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Electronic and Magnetic Structure of the Polymeric System Di-Imidazolato Iron(II)*

II. Mössbauer Investigation of the Methyl-, Ethyl-, and Phenyl-Derivatives

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For the Fe-derivatives of 2-methyl-, 2-ethyl-, and 2-phenyl-imidazoles Mössbauer spectra are measured in the temperature range 4.2 K$\leqslant T \leqslant$300 K. Their computer analysis yields isomer shifts δ, quadrupole splittings ΔE_Q, asymmetry parameters η, line widths Γ, internal magnetic fields H^{int}, sign of the main component V_{zz} of the electric field gradient tensor, and angle ζ between $\vec{H}^{\text{int}}$ and $\vec{V}_{zz}$. We find that the substituents methyl, ethyl, and phenyl have significant influence upon these parameters, i.e. upon electronic structure and magnetic ordering; only $V_{zz}>0$ and $\eta=0$ are the same for all compounds. The δ- and ΔE_Q-values indicate that the iron is in the ferrous high-spin state and tetrahedrally coordinated by imidazole nitrogens. The conclusion that the compounds are three-dimensional coordination polymers is drawn from their magnetic ordering at low temperatures. Transition temperatures are $T^*_{\text{methyl}}=33.25\pm0.05$ K, $T^*_{\text{ethyl}}=30.5\pm0.05$ K, and $T^*_{\text{phenyl}}=25.7\pm0.05$ K. Assuming a power-law dependence for H^{int} of the form $H^{\text{int}}=H(4.2)D(1-T/T^*)\beta$ we derive $D=1.52\pm0.05$ and $\beta=0.31\pm0.03$ for the three compounds. From the discussion of the saturation value of the internal magnetic field H^{int} (4.2 K) we derive for the methyl- and phenyl-compound ground state and first excited state single-electron wave function $|n\rangle=a|x^2-y^2\rangle+b|xy\rangle+c|3z^2-r^2\rangle+d|xz\rangle+e|yz\rangle+lig.$ and $|k\rangle=a'|x^2-y^2\rangle+b'|xy\rangle+c'|3z^2-r^2\rangle+d'|xz\rangle+e'|yz\rangle+lig.$, respectively, and energy separations E_k-E_n, specified by: $0.88\leqslant b\leqslant0.92$, $0.27\leqslant c\leqslant0.39$, $0.55\leqslant a'\leqslant0.57$, $-0.32\leqslant b'\leqslant-0.22$, $0.69\leqslant c'\leqslant0.77$, $a=d=e=d'=e'=0$, $E_k-E_n=4000\pm500$ cm^{-1} for the methyl compound, and $0.92\leqslant b\leqslant0.96$, $0\leqslant c\leqslant0.27$, $0.49\leqslant a'\leqslant0.52$, $0.76\leqslant c'\leqslant0.84$, $a=d=e=b'=d'=e'=0$, $E_k-E_n=4000\pm500$ cm^{-1} for the phenyl compound. The coefficients $a, \ldots, e'$ are approximate values mainly due to the assumption of isotropic covalency, due to the lack of better knowledge of the energy separation E_k-E_n, and due to the approximative procedure of estimating the orbital contribution to H^{int}. The situation for the ethyl compound is less transparent because of the non-collinearity of $\vec{H}^{\text{int}}$ and $\vec{V}_{zz}$ in this case.

1. Introduction

In the preceding paper [1] (further denoted as paper I) we described the polymeric system $\text{FeIz}_2\cdot0.71$ IzH (Iz = imidazolyl) and its investigation by Mössbauer spectroscopy and thermogravimetry. In this communication we present

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Mössbauer results of the Fe(II)-derivatives of 2-methyl-, 2-ethyl-, and 2-phenyl-imidazoles in the temperature range $4.2\ \mathrm{K} \leqslant T \leqslant 300\ \mathrm{K}$.

2. Materials

The procedure for preparing these materials is comparable with that described in paper I for $\mathrm{FeIz_2 \cdot 0.71\ IzH}$. Again the reaction schemes with either ferrocene or cyclopentadienylirondicarbonyl are applicable. In both cases we get yellow-brown powders which oxidize immediately to dark-brown Fe(II)-complexes in air. The chemical analysis yields for all three compounds the overall formula $\mathrm{FeL_2}$, with L standing for 2-methyl-, 2-ethyl-, and 2-phenyl imidazole, respectively. Thus, contrary to $\mathrm{FeIz_2 \cdot 0.71\ IzH}$, no excess imidazole (IzH) is coordinated to iron. This situation should be also reflected by Mössbauer spectroscopy.

The Mössbauer investigation was carried out with material which was filled under N_2 atmosphere into absorber holders (Cu) yielding samples with an approximate thickness of 0.5 mm and a diameter of 10 mm. The samples, mounted in a cryostat, were shielded from atmosphere (at 300 K) or vacuum (for $T < 300$ K) by indium sealed mylar windows.

3. Results

In Figs. 1a–f we show typical powder spectra for the three compounds at room temperature and in the low temperature region. From these spectra it is obvious that we are concerned with only a single iron site, in agreement with the findings of our chemical analysis, which is reflected by the formula $\mathrm{FeL_2}$. The solid curves result from a computer analysis, described in detail by Gabriel *et al.* [2], using

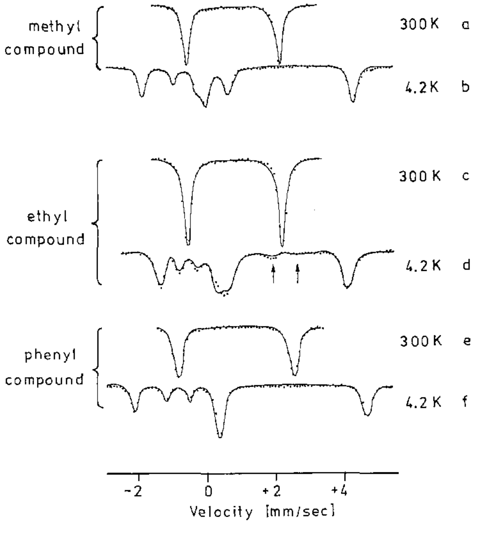

Fig. 1. Experimental and theoretical Mössbauer spectra of (*a*, *b*) methyl-, (*c*, *d*) ethyl-, and (*e*, *f*) phenyl-compounds at room temperature and 4.2 K, respectively. The parameters of the fit-curves (solid lines) are specified in Table 1. Characteristic for the non-collinearity of $\vec{H}^{\mathrm{int}}$ and $\vec{V}_{zz}$ in the ethyl-compound are the two "forbidden" lines (arrows in *d*)

isomer shifts δ, quadrupole splittings ΔE_Q, line widths Γ, and internal magnetic fields H^{int} which are specified in Table 1. In addition from Figs. 1a–f we learn that the material undergoes magnetic ordering in all three cases. From the detailed study within the temperature range $4.2\text{ K} \leqslant T \leqslant 300\text{ K}$ we find for the transition temperatures $T^*_{\text{methyl}} = 33.25 \pm 0.05$ K, $T^*_{\text{ethyl}} = 30.5 \pm 0.05$ K, and $T^*_{\text{phenyl}} = 25.7 \pm 0.05$ K, respectively. In Table 1 we summarize the Mössbauer parameters which result from least square computer fits of experimental spectra.

4. Discussion

From inspection of Table 1 we find that the influence of the substituents methyl, ethyl, and phenyl upon isomer shift, quadrupole splitting, and magnetic ordering, i.e. on the electronic and magnetic state of the iron cation is significant. The relatively large isomer shift values and quadrupole splittings, which we measure for all three Fe-derivatives, indicate that we are concerned with ferrous high-spin iron in these compounds. Comparing δ- and ΔE_Q-values, and further the sign of the main component of the electric field gradient (EFG) tensor V_{zz} and the temperature-independence of ΔE_Q from Table 1 with our findings from paper I for $\text{FeIz}_2 \cdot 0.71$ IzH we conclude that the ferrous high-spin iron in the Fe-derivatives presently under study, is tetrahedrally coordinated by either 2-methyl-, 2-ethyl-, or 2-phenyl imidazoles. This specific situation compared with the tetrahedrally *and* octahedrally coordinated iron ions in $\text{FeIz}_2 \cdot 0.71$ IzH has probably to do with the increased space required for the 2-methyl-, 2-ethyl-, and 2-phenyl imidazoles.

The further conclusion that these "substituted" Fe(II) imidazole compounds are three-dimensional coordination polymers is drawn from their magnetic ordering at low temperatures. Assuming the internal magnetic field H^{int} to have power-law dependence on the temperature of the form

$$H^{\text{int}} = H^{\text{int}}(0) D (1 - T/T^*)^{\beta}, \tag{1}$$

where $H^{\text{int}}(0)$ is the saturation value of H^{int} at low temperature (i.e. at 4.2 K) and D a correction factor matching this high-temperature formula onto the $0K$-saturation field, we are able to derive values for T^*, D and β from fitting the $H^{\text{int}}(T)$-values of Fig. 2 and Table 1 in the temperature range $0.89T^* < T < 0.99\,T^*$. Such a behavior for $H^{\text{int}}(T)$ at the nucleus of a Fe(II) ion has been previously observed [3] for threedimensional antiferromagnets with D- and β-values in the range 1.3 to 1.5 and 0.3 to 0.33, respectively (further confirmation of the assumption that the Fe(II)-imidazole compounds are antiferromagnets at low temperature will be given elsewhere [4] on the basis of Mössbauer measurements under applied magnetic field and on the basis of susceptibility measurements). Close to the D- and β-values above we find the values $D_{\text{methyl}} = 1.52 \pm 0.05$ and $\beta_{\text{methyl}} = 0.31 \pm 0.03$. Within the error range of these values we get the same results for the ethyl and phenyl compounds. The T^* values are $T^*_{\text{methyl}} = 33.25 \pm 0.05$ K, $T^*_{\text{ethyl}} = 30.5 \pm 0.05$ K, and $T^*_{\text{phenyl}} = 25.7 \pm 0.05$ K.

For the further discussion of the electronic and magnetic structure we use the results from Figs. 1b and 1f concerning the collinearity of $\vec{H}^{\text{int}}$ and $\vec{V}_{zz}$ ($\zeta = 0°$),

Table 1. Isomer shifts δ, quadrupole splittings ΔE_Q, line widths Γ, and internal magnetic fields H^{int} at various temperatures for methyl-, ethyl-, and phenyl-compounds

		Methyl compound		
T(K)	δ (mm/sec)[a, b]	ΔE_Q (mm/sec)[b, c]	Γ (mm/sec)[b]	H^{int} (kG)[d]
4.2	0.827	2.807	0.274	137.9
12.8	0.818	2.825	0.264	137.4
21.4	0.826	2.814	0.270	131.3
24.1	0.818	2.812	0.266	126.4
27.0	0.815	2.803	0.252	116.7
29.9	0.820	2.810	0.270	101.1
31.0	0.823	2.797	0.280	89.3
31.5	0.819	2.797	0.270	82.4
32.0	0.822	2.792	0.32±0.05	67.6±3.5
32.4	0.825	2.797	0.32±0.05	60.8±3.5
32.7	0.831	2.799	0.32±0.05	53.5±3.5
33.1	0.830	2.808	0.32±0.05	39.1±3.5
33.5	0.831	2.785	0.37±0.05	
33.9	0.822	2.798	0.268	—
34.2	0.825	2.784	0.37±0.05	—
51.1	0.830	2.786	0.274	—
77.3	0.827	2.787	0.260	—
300	0.718	2.718	0.260	—

Table 1 (continued):

		Ethyl compound		
T(K)	δ (mm/sec)[a, b]	ΔE_Q (mm/sec)[b, c]	Γ (mm/sec)[b]	H^{int} (kG)[e]
4.2	0.893	2.834	0.314	129.9
11.3	0.893	2.834	0.314	129.0
14.5	0.893	2.834	0.314	128.0
21.0	0.893	2.834	0.314	123.0
24.1	0.893	2.834	0.314	114.5
26.5	0.893	2.834	0.314	101.5
27.4	0.893	2.834	0.314	97.0
28.2	0.893	2.834	0.314	85.5
28.9	0.893	2.834	0.314	78.5±3.5
29.3	0.893	2.834	0.314	71.0±3.5
29.6	0.893	2.834	0.314	62.5±3.5
30.0	0.893	2.834	0.314	47.0±3.5
30.3	0.893	2.834	0.314	33.5±3.5
30.7	0.893	2.834	0.314	—
31.0	0.893	2.834	0.314	—
31.4	0.893	2.834	0.314	—
31.7	0.893	2.834	0.314	—
32.1	0.893	2.834	0.314	—
77.3	0.887	2.838	0.300	—
300	0.798	2.830	0.276	—

[a] Isomer shifts are given relative to metallic iron at room remperature.

[b] Standard deviation, if no other indication, is ±0.006 mm/sec.

[c] $V_{zz}>0$ and $\eta=|V_M-V_{xx}|/|V_{zz}|=0$.

[d] Standard deviation, if no other indication, is ±2 kG; $\vec{H}^{\text{int}}$ and $\vec{V}_{zz}$ are parallel ($\zeta=0°$).

[e] Standard deviation, if no other indication, is ±2 kG; angle ζ between $\vec{H}^{\text{int}}$ and $\vec{V}_{zz}$ is 20°.

Table 1 (continued):

T(K)	δ(mm/sec)[a, b]	Phenyl compound ΔE_Q (mm/sec)[b, c]	Γ (mm/sec)[b]	H^{int} (kG)[d]
4.2	0.899	3.455	0.244	137.9
16.2	0.898	3.410	0.254	135.6
21.2	0.902	3.481	0.282	119.1
22.4	0.905	3.481	0.290	111.1
23.4	0.903	3.485	0.290	103.4
24.0	0.995	3.482	0.32±0.03	93.0±3.5
24.6	0.912	3.479	0.33±0.03	83.0±3.5
24.9	0.914	3.471	0.32±0.03	66.1±3.5
25.5	0.918	3.478	0.32±0.03	58.5±3.5
25.8	0.910	3.474	0.330	—
26.1	0.909	3.477	0.330	—
26.8	0.908	3.476	0.298	—
47.0	0.907	3.468	0.284	—
77.3	0.900	3.467	0.272	—
300	0.792	3.329	0.330	—

which we find for the methyl and phenyl compound from computer analysis of their experimental hyperfine pattern. This result ($\zeta = 0°$) implies considerable restrictions upon $\vec{H}^{\text{int}}$ which is given by [5]

$$\begin{aligned} H_z^{\text{int}} &= H^{\text{core}} + H^{\text{cov}} + H^{\text{STHF}} + (g_z - 2)2\mu_\beta\langle r_L^{-3}\rangle\langle S_z\rangle + \tfrac{1}{7}\mu_B\langle r_D^{-3}\rangle \sum_q \langle l_{zq}\rangle\langle S_q\rangle, \\ H_y^{\text{int}} &= (g_y - 2)2\mu_B\langle r_L^{-3}\rangle\langle S_y\rangle + \tfrac{1}{7}\mu_B\langle r_D^{-3}\rangle \sum_q \langle l_{yq}\rangle\langle S_q\rangle, \\ H_x^{\text{int}} &= (g_x - 2)2\mu_B\langle r_L^{-3}\rangle\langle S_x\rangle + \tfrac{1}{7}\mu_B\langle r_D^{-3}\rangle \sum_q \langle l_{xq}\rangle\langle S_q\rangle. \end{aligned} \qquad (2)$$

$\langle S_q\rangle$ with $q = x, y, z$ are spin expectation values and μ_B is the Bohr magneton. $\langle l_{pq}\rangle$ stands for $\frac{1}{2}\langle l_p l_q + l_q l_p\rangle - \frac{1}{3}l(l+1)$, with $l = 2$ the orbital angular momentum for Fe $3d$ electrons. The remaining parameters in Eq. (2) will be defined below.

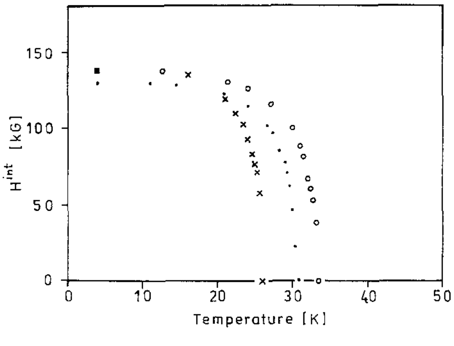

Fig. 2. Temperature dependence of H^{int} for (o) methyl, (·) ethyl, and (×) phenyl compounds

With $\vec{H}^{\text{int}} \parallel \vec{V}_{zz}$ and $\eta = 0$ Eq. (2) reduces within the principal axes system of the EFG to:

$$H_z^{\text{int}} = H^{\text{core}} + H^{\text{cov}} + H^{\text{STHF}} + (g_z - 2)2\mu_B \langle r_L^{-3} \rangle \langle S_z \rangle + \tfrac{1}{7}\mu_B \langle r_D^{-3} \rangle \langle l_z^2 - 2 \rangle \langle S_z \rangle,$$
$$H_y^{\text{int}} = H_x^{\text{int}} = 0. \tag{3}$$

From Eq. (3) we roughly estimate the various contributions to H^{int}. H^{core} gives the Fe *ns* ($n = 1, 2, 3$) polarization contribution due to the effective Fe 3*d* spin $\langle S_z \rangle$; for $3d^6$ ($S = 2$) configuration it takes the value −550 kG [6]. H^{cov} is the covalency contribution to H^{int}; its main part is due to Fe 4*s* polarization and depends therefore on the charge transfer into the Fe 4*s* atomic orbital (AO); for $3d^6$ ($S = 2$) configuration a doubly occupied Fe 4*s* shell contributes to H^{cov} by +490 kG [6]; several ferrous high-spin compounds studied by molecular orbital techniques yielded Fe 4*s* AO populations of 0.15 to 0.20 electron charges [7], thus giving a H^{cov} contribution to H^{int} of +70 kG to +100 kG. H^{STHF} is the supertransferred hyperfine field which depends on geometry and number I of iron-imidazole-iron chains [8]; for I = 6 in the antiferromagnetic $\text{LaFe}^{\text{III}}\text{O}_3$ compound H^{STHF} was calculated to be −55 kG [9]; in the present case with tetrahedrally coordinated iron we are concerned with I = 4 and somewhat larger iron-iron distances than in the iron oxide; hence we expect H^{STHF} to contribute with about −30 kG. The orbital contribution to H^{int} is given by the fourth term in H_z^{int}, with g_z being the *z*-component of the *g*-tensor which we may derive from [10]

$$g_{ii} = 2 - 2\lambda \sum_k \frac{\langle n|l_i|k \rangle \langle k|l_i|n \rangle}{E_k - E_n}. \tag{4}$$

λ is the spin-orbit coupling constant, 103 cm^{-1} in the present case [11]. $|n\rangle$ and $|k\rangle$ are the wave functions from a single-electron picture for tetrahedrally coordinated ferrous high-spin iron (Fig. 3), assuming that the "triplet" is energetically well separated from the "doublet". The dipolar contribution H^D to H^{int} is described by the fifth term in H_z^{int}. The radial expectation values $\langle r_L^{-3} \rangle$ and $\langle r_D^{-3} \rangle$ are taken to be approximately equal, and we use for the ferrous high-spin case $2\mu_B \langle r_{L,D}^{-3} \rangle = +560$ kG [12]. Since $\langle l_z^2 - 2 \rangle$ is directly proportional to V_{zz} it is easy to derive H^D without specific knowledge of $|n\rangle$ and $|k\rangle$; with $\langle S_z \rangle = 2$

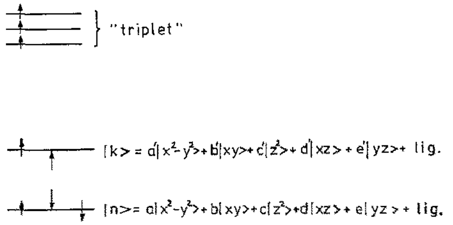

Fig. 3. Single-electron energy term scheme for tetrahedrally coordinated ferrous high-spin iron in methyl and phenyl compounds (see text)

we find $H^{D}_{\text{methyl}} = +106$ kG and $H^{D}_{\text{phenyl}} = +130$ kG. Collecting the various contributions to the saturation value of H_z^{int} (4.2 K) of about 140 kG we derive

$$-140 = -550 + 100 - 30 + H^{\mathrm{L}} + 106(+130),$$

leading to H^{L}-values of about +234 kG and +210 kG for the methyl and the phenyl compounds, respectively.

The choice of coefficients a, b, c, d, e, of the ground state single-electron orbital $|n\rangle$ of Fig. 3, which result from a linear combination of atomic orbitals, can be restricted by considering the various conditions, which already lead us to Eq. (3); in a first step we neglect ligand contributions to $|n\rangle$ and $|k\rangle$:

(1) from $\langle l_{yz}\rangle = 0$ we derive [13] $(3ae - 3bd - \sqrt{3}ce) = 0$;

(2) for $\langle l_{xz}\rangle = 0$ we get, corresponding to (1), $(3ad + 3be + \sqrt{3}cd) = 0$;

(3) zero asymmetry parameter results in $(-3d^2 + 3e^2 + 4\sqrt{3}ac) = 0$;

(4) $\Delta E_Q = 2.8$ mm/sec for the methyl compound (3.45 mm/sec for the phenyl compound), $V_{zz} > 0$, and $E_k - E_n \gg kT$ lead to [13][1] $a^2 + b^2 - c^2 - d^2/2 - e^2/2 = 0.70$ (0.85);

(5) the normalization condition of $|n\rangle$ requires $a^2 + b^2 + c^2 + d^2 + e^2 = 1$.

With the conditions (1) to (5) we find for the methyl compound $a = 0$, $b^2 = 0.85$, $c^2 = 0.15$, $d = 0$, $e = 0$, and for the phenyl compound $a = 0$, $b^2 = 0.925$, $c^2 = 0.075$, $d = 0$, $e = 0$.

In order to determine the LCAO coefficients a', b', c', d', e' for $|k\rangle$ of Fig. 3 we further take into account the conditions (6) to (10):

(6) the values for H^L require $a^2b'^2 + a'^2b^2 + d^2e'^2 = 0.255$, which corresponds to +234 kG and $E_k - E_n = 4000\ \text{cm}^{-1}$ for the methyl compound, and 0.226, which corresponds to +210 kG and $E_k - E_n = 4000\ \text{cm}^{-1}$ for the phenyl compound. An uncertainty in $E_k - E_n$ of $\pm 500\ \text{cm}^{-1}$ corresponds to an inaccuracy in H^{L} of ±30 kG (methyl) and ±26 kG (phenyl), respectively. Since $a = d = e = 0$, we get $a'^2b^2 = 0.255$ (methyl) and 0.226 (phenyl), respectively;

(7) the orthogonality condition $\langle n|k\rangle = 0$ gives $aa' + bb' + cc' + dd' + ee' = 0$;

(8) the normalization condition implies $a'^2 + b'^2 + d'^2 + e'^2 = 1$;

(9), (10) from conditions (1) to (7) we find $a'^2 = 0.30$ and $c'^2 = 5.68b'^2$; since the main contribution to $|k\rangle$ in a distorted tetrahedron usually comes from the $|z^2\rangle$-orbital (provided that $|n\rangle$ has mainly $|xy\rangle$- or $|x^2 - y^2\rangle$-character) we conclude from (8) that $d'^2 + e'^2$ has to be very small; thus we find that $d'^2 = e'^2 = 0$ is a reasonable approximation for the estimate of coefficients a' to e'.

Under the conditions (1) to (10) we finally get[2]

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[1] Neglecting ligand contributions within the five single-electron orbitals of Fig. 3 and using Fe3d AO's as basis orbitals only, the five spin-up electrons populating the "doublet"- and "triplet"-orbitals produce zero EFG because of spherical symmetric charge distribution. Thus the resulting EFG comes from the remaining spin-down electron.

[2] Without loss of generality we take $c > 0$ and $c' > 0$.

$a=0$, $b=0.922$, $c=0.387$, $d=0$, $e=0$, $a'=0.548$, $b'=-0.324$, $c'=0.771$, $d'=0$, $e'=0$, $E_k-E_n=4000\pm500$ cm^{-1} for the methyl compound, and $a=0$, $b=0.962$, $c=0.269$, $d=0$, $e=0$, $a'=0.494$, $b'=-0.234$, $c'=0.837$, $d'=0$, $e'=0$, $E_k-E_n=4000\pm500$ cm^{-1} for the phenyl compound.

So far, we totally neglected ligand contributions to $|n\rangle$ and $|k\rangle$. This might be a poor approximation since it is known from molecular orbital investigations of other ferrous high-spin compounds that covalency (α^2) can play a concomitant role in the bonding properties of ionic iron compounds [7, 13, 14]. Because of the lack of X-ray data we are not in a position to carry out MO calculations for the compounds presently under study; therefore we make the rigorous assumption that α^2 is isotropic. Within this approximation α^2 cannot be smaller than $\alpha^2=0.70$ for the methyl compound and $\alpha^2=0.85$ for the phenyl compound. Since the covalency probably does not differ drastically within the two similar compounds, we take $\alpha^2=0.85$ for both and get

$a=0$, $b=0.880$, $c=0.274$, $d=0$, $e=0$, $a'=0.574$, $b'=-0.215$, $c'=0.689$, $d'=0$, $e'=0$, $E_k-E_n=4000\pm500$ cm^{-1} for the methyl compound, and $a=0$, $b=0.922$, $c=0$, $d=0$, $e=0$, $a'=0.516$, $b'=0$, $c'=0.764$, $d'=0$, $e'=0$, $E_k-E_n=4000\pm500$ cm^{-1} for the phenyl compounds (it is interesting that the result for the phenyl compound reflects C_{2v} point symmetry of the iron cation).

Comparing the result which we derive for zero and maximum covalency, we come to the conclusion that the LCAO coefficients of $|n\rangle$ and $|k\rangle$ are in the range

$a=0$, $0.880\leqslant b\leqslant0.922$, $0.274\leqslant c\leqslant0.387$, $d=0$, $e=0$, $0.548\leqslant a'\leqslant0.574$, $-0.324\leqslant b'\leqslant-0.215$, $0.689\leqslant c'\leqslant0.771$, $d'=0$, $e'=0$ for the methyl compound, and

$a=0$, $0.922\leqslant b\leqslant0.962$, $0\leqslant c\leqslant0.27$, $d=0$, $e=0$, $0.494\leqslant a'\leqslant0.516$, $b'=0$, $0.764\leqslant c'\leqslant0.837$, $d'=0$, $e'=0$ for the phenyl compound.

The situation for the ethyl compound is less transparent. From the magnetic hyperfine spectrum at 4.2 K (Fig. 1d) with the two "forbidden" lines [2] (arrows in 1d) it follows that the direction of $\vec{H}^{\text{int}}$ deviates from $\vec{V}_{zz}$ by $\zeta=20°$; hence either H_x^{int} or H_y^{int}, or even both do not vanish in Eq. (2). And since η is still zero (Table 1), we have to assume that the spin direction is not collinear with $\vec{V}_{zz}$, thus leading to non-vanishing contributions $H_y^{\text{int}}=\frac{1}{7}\mu_B\langle r_D^{-3}\rangle\langle l_y^2-2\rangle\langle S_y\rangle$ and/or $H_x^{\text{int}}=\frac{1}{7}\mu_B\langle r_D^{-3}\rangle\langle l_x^2-2\rangle\langle S_x\rangle$. With $\zeta=20°$ and H^{int} (4.2 K)$=130$ kG the components of H^{int} become $H_z^{\text{int}}=122.1$ kG and $H_{x-y}^{\text{int}}=44.5$ kG.

As a summary of our results we draw the following conclusions:

(1) The influence of the substituents methyl, ethyl, and phenyl upon the electronic and magnetic structure of iron in the three Fe-imidazole compounds is significant.

(2) In all three cases the ferrous high-spin iron is tetrahedrally coordinated by substituted imidazole groups.

(3) The magnetic ordering at low temperatures clearly indicates that the three compounds are three-dimensional coordination polymers (this finding is comparable with the fact that these compounds are non-volatile and insoluble in organic solvents).

(4) The electronic structure in the methyl and phenyl compounds may be described by ground state and excited state single-electron wave functions $|n\rangle$ and $|k\rangle$ and energy separations $E_k - E_n$ (Fig. 3):

$0.88 \leqslant b \leqslant 0.92$, $0.27 \leqslant c \leqslant 0.39$, $0.55 \leqslant a' \leqslant 0.57$, $-0.32 \leqslant b' \leqslant -0.22$, $0.69 \leqslant c' \leqslant 0.77$, $a = d = e = d' = e' = 0$, $E_k - E_n = 4000 \pm 500\ \text{cm}^{-1}$ for the methyl compound, and

$0.92 \leqslant b \leqslant 0.96$, $0 \leqslant c \leqslant 0.27$, $0.49 \leqslant a' \leqslant 0.52$, $0.76 \leqslant c' \leqslant 0.84$, $a = d = e = b' = d' = e' = 0$, $E_k - E_n = 4000 \pm 500\ \text{cm}^{-1}$, for the phenyl compound.

The LCAO coefficients $a, \ldots, e'$ are approximate values mainly due to the assumption of isotropic covalency, due to the lack of better knowledge of the energy separation $E_k - E_n$, and due to the approximative procedure in estimating H^{L} from H^{int}. The situation for the ethyl compound is less transparent because of the non-collinearity of $\vec{H}^{\mathrm{int}}$ and $\vec{V}_{zz}$.

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