Mössbauer Spectroscopy of Hexa-ammineiron(II) Nitrate, Thiocyanate, and Sulphate

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Compounds of the type $[Fe(NH_3)_6]X_2$ ($X = NO_3$ or SCN; $X_2 = SO_4$) have been investigated between 4·2 and 340 K using the ^{57}Fe Mössbauer effect. The experiments suggest two-phase transitions occurring in the nitrate and possibly the thiocyanate which are determined by hindrance to the motion of the NH_3, NO_3, and SCN groups.

IN a large number of hexa-ammine compounds of the type $[M(NH_3)_6]X_2$ (M is a bivalent metal ion and X an anion) phase transitions at a critical temperature have been established using a variety of measurements such as specific heat, i.r. spectra, and dielectric constant. The compounds are cubic at room temperature and belong to the *Fm*3*m* space group.[1] Each iron atom is surrounded by an octahedron of ammonia molecules and the anions form a cube around each octahedron. The metal ion experiences a cubic *m*3*m* local symmetry so long as the six NH_3 molecules conform to their 4 *mm* site symmetry. This is accomplished through the motion of the ammonia groups around the C_4 symmetry axes. Below a critical temperature, T_c, characteristic of both the metal and the anion, the motional freedom of the NH_3 molecules is reduced. This phenomenon accompanies a phase transition which lowers the symmetry of the crystal and, as a consequence, that of the metal ion.

We have recently reported the phase transition in hexa-ammineiron salts with the X ions belonging to the T_d (or $\bar{4}\,3m$) symmetry of the lattice site, *e.g.* Cl^-, Br^-, I^-, $[ClO_4]^-$, and $[BF_4]^-$, using ^{57}Fe Mössbauer resonance

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[1] R. W. G. Wyckoff, 'Crystal Structures,' Interscience, New York, 1965, vol. 3.

and *X*-ray diffraction.[2] With a view to understanding the role of the X ions in the phase transitions, we have extended these measurements on hexa-ammineiron salts to compounds where the X ions have a symmetry lower than the T_d group (*e.g.* $[NO_3]^-$ and $[SCN]^-$) or in which X is the 2— anion $[SO_4]^{2-}$.

EXPERIMENTAL

The salts of hexa-ammineiron are rather unstable and deteriorate in open air. Hence their preparation and handling was carried out under an atmosphere of ammonia gas. The nitrate salt, $[Fe(NH_3)_6][NO_3]_2$, was precipitated from a hexa-ammineiron(II) acetate solution by a saturated solution of alkali nitrate; $[Fe(NH_3)_6][SCN]_2$ was produced by reaction of dry ammonia with $[Fe(py)_4][SCN]_2$ (py = pyridine) and is photosensitive. There is very little information on these salts, apart from them being yellow.[3] We obtained light blue crystals, which turned yellow when slightly oxidized. These compounds were enriched in ^{57}Fe to increase the measured resonance effect. The white $[Fe(NH_3)_6][SO_4]$ salt was obtained by flowing NH_3 gas over dry iron(II) sulphate.

Mössbauer spectra were measured between 4·2 and 340 K and analysed following conventional procedures described earlier.[2]

RESULTS AND DISCUSSION

$[Fe(NH_3)_6][NO_3]_2$.—The *X*-ray powder diffraction spectrum of $[Fe(NH_3)_6][NO_3]_2$ at room temperature agrees with the *Fm*3*m* space group and yields the lattice parameter $a = 10{\cdot}93 \pm 0{\cdot}02$ Å. The Mössbauer spectrum measured at room temperature was a single line located at $1{\cdot}12 \pm 0{\cdot}02$ mm s^{-1} relative to $Na_4[Fe(CN)_6]{\cdot}3H_2O$. This value of the centre shift, typical of previously studied hexa-ammines,[2] shows that iron is in a high-spin bivalent-charge state. The single line, which reflects the cubic symmetry experienced by the iron(II) ion, is possible only if there is *dynamic* disorder in the NH_3 molecules as well as in the NO_3 groups. The spectrum remained a single line down to 228 K, where it split into a quadrupole doublet [assigned (A) in Figure 1] having the same centre shift as the single line. Below 99 K, a second doublet, (B), appeared with a smaller quadrupole splitting. The centre shift for both the doublets were identical and their intensities were nearly equal. The intensity of the inner doublet, (B), increased at the cost of the doublet (A) on further lowering of the temperature. The area under the outer doublet, (A), was *ca.* 20% of the total resonance area at 4·2 K. All the transformations were reversible, although that between the two distorted phases [between doublets (A) and (B)] had a hysteresis: on heating, doublet (B) disappeared only above 122 K. A single line replaced doublet (A) above 228 K.

The observation of a quadrupole doublet at 228 K is indicative of a lowering of the symmetry of the Fe^{2+} ion. From the sharpness of the transition, which occurs without any line broadening, we conclude that the phenomenon is a static distortion of the crystal as found in other hexa-ammine salts.[2] Such a phase transition originates in co-operative ordering of the NH_3 motion.

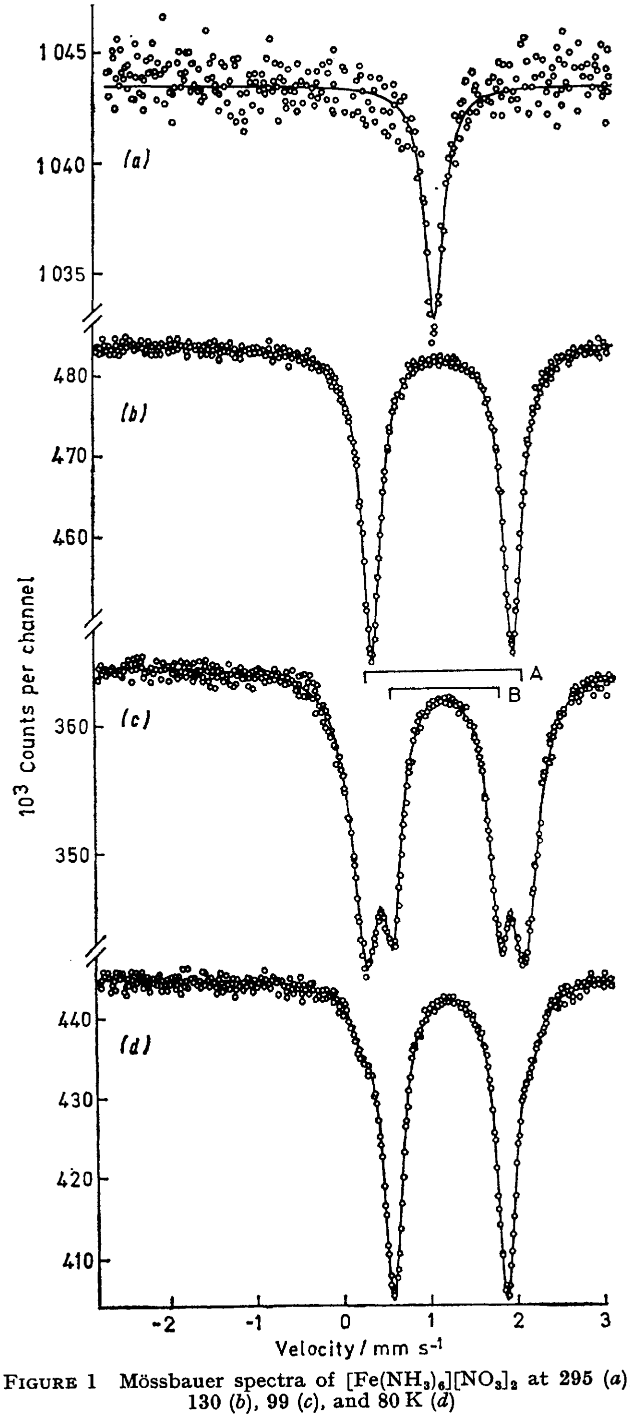

FIGURE 1 Mössbauer spectra of $[Fe(NH_3)_6][NO_3]_2$ at 295 (*a*), 130 (*b*), 99 (*c*), and 80 K (*d*)

Although no *X*-ray structure investigations have been made on this compound in the low-temperature phase, the isomorphous hexa-amminenickel nitrate has a lower symmetry at 80 K than the cubic one observed at 295 K [4]

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[2] L. Asch, G. K. Shenoy, J. M. Friedt, J. P. Adloff, and R. Kleinberger, *J. Chem. Phys.*, 1975, **62**, 2335.

[3] Gmelins Handbuch der Anorganischen Chemie, Verlag Chemie, Weinheim, 1931, no. 59, part B.

[4] S. H. Yu, *Nature*, 1942, **150**, 347.

and a phase transition has been established at 243 K from heat-capacity,[5] dilatometric,[6] and e.p.r. measurements.[7] We believe that the phase transition observed by Mössbauer spectroscopy at *ca.* 100 K in the iron salt has its origin in the hindrance to motion of the nitrate ions. In the room-temperature phase, NO_3 groups oscillate around an O–O edge; when their motion is hindered the groups will be fixed to one or the other end-points of their oscillation and hence produce two types of static distortion. There will then be two quadrupole interactions. These distortions progressively align on lowering the temperature, and are manifested in the increasing proportion of one type of distorted site. A corresponding phase transition has been observed at 80 K in hexa-amminenickel nitrate through heat-capacity measurements.[5] The e.p.r. linewidth, however, did not change [7] at *ca.* 80 K, which may be due to only a minor difference in the two distortions.

The temperature dependences of the quadrupole interactions in the low-temperature phases of the nitrate are shown in Figure 2. The variations are too steep to be accounted for by a conventional theory of the type proposed by Ingalls [8] to include the thermal populations of the crystalline electric-field levels. This failure has already been noted in other hexa-ammine compounds; [2] it has been attributed to fluctuating crystal fields due to persisting but restricted motion of the NH_3 ligands in the low-temperature phase, in agreement with dielectric measurements.[9] The time-averaged crystal field thus becomes temperature dependent.

In Figure 3 the area under the resonance curve (which is proportional to the resonance fraction) is shown as a function of temperature. While there is no discontinuity in its variation at the lower transition temperature, above the upper transition temperature of 228 K the Mössbauer effect drops to a small value. Such a phenomenon has again been observed in other hexa-ammine salts [2] and in $Eu(NH_3)_6$.[10] This may either be associated with a change in the phonon spectrum accompanying the crystallographic transformation, or with the increased scattering of the acoustic phonons by the liberons (or the motional quanta of ammonia molecules) in the cubic phase.[10]

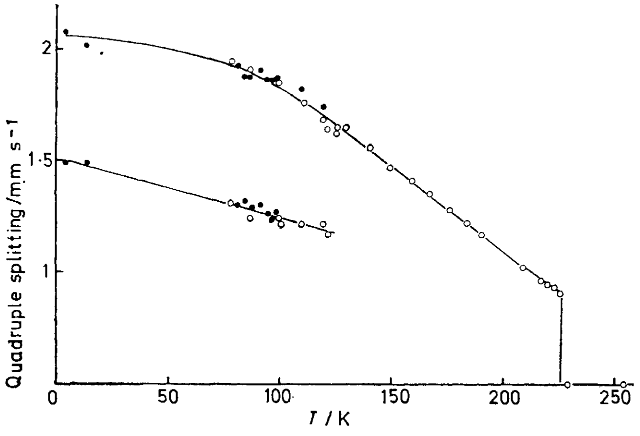

FIGURE 2 Temperature dependence of the quadrupole interaction in $[Fe(NH_3)_6][NO_3]_2$: (○), warming; (●), cooling

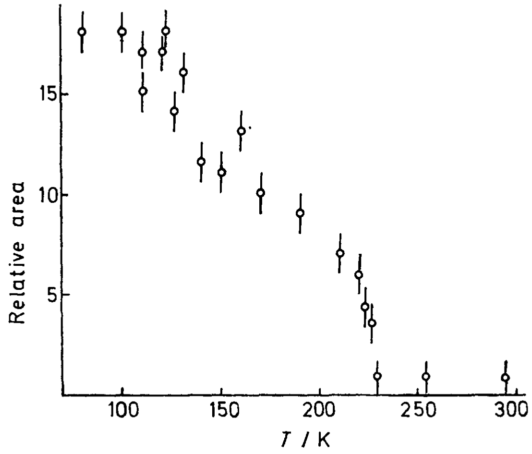

FIGURE 3 Temperature dependence of the Mössbauer resonance fraction in $[Fe(NH_3)_6][NO_3]_2$

$[Fe(NH_3)_6][SCN]_2$.—The thiocyanate has a cubic structure at 300 K, as revealed by the *X*-ray powder pattern, with $a = 11{\cdot}43 \pm 0{\cdot}03$ Å. However, the Mössbauer spectrum measured at room temperature revealed a quadrupole pattern, indicating non-cubic symmetry at the iron site. The isomer shift is the same as that measured for other hexa-ammine compounds. The lower symmetry at the metal ion can result from *static* disorder which produces distorted $[Fe(NH_3)_6]^{2+}$ clusters with a random relative orientation and results in a cubic *X*-ray structure. Alternately, the spectra could represent dynamic distortion with a fluctuation rate slower than the nuclear correlation time (*ca.* 10^{-8} s). Such behaviour has been reported in FeV_2O_4 and $FeCr_2O_4$,[11] where the fluctuation was due to a dynamic Jahn–Teller effect instead of a molecular motion as envisaged in the present case.

Below 250 K the spectrum consisted of two quadrupole patterns of nearly equal intensities. As in the nitrate, we associate this behaviour with the hindrance to motion of the anions; the $[SCN]^-$ ions are indeed known for their ability to form bonds through the S or N atoms.[12] The linewidths of the quadrupole-split lines remained unchanged down to 80 K with a value of *ca.* 0·3 mm s^{-1}, but

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[5] E. A. Long and F. C. Toettcher, *J. Chem. Phys.*, 1946, **8**, 504.

[6] D. G. Thomas, L. A. K. Staveley, and A. F. Cullis, *J. Chem. Soc.*, 1952, 1727.

[7] C. E. Hennies, Thesis, University of Sao Paulo, Brazil, 1969.

[8] R. Ingalls, *Phys. Rev.*, 1964, **A133**, 787.

[9] G. Aiello and M. B. Palma-Vittorelli, *Collective Phenomena*, 1973, **1**, 87.

[10] F. T. Parker and M. Kaplan, *Chem. Phys. Letters*, 1974, **24**, 280.

[11] M. Tanaka, T. Tokoro, and Y. Aiyama, *J. Phys. Soc. Japan*, 1966, **21**, 268.

[12] J. Danon in 'Mössbauer Spectroscopy and its Application,' I.A.E.A., Vienna, 1972, p. 281.

broadened considerably at lower temperatures (see the Table). This broadening is not due to absorber-thickness effects since the thickness saturates at low temperatures. We tentatively attribute the observed broadening to slowing down of molecular motion at low temperatures.

Width of the Mössbauer resonance line of $[Fe(NH_3)_6][SCN]_2$ at various temperatures

T/K	260	200	190	180	80	32	29	12
$\Gamma/mm\ s^{-1}$	0·29	0·30	0·30	0·32	0·34	0·45	0·48	0·58

$[Fe(NH_3)_6][SO_4]$.—The sulphate has a non-cubic *X*-ray structure at room temperature. Mössbauer spectra measured from 4·2 to 340 K showed two quadrupole patterns with the characteristic isomer shift of the hexa-ammine salts. The two doublets retained a constant area ratio throughout the temperature range and a detailed area analysis showed that one iron-lattice site has twice the population of the other. The temperature dependence of the quadrupole interaction for both sites can be explained using the conventional theory of Ingalls.[8] This tends to indicate that molecular motions are of little consequence in this salt. In fact, they must be considerably hindered in the low-symmetry electrostatic potential existing even at room temperature, unlike the other hexa-ammine compounds.

Conclusions.—From our previous [2] and present investigation it appears that the phenomenon of phase transitions in hexa-ammine compounds is closely related to molecular motion. Some understanding of this has been made by Bates [13] who qualitatively described the co-operative ordering behaviour of NH_3 molecules by merely considering the interaction between the protons within an octahedron of ammonia and that with the protons in the nearest-neighbours octahedra. Our investigation strongly suggests that symmetry and the consequent motion of the X ions is also of considerable importance in the description of the measured physical quantities. Any further understanding of these compounds demands the knowledge of at least their structures in the low-temperature phase and measurement of their heat capacity at the transition to establish the modes of molecular motion.

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[13] A. R. Bates and K. W. H. Stevens, *J. Phys.* (*C*), 1969, 1573; A. R. Bates, *ibid.*, 1970, 1825.