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Mössbauer Effect Study of the Influence of Ligand Steric Interactions on the Lattice Dynamics and Electronic Structure of Fe[B(3-isopropylpyrazol-1-yl)$_4$]$_2$

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Introduction

Coordination complexes containing various substituted polypyrazolylborate ligands have been very useful in investigating the steric properties of ligands and the electronic properties of the resulting transition metal complexes.[1] Indeed, the polypyrazolylborate ligands have been invaluable in understanding the influence of ligand steric interactions upon both the electronic spin-state of iron(II) complexes[2–6] and the important spin-state crossover, between high-spin iron(II) and low-spin iron(II), often observed in octahedral complexes.[7–9] More recently, it has been shown that polypyrazolylborate ligand steric interactions can lead to a variety of different coordination environments and coordination numbers, especially in the case of cobalt(II) complexes.[6,10–12] Indeed, ligand steric interactions are believed to be responsible for reducing the chelating nature of the tetra(3-isopropylpyrazolyl)borate ligand from the expected tridentate to the bidentate bonding found in Co[B(3-isopropylpyrazol-1-yl)$_4$]$_2$.[11]

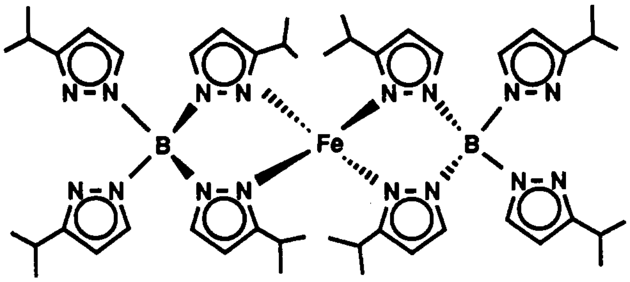
The Mössbauer effect spectral hyperfine parameters have been extensively used to characterize the electronic properties of iron polypyrazolylborate complexes as a function of temperature,[2–5] pressure,[4] and spin-state.[4,5] In contrast, there has been relatively little use of the Mössbauer effect to study the lattice properties and lattice dynamics of these coordination complexes. The utility of the Mössbauer effect in the study of the lattice properties of a series of organoiron compounds has been nicely demonstrated by Herber and his colleagues.[13,14] More recent studies have dealt with ligand dynamics in some organoiron compounds[15] and with the lattice dynamics in several iron(III) dithiocarbamate complexes.[16] The purpose of this note is to illustrate the use of the Mössbauer effect in the study of the unusual lattice properties which are found in Fe[B(3-isopropylpyrazol-1-yl)$_4$]$_2$, I; properties which can be attributed to coordinated ligand steric interactions.

Experimental Section

Fe[B(3-isopropylpyrazol-1-yl)$_4$]$_2$, I, was prepared as described previously.[11] The Mössbauer effect spectra were obtained under constant geometry conditions on a Harwell constant acceleration spectrometer which utilizes a room-temperature rhodium matrix cobalt-57 source and was calibrated at room temperature with α-iron foil. The absorber contained 90 mg/cm^2 of finely divided crystals which were dispersed in vaseline. The observed spectra were fit by using standard computer least-square minimization techniques with two quadrupole doublets of equal area and linewidth. The left and right components of both doublets had slightly different areas, presumably as a result of texture in the absorber.

Results and Discussion

The Mössbauer effect spectra of Fe[B(3-isopropylpyrazol-1-yl)$_4$]$_2$, I, have been measured between 85 and 296 K and three typical spectra are shown in Figure 1. As this figure reveals, the Mössbauer spectra exhibit a non-symmetric doublet with a large quadrupole splitting. It is not possible to fit the observed spectra satisfactorily with a single asymmetric quadrupole doublet and we have been forced to fit them with two quadrupole doublets of equal area. These two doublets are shown as the solid line component fits in Figure 1 and the resulting hyperfine parameters, as a function of temperature, are given in Table I.



I

To understand the Mössbauer spectral hyperfine parameters, it would be useful to have the single crystal structure of Fe[B(3-isopropylpyrazol-1-yl)$_4$]$_2$. Unfortunately, we have been unable to obtain the crystal structure of this compound, but have found that its X-ray powder diffraction pattern is similar to, but surely not identical to, that of Co[B(3-isopropylpyrazol-1-yl)$_4$]$_2$. As a result, we conclude that the molecular structure of the former is similar to that of the cobalt compound but that the iron compound probably crystallizes in a less symmetric space group than does the latter. The single crystal X-ray structure of Co[B(3-isopropylpyrazol-1-yl)$_4$]$_2$ indicates that the inner coordination sphere of the cobalt atom is best described as a flattened tetrahedron[11] comprised of two imidazole nitrogen atoms from each of the two coordinated ligands. In other words, only two of the four available pyrazolyl nitrogen donor atoms on each of the ligands are coordinated to the cobalt(II) ion. The four-coordinate bonding found in this compound is unexpected and, no doubt, results from steric interactions between the two coordinated ligands. Indeed, molecular models have indicated[11]

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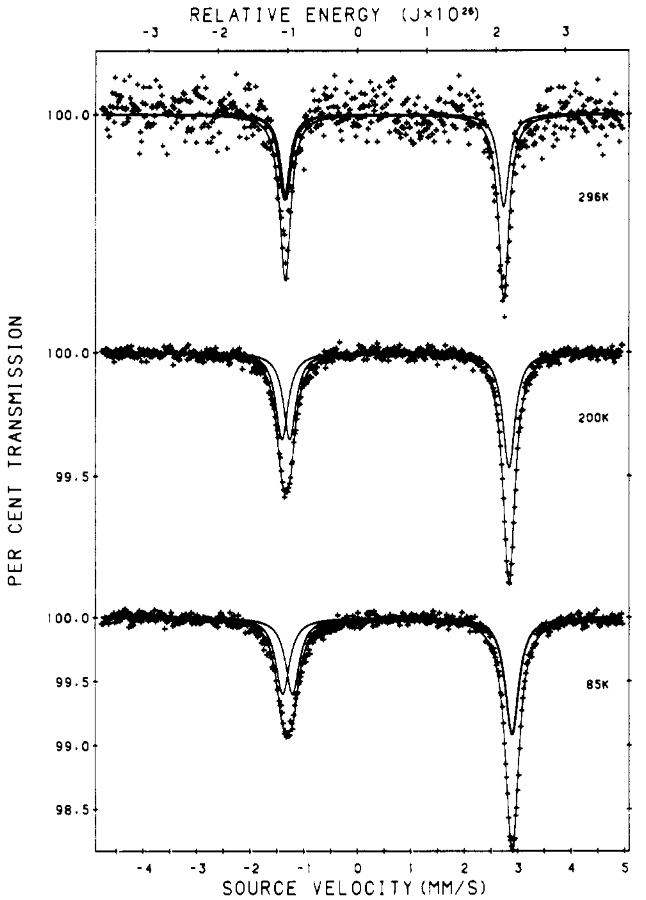

Figure 1. Mössbauer effect spectra of Fe[B(3-isopropylpyrazol-1-yl)$_4$]$_2$ obtained at several temperatures.

that an octahedral structure with the two ligands in a tridentate coordination mode would be highly strained because of steric interactions of the six isopropyl groups, groups which would lie in the equatorial belt of this complex. Apparently to relieve this strain, the ligand adopts a bidentate distorted tetrahedral bonding mode with two rather long but similar cobalt to nitrogen bond lengths[10,17-19] of 1.970(3) and 1.980(3) Å. Co[B(3-isopropylpyrazol-1-yl)$_4$]$_2$ crystallizes in the monoclinic $C2/c$ space group with four crystallographically identical molecules in its unit cell.

The Mössbauer spectra and powder diffraction pattern indicate that Fe[B(3-isopropylpyrazol-1-yl)$_4$]$_2$ most likely crystallizes in a space group which has two crystallographically distinct molecules, but which retains the distorted tetrahedral coordination geometry. Indeed, as indicated above, two quadrupole doublets, with very similar hyperfine parameters, see Table I, are required to successfully fit the observed Mössbauer spectra. Very similar hyperfine parameters would be expected for the two crystallographically non-equivalent, but chemically very similar, molecules. As indicated in Table I, the area ratio of the left and right components, A, of each doublet is ca. 0.75 and independent of temperature. The less than unit value of this ratio reveals the presence of texture in the Mössbauer absorber. However, this texture cannot account for the broadening observed in the left spectral line. This broadening can only be accounted for with two doublets. The Mössbauer effect isomer shifts of the two doublets found in Fe[B(3-isopropylpyrazol-1-yl)$_4$]$_2$, are very characteristic of those expected for iron(II) in a tetrahedral environment.[20-22] The temperature dependence of the isomer shift for the two sites is completely consistent with that expected from the second order Doppler shift,[23] and yields $d\delta/dT$ values of -3.38×10^{-4} and -4.84×10^{-4} mm/(s·K). The quadrupole splittings for the two sites are similar but rather larger than those typically observed in distorted tetrahedral high-spin iron(II) complexes.[20-22,24] The maximum expected[25,26] valence contribution to the quadrupole splitting for iron(II) is 3.717 mm/s. Hence the observed splittings indicate that the valence and lattice contributions to the electric field gradient must have the same sign. These large values also indicate that, almost surely, the coordination sphere about the iron must be more highly distorted than that observed in the analogous cobalt compound.[11] The very small temperature dependence observed for the two quadrupole splittings is consistent with this large distortion and indicates a large splitting of the tetrahedral ^5E_g ground state, such that only one of the two ground state e_g orbitals is doubly occupied between 85 and 296 K. Hence, the splitting of the $d_{x^2-y^2}$ and d_{z^2} orbitals must be at least on the order of 600 cm^{-1}, a splitting not unreasonable for this type of coordination environment.[24,26] Unfortunately, because the sign of the quadrupole splitting is unknown, it is not possible to determine which orbital is the ground state orbital.[27]

The most unusual aspect of the Mössbauer spectra of Fe[B(3-isopropylpyrazol-1-yl)$_4$]$_2$ is the temperature dependence of the spectral absorption area given in Table I. This dramatic temperature dependence is indicated by the time required to obtain the spectra shown in Figure 1. The 85 K spectrum was obtained in ca. 6 h, but more than 150 h were required to obtain the 296 K spectrum, which, even after this length of time, has a rather poor signal to noise ratio.

The temperature dependence of the Mössbauer spectral absorption area is best understood in terms of the Debye model for lattice vibrations. This model predicts a linear decrease in the logarithm of the Mössbauer spectral absorption area above approximately half the lattice Debye temperature.[14,23,28,29] It is apparent in Figure 2 that the temperature dependence of the logarithm of the Mössbauer spectral absorption area in Fe[B(3-isopropylpyrazol-1-yl)$_4$]$_2$ is linear below ca. 170 K. However, above these temperatures, the spectral absorption area decreases much more rapidly than expected from the Debye model. The linear behavior observed between 85 and 160 K yields a slope, d (ln A)/dT, of -1.02×10^{-2} K^{-1} and a Debye temperature, θ_D, of 115 K. The straight line shown in Figure 2 corresponds to the Debye model with this Debye temperature and a mass of 57 g/mol for the iron nucleus. Alternatively, we can calculate a Mössbauer temperature, θ_M, which is equivalent to the Debye temperature, but takes into account the effective recoil mass which can be determined from the second order Doppler shift.[13,14] The second order Doppler shift, as obtained from the temperature dependence of the isomer shift given above, yields values for the effective recoil masses of 123 and 86 g/mol and Mössbauer

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Table I. Mössbauer Spectral Hyperfine Parameters Obtained for Fe[B(3-isopropylpyrazol-1-yl)$_4$]$_2$

	doublet A		doublet B					
T, K	δ,[a] mm/s	ΔE_Q, mm/s	δ,[a] mm/s	ΔE_Q, mm/s	Γ, mm/s	A[b]	abs area (% ϵ)(mm/s)	ln area
85	0.76	4.30	0.84	4.12	0.30	0.75	2.81	1.03
100	0.76	4.29	0.84	4.11	0.31	0.74	2.35	0.85
120	0.75	4.28	0.84	4.11	0.30	0.74	1.94	0.66
140	0.75	4.27	0.83	4.11	0.30	0.74	1.61	0.48
160	0.74	4.26	0.81	4.10	0.29	0.75	1.29	0.25
180	0.73	4.25	0.80	4.10	0.28	0.75	0.96	−0.045
200	0.72	4.25	0.79	4.10	0.28	0.75	0.70	−0.36
220	0.72	4.24	0.79	4.10	0.27	0.77	0.38	−0.96
240	0.72	4.23	0.78	4.08	0.27	0.75	0.27	−1.31
260	0.71	4.23	0.76	4.04	0.25	0.79	0.18	−1.74
280	0.69	4.18	0.75	4.04	0.26	0.77	0.10	−2.28
296	0.69	4.17	0.74	4.04	0.24	0.92	0.032	−3.44

[a] Measured relative to room-temperature natural abundance α-iron foil. [b] The ratio of the area of the left component of the two quadrupole doublets to the area of the right component of the two quadrupole doublets.

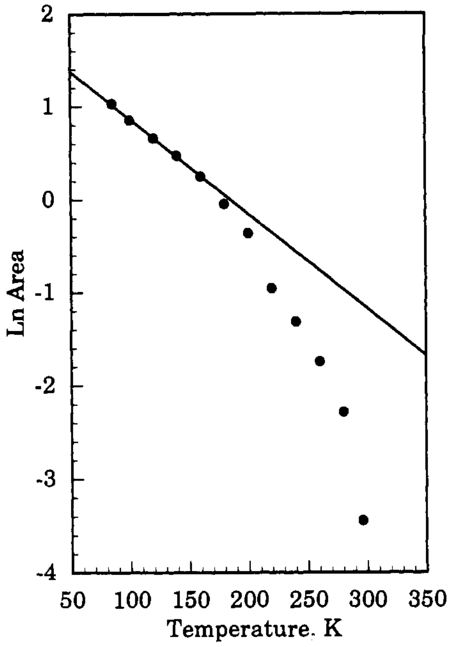

Figure 2. Temperature dependence of the logarithm of the Mössbauer spectral absorption area for Fe[B(3-isopropylpyrazol-1-yl)$_4$]$_2$. The straight line corresponds to a Debye model fit of the data between 85 and 160 K.

Table II. Mössbauer Derived Lattice Dynamic Properties of Fe[B(3-isopropylpyrazol-1-yl)$_4$]$_2$

T, K	ln A	ln A_D[a]	ln A − ln A_D	$\langle u^2\rangle$, Å^2	$\langle u^2\rangle_{rms}$, Å
180	−0.045	0.055	−0.010	0.0056	0.075
200	−0.36	−0.15	−0.21	0.012	0.11
220	−0.96	−0.35	−0.61	0.034	0.18
240	−1.31	−0.56	−0.75	0.043	0.21
260	−1.74	−0.76	−0.98	0.055	0.24
280	−2.28	−0.96	−1.32	0.074	0.27
296	−3.44	−1.13	−2.31	0.130	0.36

[a] ln A_D is the logarithm of the absorption area as computed from the Debye model represented by the straight line shown in Figure 2.

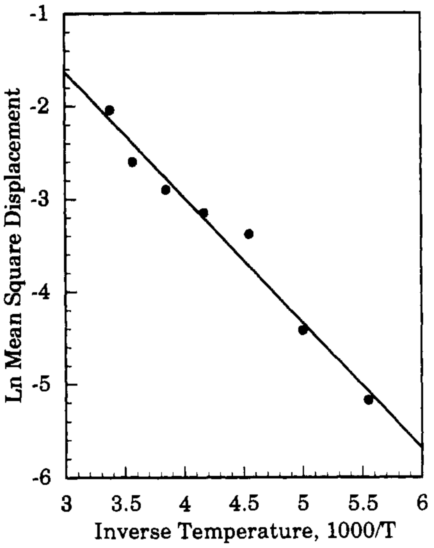

Figure 3. Logarithm of the mean square displacement of the iron nuclide in Fe[B(3-isopropylpyrazol-1-yl)$_4$]$_2$ as a function of the inverse temperature.

temperatures, θ_M, of 79 and 94 K. Both the Debye and Mössbauer temperatures are reasonable[16,23,30] for a compound which consists of well separated neutral monomeric Fe[B(3-isopropylpyrazol-1-yl)$_4$]$_2$ molecules which are bound into the lattice by only van der Waals forces, as was found to be the case[11] for Co[B(3-isopropylpyrazol-1-yl)$_4$]$_2$. The increased recoil masses of the iron-57 nuclide indicate the presence of covalent bonding with the two ligands, bonding which apparently is rather different for the two sites.

As shown in Figure 2, above 160 K the Mössbauer spectral absorption area deviates substantially from that expected for Debye model behavior. This deviation indicates that the iron nuclide is undergoing, in addition to the usual lattice vibration, another, more highly temperature dependent, displacement.[31] In order to describe this additional displacement, we have used an approach similar to that proposed by Wordel and Wagner,[32] which we have recently applied to hydride motion in some organoiron compounds.[15] The difference, ln A − ln A_D, between the experimental Mössbauer spectral absorption area and the area expected on the basis of the Debye model, see Figure 2 and Table II, is used to calculate the additional mean-square displacement of the iron nuclide, $\langle u^2\rangle$, above 160 K. If we assume that the additional iron displacement is controlled by a thermally activated process,[33] the logarithm of the mean-square displacement should obey the Arrhenius law. Figure 3 shows the expected linear behavior for the Arrhenius plot and yields an activation energy of 1350 K or 940 cm^{-1} for the displacement in Fe[B(3-isopropylpyrazol-1-yl)$_4$]$_2$. This activation energy is reasonable for a displacement which surely must involve some ligand motion. The magnitude of the displacement, $\langle u^2\rangle_{rms}$, increases from zero at 160 K up to 0.36 Å at 296 K; values which are twice that expected for the normal Debye lattice vibrational displacement. Although the 296 K displacement seems rather large, it should be remembered that ligand-ligand steric interactions produce a

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rather large chelation cavity for the metal ion. Further, it should be noted that typical octahedrally coordinated cobalt polypyrazolylborate complexes have, at 200 K, cobalt to nitrogen bond distances[10-12] which fall in the range from 2.05 to 2.21 Å. These values are 0.08–0.14 Å larger than the average cobalt to nitrogen bond distance found[11] in $Co[B(3\text{-isopropylpyrazol-1-yl})_4]_2$, and are of the same order of magnitude as the additional iron displacement calculated at 200 K; see Table II.

It is difficult to understand exactly why $Fe[B(3\text{-isopropylpyrazol-1-yl})_4]_2$ should show both the normal Debye lattice vibrations and the additional iron displacement, but we believe this may be due to the strong ligand–ligand steric interactions in the coordination sphere of the iron(II) ion. The packing energy of the individual neutral $Fe[B(3\text{-isopropylpyrazol-1-yl})_4]_2$ molecules in the extended lattice is controlled by the van der Waals potential between the peripheral portions of the ligands. It is this packing which results in the Debye model vibrational behavior at low temperature. However this packing does not necessarily yield the ideal binding of the iron atom into the lattice, especially in view of the ligand steric interactions mentioned above and found[11] in $Co[B(3\text{-isopropylpyrazol-1-yl})_4]_2$. We believe it is this non-ideal binding of the iron nuclide in the lattice which yields, at higher temperature, the additional thermally activated displacement. This additional displacement produces destructive interference[31] between the absorbed Mössbauer γ-rays and, as a consequence, decreases the recoil free fraction, and hence, the observed Mössbauer spectral absorption area. It would be interesting to compare this behavior with that observed in the less sterically hindered five and six coordinate complexes.

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Additions and Corrections

1992, Volume 31

Eiichi Kimura,* Hiromasa Kurosaki, Yasuhisa Kurogi, Mitsuhiko Shionoya, and Motoo Shiro: pH-Dependent Coordination Mode of New Bleomycin Synthetic Analogues with Copper(II), Iron(II), and Zinc(II).

Pages 4314 and 4317. The interaxial angles, $\alpha = 105.13\ (1)^\circ$, $\beta = 101.14\ (1)^\circ$, and $\gamma = 98.84\ (1)^\circ$, should be added to the Abstract and Table I. The space group $P1$ should be also corrected to $P\bar{1}$.—Eiichi Kimura

Kattesh V. Katti,* Prahlad R. Singh, and Charles L. Barnes: Transition Metal Chemistry of Main Group Hydrazides. 1. Synthesis and Characterization of Cyclometallaphosphohydrazides of Cobalt(I), Copper(I), and Palladium(II). X-ray Structures of Cobalt(I) and Palladium(II) Representatives.

Page 4589. Table I should include the values $\alpha = 86.318\ (15)^\circ$ and $\gamma = 72.183\ (19)^\circ$ for the triclinic compound 7.—Kattesh V. Katti