Mössbauer spectroscopy in external magnetic fields has been used to measure the signs of the principal components of the electric field gradient $V_{zz}$ in the two forms of $[\text{Fe(H}_2\text{O)}_6]\text{[ClO}_4\text{]}_2$. The signs are $V_{zz}$ negative for the low temperature form (A) with quadrupole splitting $\Delta E_A = 3.4$ mm/sec, and $V_{zz}$ positive for high temperature form (B) with $\Delta E_B = 1.4$ mm/sec. This implies a trigonally distorted ligand field and the transition (A) $\rightarrow$ (B) corresponds to compression $\rightarrow$ elongation with respect to the trigonal axis.

Mössbauer spectroscopy of $[\text{Fe(H}_2\text{O)}_6]\text{[ClO}_4\text{]}_2$ was first reported by Dezsi and Keszthelyi [1] who observed a low temperature ($T < 223^\circ$K) form (A) characterized by a quadrupole splitting $\Delta E_A = 3.4$ mm/sec and a high temperature ($T > 253^\circ$K) form (B) characterized by a quadrupole splitting $\Delta E_B = 1.4$ mm/sec. For $223^\circ < T < 253^\circ$K, both forms exist simultaneously with the ratio of the amount of (B) to the amount of (A) increasing as a function of increasing $T$. The isomeric shift 1.34 mm/sec (relative to iron metal) is the same for all the spectra and is consistent with high-spin Fe(II). In this letter we report Mössbauer measurements in applied magnetic fields from which we obtain the sign of the principal component of the electric field gradient $V_{zz}$ in form (A) and in form (B). As we show subsequently these measurements allow us to deduce that the low-symmetry ligand field component at the metal site is trigonal and that the transition (A) $\rightarrow$ (B) corresponds to a transition from elongation along the three fold axis to compression along this three fold axis. The behavior of this system is thus similar to the analogous material Fe(N,N'-dicyclohexyl thiourea)$_6\text{[ClO}_4\text{]}_2$ which has recently been investigated in detail [2].

The Mössbauer measurements were made with conventional constant-acceleration spectrometers. The room temperature spectrum obtained in an external magnetic field of 20 kOe is shown in fig. 1a, and consists of a doublet and an apparent triplet with the doublet occurring at higher energy. As several authors have discussed [3–5], this determines the sign of $V_{zz}$ to be positive in (B). The $H_0 = 0$ spectrum at 4.2$^\circ$K is shown in fig. 1b; the quadrupole splitting is 3.48 mm/sec, changed only slightly from the value of 3.4 mm/sec at 200$^\circ$K obtained by Dezsi and Keszthelyi [1]. The 4.2$^\circ$K, $H_0 = 25$ kOe spectrum is shown in fig. 1c; now the spectral doublet is at lower energy than the apparent triplet and hence the sign of $V_{zz}$ is negative.
for (A). The magnitudes of $\Delta E$ are typical [6, 7] of high-spin Fe$^{2+}$ with an orbital singlet and an orbital doublet ground state for (A) and (B), respectively. Thus (A) is an orbital singlet with negative $V_{zz}$; (B) is an orbital doublet with positive $V_{zz}$.

We now consider the different situations that can arise in a hexa-coordinated high-spin Fe(II) complex. The $S$D term is split into $5E_g$ and $5T_g$ terms by an octahedral field, the latter lying lowest. If the site symmetry is lower than octahedral, the $5T_g$ 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 $5T_g$ term is split into a singlet (xy) and a doublet (xz, yz). $V_{zz}$ is positive for the singlet term (oblate) and negative for the doublet (prolate). In the case of a trigonal distortion $5T_g$ splits into a singlet term with wavefunction $|t_{2g}^0\rangle = |z^2\rangle$ and a doublet with wavefunctions $|t_{2g}^\pm\rangle$ and $|t_{2g}^-\rangle$.

In trigonal symmetry the singlet now has negative $V_{zz}$ and the doublet positive $V_{zz}$. 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.

Comparison with the experimental results cited above shows that the only consistent interpretation is in terms of a trigonally distorted octahedral environment for the Fe$^{2+}$ in both (A) and (B). Furthermore, 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 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 $|t_{2g}^+\rangle$ relative to $|t_{2g}^-\rangle$ and $|t_{2g}^0\rangle$. Thus (A) $\rightarrow$ (B) corresponds to compression $\rightarrow$ elongation with respect to the trigonal axis.

Recent X-ray diffraction measurements [9, 10] in Ti(urea)$_6$(ClO$_4$)$_2$ at 300 and 90 K have shown that the perchlorate anions become disordered among configurations which differ from tetrahedral at the higher temperature [10]. The disorder is energetically favored

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**Fig. 1. Mössbauer spectra of [(Fe(H$_2$O)$_6$)(ClO$_4$)$_2$] (a) $T = 300$ °K and $H_0 = 20$ kOe; (b) $T = 4.2$°K, $H_0 = 0$; (c) $T = 4.2$°K, $H_0 = 25$ kOe.**
because of increased hydrogen bonded interaction with coordinated urea. At the lower temperature the disorder disappears. In addition, recent measurements of the magnetic anisotropy in this material [11] suggest a temperature dependence of the trigonal splitting (Δ) of the ground state orbitals although crystallographic study indicates no temperature dependence to the coordination. In fact, difficulty in fitting the magnetic data and temperature dependence of Δ is attributed to crystallographically undetected compression or elongation with respect to the three fold axis [11]. Mooy et al. [12] have found that in Al(urea)$_6$ (ClO$_4$)$_2$ doped with Cs$^{3+}$ the order–disorder transition is of second order thermodynamically. However, in Fe(N,N'-dicyclohexylthiourea)$_6$(ClO$_4$)$_2$ there is evidence for a latent heat connected with the transitions (A) → (B) which would rule out a second order transition in that material [2]. We speculate that the transition (A) → (B) we observe in Fe(H$_2$O)$_6$(ClO$_4$)$_2$ is connected with a perchlorate disorder phenomenon analogous to those cited above. The T dependence of the disorder changes the hydrogen bonded interaction with the water of the Fe$^{2+}$ coordination sphere which in turn results in changes in the local crystalline field. Such changes of metal–oxygen ligation would probably be too small to be detected crystallographically but are amenable to Mössbauer study. Detailed susceptibility measurements are in progress.

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References