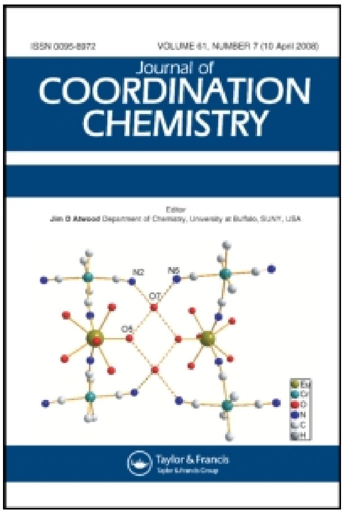

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THE SINGLE CRYSTAL POLARIZED OPTICAL SPECTRA OF HEXAAQUOIRON(II) PERCHLORATE

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THE SINGLE CRYSTAL POLARIZED OPTICAL SPECTRA OF HEXAAQUOIRON(II) PERCHLORATE

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The single crystal polarized spectra of the $Fe(H_2O)_6^{++}$ ion as the perchlorate salt have been obtained at room temperature and 10°K. The spectra are very dichroic at low temperature. The major bands show a large decrease in area upon cooling suggesting that the band intensities result from a vibronic coupling mechanism. The spectra are interpreted in terms of D_{3d} symmetry where the C_3 axis is collinear with c_0 of the pseudohexagonal unit cell. The major features of the spectra are assigned and an analysis of the vibronic mechanism is presented.

INTRODUCTION

The $Fe(H_2O)_6^{2+}$ ion has been studied in several crystalline compounds. Most extensive have been the investigations of $[Fe(H_2O_6]SiF_6$, in which the iron exists in a trigonally distorted environment.[1,2] There have appeared reports of its optical spectra at ambient[3,4] and low temperatures,[5,6] its Mössbauer spectrum,[7] its magnetic susceptibility,[8,9] its electron spin resonance (esr) spectrum[10,11] and the esr spectrum of Fe^{2+} in the isomorphous zinc compound.[12] Despite all this work some ambiguity about the sign of the trigonal distortion persists; the neutron diffraction study[2] indicates a stretching along the three-fold axis, and magnetic measurements[13] are best interpreted in terms of a contraction.

The $Fe(H_2O)_6^{2+}$ ion exists in an approximately tetragonally distorted environment in $(NH_4)_2[Fe(H_2O)_6](SO_4)_2$.[14] This compound belongs to the monoclinic system, and for it there is evidence of symmetry lower than tetragonal, especially at lower temperatures.[15] Again, rather extensive magnetic measurements have been reported[8,9,16] in addition to Mössbauer[7,15] and room temperature spectral data.[3,4] Neither low-temperature crystal spectra nor esr measurements have been reported.

Holmes and McClure[17] have measured the crystal spectrum of $Fe(H_2O)_6^{2+}$ in $FeSO_4 \cdot 7H_2O$ at 77°K, but they could not tell from the spectrum whether the chromophore's distortion is tetragonal or rhombic. Its Mössbauer spectrum has also been studied.[7]

In order to gain more detailed information about trigonally distorted $Fe(H_2O)_6^{2+}$ we have studied in detail and here report the low-temperature polarized optical spectra of $[Fe(H_2O)_6](ClO_4)_2$ in which the chromophore is trigonally distorted.[18] To date, only an unpolarized room-temperature crystal spectrum has appeared.[4]

EXPERIMENTAL

$Fe(ClO_4)_2 \cdot 6H_2O$ was prepared by dissolving powdered iron in dilute $HClO_4$ (~6 M) to which had been added a small amount of thiourea. The solution was filtered and left to evaporate. The thiourea maintains a reducing environment for the Fe(II) so the evaporation can be done in contact with atmospheric oxygen. The crystals separate as long, pale-green rods. They are somewhat deliquescent; extended storage over a mild drying agent such as $CaCl_2$, however, appears to cause a small loss of water. The partially deuterated iron complex and the mixed iron–zinc complex were prepared in a similar manner. The zinc and iron complexes are isomorphous, and belong probably to space group $Pmn2_1$ (C_{2v}^7, No. 31).[18]

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Anal.: Calcd. for $[Fe(H_2O)_6](ClO_4)_2$: Cl, 19.54; Fe, 15.4. Found: Cl, 19.49; Fe, 15.6. The chlorine analysis was carried out by Galbraith Laboratories, Inc., Knoxville, Tennessee.

All spectra were run on a Cary 14 spectrophotometer with the sample mounted in the chamber of an Air Products Displex cryogenic refrigerator. This enabled spectra to be recorded at any temperature from room temperature down to ca. 10°K. For the polarized spectra two Glan-Thompson polarizers obtained from Karl Lambrecht Corporation were used.

Many of the crystals partially fragment into domains when they pass through the transition temperature (see below). This did not prevent the recording of the spectra, but caused some uncertainty in the position of the base line. This in turn prevented accurate measurement of the areas under the peaks and precluded any attempt to estimate the frequency of the intensity-producing vibrations.

RESULTS AND DISCUSSION

The polarized crystal spectra of $[Fe(H_2O)_6](ClO_4)_2$ at room temperature and 10°K are shown in Figure 1. The absorptions are somewhat more intense in the σ spectrum (electric vector of light perpendicular to the unique axis (see below)) than in the π spectrum (electric vector of light parallel to the unique axis). The major bands show a rather large decrease in area upon cooling; this suggests that the band intensity is due largely to vibronic mechanisms. As expected, the band maxima shift to higher energy on cooling due to a depopulation of vibrational levels associated with the electronic ground state. The most noticeable feature, however, is the strong dichroism. In high-spin, octahedral d^6 complexes a single spin-allowed band is expected, sc., $^5T_2 \rightarrow {}^5E$. In Fe(II) complexes this is almost invariably found to be split even when the iron is situated on an octahedral site.[19] Therefore, in such cases the degeneracy of the excited state is

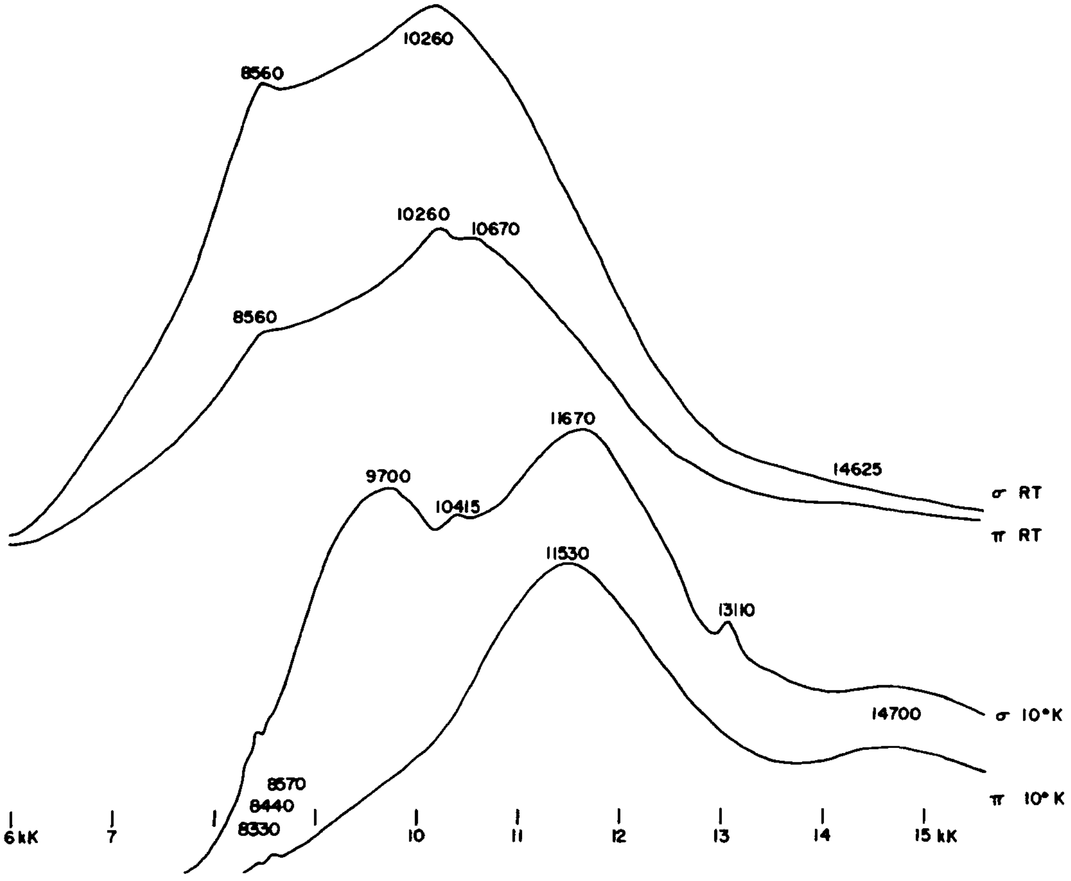

FIGURE 1 Room temperature and 10°K spectra of $[Fe(H_2O)_6](ClO_4)_2$. Band positions are given in cm^{-1}. The strong water overtone band ~6950 cm^{-1} has been omitted from the spectra.

removed as a result of the electronic transition. In the present compound the expected two bands are seen in the $\sigma(\perp C_3)$ spectrum separated by 1970 cm^{-1}. In the $\pi(\| C_3)$ spectrum, however, only the higher energy band appears as a peak; the lower energy band, if present at all, appears as a very weak shoulder. It is this feature of the spectrum especially which must be explained.

When light passes down the long axis of the crystal, there is complete extinction under crossed polarizers. This indicates a unique axis (C_3 or C_4). A C_3 axis is compatible with the space group of the crystal. Although the crystal is orthorhombic, the unit cell is pseudohexagonal with the three-fold axis (C_3) lying along c_0. The crystal study of the isomorphous magnesium compound indicates that this three-fold axis is collinear with the C_3 axis of the MO_6 octahedron.[18]

Confirmation of the choice of C_3 as the unique axis comes from the Mössbauer studies of $[Fe(H_2O)_6](ClO_4)_2$ carried out by Dészi and coworkers.[20,21,22] They first noted that the quadrupole splitting changes from ca. 1.4 mm sec^{-1} at 296°K to ca. 3.5 mm sec^{-1} at 5°K.[20] The transition begins to occur at 243°K on cooling; it occurs at 258°K on heating and is spread over less than 5°K.[21] Application of magnetic fields of up to 50 kOe indicates that the increase of quadrupole splitting on cooling is accompanied by a change in sign of the electric field gradient.[21] On the basis of the analysis of Collins[23] this has been interpreted as a change in the direction of distortion of the $Fe(H_2O)_6^{2+}$ octahedron, which is assumed to be axially extended above 243°K and axially compressed below this temperature. This would cause the ground state to be an orbital doublet above the transition temperature and a singlet below it. A combination of the size of the quadrupole splitting and the sign of the electric field gradient indicates unambiguously that the low-temperature orbital singlet is $|z^2\rangle$. The ground state term at low-temperature is ${}^5A_{1g}$. We may assume that the FeO_6 octahedron belongs to the point group D_{3d}, and we will analyse its spectra on this basis.

First of all, we note that for the principal bands, the axial spectrum is identical with the $\sigma(\perp C_3)$ spectrum. This indicates that, as expected, the observed absorption bands are due to electric dipole transitions.

The ${}^5E_g\,(O_h)$ excited state is not split by the lowering of the symmetry to D_{3d}. It is probable that here, as in other Fe^{2+} high spin complexes, the splitting is due the Jahn–Teller effect.[17] To a first approximation, the vibrations involved may be assigned to those of the FeO_6 group. In D_{3d} the 15 normal vibrations of FeO_6 are $2a_{1g}$, a_{1u}, $2a_{2u}$, $2e_g$ and $3e_u$. The Jahn–Teller distortion can be brought about by the coupling of an e_g vibration with the ${}^5E_g$ excited state.[24] This results in the formation of three vibronic states as follows: ${}^5E_g \times e_g = {}^5A_{2g}^{VIB} + {}^5A_{1g}^{VIB} + {}^5E_g^{VIB}$. Transitions to these states are electric dipole forbidden unless some odd crystal field or some u vibration be mixed in. Since the intensity of the spectral bands decreases markedly with lowering of the temperature, the latter is likely the case. Since only two bands are seen in the spectrum, we must assume that two of the three vibronic states are rather close in energy. If ${}^5A_{1g}^{VIB}$ and ${}^5E_g^{VIB}$ lie close together but about 2 kK above ${}^5A_{2g}^{VIB}$, then the observed spectrum can be explained. The u vibrations which make the transitions allowed are indicated on the right side of Figure 2. In the $\pi(\| C_3)$ spectrum the ${}^5A_{2g}^{VIB}$ state is accessible only by coupling with an a_{1u} vibration. This vibration involves twisting of the plane of the three oxygens above the Fe in one sense around C_3 while the plane of the three oxygens below the Fe is twisted in the opposite sense. The motion of the atoms in this normal mode is confined to the xy plane.[25] So the vibration has no component in the z direction and will be inactive in the $\pi(\| C_3)$ spectrum. It may noted that further Jahn–Teller splitting of the ${}^5E_g^{VIB}$ state may occur because of the spin degeneracy. This is expected to be smaller than that due to orbital degeneracy, and in fact we see no evidence of this further splitting.

The exact magnitude of the splitting of the ${}^5T_2(O_h)$ level is not known for any Fe(II) complex. For the trigonally distorted $[Fe(H_2O)_6]SiF_6$ and for $(NH_4)_2[Fe(H_2O)_6](SO_4)_2$, which has tetragonal (or lower) symmetry, it appears that the total splitting may be of the order of several hundred to about 1000 cm^{-1}.[9] The same is probably the case here. At low temperature it is clear that only the states arising from ${}^5A_{1g}$ may be populated. Under second order spin–orbit coupling ${}^5A_{1g}$ becomes $A_{1g} + 2E_g$ in D'_{3d} with A_{1g} lowest in energy.[26] In $[Fe(H_2O)_6]SiF_6$ the two lowest levels have been calculated to be separated by ca. 10–12 cm^{-1}.[27,28,29] In the present compound the splitting of the lowest levels is probably of the same order of magnitude. From the Boltzmann distribution function it can be calculated that at the temperature of the optical spectra (~10°K) the population of these levels would be in a ratio of ~1 to 5 for a separation of 10–12 cm^{-1}. If the crystal temperature is near 15°K (which is quite possible) the relative populations would be ~1 to 3 for this same splitting. So at the temperature of measurement both levels would be significantly populated and transitions could occur from both ground state components. The second E

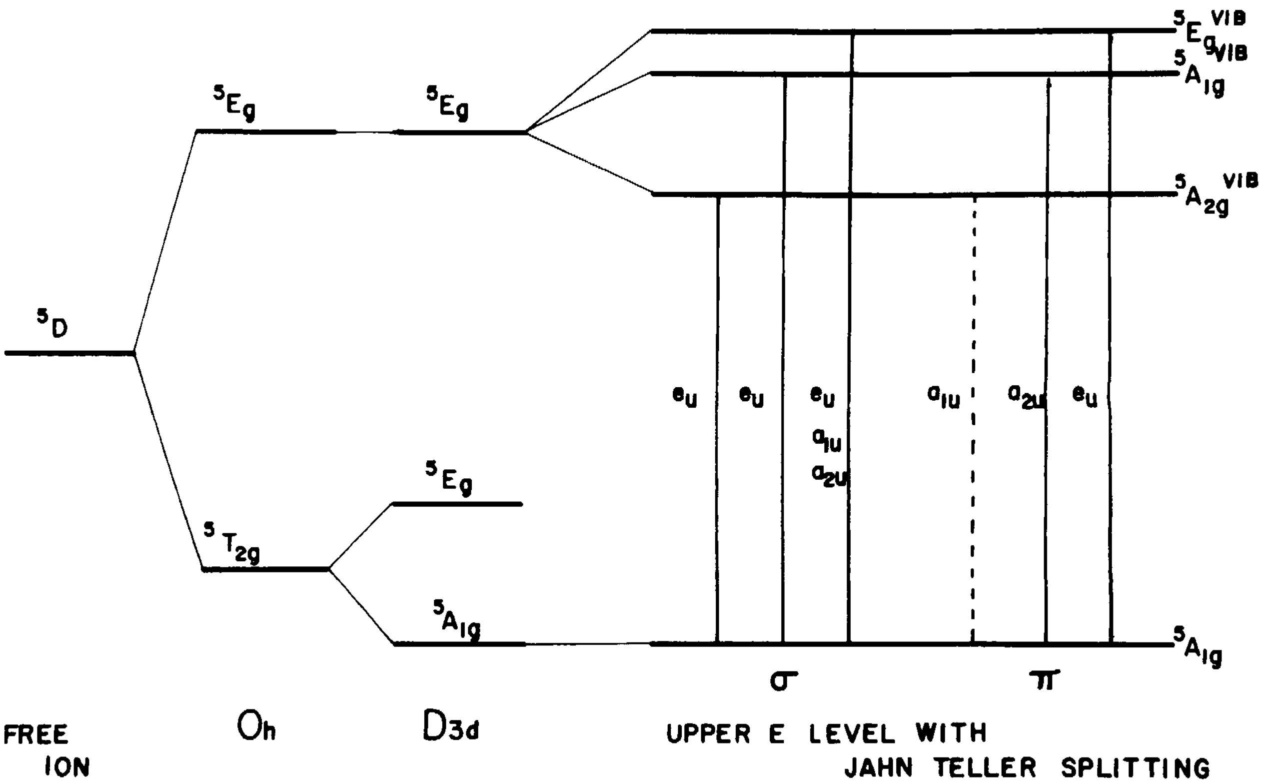

FIGURE 2 Energy diagram for $[Fe(H_2O)_6](ClO_4)_2$. The activating vibration for the Jahn–Teller splitting is of e_g symmetry. The right of the diagram indicates which u vibrations will make the various transitions allowed. The dotted line indicates that there will be no transition to $^5A_{2g}^{VIB}$ in $(\pi \| C_3)$ because the a_{1u} vibration is not active along the C_3 axis.

level is expected to lie ~40–50 cm^{-1} above the first E state.[13,27] So its population at low temperature would be negligible.

The shoulder of moderate intensity at 14.7 kK may with some confidence be assigned to the lowest quintet–triplet transition ($^5T_{2g} \rightarrow {}^3T_{1g}$ in O_h; $^5A_{1g} \rightarrow {}^3A_{2g} + {}^3E_g$ in D_{3d}). The two excited states yield spinor states ($A_{1g} + E_g$) and ($A_{1g} + A_{2g} + 2E_g$). Transitions from the $A_{1g} + E_g$ ground states are allowed in both polarizations to several of these spinor states. So it is not surprising that the band is rather broad and appears in both polarizations. This same assignment was made for the analogous band in the spectrum of $RbFeF_3$ by Ferguson *et al.*[30] on the basis of weak-field d^6 calculations. They were also able successfully to assign several of the other higher energy triplet states in $RbFeF_3$. The spectra of thick crystals of $[Fe(H_2O)_6](ClO_4)_2$, however, show at 10°K only a few broad and ill-defined peaks in the region 16–37 kK. This may have been due in part to crystal fragmentation and consequent poorer resolution. Since this region is dotted with a large number of triplet states (even in O_h symmetry), it would be quite uninformative to do ligand field calculations without more and better-defined bands.

In addition to these bands there are several other features of the spectra to be assigned. Weak bands at 8.3–8.6 kK and at 10.4 and 13.1 kK appear to be overtones and combination bands of the principal water vibrations at ~3370 cm^{-1} and 1620 cm^{-1}. Thus, for example, the band at 10 417 cm^{-1} ($\sigma, \perp C_3$) is 3 x 3472 cm^{-1} and there is a very strong band also at 6973 (= 2 x 3486) cm^{-1} ($\sigma, \perp C_3$). Furthermore, all of these features decrease in relative size upon partial deuteration.

We hoped that more information about the ground state would be forthcoming from esr measurements at 5°K, but no esr spectrum was observed either in the pure compound or in $[Zn(Fe)(H_2O)_6](ClO_4)_2$. This, however, is not surprising. In octahedral symmetry the ^5D state of a d^6 ion has three orbital states for the ground state which are connected by spin-orbit coupling. This produces a short spin-lattice relaxation time and a very large zero-field splitting. When the octahedral symmetry is further lowered, this large zero-field splitting makes detection of the esr signal very difficult.[12]

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