Orbital ground state reversal in the high-spin complex Fe(II) (*N, N'*-dicyclohexylthiourea)₆(ClO₄)₂

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(Received 10 May 1973)

Mössbauer spectroscopy of iron (II)(*N, N'*-Dicyclohexylthiourea)₆(ClO₄)₂ shows the existence of two isomers. At low temperatures ($T < 200^\circ\text{K}$) a form *A* with quadrupole splitting $\Delta E = 3.31$ mm/sec is stable. At and above room temperature a form *B* with $\Delta E = 1.32$ mm/sec is stable. For $200^\circ\text{K} < T < 300^\circ\text{K}$ both forms are observed with the *B/A* ratio increasing with increasing temperature. The values of ΔE are typical of Fe^{2+} with an orbital singlet and an orbital doublet ground state for *A* and *B*, respectively. The isomer shift and magnetic susceptibility results indicate that both forms of the molecule contain high-spin ferrous ions. Infrared spectra show that in both forms the iron is bound to the sulphur atoms of each of the six dicyclohexylthiourea ligands. Mössbauer spectra in external magnetic fields show that the sign of the principal component of the electric field gradient is negative for form *A* and positive for form *B*, and that the asymmetry parameter of the electric field gradient tensor is negligible in both forms. The only consistent interpretation of all the results outlined above is in terms of a trigonally distorted octahedral coordination of the Fe^{2+} for both isomers. In form *A*, the distortion is such that the prolately deformed (t_{2g}^0) orbital is lowest while in form *B* the oblatelly deformed degenerate pair (t_{2g}^+) and (t_{2g}^-) are lowest. The foregoing suggest a low symmetry ligand field component (Δ) of variable sign, going from a compression ($\Delta > 0$) along the trigonal axis at low *T* to an elongation ($\Delta < 0$) at higher temperatures. The transition is discussed in terms of perturbations of the coordination sphere possibly induced by temperature dependent changes in the hydrogen bonding to the perchlorate anions.

I. INTRODUCTION

In this paper we report the results of a Mössbauer spectroscopy study of iron (II)(*N, N'*-dicyclohexylthiourea)₆(ClO₄)₂, hereafter FeDCTU, for which we show there to be an unusual temperature dependence of the electronic environment of the ferrous ion. We have found that the compound exists in two isomeric forms *A* and *B* with quadrupole splittings $\Delta E_A = 3.31$ mm/sec and $\Delta E_B = 1.32$ mm/sec. Above 200°K both isomers are found in thermal equilibrium, while at lower temperatures only *A* is present and at room temperature and above, only *B* is present. The equilibration time for interconversion between the two isomers is of the order of hours and a kinetic study will be published separately.

The sign of the principal component of the elec-

tric field gradient, V_{zz} , has been determined by measurements in an external magnetic field. V_{zz} is negative for *A* and positive for *B*. As we will show below, this uniquely determines: (a) the symmetry of the ligand field to be a trigonally distorted octahedral; and (b) the nature of the transformation to involve changes in the sign of the trigonal distortion.

II. EXPERIMENTAL

The compound was prepared as described by Yagupsky.¹ Hot, concentrated methanol solutions of ferrous perchlorate and *N, N'*-dicyclohexylthiourea (DCTU) were mixed in stoichiometric proportions (1:6). When the mixture was allowed to cool a faintly yellowish precipitate was obtained. The precipitate was filtered and washed with cold ethanol and dried in vacuum. Elemental analyses are

in agreement with the formula $\text{Fe}(\text{DCTU})_6(\text{ClO}_4)_2$.
 Calculated: C: 55.1%; H: 8.5; N: 9.8; Fe: 3.6.
 Found: C: 54.1%; H: 9.2; N: 9.2; Fe: 3.5.

Infrared spectra of $\text{Fe}(\text{DCTU})_6(\text{ClO}_4)_2$ in KBr pressed disks and in nujol mulls were taken in the region between 4000 and 400 cm^{-1} at room temperature using a Perkin Elmer spectrometer. Spectra in KBr disks were also taken at 77°K. The magnetic susceptibility was measured at room temperature by the Gouy method and at temperatures between 4 and 300°K in a vibrating sample magnetometer.

Mössbauer spectra were taken in a conventional constant acceleration spectrometer at 4, 77, and 300°K and at several temperatures between 77 and 315°K. Spectra at 4, 77, and 300°K in external magnetic fields were also taken. At 4 and 77°K a Nb_3Sn superconducting solenoid was used with the magnetic field parallel to the direction of propagation of the gamma rays. The room temperature measurements were made using a Varian Associates 4 in electromagnet with cylindrical pole pieces tapered to 1 in. and capable of yielding up to 20 kG.

The experimental results are described and discussed in the next section.

III. RESULTS AND DISCUSSION

A. Thermal Equilibrium Between Two Isomers of FeDCTU

The infrared spectra of FeDCTU are similar to those reported in previous investigations of thiourea and substituted thiourea complexes of nickel, cobalt, and iron which have shown that the thiourea ligands are coordinated to the metal by the sulfur atoms.¹⁻⁵ Furthermore, there were no differences in the absorption frequencies in the spectra between 300 and 77°K, ruling out temperature dependent changes in the atoms in the coordination sphere.⁶

The magnetic measurements at room temperature yielded a magnetic moment of 5.2 μ_B , typical of high spin Fe(II) complexes. Between 20 and 200°K the magnetic moment was found to be equal to 5.0 μ_B and there was a small but apparent discontinuity in the moment at 250°K. In any event the magnetic data confirm the presence of a ground state spin quintet over the entire temperature range and rule out the possibility of spin state equilibria as responsible for the temperature dependent phenomena we observe.

In Fig. 1 we show the Mössbauer spectra of FeDCTU at 77 and 300°K, with quadrupole splittings ΔE of 3.31 and 1.32 mm/sec, respectively. At 4.2°K, $\Delta E = 3.54$ mm/sec; no measurements

were made above 315°K.

Examination of the spectra shows that while the quadrupole splitting changes, the isomer shift is unchanged, i.e., both quadrupole doublets have the same centroid. The isomer shift is +1.20 mm/sec (relative to iron metal) which is consistent with high-spin Fe(II) octahedrally coordinated to sulfur. Spectra taken at intermediate temperatures are shown in Fig. 2. The simultaneous appearance of the two sets of quadrupole splittings and their relative intensities as a function of temperature in this region of temperature point to the existence of the two isomers we have called A and B. The transformation of A into B does not, however, seem to involve a gross crystallographic phase transition; in that case we would have expected a sudden change in the quadrupole splitting for all sites at the transformation temperature. For example, Asch *et al.*⁷ found that in $\text{Fe}(\text{NH}_3)_6\text{Cl}_2$ the spectra changed suddenly from a quadrupole splitting of ~1.4 mm/sec below 110°K to a single unsplit line

FIG. 1. Mössbauer spectra of FeDCTU at (a) 300°K and (b) 77°K.

FIG. 2. Mössbauer spectra of FeDCTU at (a) 205 °K and (b) 225 °K.

above. However, Deszi and Keszthelyi⁸ reported spectra of $\text{Fe}(\text{ClO}_4)_2 \cdot 6 \text{H}_2\text{O}$ which show the simultaneous existence of two quadrupole doublets between 223 and 253 °K and would seem to be analogous to the effect we are reporting here.

B. Quadrupole Interactions and the Electronic Ground State

In most of the ferrous compounds studied by Mössbauer spectroscopy the crystal field of the ligands splits the orbital degeneracy so as to result in an orbital singlet ground state. In these cases, quadrupole splittings ranging from 2.5 to 4.0 mm/sec are obtained.⁹ In those cases, however, where an orbital doublet lies lowest, the quadrupole splittings are smaller.¹⁰ According to simple crystal field theory, the splittings are one half of those in singlet states. For example FeCO_3 has a trigonally distorted crystal field and an orbitally degenerate ground state; the measured quadrupole splitting¹¹ is 2.06 mm/sec at 4 °K and 1.80 mm/sec at 300 °K and is positive.¹² Another case is ferrous formate dihydrate in which there are two iron sites that

have different local symmetry. At one of these sites the ground state is an orbital doublet state and at the other an orbital singlet; the quadrupole splittings at 4 °K are 1.48 and 3.36 mm/sec, respectively.¹³

Thus the quadrupole splitting in FeDCTU may be interpreted in terms of the isomer *A* at low temperatures having an orbital singlet ground state and the isomer *B* at higher temperatures having an orbital doublet ground state. The splitting between the singlet and the doublet is due to the distortions of the local crystal field from octahedral symmetry. This distortion can be tetragonal, trigonal, or lower symmetry and will determine the symmetry of the ground state wave functions. Because the symmetry of wavefunctions determines the sign of the principle component of the electric field gradient, V_{zz} , a knowledge of the magnitude and the sign of V_{zz} provides a detailed description of the wave functions. The sign of V_{zz} can be obtained from measurements in an external magnetic field, as have been discussed by several authors.¹⁴⁻¹⁶ There is however, some confusion of nomenclature and so we briefly outline the theory below.

C. Mossbauer Spectra in External Magnetic Fields

In the absence of significant deviations from axial symmetry (small η) the quadrupole doublet is due to transitions between the $m_I = \pm 3/2$ and $m_I = \pm 1/2$ of the nuclear excited state and the nuclear ground state ($m_I = \pm 1/2$). In polycrystalline samples the two lines have equal intensity and it is not possible to determine whether the $m_I = \pm 3/2$ states lie above the $m_I = \pm 1/2$ states or vice versa. The first instance, $m_I = \pm 3/2$ at higher energy, corresponds to the case where the principal component of the electric field gradient, V_{zz} , is positive, resulting from a charge distribution surrounding the nucleus which is oblatelly deformed. The other instance, $m_I = \pm 1/2$ at higher energy, corresponds to the case of negative V_{zz} , resulting from a charge distribution which is prolately deformed.

The degeneracy of the nuclear states can be lifted by an external magnetic field. Usually, the magnetic fields of the order of 20–40 kOe are intense enough to allow for resolution of the spectra, and the two situations are easily distinguished because the spectrum consists of a doublet and an apparent triplet. For Fe^{57} , since $Q > 0$, the doublet lies at higher energy in case of positive V_{zz} . In the case of negative V_{zz} , the doublet lies at lower energy. If η is appreciable, the spectra for the polycrystalline samples are not so easily distinguished and comparisons should be made with computer generated spectra (see for example, Collins and Travis¹⁵).

We now consider the different situations that can arise in a hexacoordinated high spin Fe(II) complex. The 5D term is split into 5E_g and $^5T_{2g}$ terms by an octahedral field, the latter lying lowest. If the site symmetry is lower than octahedral, then the $^5T_{2g}$ term is split into a doublet and a singlet or three singlets. The first case corresponds to an axial distortion (trigonal or tetragonal) and the second case to a rhombic distortion. In the case of a tetragonal distortion along the z axis the $^5T_{2g}$ term is split into a singlet $|xy\rangle$ and a doublet $|xz\rangle$, $|yz\rangle$. V_{zz} is positive for the singlet term (oblate) and negative for the doublet (prolate). In the case of a trigonal distortion $^5T_{2g}$ splits into a singlet term with wave function¹⁷ $|t_{2g}^0\rangle = |z^2\rangle$ and a doublet with wavefunctions $|t_{2g}^+ \rangle = \sqrt{2/3} |x^2 - y^2\rangle - \sqrt{1/3} |xz\rangle$ and $|t_{2g}^- \rangle = \sqrt{2/3} |xy\rangle + \sqrt{1/3} |yz\rangle$. In trigonal symmetry the singlet has negative V_{zz} and the doublet positive V_{zz} . This is summarized in Table I. The latter doublet may be further split in accord with the Jahn-Teller effect, although Jahn-Teller distortion is usually small for t_{2g} configurations. In any event, V_{zz} remains positive.

Another possible distortion consists of twisting of one triangular face with respect to the other, from O_h (trigonal antiprismatic) toward D_{3h} (trigonal prismatic). For small distortions of this type, the sign of V_{zz} is not expected to change.

In Fig. 3 we show the spectrum of FeDCTU at 77°K in an external magnetic field at 20 kOe. The doublet clearly lies at lower velocities and the triplet at higher velocities and η is very nearly zero. This indicates that V_{zz} is negative. Thus isomer A is an electronic singlet state with negative V_{zz} ; referring to Table I, the ground state of A is described by a wave function of $|z^2\rangle$ symmetry which arises from a trigonal distortion of the crystal field. Figure 4 shows the spectrum of FeDCTU at 300°K and $H_0 = 20$ kOe. Now the situation is the reverse of Fig. 3, indicating V_{zz} positive. Thus B is an electronic doublet state with positive V_{zz} ; again referring to Table I, we find a trigonal distortion (elongation) which this time stabilizes the electronic doublet lowest. The results are sum-

TABLE I. Effects of axial crystal field distortions on the sign of V_{zz} .

	Tetragonal	Trigonal
Doublet wavefunction	$ xz\rangle, yz\rangle$	$\sqrt{2/3} x^2 - y^2\rangle - \sqrt{1/3} xz\rangle$ $\sqrt{2/3} xy\rangle + \sqrt{1/3} yz\rangle$
Sign of V_{zz}	-	+
Relative magnitude of V_{zz}	1/2	1/2
Singlet wavefunction	$ xy\rangle$	$ z^2\rangle$
Sign of V_{zz}	+	-
Relative magnitude of V_{zz}	1	1

TABLE II. Parameters for FeDCTU.

	Form A	Form B
Quadrupole splitting	3.31 mm/sec	1.32 mm/sec
Sign of V_{zz}	-	+
Temperature range	$T < 300^\circ\text{K}$	$T > 200^\circ\text{K}$
Ground state wavefunction	$ z^2\rangle$	$\sqrt{2/3} x^2 - y^2\rangle - \sqrt{1/3} xz\rangle$ $\sqrt{2/3} xy\rangle + \sqrt{1/3} yz\rangle$
Isomer shifts relative to iron metal	+1.20 mm/sec	+1.23 mm/sec

marized in Table II.

On the basis of simple crystal field theory it is possible to account for the transition $A \rightarrow B$ as T increases in terms of a change in sign of the trigonal term Δ in the crystal field expansion. A compression along the trigonal axis lowers the energy of $|t_{2g}^0\rangle$ relative to $|t_{2g}^+\rangle$ and $|t_{2g}^-\rangle$ while an elongation raises the energy of $|t_{2g}^0\rangle$ relative to $|t_{2g}^+\rangle$ and $|t_{2g}^-\rangle$. Thus $A \rightarrow B$ corresponds to compression-elongation with respect to the trigonal axis (Fig. 5).

The actual situation may be more complicated. Gerloch *et al.*⁸ have made a crystal field point charge calculation and have shown that the sign of the distortion (compression or elongation) is not sufficient to determine the sign of the trigonal term and hence the sign of Δ . They find that the sign also depends on the magnitude of the second-order radial parameter Cp . For example, for small values of Cp ($< 1000 \text{ cm}^{-1}$), a compression stabilizes the orbital doublet lowest, while for large values of Cp ($> 1000 \text{ cm}^{-1}$), a compression stabilizes the orbital singlet lowest. In the case of FeDCTU, if we make the reasonable assumption that Cp is the

FIG. 3. Mössbauer spectrum of FeDCTU in an axial magnetic field of 20 kOe at 77°K.

same for both A and B , then we can identify the transition $A \rightarrow B$ with a compression $\rightarrow$ elongation or an elongation $\rightarrow$ compression with respect to the trigonal axis, but we cannot say which without knowledge of the magnitude of C_p . Gerloch *et al.*¹⁸ point out that in general $C_p \approx 5 Dq$ ($\sim 5000 \text{ cm}^{-1}$); hence $A \rightarrow B$ probably corresponds to compression $\rightarrow$ elongation, as noted above.

D. The Nature of the Transition: Perchlorate Disorder?

We suppose that the transformation $A \rightarrow B$ results from a subtle perturbation of the sulfur coordination environment. One possibility is a temperature dependence of the packing of the bulky cyclohexyl substituents (twelve per molecule) in the thiourea ligands. Another possibility is a temperature dependence of perchlorate disorder and thus hydrogen bonding between the perchlorate anions and the thiourea amines, causing small changes in the metal sulfur ligation. In either case the small changes of the inner coordination sphere may not be discernible from x-ray measurements but could be detectable by the Mössbauer effect.¹⁸ X-ray measurements above and below the transition region would certainly be valuable in this connection.

The aforementioned temperature dependence of the perchlorate-amine hydrogen bonding is presumed by analogy to the work of Figgis, Wadley, and Graham.^{19,20} They have determined the crystal structure of $\text{Ti}(\text{urea})_6(\text{ClO}_4)_3$ at 300 and 90 °K. They find that structure of the immediate coordination environment is unchanged from 300 to 90 °K and the distortion of the octahedron consists only of a rotation of one triangular face with respect to

FIG. 4. Mössbauer spectrum of FeDCTU in an axial magnetic field of 20 kOe at 300 °K.

FIG. 5. Energy level diagrams for Form A and Form B of FeDCTU.

the other one of 5° about the trigonal axis, with no apparent elongation or compression along this axis. There are changes, however, in the configurations of the perchlorate ions, and Figgis *et al.*^{19,20} have promulgated a model which involves disorder at room temperature, between two of the perchlorate ions in which two of the oxygens have different interatomic angles. This enables the oxygen atoms to form stronger hydrogen bonds to the urea nitrogens than does a regular tetrahedral arrangement. At 90 °K, the disorder is frozen out²⁰ and each perchlorate possesses one or the other of the possible configurations. Furthermore, although no temperature dependent crystallographic changes are observed in the coordination sphere, recent measurements of the susceptibility of this material by Figgis, Wadley, and Gerloch²¹ suggest a temperature dependence of the axial ligand field component Δ .

In addition, Mooy *et al.*²² have studied the ESR of Cr^{3+} in $\text{Al}(\text{urea})_6(\text{ClO}_4)_3$ between 77 and 360 °K. At 77 °K they find there are six complexes per unit cell, differing in the orientation of their x axes. Above 77 °K, the ESR spectrum is strongly temperature dependent, with the E parameter in the spin Hamiltonian going to zero at 295 °K. Below 295 °K both the D and E parameters in the spin Hamiltonian vary approximately as $(295 - T)^{0.5}$ (the D parameter also has a component which is linear in T above and below 295 °K). The authors cite these observations as evidence for a second-order phase transition, possibly of an order-disorder type involving the occupancy of sites in the perchlorate tetrahedra. Above 295 °K, there is rapid interconversion between the oxygen sites; below 295 °K one site or the other is increasingly occupied leading to an ESR spectrum of lower symmetry.

These results suggest by analogy, a similar mechanism in FeDCTU. However, in this case the transition does not appear to be second order, be-

cause the varying equilibrium between the two forms as a function of temperature implies a latent heat. Furthermore, there is some evidence for hysteresis effects in the equilibrium value. These points will be further elaborated in a study of the transformation kinetics which will be published separately. We note that if the transition were second order in FeDCTU, we would have expected to see the quadrupole splitting change smoothly with decreasing T below the transition temperature T_c , perhaps with a $(T_c - T)^{1/2}$ temperature dependence. We would not expect to see both quadrupole pairs simultaneously over a considerable temperature interval.

IV. CONCLUSION

We have seen that from the respective magnitudes and signs of the quadrupole splittings one is able to characterize uniquely the ground state electronic wavefunctions for the two isomeric forms of FeDCTU. As noted previously, another case of such a possible transformation is that of $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, studied by Deszi and Keszythelyi⁸ as a function of temperature in zero magnetic field. We have now studied this material in external magnetic fields as well and the results will be reported separately.²³ Our initial measurements indicate that for this compound too, the crystal field has a trigonal distortion and a compression to elongation transformation is responsible for the two isomers. In addition, we have investigated other substituted thiourea complexes and have found some of them to exhibit the two isomer behavior as in FeDCTU. Thus there seems to be a number of systems, perhaps involving hydrogen bonded interaction with "uncoordinated," disordered perchlorate anions, in which this behavior occurs.

ACKNOWLEDGMENTS

We would like to thank Mr. Mario Weber for advice and help with the Mössbauer measurements, Dr. Simon Foner for help with the susceptibility measurements, and Dr. Brian B. Schwartz for useful discussions. R. L. would like to acknowledge support from the Forge Foundation. W. M. R. would like to acknowledge support from the Petroleum Research Fund and the Research Corporation. This research was also supported in part by grant number RR 07143, Department of Health, Education and Welfare. R. B. F. would like to acknow-

ledge the Organization of American States for partial support and thank the University of Chile for hospitality while working on part of this investigation. We thank Grace M. Lynch for editorial assistance.

*Partially Supported by an Organization of American States Fellowship.

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