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Mössbauer Spectroscopy of Iron(II) Diimine Complexes

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The influence of alkyl and aryl groups attached to the diimine ring of the ligand on the properties of several iron(II) diimine complexes was investigated by ^{57}Fe Mössbauer spectroscopy. The Mössbauer spectra, taken at 295 and 4.2° K, showed that the isomer shift (δ) remains almost constant in all the series, whereas the quadrupole splitting (ΔE_Q) changes markedly when a phenyl group is present in the ligands. Measurements with external applied magnetic field indicated a negative sign for the electric field gradient at the iron nucleus. The results are discussed on the basis of the comparison with the electronic spectra, taking into account the special features which arise from the presence of a phenyl group at the ligands.

Introduction

The complexes of low-spin iron(II) with the diimine ligands, 1,10-phenanthroline (phen) and 2,2′-dipyridine (dipy), are known since the end of the nineteenth century[1]. Two other complexes, with glyoxal bis(methylimine) (GMI) and biacetyl bis(methylimine) (BMI) of this class have been prepared by Krumholz, using non-aromatic ligands[2]. The study of this class of complexes[3] has been recently extended with the synthesis of six new complexes[4]. In this series gradual changes in the ligands were introduced (Figure 1) in order to observe their influence on the electronic spectra[4] and nuclear hyperfine interactions.

The Mössbauer spectra of the phen and dipy iron(II) complexes are known since 1962[5–9]. The large values obtained for the quadrupole splitting (ΔE_Q) were interpreted as good evidence of distortion from the O_h symmetry. Mössbauer spectroscopy has also proved to be useful to study the participation of the ligand orbitals in the metal–ligand bonds[8]. The existence of the so-called "back-donation" in these complexes has been also evidenced[9]. In the case of the complexes $Fe(GMI)_3^{2+}$ (R and R′ = H) and $Fe(BMI)_3^{2+}$ (R and R′ = CH_3) the Mössbauer spectra have been first investigated by Epstein[6], in comparison to the analogous phen and dipy complexes. This author, however, was not successful in obtaining good numerical values for the Mössbauer parameters, probably due to impurities in his samples. In 1974 Schlosser *et al.*[10] reported a study on a series of diimine complexes, including the two above-mentioned complexes, giving more precise results.

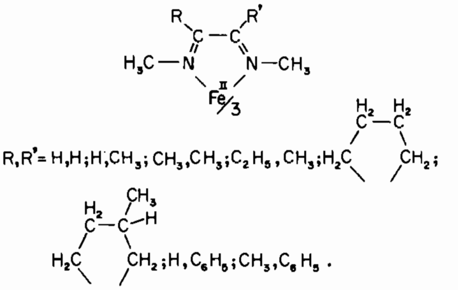

Figure 1. The iron(II) tris-diimine complex series studied in this work.

The electronic spectra of these diimine complexes, recorded in solid state at liquid nitrogen temperature, have indicated the occurrence of three metal to ligand electron transfer (MLET) bands[4], in the visible region. These bands have been associated to transitions from the filled metal e and a_1 orbitals to the ligand π^* orbitals (e and a_2), considering the complex as having D_3 symmetry. The main bonding interactions in the ground state were postulated to involve the filled "d_{xy}, d_{xz} and d_{yz}" metal orbitals and the empty π^* ligand orbitals, with some degree of back-bonding stabilization. The changes on the diimine ligand lead to appreciable variation in the electronic spectra, principally in the case of the complexes of ligands containing a phenyl group[4]. In the present work we attempted to determine the effect of the R and R′ substituents on the Mössbauer parameters, in order to evaluate how and how

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much the variations in these ligands can perturb the metal–ligand bonds.

Experimental

The iron(II) diimine complexes were prepared and characterized as reported in reference 4.

The Mössbauer spectra were recorded using 1024 channels of a Hewlet–Packard Multichannel Analyser. The data were accumulated in the multiscaling mode with a dwell time of 50 μsec per channel. The drive unit, made in the Physik Department of the Technische Universität München, provides a sinusoidal motion to the source. The phase and frequency of the source motion was synchronized to the external advance address control of the multichannel analyser. The detector used was a proportional counter of Kr/CO_2 obtained from Harshaw and the source was a 23 mC of ^{57}Co diffused in a Cu matrix. A natural iron foil was used as absorber for the velocity calibration determination. The 4.2° K absorption spectra have been taken with both source and absorber kept in liquid helium. For this measurement a modified Sulfrian Cryogenics Inc. Cryostat has been employed.

The measurements with external magnetic field have been done with a 50KG superconducting solenoid obtained from Oxford Instrument. The absorbers, kept at 4.2° K, were microcrystalline and thin typically of the order of 7 mg/cm^2 of natural iron, in order to avoid any broadening of the resonance lines.

The data were folded and linearized with a 370/175 IBM computer, and an iterative curve fitting procedure was used to determine the Mössbauer parameters (isomer shift, quadrupole splitting and peak height). The solid line for all Mössbauer patterns appearing in this paper represents the Lorentzians least squares fit of the data. The isomer shift data are referred to a ^{57}Co/Cu source.

Results

The Mössbauer spectra of all studied iron(II) diimines consist of a well resolved doublet. Figure 2 illustrates the room temperature spectra for some of the compounds which, in general, have low absorption. The resonance is markedly increased when source and absorber are cooled down to liquid helium temperature, as can be seen from the spectra shown in Figure 3. The parameters obtained from the least squares fitting of the data are reported in Table I. In the spectrum of the $[Fe(CMI)_3](ClO_4)_2$ complex, the deviations from the calculated Lorentzians curves are, probably, due to another iron species arising from ligand oxidation[11].

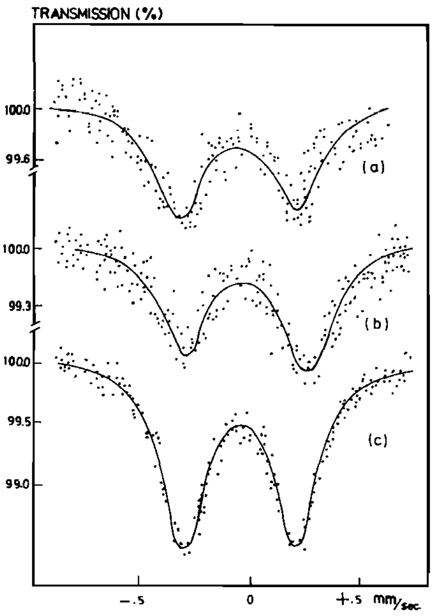


Figure 2. Room temperature Mössbauer spectra of the complexes with ligands: a) EMI, b) CMI and c) MMI.

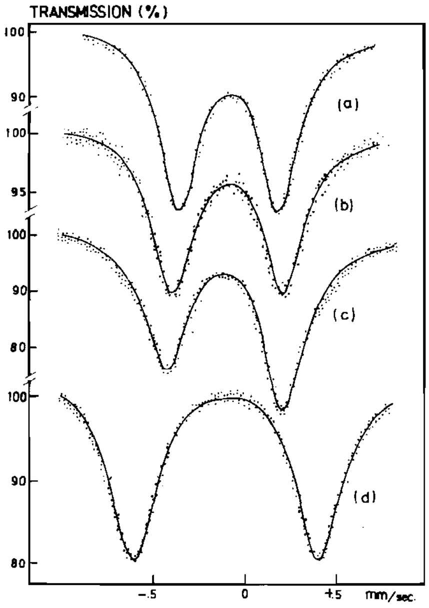
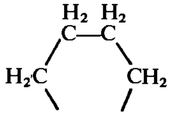
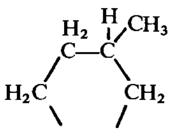


Figure 3. Liquid helium temperature Mössbauer spectra of the complexes with ligands: a) MMI, b) EMI, c) CMI and d) FMI.

The Mössbauer parameters reported in Table I are closely related to the characteristic parameters of the known tris-bidentate low-spin iron(II) complexes[5–7]. In some cases they seem to indicate a rather large static distortion relative to other diamagnetic six-coordinate polyimine systems whose quadrupole splitting is smaller. Less information is available from the isomer

TABLE I. Mössbauer Parameters for the Iron(II) Tris-diimine Complexes. The error in δ and ΔE_Q is about ± 0.005 and the Γ for the doublet varies from 0.23 to 0.26 mm/sec. The isomer shift values are referred to a ^{57}Co/Cu source.

	Iron(II) Complexes		δ (mm/s)		ΔE_Q (mm/s)	
		R, R′	295°K	4.2°K	295°K	4.2°K
1	BMI	CH_3, CH_3	–0.029	–0.078	0.525	0.553
2	MMI	H, CH_3	–0.042	–0.096	0.508	0.532
3	GMI	H, H	–0.064	–0.113	0.549	0.582
4	EMI	CH_3, C_2H_5	–0.060	–0.106	0.553	0.593
5	CMI		–0.063	–0.124	0.592	0.635
6	MCMI		–0.059	–0.118	0.585	0.601
7	FMI	H, C_6H_5	–0.060	–0.109	0.934	0.946
8	MFMI	CH_3, C_6H_5	–0.058	–0.107	0.950	0.980

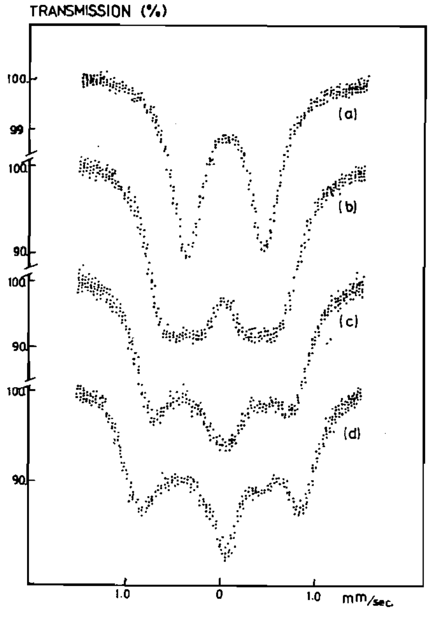


Figure 4. Mössbauer spectra of the $[Fe(BMI)_3](ClO_4)_2$ complex with applied magnetic filed parallel to incident gamma rays. H_{ex} equal to: a) O KG, b) 11 KG, c) 18 KG and d) 23.5 KG.

shift since its values fall in a very narrow span of values.

The observation of the Mössbauer spectra of polycrystalline samples in an external magnetic field enables us to determine the sign of the principal component of the electric field gradient (EFG) as well as an estimate of the asymmetry parameter[12].

The computed magnetic perturbed spectra of Collins and Travis[13] show that when the asymmetry parameter (η) is zero, an applied magnetic field causes the $\pm 1/2 \rightarrow \pm 3/2$ line to split into a poorly defined doublet and the $\pm 1/2 \rightarrow \pm 1/2$ line to split into a triplet with well resolved outer lines and a weak inner line. The spectra progress smoothly, as η goes from zero to one, from a doublet–triplet to a symmetrical triplet–triplet. Such measurements have been performed at 4.2° K for the $[Fe(MFMI)_3](ClO_4)_2$ complexes in which a strong effect has been observed from the substitution of the R′ radical. The spectra of the BMI complex are shown in Figure 4. In the case of the MFMI complex, we observed a larger splitting of the bands.

These spectra were compared to the theoretical ones[14] for the case of randomly oriented EFG and detection axis parallel to the applied field. The conclusions derived from the examination of these spectra are: a) V_{zz} is negative for both EMI and MFMI complexes. b) One can establish a lower limit of about 0.4 for η in both cases. c) No internal magnetic field induced by the external field at 4.2° K was observed as expected with such diamagnetic complexes.

Discussion

In this series of tris-diimine complexes, as well as for the other complexes with bidentate ligands, it is generally assumed that the symmetry around the central ion is the D_3 point group symmetry. We do not take into account the possibility of a further decrease in symmetry due to different R and R′ substituents in *cis*-position. The metal *d* orbitals of cubic t_{2g} parentage will split into a singlet and a doublet which transform as the A_1 and E irreducible representations of the point group D_3, whereas the *d* orbitals of cubic e_g parentage still belong to a doublet which transforms as the E representation. Figure 5 illustrates a MO energy level diagram obtained from a correlation scheme with octahedral symmetry.

These arguments do not indicate the relative energies of the orbitals and no information is available about their metal character. The electronic distribution around the iron nucleus is determined by the order of occupancy of the complex MO's in addition to the metal character they adopt. Strong ligands as tris-diimine produce a spin-pairing in iron(II) giving a $(a_1)^2(e)^4$ configuration.

The degree of covalent overlap between the iron metal orbitals and ligand orbitals depends on the σ and π donor and π-acceptor ability of the ligands. The information obtained from Mössbauer spectroscopy about the nature of the bonds is concerned mainly with the 4*s* and 3*d* orbital population[14,15]. Most authors[3,16–18] agree that the stabilization of spin-paired iron(II) diimine complexes is due to the extent to which electrons in filled d_π orbitals are delocalized into vacant π^* ligand orbitals. This participation of empty ligand orbitals in the MO localized essentially on the metal is often called back-donation.

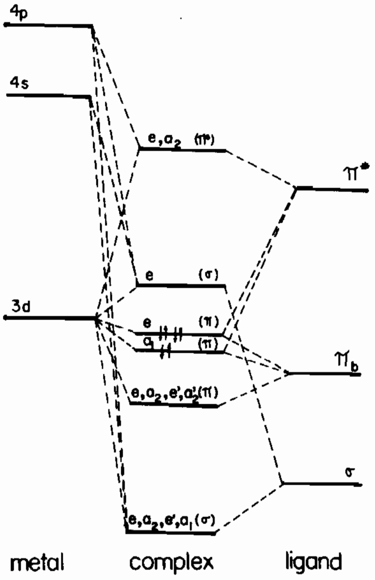


Figure 5. Molecular orbital energy level diagram for iron(II) tris-diimine complexes, considering a D_3 point group symmetry.

This series of tris-diimine complexes allows us to correlate the experimental results with changes in the covalency ability of the ligands due to the systematic variation of alkyl substituents, since they perturb the molecule by changing the energy of the complex MO's.

Isomer Shift

The isomer shift is related to the total *s* electron density at the iron nucleus and it becomes more negative with the increase of *s* electron density at the nucleus. The degree of covalent overlap between the central metal and the ligands can affect the charge density at the nucleus mainly by the direct increase of 4*s* population or by the change in the 3*s*–4*s* shielding due to modification in the 3*d* population. The isomer shift will become more negative both with increasing σ-donor and π-acceptor ability of the ligands[14,19] in such a way that the change in the isomer shift for different ligands cannot be attributed exclusively to σ-bonding or π back-donation. No unequivocal conclusion as to the extent of each effect can be achieved purely on the basis of this parameter.

No systematic variation in the isomer shift was observed in all the series of different substituents in the tris-diimine complexes studied since the values of isomer shift fall within a very narrow range. This fairly low variation of δ correlates very well with the observation that 10Dq was assumed to be nearly constant for the whole series in the electronic spectra studies[4], since this parameter is also sensitive to the covalence abilities[20] of the ligands.

The trend of the isomer shift value for complexes 1 to 3 could be correlated to the perturbation introduced by the methyl group. A similar trend is also observed in the MLET bands of the electronic spectra. These results suggest that the methyl substituents induce a slight decrease either in the σ-donation or π back-donation ability of the diimine ligands.

Quadrupole Splitting

The ΔE_Q values are valuable in giving information about the symmetry of iron complexes. They are also useful in examining the σ and π bonding ability of the ligands, especially when examined together with the isomer shift values[21].

The EFG at the nucleus[22] of a given atom may be considered to be the sum of two contributions: the field gradient generated by the atom's own electron cloud (q_{val}) and that generated by distant charges. Of these two effects the former is usually by far the most important and we will consider only the immediate environment of the nucleus. Thus the principal component of the EFG at the nucleus can be taken to be the sum of the contribution made by the non-spherical *d* electrons multiplied by the Sternheimer factor (1–R) which corrects for the polarization of the electrons in spherical orbitals[23].

For the low spin iron(II) complexes no odd electron contribution exists and the EFG due to valence electrons depends only on the symmetry of the complex and the nature of metal–ligand bonds.

The main contribution from the tris-diimine complex MO's to the EFG should come from the a_1 and e filled orbitals since they have stronger component of the EFG at the nucleus and will depend on the participation of different d orbitals on the symmetry adapted wave function which represents the a_1 and e orbitals and from the overlap distortion effects which determine their "effective" population[24]. If we assume that the z axis is along the three fold symmetry axis C_3[25] the orbital singlet a_1 wave function will have a d_{z^2} character, with $V_{zz}<0$ and the orbital doublet e wave function will be:

$$e_a = \frac{1}{\sqrt{3}}(\sqrt{2}|d_{x^2-y^2}> + |d_{xz}>) \text{ and}$$

$$e_b = \frac{1}{\sqrt{3}}(\sqrt{2}|d_{xy}> - |d_{yz})$$

with $V_{zz}>0$.

In the system under consideration (distorted strong field complexes) σ and π bondings effects are not readily separated. However, the existence of intense MLET transitions[4] can be taken as evidence that the bonding of importance for the stabilization of the tris-diimine complexes is the result of the delocalization of metal electrons on the empty ligand π^* orbitals[3]. Let us consider only the π acceptor properties of the ligands.

The electronic spectra studies suggest that the metal a_1 orbital should have a lower energy than the metal e orbitals[4]. This is an agreement with the negative sign found by us for the EFG in the BMI and MFMI complexes if we take into account the π back-donation. Electrons in e orbitals make positive contributions to the q_{val} and these contributions will decrease in magnitude as these electrons become more delocalized, with the predominance of negative contribution due to electrons in a_1 orbital ground state. The extent to which the d_e metal orbital population decreases due to back-donation makes the electronic distribution more asymmetric with increasing ΔE_Q.

The small variation of ΔE_Q values in the series from complex 1 to 6 indicates that the change in π-acceptor ability of the ligand is very slight, maintaining the complex orbital energy and population nearly undisturbed. However, the slight trend observed in the isomer shift values for complexes 1, 2 and 3 does not work properly for the quadrupole splitting on the basis of π back-bonding, since a correlation between δ and ΔE_Q is not observed.

The introduction of a phenyl group in the ligands induces a perturbation on the complex MO which is seen in the electronic spectra by the increasing splitting of the MLET band[4] and induces an increase of 80% on the magnitude of ΔE_Q as observed by Mössbauer spectroscopy. Two assignments can be made for this result: one is a purely steric effect causing a decrease of symmetry, and the other is the increase of the π-acceptor ability of the ligand by extension of conjugation. The most probable effect is the steric one, since the conjugation is expected to be decreased by the non-coplanar structure of the ligand as shown by Favini and Simonetta[26]. This hypothesis seems to be confirmed when we observe that ΔE_Q markedly increases when a phenyl group is introduced in the ligands while δ remains nearly constant. Moreover, the phenyl group planarity should be hindered more by the methyl than by the hydrogen, which is consistent with the ΔE_Q values reported for complexes 7 and 8 in Table I. Thus the distortion introduced by the phenyl substituent can lead to a further splitting of the e metal orbital without change in the π bonding ability in such a way that ΔE_Q becomes more negative and the isomer shift remains almost unchanged.

Our discussion of ΔE_Q overestimates the π back-donation in these complexes. We have neglected the effects arising from the σ-donor strength of the ligands. The σ contribution is suggested by the absence of a correlation between the isomer shift and the quadrupole splitting. If the only effect was the π-acceptor strength, the isomer shift should decrease with increasing quadrupole splitting, which is not the case in the present series of complexes. A counterbalance between the π back-donation and σ effects could be responsible for the nearly constant values of δ and ΔE_Q in this tris-diimine iron(II) complex series. It is unlikely that the whole of this difference is due to back-donation, particularly because of the synergic interaction between metal–ligand σ and π bondings[27].

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