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Electronic and Mössbauer Spectroscopy Studies of Iron(II) Complexes with Tridentate Unsaturated Nitrogen Containing Ligands

E. BAGGIO-SAITOVITCH*
Centro Brasileiro de Pesquisas Fisicas, Wenceslau Braz 71, Rio de Janeiro, Brasil
and
M. A. DE PAOLI
Instituto de Quimica, Universidade de Campinas, Caixa Postal 1170, Campinas, SP, Brasil
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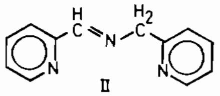
The effect of the fusion of a further N-donor coordination site to a diimine giving tridentate unsaturated chelate ligands in iron(II) complexes was investigated by using electronic and ^{57}Fe Mössbauer spectroscopy. The electronic spectra, measured at 77 °K, showed that the tridentate ligands produce with iron(II) complexes, $[Fe(ligand)_2]^{++}$, having characteristic spectral features connected with the structure of the complex ion. The Mössbauer spectra taken at 295 and 4.2 °K, showed a variation of the isomer shift and quadrupole splitting in the series of complexes. The spectra taken with a external magnetic field showed for all complexes a negative sign for the principal component of the EFG tensor (V_{zz}). The results are discussed on the basis of a strong σ-bonding along a unique axis, considering the D_{2d} point group symmetry.

Introduction

The iron(II) complexes studied in this work have two tridentate ligands which are constituted of a diimine ring with a second amine or imine ring fused to it, mainly: terpyridine [1] (I), 2-(2′-pyridylmethyleneaminomethyl)pyridine [2] (II), 2,6-pyridinedialbis(methylimine) [3] (III), 1-(2′-pyridylmethyleneaminomethyl)-2-aminoethane [4] (IV) and 1- (2′-pyridylmethyleneaminomethyl)-2-aminopropane(V).

Recently we have made a systematic Mössbauer and electronic spectra study on a series of tris(diimine)iron(II) complexes [5, 6]. The object of this work is to investigate the effect of the electronic and Mössbauer spectral properties of the respective iron(II) complexes produced by the second ring fusion or annelation in the ligand. In this work we also want to show how these two spectral techniques complement each other in the study of the bonding between iron and these nitrogen containing ligands.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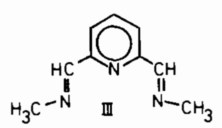
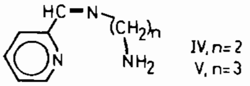

III


IV, n=2
V, n=3

These complexes, as pointed out by Krumholz [7], belong to a single class having characteristic spectral features which should be connected with the structure of the complex ion. The mere fact of having a second chelate loop fused to the diimine ring therefore was assumed to be responsible for the change of the spectral pattern as one passes from the complexes of the bidentate diimines to those of the terdentate ligands.

The coordination of the second ring in the case of the complex with ligand IV is unfavourable, due to the saturated character of the bonds. We prepared the complex with the ligand V in order to observe if the six membered saturated ring would close as well as the five membered one of IV. It was observed that the formation of the complex is more favourable than in the five membered case, probably due to a lower steric hindrance of the six membered ring.

Experimental

The perchlorate salts of the complexes with ligands I, II, and III were prepared according to references 1, 2, and 3, respectively. The two others were obtained according to Krumholz [7] but crystallized

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*Present address: Physik Dept. E-15, Technische Universität München, 8046-Garching bei München, West Germany.

TABLE I. MLET Band Position in kK Calculated by the Log–Normal Components Computer Fitting for the Iron(II) Complexes, Fe(Ligand)$_2^{2+}$, from KBr Pellet Spectra. The values in parenthesis represent the calculated relative intensity of the bands.

Ligand	I	II	III	IV	V
	15.87 (.75)	15.1 (.12)	14.8^a (.32)	13.5^a (.18)	13.4^a (.13)
	17.93 (1.0)	17.05 (1.0)	16.85 (1.0)	15.43 (1.0)	15.24 (1.0)
	18.9^a (.12)	–	17.1^a (.61)	16.25 (.98)	–
	20.0^a (.18)	18.6^a (.57)	18.12 (.13)	17.5^a (.89)	16.6^a (.45)
	20.6^a (.38)	–	19.2^a (.47)	–	–
	–	10.18 (.58)	20.31 (.32)	19.22 (.47)	18.45 (.65)
	–	21.7^a (.24)	21.73^a (.52)	19.87 (.50)	–
	26.3^a (.16)	26.05^c (.78)	–	24.31^b (.87)	23.45^b (.61)
	–	–	–	26.91^b (.91)	26.56^b (.75)

^{a}Shoulder. ^{b}Broad. ^{c}Very broad.

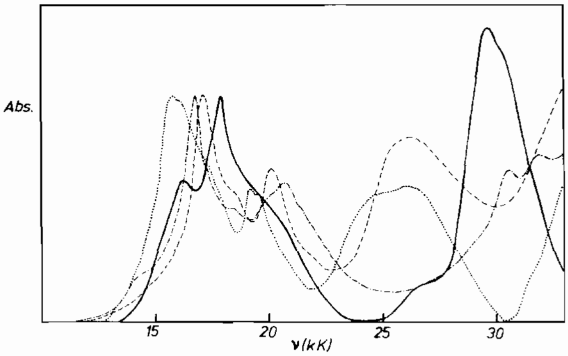

Figure 1. Electronic spectra of the complexes, Fe(ligand)$_2^{+2}$, measured at 77 °K in KBr pellets; —— ligand I, ----- ligand II, -·-·- ligand III and ···· ligand IV. The spectrum of the complex with ligand V is very similar in shape to that with ligand IV.

in absence of air in order to prevent oxidation; this gives a higher yield and a higher degree of purity with a less complicated crystallization procedure.

The electronic absorption spectra of these complexes, at 77 °K, were measured with a Cary-17 Recording Spectrophotometer using a "Cary Liquid Helium Dewar". The samples were measured in solid state as KBr pellets. A pure KBr pellet with the same thickness of the sample was taken as blank. These pellets were prepared as thin as possible in order to have a reasonable slit aperture in the UV region. The spectra measured in the Absorbance *versus* nm scale were transposed to the Absorbance *versus* kK scale and analysed in their log–normal [8] components using a Burroughs 6700 computer.

For the infra-red spectra KBr pellets were used in a Perkin-Elmer model 180 Infra-Red Spectrophotometer.

The Mössbauer spectra were recorded using a 1024 channel of a Hewlet–Packard Multichannel Analyser with a sinusoidal drive unit, previously described [6]. The 4.2 °K data were obtained with the source and absorber at liquid helium temperature. An Oxford Instrument Superconducting Solenoid was used to determine the Mössbauer spectra in a longitudinal magnetic field. The absorber was microcrystalline with thickness of about 10 mg/cm^2 of natural iron and the source was 25 mC of ^{57}Co in a Cu matrix.

The Mössbauer data were folded and linearized with a 370/175 IBM computer and an iterative curve fitting procedure was used to determine the Mössbauer parameters. The solid lines for all the Mössbauer patterns appearing in this paper represent the Lorentzian least squares fit of the data. The isomer shift values are referred to the source of ^{57}Co/Cu in all the figures whereas in Table II the values are related to a metallic ion absorber.

Results

Electronic Spectra

The absorption spectra of the iron(II) complexes with the tridentate imine ligands are shown in Figure 1; these spectra taken at 77 °K present better resolution than the room temperature spectra already reported [7, 9]. In Table I we report the best position of the bands that appear superimposed in the spectra, as obtained from the log–normal function analysis of the data. A bathochromic shift of the bands is observed in the spectra measured in KBr pellets compared to the solution spectra.

Despite significant structural differences between the individual ligands, these complexes seem to belong to a similar spectral class. The shape of the spectra differ from the electronic spectra of the iron(II) complexes with bidentate α-diimine ligands, which remain nearly invariant in a large number of derivatives [5].

The complexes with ligands II, IV and V show three main groups of absorption bands: the first one from 13.0 to 17.0 kK, the second one from 18.5 to 21.7 kK and the last from 23.5 to 26.0 kK. The complexes with ligands I and III do not have absorp-

TABLE II. Mössbauer Data Obtained for the Iron(II) Complexes, Fe(Ligand)$_2$. The average line width is 0.24 mm/s and the accuracy of the parameter values is ±0.007 mm/s. The isomer shifts are related to a metallic iron absorber. ν_{max} values from the room temperature solution spectra.

Ligand	ν max (kK)	δ (mm/s)		ΔE_Q (mm/s)	
		295 °K	4.2 °K	295 °K	4.2 °K
I	18.12	.211	.178	−1.06	−1.06
II	17.09	.188	.135	−0.925	−0.930
III	17.61	.122	.068	−0.805	−0.770
IV	16.84	.210	.165	−0.926	−0.940
V	16.03	.333	.285	−0.630	−0.650

tion in the third region. These bands are assigned to metal to ligand electron transfer (MLET) transitions. The terpyridine complex seems to be an exception since it has absorption bands at 15.87 kK and 17.93 kK and a very broad continuum to higher energies, which seems to be a Franck–Condon envelope.

An absorption band at 30 kK observed in the spectrum of the complex with terpyridine is also present in the spectrum of the free ligand and consequently assigned to an internal ligand electron transfer (ILET) transition, although it can be masking a less intense metal to ligand electron transfer band. The spectra of the free ligands of the remaining complexes were not obtained, due to their thermodynamic instability in the free form. However, the spectra of the corresponding ketones are well known and they show intense absorption bands near 30.0 kK. Extending this observation to the imine ligands, we could assign the bands observed in this region to ILET transitions.

The appearance of three groups of bands in the spectra of these complexes shows the effect of lower symmetry, compared to tris(diimine) complexes. The intense transitions about 16–18 kK correspond to the ET excitations typical for all low spin diimine iron(II) complexes. The second group of bands (18–22 kK) is stronger in intensity than the second $^1A_1 \rightarrow {}^1E$ ET transition in tris(diimine) complexes. A third group of transitions (24–27 kK) is only apparent in the complexes with unsymmetrical ligands II, IV, and V what can be regarded to the bis (unsymmetric diimine)iron(II) components, with two further σ-electron donor ligands (either pyridine nitrogen or saturated nitrogen). These σ-donors should raise the d-electron energy. For bipy complexes it is known that a second ET transition M → L is shifted from the UV to the visible spectrum under such conditions [10].

The possibility of a further oxidation of the ligands IV and V to produce an imine in the second ring is excluded since the infra-red spectra of these complexes present sharp peaks in the N–H stretching frequency region (3170 to 3280 cm^{-1}).

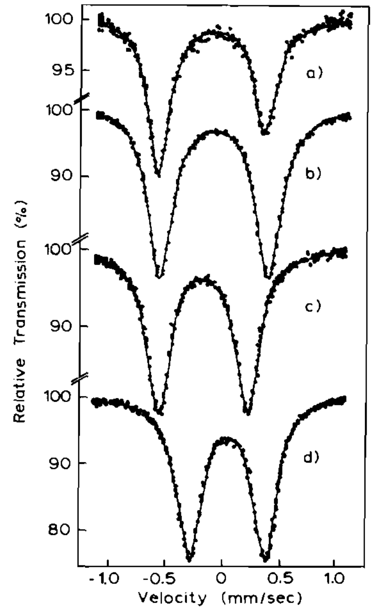

Figure 2. Mössbauer spectra at 4.2 °K of the complexes Fe(ligand)$_2^{2+}$, with ligands: III(a), IV(b), II(c), V(d).

The nature of the bonding in the ligand skeleton which forms the second fused chelate ring system affects the position of the absorption maxima of the respective iron(II) complexes. It is shifted toward the blue as the number of aromatic rings increases.

Mössbauer Spectra

The unperturbed Mössbauer spectra at 4.2 °K for the iron(II) complexes with these tridentate ligands are shwon in Figure 2. The Mössbauer parameters obtained from the least squares fitting of the data for liquid helium and room temperature are reported in Table II. The isomer shift is more sensitive to the different tridentate ligands in this series of complexes than was observed for the complexes with diimine ligands [6]. The quadrupole splitting is almost temperature independent and large in comparison with other diamagnetic six coordinated polyimine systems

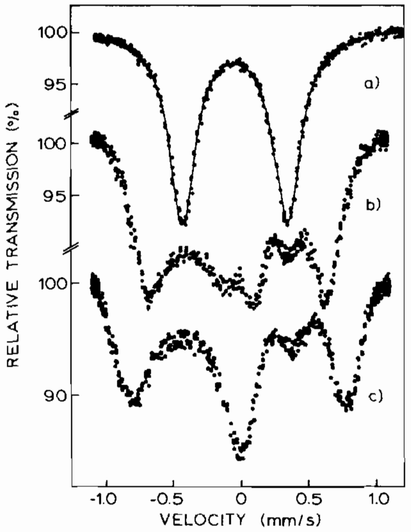

Figure 3. Mössbauer spectra of the complex with ligand III in an applied magnetic field parallel to the incident gamma rays. H_{ex} equal to: a) 0 KG, b) 22.5 KG, c) 34 KG.

[11]. This is indicative of a large static distortion from an octahedral symmetry.

The Mössbauer spectra have been obtained for all the samples in an external magnetic field. In Figure 3 the spectra obtained for the complex with ligand III is presented: the triplet observed at positive velocity implies, in the case of nuclear transition of ^{57}Fe, that the principal component of the electric field gradient (EFG) at iron site is negative. A similar pattern of Mössbauer spectra was maintained for all the ligands in the present series of complexes.

From the observed triplet splitting one can estimate the effective magnetic field at the iron nucleus which turns out to be equal to the applied one, reflecting the diamagnetic nature of these complexes.

Discussion

Geometrical considerations lead one to expect that in the case of iron(II) complexes with tridentate ligands, Fe(ligand)$_2^{+2}$, non cubic components become rather important. The highest symmetry possible for these complexes would be the point group D_{2d}. To achieve this, it is necessary to assume that the three nitrogens in each ligand lie in a single plane. In D_{2d} symmetry the metal d-orbitals of cubic t_{2g} parentage will split in a singlet and a doublet which transform as the B_2 and E irreducible representation of the group, whereas the metal d orbitals of e_g cubic parentage will split in two singlets which transform as the B_1 and A_1 irreducible representation of the group.

As a consequence of the lower symmetry of these complexes the π^* ligand orbitals also split, which may explain the high number of absorption bands in the electronic spectra. An assignment of the bands could be done only on the basis of Molecular Orbital Calculations.

It is well stablished that the EFG at the nucleus of a covalently bound atom is determined mainly by the asymmetry of the charge distribution in the innermost valence shell [12]. The magnitude and sign of the EFG in the case of diamagnetic Fe(II) complexes with its nominal d^6 configuration is defined by the occupancy of the different 3d valence orbitals [13]. This occupancy may reflect the extent to which the metal orbitals mix with appropriate ligand orbitals to form the molecular orbitals [14].

The existence of intense MLET bands in these complexes can be taken as evidence for the importance of the delocalization of the metal electrons into empty π^*-ligand orbitals [7, 9, 15]. The π-back-donation was used to explain the negative EFG for a series of tris(diimine)iron(II) complexes [6]. If we take into account only the π-back-donation we will end up with the wrong sign for the EFG, since mainly electrons with d_{xz} and d_{yz} character will be delocalized. This would lead to a predominance of the positive contribution to the EFG made by electrons in the d_{xy} orbital. The fact that the central nitrogen is more strongly bonded to the metal in the case of the terpyridine ligand [16] indicates that for the complexes with tridentate ligands the σ-bonding is important [17]: electrons transferred from the ligands, in the present case, will populate mainly the metal d_{z^2} empty orbital. So the σ-bonding brings a negative contribution for the EFG, in agreement with our experimental results.

The well known equation for the principal component of the EFG can be written as [14]:

$$V_{zz} = -4/7e(1 - R)\langle r^{-3}\rangle_d(N_\sigma - N_\pi)$$

where

$$N_\sigma = n_{z^2} - n_{x^2-y^2}$$

$N_\pi = n_{xy} - 1/2(n_{xz} + n_{yz})$, the n_i is the effective population of the "i" ortibal.

The sign of EFG will be negative as long as the σ-bonding along the z-axis is stronger than π-back-bonding.

If it is possible to distinguish the contribution to the EFG coming from the σ-bonding and π-back-bonding the same is not true for the isomer shift. This hyperfine parameter reflects the total "*s*" electron density at the iron nucleus and becomes more negative with increasing "*s*" electron density. A direct increase is due to the population of the empty 4*s* metal orbital via σ-bonding, whereas the delocalization of electrons by π-back-bonding reduces the shielding on the 3*s* and 4*s* electrons [14]. No unequivocal conclusion as to the extent of each effect purely on the basis of the isomer shift can be achiev-

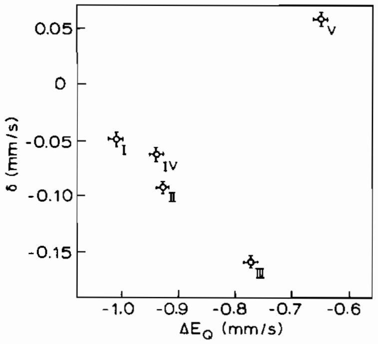

Figure 4. Isomer shift *versus* quadrupole splitting in mm/sec, measured at 4.2 °K, for the compounds listed in Table II.

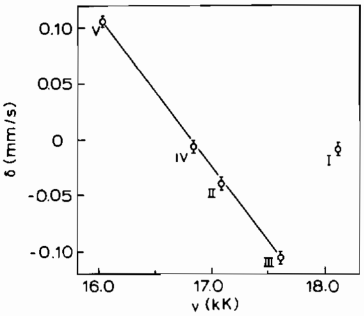

Figure 5. Isomer shift (mm/sec) at 295 °K *versus* ν_{max} (kK) for the series of complexes studied in this paper (ν_{max} from the room temperature solution spectra).

ed since the increase in strength of both bonds makes it more negative.

The correlation between the EFG and the isomer shift can indicate which bonding is reinforced along a series of compounds [18]. Since the isomer shift is dependent on the sum of the σ and π bonding ability of the ligands and the quadrupole splitting on the difference, a linear relationship between these two Mössbauer parameters for a given series of complexes implies that one of the effects is relatively constant.

For the complexes studied in this work the correlation between δ and ΔE_Q is shown in Figure 4. The negative slope can be understood if we assume that the π-back-bonding is increasing as compared with the σ-bonding: the isomer shift becomes more negative and the positive contribution to the EFG increases.

The complex with ligand V does not fit into this correlation, which can be understood if we assume that the increase of the second fused chelate ring size leads to a further distortion of the molecule due to a hindrance from the rings. As a consequence the overlap of the metal d_{z^2} orbital will be modified and the σ-bonding will decrease. This picture is in agreement with the position of the complex with ligand V in Figure 4, since a decrease of the σ-bonding should result in a simultaneous decrease of EFG and increase of isomer shift, as described above.

The energy of the principal absorption band in the electronic spectra is also sensitive to the modification of the π-back-donation. A plot of the position of the more intense band, ν, *versus* the isomer shift for these five compounds is shown in Figure 5. It is evident that there exists a considerable degree of correlation between these parameters, except for the terpyridine complex which shows a peculiar electronic spectrum. In this case, the non-correlation of the complex with terpyridine could be attributed to an electronic effect induced by the conjugation in the three aromatic rings of the ligand. The present correlation indicates that the decrease of the isomer shift is due to an increase of the extent of π-back-donation. This result supports the explanation which attributes the decrease in the EFG for the complex with ligand V as due to a modification of the molecular architecture with a consequent decrease of the σ-bonding.

Conclusion

The negative sign of the EFG in this series of iron(II) complexes with tridentate ligands, where the metal atom is in a D_{2d} point group symmetry, can be explained on the basis of strong σ-bonding mainly along a unique axis with the consequent population of the empty d_{z^2} metal orbital. The correlation between the Mössbauer parameters, isomer shift and quadrupole splitting suggests that if the molecular architecture leads to a strong σ-bonding, it is the π-back-bonding that is more sensitive to the modifications introduced by the different ligands.

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