the substituents to the iron atom. The fact that the different radicals are bonded to the imino nitrogen suggested to us that these compounds could be more suitable for systematic studies.



I - R = H ; R' = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9
II - R = CH_3 ; R' = H, CH_3, C_6H_5

Fig. 1. The iron(II) complexes studied in the present work. I) Tris-(2-pyridinalimine); II) Tris-(2-pyridilketoimine).

Experimental

The tris(2-pyridinalimine)- and tris(2-pyridilketoimine)iron(II) complexes were prepared by literature methods [8, 9].

The Mössbauer spectra were recorded in 1024 channels of a Hewlett–Packard Multichannel analyser with a drive unit which provides a sinusoidal motion to the source. The data were collected at room temperature and 4.2 °K, the source and absorber were kept at the same temperature. The detector was a proportional counter with a Kr/CO_2 gas mixture and the source was 23 mCi of ^{57}Co diffused in a copper matrix. Calibration of the spectrometer was accomplished by the Mössbauer spectra of an iron metal standard foil, after each measurement. The data folding and linearization were carried out on a 370/175 IBM computer. An iterative least-squares Lorentzian line shape program was used to obtain the Mössbauer parameters. The isomer shift values are referred to the $^{57}Co/Cu$ source in the figures.

The average linewidth for the doublet was 0.25 mm/s and the reproducibility of the data in three measurements gave an error of *ca.* 0.008 mm/s.

Results and Discussion

A representative set of Mössbauer spectra for some of the complexes is shown in Figure 2. Although the series include ligands with varying structures their spectra are very similar showing small resolved doublets. The Mössbauer parameters obtained from the computer fitting of our data are shown in Table I. The indicated geometrical isomers have been chemically separated.

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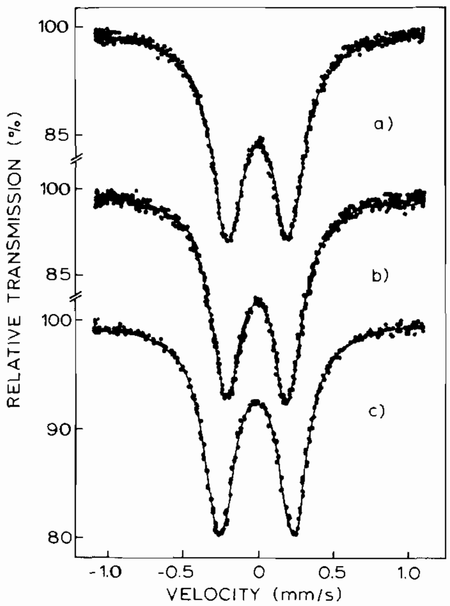

Fig. 2. Mössbauer spectra obtained at 4.2 °K for the complexes with the following R,R′ substituents: a) H, CH_3; b) H, C_4H_9 and c) CH_3, CH_3.

TABLE. Mössbauer Parameters Obtained for the Tris(2-pyridinalimine) and Tris(2-pyridilketoimine)–Iron(II) Complexes Shown in Figure 1.*

No.	R; R′	δ (mm/s)		ΔEq (mm/s)	
		295 °K	4.2 °K	295 °K	4.2 °K
1	H; CH_3	0.247	0.196	0.370	0.395
2	H; C_2H_5	0.265	0.212	0.366	0.393
3	H; n-C_3H_7 a	0.274	0.216	0.365	0.389
	b	0.271	0.209	0.350	0.367
4	H; n-C_4H_9	0.267	0.216	0.370	0.392
5	CH_3; H	0.205	0.163	0.570	0.581
6	CH_3; CH_3 a	0.242	0.207	0.461	0.486
	b	0.248	0.210	0.456	0.480
7	CH_3; C_6H_5	0.308	0.257	0.361	0.382

*The error in δ and ΔEq is about ± 0.008 mm/s and the linewidth of the doublet is on average 0.25 mm/s. The isomer shifts are referred to a metallic iron absorber. (a) and (b) are geometrical isomers.

In a study of a series of similar complexes the decrease in isomer shift cannot be unequivocally attributed to the increase of either σ-bonding or backbonding. But if a regular correlation exists between the Mössbauer parameters, at least qualitative information can be obtained concerning which bonding is mainly modified along the series.

It is already established that forward σ-coordination as well as back-donation [5] both lead to an increase in the *s* electron density at the iron nucleus with a consequent decrease in the isomer shift ($\Delta R/R < 0$ for ^{57}Fe): through σ-bonding electrons are transferred from the ligands to appropriated iron empty orbitals, hybridized as may be required by geometry, which have at least partial 4*s*-character; back-donation transfers *d*-electrons from the iron atom to appropriate ligand empty orbitals and consequently decreases the shielding of *s* electrons.

The considerations regarding the quadrupole splitting for the present compounds are the same which have been made for the tris-diimineiron(II) complexes [7], since in both cases the iron atom, with d^6 configuration, is covalently bonded to six nitrogens and has a D_3 point group symmetry. It is mainly the *d*-electrons which give a positive contribution to the electric field gradient that will be delocalized into the ligands empty orbitals, and as a result the negative contribution to the EFG given by electrons in the d_{z^2} iron orbital will predominate if back-donation becomes important. The σ-forward coordination should populate empty *d*-orbitals which give a positive contribution to the EFG, and as a consequence if this bonding is mainly increased along a series of compounds the isomer shift should become more negative while the quadrupole splitting should become more positive.

A plot of the quadrupole splitting, ΔEq, *versus* the isomer shift relative to the copper source, δ_{Cu}, for these seven compounds is shown in Figure 3. A considerable degree of correlation exists for the compounds with pyridilketoimine ligands (II), but the same is not true for the compounds with pyridinalimine ligands (I) since their Mössbauer parameters are distributed in a very narrow range of values.

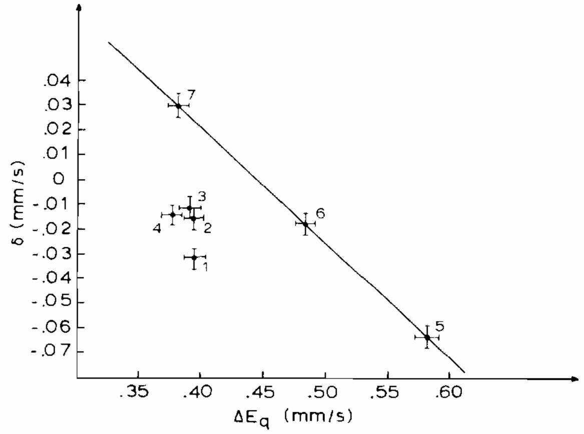

Fig. 3. Isomer shift *versus* quadrupole splitting, in mm/s, measured at 4.2 °K for the compounds listed in Table I.

To discuss the bonding information obtained from Figure 3 it will be assumed that the EFG is negative as has been observed to be the case for similar iron(II) complexes [7, 9–13]. On this basis one may conclude that in the pyridilketoimine series of complexes the back-donation decreases along compounds 5, 6 and 7 (see Table I): the back-donation strength is reduced as the size of R′-substituent increases. This result supports the assumption made by Krumholz [1, 8], to explain the shift of the charge transfer bands in the electronic spectra: the hindrance between the R′-substituents and the CH_3 can cause a shift from the coplanar structure of the ligands, leading to a decrease in π-back-coordination since conjugation is less favourable. The twisting angles should increase with substituent size as has been discussed by Favini and Simonetta [14]. This result is qualitatively different from the one which was obtained in the series of tris-diimineiron(II) complexes [7]. There the phenyl substituent induced 80% increase in the quadrupole splitting while the isomer shift was not affected: what was observed is mainly a decrease in the complex symmetry. In the present case the modification of quadrupole splitting is followed by a change in the isomer shift in such a way that one may assume that the ligand π-acception ability is sensitive to the R′-substituents.

In the case of tris(pyridinalimine)iron(II) compounds very small modifications are introduced by the different R′-substituents: the Mössbauer parameters are the same, within the experimental accuracy, for the complexes 2, 3 and 4 (Table I). However, compound 1 which has the smaller R′-substituents shows a small increase in back-bonding. In this case the hindrance cannot be between the R and R′-substituents but may occur between the pyridine and the R′-substituent belonging to different ligands, the effect being much weaker as should be expected.

It is not possible to get enough information from these compounds about the effect of the R-substituent since only compounds 1 and 6 (Table I) have the same R′-substituent. More data are being prepared to further investigate this aspect of the problem.

Conclusion

The Mössbauer studies in these series of iron(II) compounds with bidentate ligands confirm that the characteristics of such complexes are determined mainly by the electron delocalization within the five membered chelate ring. This delocalization is strongly affected when the substituents induce a decrease in the conjugation: due to hindrance effects back-donation decreases and the Mössbauer parameters are sensitive to this effect.

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