

A Mössbauer Spectroscopic Investigation of a Series of Boron-Capped Iron II Clathrochelates

ROBERT L. ASHER¹ AND JOHN G. STEVENS²

*Department of Chemistry, University of North Carolina at Asheville,
Asheville, North Carolina 28804*

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A series of boron-capped iron (II) clathrochelates has given excellent Mössbauer intensities for room and liquid nitrogen temperatures. The quadrupole splittings for these clathrochelates decrease slightly between room and liquid nitrogen temperatures, having values between 0.4 and 1.2 mm/sec. The isomer shifts are close to 0.0 mm/sec relative to α -Fe. This is an indication of iron (II) in a low and/or intermediate spin state. While the isomer shift differences are nominal, the quadrupole splittings correlate with the size of the atom or atomic group at the boron site and the distortion of the complex from a trigonal prismatic structure. There is evidence of a phase change for two of the complexes ($\text{Fe}(\text{DMG})_3(\text{BH})_2$ and $\text{Fe}(\text{DMG})_3(\text{BF})_2$) between room and liquid nitrogen temperatures. © 1990 Academic Press, Inc.

Introduction

A clathrochelate is a special type of complex that contains an encapsulated central atom which is also bound by the chelating groups. The synthesis of these types of compounds was first proposed by D. H. Busch who coined the term clathrochelate (1). The series of clathrochelates investigated in this study were prepared by Grzybowski and co-workers (2, 3) at Gettysburg College using a method similar to that reported in the literature by Rose and co-workers (4, 5).

Clathrochelates studied are shown in Fig. 1. Jackels and Rose (6) have previously studied complexes of the type seen in Fig. 1a. They reported that the quadrupole

splitting and isomer shift values for the various complexes had noticeable differences (6). In Mössbauer spectroscopy it is not very common to see effects from groups that are more than two atoms removed from the Mössbauer isotope, because the Mössbauer parameters depend only upon the electron densities of the Mössbauer isotope, ⁵⁷Fe. It is, therefore, interesting to note that a group attached to the boron, four atoms away, produces significant changes in the quadrupole splitting. From Fig. 1 it can be seen that these clathrochelate complexes have a very symmetric structure, forming a nearly trigonal prismatic structure about the iron. It is this less common symmetry and the effects of distant atoms on quadrupole splitting values that prompted further investigation of these complexes. Jackels and Rose (6) concluded that the electronegativity of the group attached to the boron had an effect on

¹ Presently at the Chemistry Department, University of Florida, Gainesville, FL 32611.

² To whom correspondence should be addressed.

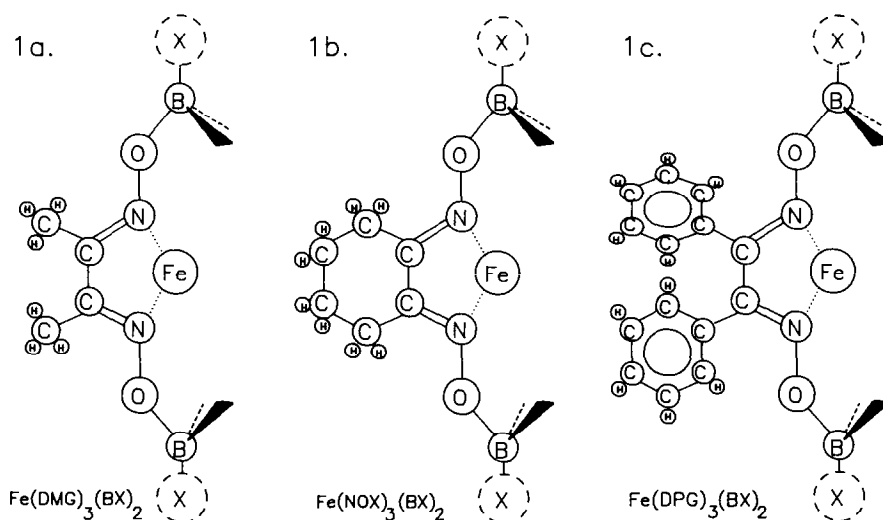


FIG. 1. Types of clathrochelates investigated (DMG, NOX, and DPG).

the isomer shift value. As the attached group was changed from F^- to alkoxy the isomer shift decreased, probably indicating the greater electron-releasing nature of the alkoxy group (6). The motivation for the present investigation was to ascertain whether this is the only correlation and whether this correlation is valid for other clathrochelate series.

Experimental

A list of the clathrochelates investigated, as well as their Mössbauer fitting parameters, are reported in Table I. The different chelating groups in the series of clathrochelates studied include DMG (dimethylglyoxime), NOX (1,2-cyclohexanedione dioxime or nioxime), and DPG (diphenylglyoxime). Mössbauer spectra of all of the complexes were obtained using a 3- to 5-mCi Rh^{57}Co source, a Reuter-Stokes xenon proportional detector, an Elscint Mössbauer spectrometer, and a Nuclear Data ND600 multi-channel analyzer. Samples were prepared by mixing a portion of 99% hygroscopic bo-

ron nitride and enough complex to contain 10 mg/cm² of natural iron. Initial spectra were observed to have quadrupole splittings of unequal intensities. When these samples were ground more carefully, the differences in intensities were no longer observed. Apparently, these intensity differences were due to texture effects, i.e., orientation of the crystals in the sample. Liquid nitrogen temperature spectra were obtained using a Janis Dewar with a Lake Shore Cryotronics temperature controller. Room temperature spectra of the samples required approximately 18 to 24-hr acquisition times, while liquid nitrogen spectra required 10–14 hr. Each spectrum was fit using the Mössbauer Spectra Fitting Program for UNiversal Theories (MOSFUN) (7), (see sample spectra Fig. 2). Isomer shift values are reported relative to room temperature α -Fe spectra.

Results and Discussion

The Mössbauer spectra of the complexes consist of quadrupole splittings which are in the range from 0.4 to 1.2 mm/sec. It should

TABLE I
 MÖSSBAUER PARAMETERS OF THE CLATHROCHELATES INVESTIGATED

Compound	<i>T</i> (K)	$\delta^{a,b}$ (mm/sec)	Δ^b (mm/sec)	<i>I</i> ₁ (%)	<i>I</i> ₂ (%)	<i>R</i> ^c
Fe(DMG) ₃ (BCH ₃) ₂	295	0.06	0.71	2.4	2.4	
Fe(DMG) ₃ (BOH) ₂	295	0.07	0.76	7.9	8.2	
Fe(DMG) ₃ (BH) ₂	295	0.07	0.86	1.0	1.0	
Fe(DMG) ₃ (BF) ₂	295	0.08	0.87	3.9	4.0	
Fe(NOX) ₃ (BOCH ₃) ₂	295	0.04	0.49	7.2	7.2	
Fe(NOX) ₃ (BC ₄ H ₉) ₂	295	0.05	0.58	6.4	6.6	
Fe(NOX) ₃ (BC ₆ H ₅) ₂	295	0.04	0.63	8.4	8.4	
Fe(NOX) ₃ (BOH) ₂	295	0.05	0.64	10.9	11.2	
Fe(NOX) ₃ (BH) ₂	295	0.06	0.64	2.6	2.5	
Fe(NOX) ₃ (BF) ₂	295	0.07	0.70	0.7	0.7	
Fe(NOX) ₃ (BBr) ₂	295	0.05	0.75	1.1	1.1	
Fe(DPG) ₃ (BC ₆ H ₅) ₂	295	0.00	0.23	1.1	1.1	
Fe(DMG) ₃ (BCH ₃) ₂	77	0.00	0.66	2.8	2.8	1.29
Fe(DMG) ₃ (BOH) ₂	77	0.03	0.74	13.0	13.0	1.59
Fe(DMG) ₃ (BH) ₂	77	0.08	1.15	1.9	1.9	2.00
Fe(DMG) ₃ (BF) ₂ ^d	77	0.09	1.08	5.4	5.4	1.51
		0.04	0.81	6.1	6.1	3.28
Fe(NOX) ₃ (BOCH ₃) ₂	77	0.01	0.45	13.0	13.3	1.88
Fe(NOX) ₃ (BC ₄ H ₉) ₂	77	0.01	0.57	10.8	10.8	1.67
Fe(NOX) ₃ (BC ₆ H ₅) ₂	77	0.01	0.58	13.4	11.9	1.70
Fe(NOX) ₃ (BOH) ₂	77	0.01	0.57	15.2	16.1	1.40
Fe(NOX) ₃ (BH) ₂	77	0.01	0.56	6.1	5.7	2.39
Fe(NOX) ₃ (BF) ₂	77	0.01	0.66	0.9	1.0	1.38
Fe(NOX) ₃ (BBr) ₂ ^e	77	0.04	0.70	<1	<1	—
Fe(DPG) ₃ (BC ₆ H ₅) ₂	77	0.02	0.19	0.7	0.6	1.19

^a These values are reported relative to α -Fe standard at 298 K.

^b These values are reported +0.02 mm/sec.

^c Ratio of liquid nitrogen peak area to room temperature peak area.

^d There are two iron sites seen in this spectrum.

^e The spectrum for this compound at 77 K is very poor, i.e., the data are less reliable.

be noted that the quadrupole splittings are slightly smaller at liquid nitrogen temperature for most of the complexes. The isomer shifts have values ranging from 0.0 to 0.1 mm/sec relative to α -Fe. These results suggested that the iron (II) in these complexes is in a low and/or intermediate spin state. The large intensities observed in the room temperature spectra are an indication that

there are both covalent bonding between the nitrogens of the chelating groups and the encapsulated iron and strong intermolecular bonding between the clathrochelate molecules.

The correlation between isomer shift values and electronegativities, which Jackels and Rose report, is not observed in the present reported series of clathrochelates (6).

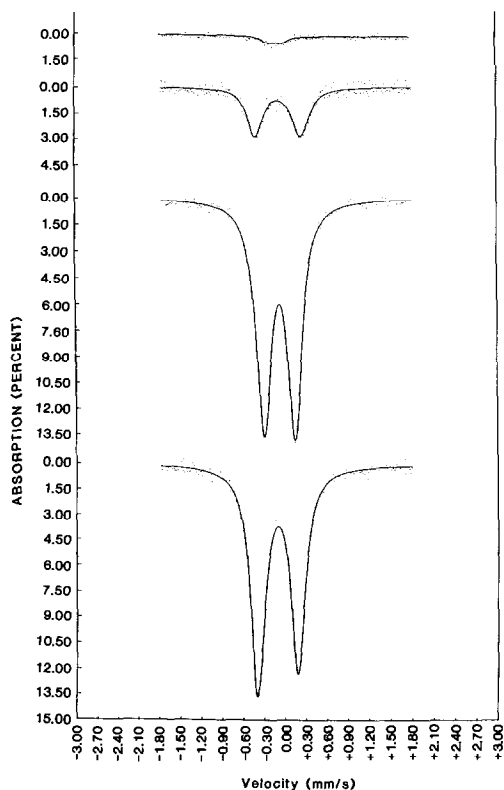


FIG. 2. Example Mössbauer spectra: $\text{Fe}(\text{DMG})_3(\text{BCH}_3)_2$, $\text{Fe}(\text{NOX})_3(\text{BOCH}_3)_2$, $\text{Fe}(\text{DMG})_3(\text{BC}_6\text{H}_5)_2$, and $\text{Fe}(\text{DPG})_3(\text{BC}_6\text{H}_5)_2$.

The isomer shift values for all of the complexes in the present investigation are the same, within experimental error of each other, except for the $\text{Fe}(\text{DMG})_3(\text{BF})_2$ and $\text{Fe}(\text{DMG})_3(\text{BH})_2$ complexes. It should be further noted that these two complexes do not follow the trend of decreasing in isomer shift value from room temperature to liquid nitrogen temperature (see Fig. 3 for this departure from the trend). A new phase is apparently present for these two samples at liquid nitrogen temperature. In fact, the Mössbauer spectrum of the $\text{Fe}(\text{DMG})_3(\text{BF})_2$ complex at liquid nitrogen temperature gives two sets of quadrupole splittings. The peak with the larger quadrupole splitting corresponds to the new phase, while the

smaller corresponds to the phase seen at room temperature.

The general trends in quadrupole splitting can be understood by considering the crystal field splitting for low-spin d^6 systems (8) of trigonal prismatic (TP, dihedral twist angle, $\beta = 0^\circ$), antitrigonal prismatic (TAP or octahedral, $\beta = 60^\circ$), or something in between these two geometries (see Fig. 4). Reiff has reported the effect of geometry on the quadrupole splittings of other, less symmetric, clathrochelates (9). He concluded that the main reason for quadrupole splitting differences in these complexes is a consequence of varying amounts of distortion in the trigonal prismatic geometry about the iron nucleus. Octahedral and pseudooctahedral complexes are not expected to make any significant contributions to quadrupole splitting, because the d -orbitals occupied (d_{xy} , d_{xz} , and d_{yz}) form a spherically symmetric charge distribution. However, in trigonal prismatic complexes the orbitals occupied (d_{xy} , $d_{x^2-y^2}$, and d_{z^2}) do not form a spherically symmetric charge distribution. The $d_{x^2-y^2}$ and d_{z^2} orbitals together give a spherical charge distribution, but the remaining d_{xy} orbital causes a quadrupole splitting. The resulting quadrupole splitting would be negative because the d_{xy} orbital decreases the electric field gradient (EFG) in the z direction. It is unfortunate that in ^{57}Fe Mössbauer spectroscopy, the sign of the quadrupole splitting cannot be determined without the application of a strong magnetic field. It is expected that those complexes with large quadrupole splitting probably have geometries closest to the TP structure. As the quadrupole splitting decreases, the dihedral twist angle increases and the structure becomes a distorted trigonal prism. Eventually, at $\beta = 60^\circ$, the geometry is antitrigonal prismatic. Unfortunately, there is very little structural data available in the literature. However, Jackels and Rose report a twist angle of 16.5° for the $\text{Fe}(\text{DMG})_3(\text{BF})_2$ complex (6).

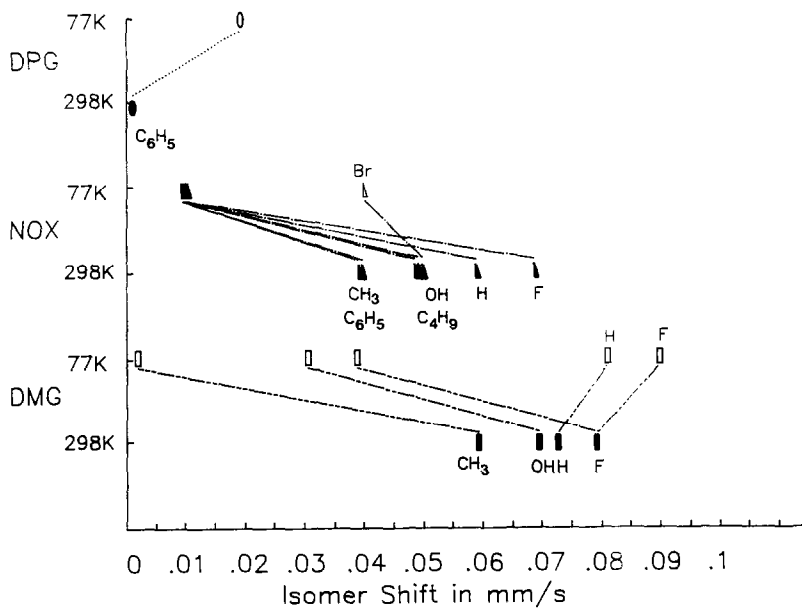


FIG. 3. Plot of slight decreasing trend of isomer shift data at room and liquid nitrogen temperature.

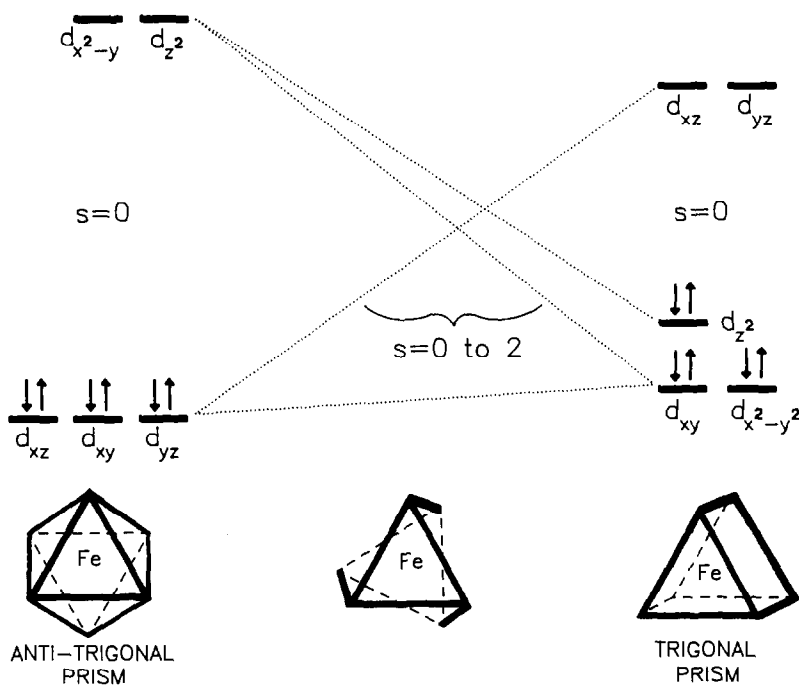


FIG. 4. Crystal field splitting for d^6 systems (TAP and TP).

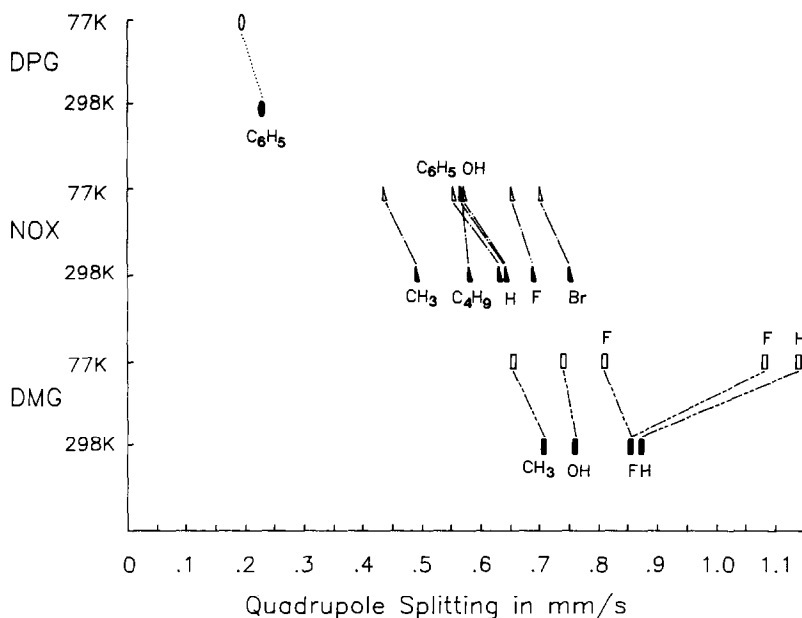


FIG. 5. Plot of quadrupole splitting trends for DPG, NOX, and DMG chelating complexes. (Note the general trend in quadrupole splitting is DPG < NOX < DMG.)

The overall geometry and, in particular, the twist angle of the complexes may be affected in two ways. First, there is the effect of the chelating group itself and, second, the effect of the group attached to the boron site. There is an apparent effect on the quadrupole splitting related to the "bulkiness" of substituents to the ring that encapsulates the iron. As the chelating group is changed from DPG to NOX to DMG there is a general increase in the quadrupole splitting (see Fig. 5). The twist angle is affected by the size of the substituents and, likely, by their electron donating ability. As the chelating group becomes less complex in size and shape, there is freedom to form a trigonal prismatic structure. There is a trend in the Mössbauer data which links the quadrupole splitting to the size (or massiveness) of the group substituted at the boron site. As the size of the group increases, the quadrupole splitting decreases. For example, in the DMG series a definite decrease

in quadrupole splitting can be seen as the group attached to the boron is changed from H to CH₃. This trend is even more obvious in the NOX series of complexes. Organic and alkoxy substitution at the boron in this series shows this correlation best. The increase in "bulkiness," OCH₃ < C₄H₉ < C₆H₅, parallels the increasing quadrupole splitting values for the complexes. This trend is probably a demonstration that the axial groups attached to the boron perturb the crystal solid from antitrigonal prismatic towards trigonal prismatic. The larger the group, larger the trend toward the more common antitrigonal prismatic structure.

There is a small decrease in the quadrupole splitting from room to liquid nitrogen temperature for all the complexes, except for Fe(DMG)₃(BF)₂ and Fe(DMG)₃(BH)₂. Normally, quadrupole splittings increase as the temperature decreases. This is due to the Maxwell-Boltzmann distribution of the *d* electrons: as the temperature is lowered,

there is an increase in the difference in the population of some of the d levels in the usual octahedral structure. However, because of the nature of the d orbital splittings for these complexes, i.e., the intermediate spin state (see Fig. 5), the quadrupole splitting will actually decrease with a decrease in temperature. In particular there are intermediate structures TP and TAP where four of the d levels ($d_{x^2-y^2}$, d_{z^2} , d_{xz} , and d_{xy}) differ in energy by only a small amount. It is at this stage that there is an opportunity for the spin to be 0, 1, or 2 depending upon the energy differences and thermal population of the levels (see Fig. 4).

As previously mentioned, there is strong covalent interaction between the iron and the nitrogens. In addition, several of the complexes exhibit strong intermolecular bonding. In particular the $\text{Fe}(\text{DMG})_3(\text{BOH})_2$ and $\text{Fe}(\text{NOX})_3(\text{BOH})_2$ complexes have very large intensities at room temperature (see Table I). The spectral areas of these two complexes do not increase as significantly as the other complexes when lowering the temperature from room temperature to liquid nitrogen temperature spectral areas to liquid nitrogen areas. Conversely the $\text{Fe}(\text{DMG})_3(\text{BH})_2$ and $\text{Fe}(\text{NOX})_3(\text{BH})_2$ are complexes which exhibit weak intermolecular bonding.

Conclusions

There is a correlation between quadrupole splitting values and amount of distor-

tion in the trigonal prismatic structure for the boron capped iron II clathrochelates studied. The decrease in quadrupole splitting from room to liquid nitrogen temperature is due to an electron distribution resulting from intermediate spin states. While all the complexes studied have strong intramolecular bonding, the intermolecular bonding differs considerably.

Acknowledgments

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