A High-Pressure and Low-Temperature Mössbauer Effect Study of an Iron(III) Squarate Complex

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Several investigators [1–4] have prepared and studied the electronic and magnetic properties of the iron complexes obtained with 3,4-dihydroxy-3-cyclobutene-1,2-dione, $H_2C_4O_4$, commonly referred to as squaric acid. The structure of the iron(II) complex, $FeC_4O_4(H_2O)_2$, is now well established because of its isomorphism with $NiC_4O_4(H_2O)_2$ whose single crystal X-ray structure has been determined [5]. The iron(II) ion is coordinated to four different squarate dianions and to two trans water ligands to yield a pseudooctahedral complex. The squarate dianions bridge four separate iron(II) ions to form a cubic three dimensional structure [4]. In contrast, the structure of the iron(III) complex, $FeC_4O_4(H_2O)_3(OH)$, is less certain because its X-ray structure has not been reported. This may be because the material precipitates as a very fine extremely insoluble black-violet microcrystalline solid when prepared by the method of West and Niu [1]. However, the results of extensive magnetic measurements indicate that it most likely is a dimeric complex with two bridging hydroxy groups, four coordinated trans water molecules and two waters of hydration, as is illustrated in the proposed structure [2, 3, 6] shown in Fig. 1. The low temperature magnetic properties of this complex [2] indicate that it behaves as a normal Heisenberg-Dirac-VanVleck antiferromagnetic dimer with $S_1 = S_2 = 5/2$, $g = 2.00$, and $J = -7.0$ cm^{-1}, and with a Neel temperature of 55 K.

The purpose of this paper is to report our investigation of the Mössbauer spectral properties of $[FeC_4O_4(H_2O)_2OH]_2 \cdot 2H_2O$ at low-temperature in a variety of magnetic fields and at room temperature at high-pressure. This work was undertaken to obtain

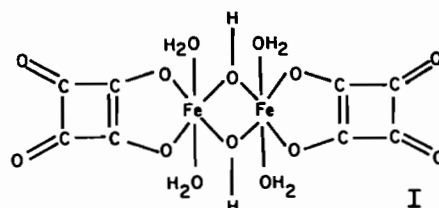*Author to whom correspondence should be addressed.

Fig. 1. Structure of the iron(III) squarate complex, $[FeC_4O_4(H_2O)_2OH]_2 \cdot 2H_2O$.

further information about the magnetic properties of this material at low temperature in order to further support the structure proposed earlier [2].

Experimental

The complex $[FeC_4O_4(H_2O)_2OH]_2 \cdot 2H_2O$ was prepared by the method of West and Niu [1]. The black-violet material is stable indefinitely and does not lose water on standing. *Anal.* Calcd. for $FeC_4H_7O_8$: Fe, 23.37; C, 20.11; H, 2.95. Found: Fe, 23.6; C, 20.45; H, 3.07%.

The Mössbauer effect spectra were obtained on a Harwell constant-acceleration spectrometer which utilized a room-temperature rhodium-matrix source. The spectrometer was calibrated at room temperature with natural α-iron foil. The magnetically perturbed spectra were obtained with the sample placed directly in liquid helium in a British Oxygen Corp. cryostat with a superconducting magnet which produced a transverse magnetic field. The magnetic field was calibrated by measuring the change in the iron foil internal hyperfine field at 4.2 K produced by the magnet. The temperatures of the samples studied below 4.2 K were obtained by pumping on the liquid helium and measuring the vapor pressure of gaseous helium above the liquid. The high-pressure Mössbauer spectra reported herein were obtained by using an opposed diamond anvil cell. The details of the placement of the high-pressure cell in the spectrometer and the calibration of the pressure has been discussed earlier [7]. The spectra were measured on natural abundance iron samples and required several days for data collection. The Mössbauer spectra were evaluated by using least-squares minimization computer programs and the Harwell IBM 370/168 computer facilities.

Results and Discussion

The Mössbauer effect spectra of $[FeC_4O_4(H_2O)_2OH]_2 \cdot 2H_2O$ obtained at 4.2 K and 1.6 K and in

TABLE I. Mössbauer Effect Spectral Parameters.[a]

T, K	P, kBar	H_{app}, Tesla	ΔE_Q	δ	Γ	H_{int}, Tesla	$I_{2/5}$
298	0	0	0.13	0.42	0.34	0	–
298	45	0	0.50	0.40	0.45	0	–
78	0	0	0.13	0.52	0.28	0	–
4.2	0	0	0.14	0.57	0.28	0	–
4.2	0	1.5	~0	0.42	–	1.5	2.1
4.2	0	3.0	~0	0.41	–	3.1	2.1
4.2	0	4.5	~0	0.41	–	4.3	2.5
4.2	0	6.0	~0	0.41	–	5.8	4.0[b]
1.35	0	0	0.16	0.56	0.32	0	–
1.6	0	6.0	~0	0.41	–	6.3	4.0[b]

[a]All data in mm/s relative to natural α-iron foil. [b]Constrained to this value.
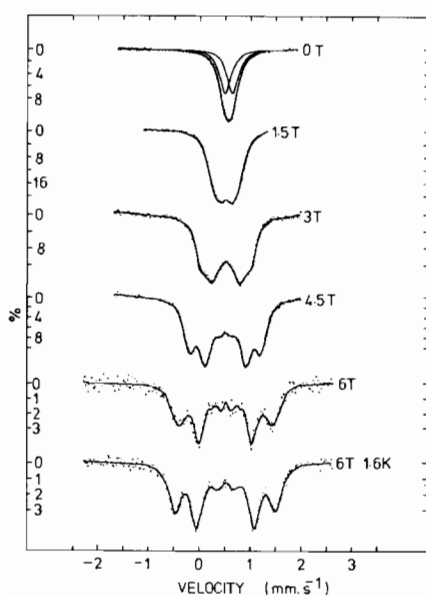
Fig. 2. The Mössbauer effect spectrum of $[FeC_4H_4(H_2O)_2-OH]_2 \cdot 2H_2O$ obtained at various temperatures and transverse applied magnetic fields.

several transverse applied magnetic fields are illustrated in Fig. 2. The solid lines shown in this figure correspond to computer optimized best fits to the experimental data. The computed model assumed six lines corresponding to the six allowed transitions expected in the presence of a magnetic field. The relative intensity of the two and five line was unconstrained except for the spectra obtained at six Tesla in which case they were constrained to a value of 4.0. The resulting Mössbauer effect spectral parameters are presented in Table I.

The Mössbauer effect spectral parameters observed for $[FeC_4H_4(H_2O)_2OH]_2 \cdot 2H_2O$ are reasonable

for a pseudooctahedral high-spin iron(III) compound with strong antiferromagnetic coupling. The iron-(III) ion with a symmetric $^6A_{1g}$ ground state electronic configuration would be expected to make little if any valence contribution to the electric field gradient at the iron nucleus. Hence the small value observed must result mainly from a lattice contribution to the electric field gradient. The small value (*ca.* 0.15 mm/s) observed at ambient pressure and zero applied field is consistent with the non-cubic ligand field which would be generated by the proposed structure (Fig. 1). The isomer shift is also reasonable for a high-spin iron(III) ion and decreases with increasing temperature, as a result of a second order Doppler shift arising from differences in the source and absorber temperature. We have no explanation for the rather small isomer shift values observed in an applied field. The small values may result because of the very different techniques used in fitting the applied field spectra as compared with the zero field spectra.

The internal hyperfine field, H_{int}, as indicated in Table I, is always found to be within *ca.* five percent of the transverse applied magnetic field, H_{app}. This indicates that in all cases the H_{int} is essentially the same as H_{app} to within experimental error limits. This agreement is consistent with the proposed dimeric structure for this compound. Magnetic susceptibility measurements [2] indicate that this compound is strongly antiferromagnetically coupled with $J = -7.0$ cm^{-1}. Thus at 4.2 K, only the dimeric S = 0 ground state is significantly populated. At 4.2 K the population of the next highest state, with S = 1, would be less than 2×10^{-9} relative to the ground state. Hence at 4.2 K and 1.6 K this material would be expected to behave as a diamagnetic material in which the internal hyperfine field would be equivalent to the applied field. The relative intensity of the second and fifth line in the hyperfine field split Mössbauer spectrum will depend on the angle between the internal hyperfine field and the γ-ray direction. For a powdered material at zero or low applied fields the relative intensity expected would be two. As the magnitude of the transverse applied magnetic field increases, this field becomes strong enough to align the internal field parallel with the applied field and hence normal to the γ-ray direction. In the limit of perfect alignment, the relative intensity would be expected to be four for the second and fifth line. Hence the observed increase in the intensity of the two and five line (see Table I) is reasonable. Essentially the same $I_{2/5}$ value is found at 4.2 K and 1.6 K and six Tesla even if the constraint is removed.

The Mössbauer effect spectra of $[FeC_4O_4(H_2O)_2-OH]_2 \cdot 2H_2O$ obtained at room temperature and zero and 45 kBar applied pressure are illustrated in Fig. 3. The resulting Mössbauer spectral parameters are given
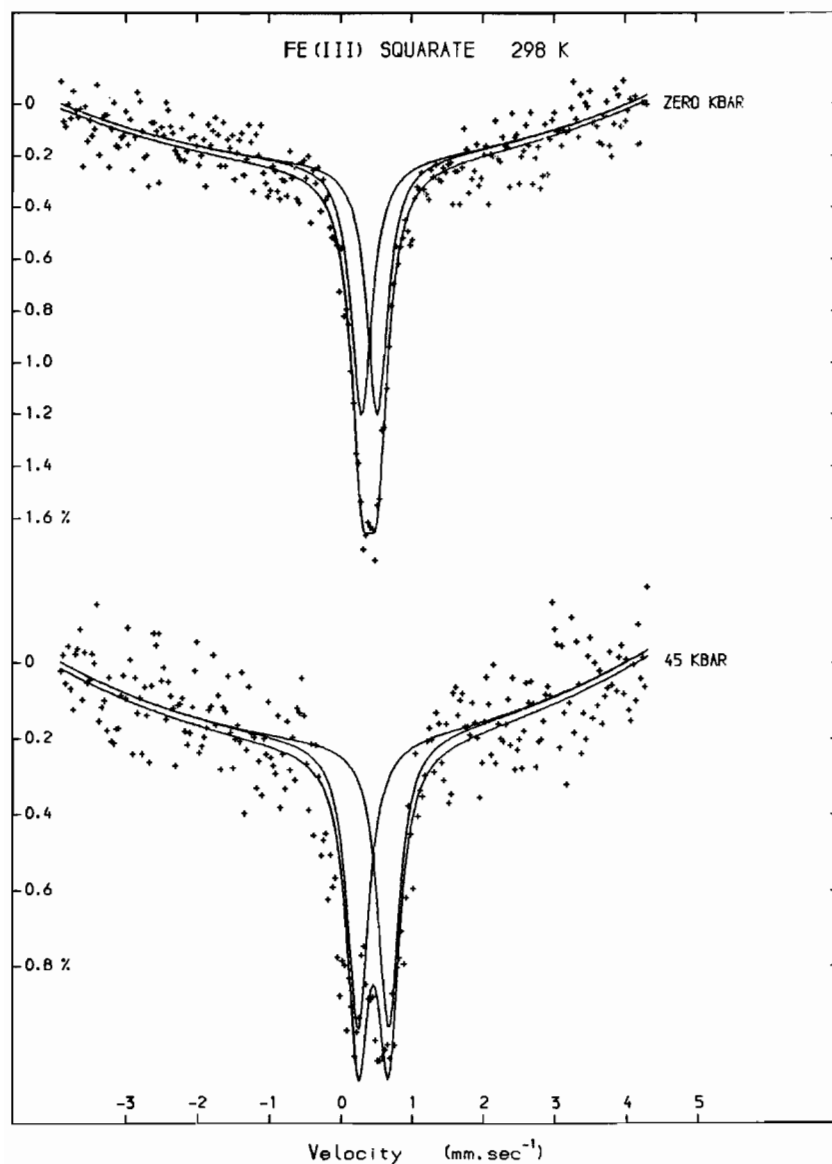
Fig. 3. The Mössbauer effect spectrum of $[FeC_4H_4(H_2O)_2]_2 \cdot 2H_2O$ obtained at room temperature at ambient and 45 kBar pressure in an opposed diamond anvil cell.

in Table I. The most striking change in the spectrum with increasing pressure is the increases in the quadrupole interaction. The magnitude of this splitting increases by a factor of four in going from zero to 45 kBar pressure. As noted above, the splitting must arise predominately from a lattice contribution to the electric field gradient in this iron(III) compound. Apparently this material has a high degree of anisotropy in its compressibility which leads to a change in the electric field gradient at the nucleus with increasing pressure. This anisotropy would be reasonable in view of the distorted structure proposed in Fig. 1. The observed decrease in the isomer shift with increasing pressure, if real, may result from an increase in the s-electron density at the iron nucleus with increasing pressure.

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