The Fe^{2+} Chelate of Hydrazinecarboxylic Acid Studied by the Mössbauer Effect

D. HANŽEL AND F. SEVŠEK

J. Stefan Institute, University of Ljubljana, Ljubljana, Yugoslavia

The chelate compounds K[Fe(hyc)$_3$] and N$_2$H$_5$[Fe(hyc)$_3$]·H$_2$O (hyc = N$_2$H$_3$COO) were studied by the Mössbauer effect of ^{57}Fe at various temperatures. At room temperature the quadrupole splitting parameter is 2.77 mm/sec for K[Fe(hyc)$_3$] and 2.35 mm/sec for N$_2$H$_5$[Fe(hyc)$_3$]·H$_2$O, and the center shift is 1.08 mm/sec for both compounds. The temperature dependences of the quadrupole parameters yielded the crystal field splittings of the $^5T_{2g}$ levels of the Fe^{2+} ions which indicate large trigonal distortion of the Fe(hyc)$_3$ anion. Using a molecular crystal-like treatment of the ferrous ion vibrations the temperature dependence of the recoilless fraction gave an effective Debye temperature $\Theta_D = 71°$K for K[Fe(hyc)$_3$] and $\Theta_D = 90°$K for N$_2$H$_5$[Fe(hyc)$_3$]·H$_2$O. No evidence for magnetic ordering was found down to 4.5°K in either compound.

Introduction

In this work we report the results of the Mössbauer effect study of ^{57}Fe in the piezo-electric chelate compounds K[Fe(hyc)$_3$] and N$_2$H$_5$[Fe(hyc)$_3$]·H$_2$O, where hyc = N$_2$H$_3$COO. The former belongs to the trigonal series K[Me(hyc)$_3$], and the latter to the series N$_2$H$_5$[Me(hyc)$_3$]·H$_2$O, where Me = Fe, Co, Ni, Zn. The space group of K[Fe(hyc)$_3$] is considered as R_{3c} with six molecules in the unit cell (2). N$_2$H$_5$[Fe(hyc)$_3$]·H$_2$O belongs to the space group C_c, and there are four molecules in the monoclinic unit cell. The complex anion Fe(hyc)$_3^-$ has a chelate structure in both compounds. Three N$_2$H$_3$COO ligands in *cis* position form a nearly octahedral arrangement around the metal ion with three oxygen and three nitrogen atoms (Fig. 1). Compounds of the N$_2$H$_5$[Me(hyc)$_3$]·H$_2$O series were extensively studied by X-ray (3) and infrared (4) spectra, while the Mössbauer effect (5) of ^{57}Fe in

N$_2$H$_5$[Fe(hyc)$_3$]·H$_2$O gave information about the EFG tensor of Fe^{2+} ion as well as the crystal field parameters. Both compounds are considered piezoelectric.

Experimental

The crystals of N$_2$H$_5$[Fe(hyc)$_3$]·H$_2$O and K[Fe(hyc)$_3$] are pale green. The former were grown from a saturated aqueous solution containing the ferrous salt FeCl$_2$·4H$_2$O and hydrazine carboxilic acid (N$_2$H$_3$COOH) (1). The latter were obtained from the mother liquor of the compound
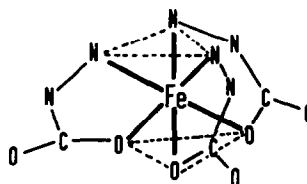

FIG. 1. Local symmetry of iron in K[Fe(hyc)$_3$] and N$_2$H$_5$[Fe(hyc)$_3$]·H$_2$O as taken from Ref. (1).

$N_2H_5[Fe(hyc)_3]\cdot H_2O$ by addition of potassium hydroxide as has been described previously (2). The products were confirmed by chemical analysis and X-ray patterns. Finely powdered samples having $10\ mg/cm^2$ of natural iron were used as absorbers for Mössbauer measurements in transmission geometry. The ^{57}Co in Pd source was kept at room temperature and spectra of the absorber were measured in the region from 4.5 to 500°K with a 512-channel analyzer operated in the time mode, using Elron's constant-acceleration equipment. The velocity scale was calibrated with iron, and it was also used as a reference for the center shift parameters. The spectra were analyzed by nonlinear least-squares program assuming Lorentzian lineshapes.

Results and Discussion

In the temperature range 4.5–470°K the spectra of ^{57}Fe in $N_2H_5[Fe(hyc)_3]\cdot H_2O$ and $K[Fe(hyc)_3]$ are similar in form with two resolved lines, typical of quadrupole interaction of the iron nucleus with the electric field gradient (efg) tensor. The characteristic spectrum of ^{57}Fe in $K[Fe(hyc)_3]$ is given in Fig. 2.

The relatively narrow $\Gamma\ exp \approx$ 0.28 mm/sec and temperature-independent widths of the absorption peaks of ^{57}Fe indicate the existence of only one type of iron in the unit cell, with no evidence of relaxation or magnetic ordering down to 4.5°K for either compound.

At 500°K new broad doublets with hyperfine parameters typical of Fe^{3+} were found in spectra of both compounds, indicating decomposition to ferric forms.

Quadrupole Coupling

Temperature dependences of the quadrupole splitting parameters of ^{57}Fe in $K[Fe(hyc)_3]$ and $N_2H_5[Fe(hyc)_3]\cdot H_2O$ are shown in Fig. 3.

In Fe^{2+} compounds the electric field gradients arise mainly from the valence electrons, and the temperature dependence of the quadrupole splitting parameter has been discussed in detail by Ingalls (6). The contribution to the efg from atoms in the lattice is usually smaller and temperature independent. Therefore the quadrupole splitting parameter ΔE_Q can be written in the
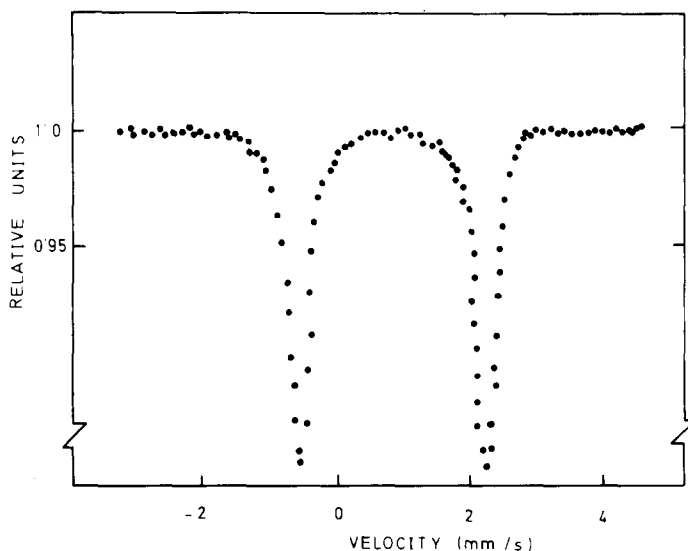

FIG. 2. Mössbauer spectrum of ^{57}Fe in $K[Fe(hyc)_3]$ at 77°K taken witn a source of ^{57}Co in Pd.
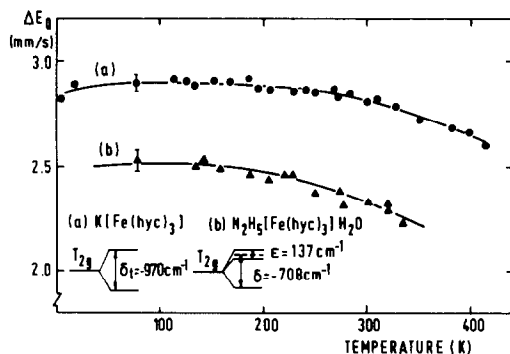
FIG. 3. Temperature dependence of the quadrupole splitting parameter of ^{57}Fe in K[Fe(hyc)$_3$] and N$_2$H$_5$[Fe(hyc)$_3$]·H$_2$O. Theoretical curves, (a) and (b), have been calculated with the crystal field parameters as given in the text. The energy-level diagrams show schematically the influence of trigonal distortion on K[Fe(hyc)$_3$] and rhombic distortion on N$_2$H$_5$[Fe(hyc)$_3$]·H$_2$O.

form

$$\Delta E_Q(T) = \tfrac{1}{2}e^2 Q(1-R)\langle r^{-3}\rangle_0$$

$$\alpha_{MO}^2 F(\delta_t,\, \varepsilon_1\alpha^2\lambda_0,\, T)(1+\eta^2/3)^{1/2}$$

$$+\Delta E_Q^{lat}, \qquad (1)$$

where $(1-R)$ is the Sternheimer shielding factor (7) for iron, α_{MO}^2 the covalency factor (8) which reduces the free ion parameter $\langle r^{-3}\rangle_0$ due to complex formation, η the parameter of asymmetry, and F the reduction factor which describes the averaging of the efg through the Boltzmann population of the crystal field and spin–orbit levels. It depends on the point symmetry of the Mössbauer atom, the strength of the crystal field, the covalency, and the temperature.

The ligand configuration of the compound K[Fe(hyc)$_3$] is of octahedral type with a threefold axis passing through the ferrous site. Thus the crystal field potential at the Fe^{2+} ion in K[Fe(hyc)$_3$] is predominatly of cubic symmetry, with a small trigonal component $V_t = -\delta_t(L_z^2 - 2/3)$ which splits the orbital ground-state triplet $T_{2g}(O_h)$ into a doublet and a singlet. Further splitting

might be caused by the spin–orbit interaction $\alpha^2\lambda_0 LS$. The reduction factor F of Fe^{2+} in K[Fe(hyc)$_3$] was calculated with these two contributions considered as the Hamiltonian perturbation. It was applied to the T_{2g} basic functions quantized along the trigonal axis (9). The E_{2g} levels were not considered in this treatment because they are usually about 10^4 cm^{-1} higher than the T_{2g} levels. The theoretical quadrupole splitting parameter ΔE_Q [curve (a) in Fig. 3] was obtained by a least-squares-fitting routine where the crystal field splitting parameter δ_t, the covalency factor α^2, and ΔE_Q^{lat} were treated as free variables. The difference between the covalency factors α^2 and α_{MO}^2 was not considered in this calculation. The best agreement between the experimental values of the quadrupole splitting parameter and the theoretical values was obtained with the following set of parameters:

$$\delta_t = -970 \pm 80 \text{ cm}^{-1},$$

$$\alpha^2 = 0.7 \pm 0.1,$$

$$\Delta E_Q^{lat} = +0.15 \pm 0.07 \text{ mm/sec}.$$

The negative value of the crystal field splitting parameter δ_t gives evidence that the ferrous ion in K[Fe(hyc)$_3$] is characterized by an orbitally nondegenerate ground term. These results suggest that the maximal principal component of the efg tensor is negative.

The value of the quadrupole coupling constant and its temperature dependence as measured in N$_2$H$_5$[Fe(hyc)$_3$]·H$_2$O is different from that of K[Fe(hyc)$_3$]. N$_2$H$_5$[Fe(hyc)$_3$]·H$_2$O is monoclinic, and the symmetry of the crystal field potential at the ferrous site could be nonaxial. Therefore the perturbation treatment with the rhombohedral crystal field potential was carried out, taking into account the spin–orbit interaction. The temperature dependence of the quadrupole splitting parameter [curve (b) in Fig. 3] gave the best agreement with the experimental data using the following crystal

field variables:

$$\delta = -708 \pm 80 \text{ cm}^{-1},$$

$$\varepsilon = 137 \pm 50 \text{ cm}^{-1},$$

$$\alpha^2 = 0.6 \pm 0.1,$$

$$\Delta E_Q^{\text{lat}} = +0.4 \pm 0.1 \text{ mm/sec},$$

$$\eta = 0.15,$$

where δ and ε are the crystal field splittings of the $^5T_{2g}$ level as shown in Fig. 3. The ground-state wavefunction of the ferrous ion could not be determined uniquely from these results, since different crystal field potentials can give the same energy separations (10). Therefore additional experimental evidence concerning the detailed type of distortion of the crystal field potential was needed. From the analysis of the single crystal spectra of $N_2H_5[Fe(hyc)_3] \cdot H_2O$ measured for different directions of the incident γ ray relative to the crystallographic axis, a negative largest principal component of the efg tensor had been already obtained (5). Considering these results the crystal field potential at Fe^{2+} in $N_2H_5[Fe(hyc)_3] \cdot H_2O$ should be mainly trigonally distorted, similar to that found for $K[Fe(hyc)_3]$. The negative V_{zz} would then suggest that the $Fe(hyc)_3$ anion in $N_2H_5[Fe(hyc)_3] \cdot H_2O$ might be elongated in the direction of the pseudotrigonal axis. The small value obtained for the parameter of

asymmetry ($\eta = 0.15$) gives further support for this supposition.

Recoilless Fraction

The relative recoilless fraction (f) of ^{57}Fe in $K[Fe(hyc)_3]$ and $N_2H_5[Fe(hyc)_3] \cdot H_2O$ was estimated at various temperatures from the areas of the experimental spectra, which were corrected due to background from nonresonant radiation (11) and finite thickness effects (12). At room temperature the following values were obtained:

$f = 0.20 \pm 0.02$

for $K[Fe(hyc)_3]$;

$f = 0.35 \pm 0.04$

for $N_2H_5[Fe(hyc)_3] \cdot H_2O$.

The linear dependences of $\ln f$ on the temperature above 100°K (Fig. 4) indicate that the vibrations of the iron ion can be approximated by the high-temperature Debye model with constant Debye temperature.

The $Fe(hyc)_3$ anions apparently resemble each other in the two compounds, as seen from their infrared spectra(4) and center shift parameters. Thus the difference in the recoilless fractions must arise primarily from three factors: (i) different bonds in the $Fe(hyc)_3$ anions, (ii) different bonds between
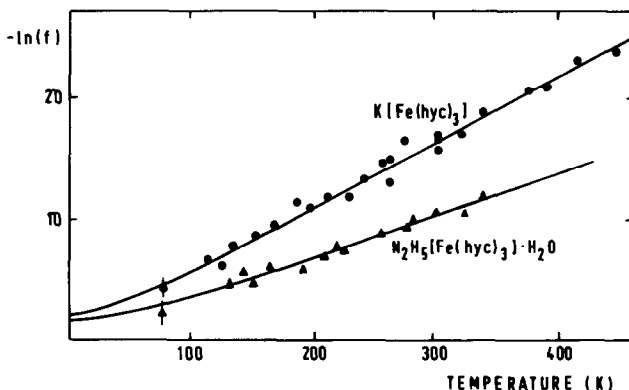

FIG. 4. Logarithm of the recoilless fractions ($-\ln f$) versus temperature in $K[Fe(hyc)_3]$ (●) and $N_2H_5[Fe(hyc)_3] \cdot H_2O$ (▲).

the Fe(hyc)₃ anions and the cations, and (iii) different crystal packings.

The recoilless fraction is proportional to the mean square of the displacement of the iron ion, which is mostly sensitive to low-frequency vibrations (13). These can be approximated by supposing the Fe(hyc)₃ anions to be rigid spheres which vibrate as a whole. In addition, the vibrations of the ferrous ion relative to the center of mass of the Fe(hyc)₃ anion must also be considered. But the linear variations of $-\ln f$ with temperature indicate that these modes are lying at much higher frequencies and do no contribute significantly to the measured temperature dependences of the recoilless factors in the temperature region of interest. From the high-temperature approximation of the experimental data shown in Fig. 4, extrapolated to zero temperature, this contribution has been estimated to be greater than 0.9 for both compounds. This implies that it should be nearly constant over the entire measured temperature region. In this case the thermal variation of the recoilless fraction should be mainly due to vibrations of the rigid Fe(hyc)₃ anions in the crystal, which can be fairly well approximated by a simple Debye model where the effective mass is taken to be that of the Fe(hyc)₃ anion (13). The appropriate Debye temperatures have been obtained from the experimental data as: $71 \pm 4°K$ for K[Fe(hyc)₃] and $90 \pm 4°K$ for N₂H₅[Fe(hyc)₃]·H₂O.

Center Shift

The values of the center shift and its temperature dependence are the same within experimental error for N₂H₅[Fe(hyc)₃]·H₂O and K[Fe(hyc)₃] (Fig. 5). This implies that the electron densities at the iron nuclei and thus the chemical structure of the Fe(hyc)₃ anions are very similar in both compounds. The temperature variation of the center shift can be interpreted in terms of a second-order Doppler shift and the thermal volume
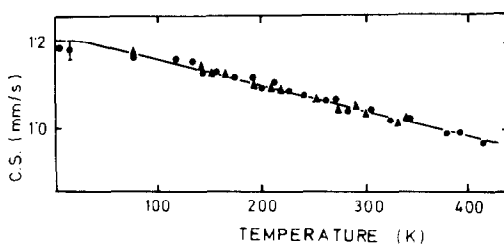

FIG. 5. Temperature dependence of the center shift of ⁵⁷Fe in K[Fe(hyc)₃] (●) and N₂H₅[Fe(hyc)₃]·H₂O (▲) relative to metallic iron at 295°K.

expansion (14, 15):

$$\text{C.S.} = \delta_0 - 3\hbar E_0/(2mc^2)\langle\omega\rangle - \gamma T, \quad (2)$$

where δ_0 is the sum of the isomer shift and the second-order Doppler shift contribution of the source, and γ the thermal volume expansion coefficient. The second-order Doppler shift has been expressed by the first moment of the phonon spectra using the relation: $\langle v^2 \rangle = 3\hbar\langle\omega\rangle/m$ (16). E_0 is the energy of the γ-ray, m the effective mass of the oscillating atom, and $\langle\omega\rangle$ the first moment of the phonon spectra. The high-temperature approximation of Eq. [2] yields a nearly linear variation of the center shift with temperature. The slope of the curve depends mainly on the thermal expansion coefficient (γ) and the effective vibrational mass (m) and is independent of any particular model of lattice vibrations. If the mass of the Fe(hyc)₃ anion is considered in Eq. (2) the thermal volume expansion coefficient $\gamma = 4.4 \times 10^{-4}$ mm/sec °K is obtained for both compounds. This value is rather large and would mean that the thermal volume expansion term is dominant in Eq. (2) and is thus the principal reason for the temperature variation of the center shift. But if the effective mass is taken to that of ⁵⁷Fe, the thermal expansion coefficient is found to vanish for K[Fe(hyc)₃] and N₂H₅[Fe(hyc)₃]·H₂O. This result seems much more reasonable and indicates that the vibrations of the ⁵⁷Fe ion in Fe(hyc)₃ ion are the most important contributions to the thermal variation of the center shift. Since

the second-order Doppler shift is proportional to the first moment of the phonon spectral density, the short wavelengths are expected to be the most important ones. These arise principally from the motion of the iron relative to the center of mass of the $Fe(hyc)_3$ anion. The second-order Doppler shift thus reflects the local structure, which is nearly the same for both compounds. On the contrary, the recoilless fraction is proportional to $\langle \omega^{-1} \rangle$ and thus depends mainly upon the long-wavelength vibrations which reflect most of all the crystal structure of the compound.

Our results show that the thermal behavior of the recoilless fraction and that of the center shift of ^{57}Fe in $K[Fe(hyc)_3]$ and $N_2H_5[Fe(hyc)_3]\cdot H_2O$ can be explained on the basis of a molecular crystal-like treatment in which the motion of the iron atom was considered as a superposition of the vibrations of the $Fe(hyc)_3$ anions as a whole and of those of the iron relative to this anion. This confirms the existence of a frequency gap between these two kinds of vibrations.

Acknowledgments

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