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The Configurations of $[FeCl_2(OH_2)_4]^+$: a Mössbauer Study

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Mössbauer spectra have been measured at 90 K for the compounds $FeCl_3 \cdot nH_2O$; n = 2, 2½, 3½ and 6. In all cases, the structure is that of $FeCl_2(OH_2)_4^+$ with an appropriate complex anion. The configuration is trans *for n = 2 and 6, while it is* cis *where n = 2½ and 3½.*

Introduction

The series of compounds $FeCl_3 \cdot nH_2O$ were first made known in 1892 by Roozeboom [1] through a study of the ferric chloride–water phase diagrams. The four hydrates found were $FeCl_3 \cdot 2H_2O$, $FeCl_3 \cdot 2½H_2O$, $FeCl_3 \cdot 3½H_2O$ and $FeCl_3 \cdot 6H_2O$. An understanding of their configurations is of possible importance to a long term study [2] of the mechanisms of the leaching of various ores using aqueous $FeCl_3$ as oxidant [3].

The hexahydrate (n = 6) has been studied crystographically by Lind [4] and found to consist of *trans*-$[FeCl_2(OH_2)_4]Cl \cdot 2H_2O$: a D_{4h} structure with two lattice water molecules. The dihydrate has been studied by infrared spectroscopy [5] and found to be a dimeric *trans*-$[FeCl_2(OH_2)_4][FeCl_4]$.

Recently, the 2½ hydrate has been studied by X-ray crystallographic methods [6] and was found to depart from the *trans* configuration and is instead *cis*-$[FeCl_2(OH_2)_4][FeCl_4] \cdot H_2O$.

As part of a study of Fe(III)–chloride complexes, we have made measurements of the Mössbauer spectra of all members of this series to confirm and extend structural understanding.

Experimental Section

The compounds were prepared by known methods [7]. Since some of them – particularly the 2½ hydrate and the 3½ hydrate – are quite hygroscopic, it was necessary to handle them under dry nitrogen. Crushing of the crystals was done under dried low-boiling petroleum ether to prevent local overheating. Mounting of the powdered compounds for Mössbauer study was between mylar sheets in a gold-plated copper plate. In some experiments the gold plating was defective and reaction of Fe(III) with the underlying copper gave rise to Fe(II) peaks in the spectrum.

The Mössbauer spectra were recorded using a constant acceleration spectrometer coupled to a Northern Scientific N.S. 636 multichannel analyzer. The samples were mounted in a Janis DT-1954 cryostat for low temperature studies. The ^{57}Co radiation source was embedded in a palladium matrix. Calibration of the velocity of the instrument was done by use of a 0.001 inch pure iron foil. The peak positions were found to be linear and were adjusted to agree with the values recommended by Violet and Pipcorn [8]. Peak-widths between 0.24 and 0.29 mm s^{-1} were obtained in most cases. The data were analysed on 600 points using a curve fitting program with non-linear regression [9] assuming Lorentzian line shapes and equal widths for both peaks in a doublet. In all analyses a plot was obtained of the residual differences between the calculated spectra and the experimental data, so as to confirm that no peaks were incompletely analysed. The total number of counts was about 3×10^5 per channel, so as to give a statistical uncertainty of ±0.2% on each point.

Results and Discussion

Mössbauer spectra measured at 90 K are given in Figs. 1–4 for the four hydrates n = 2, 2½, 3½ and 6, respectively. Clearly evident in Fig. 4 are two peaks constituting a quadrupole split pair. Figures 1–3 show the four peaks of two quadrupole doublets.

The results obtained for the centre shifts and quadrupole splittings for these compounds are given in Table I. Also summarized in Table I are the stereochemical assignments indicated by the Mössbauer data.

The structure of $FeCl_3 \cdot 6H_2O$ was determined by Lind [4] to be *trans*-$[FeCl_2(OH_2)_4]Cl \cdot 2H_2O$.

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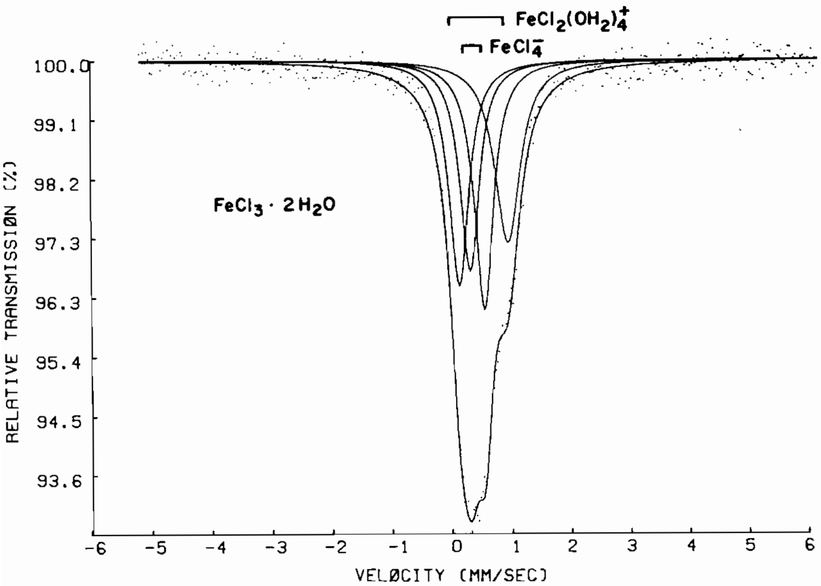

Fig. 1. Mössbauer spectra measured at 90 K for $FeCl_3 \cdot 2H_2O$.

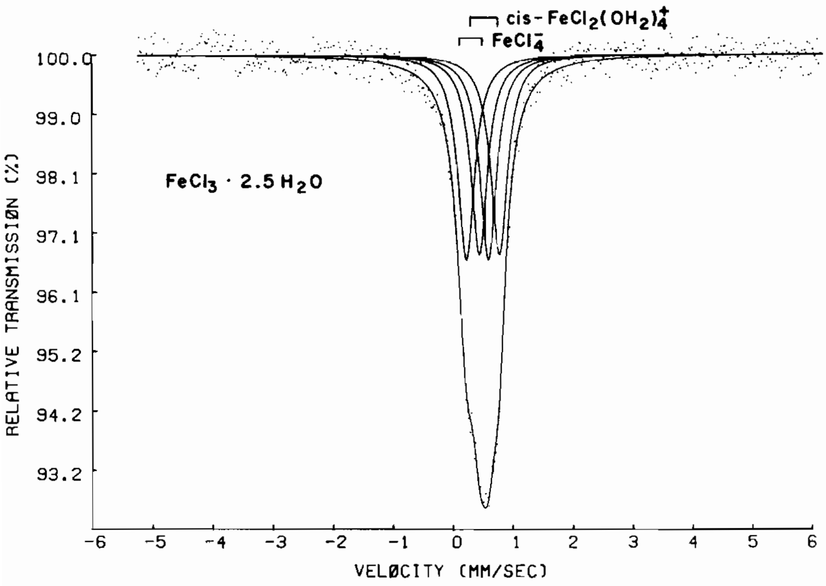

Fig. 2. Mössbauer spectra measured at 90 K for $FeCl_3 \cdot 2\frac{1}{2}H_2O$.

Its centre shift, δ, is 0.580 mm s^{-1} and is in keeping with the expected values for octahedral Fe(III) compounds [10]. The high quadrupole splitting value, Δ, of 0.871 mm s^{-1} is indicative of a large electric asymmetry, such as one finds in a *trans*-configuration. Our measurements are thus in keeping with the known structure. The asymmetry of line width and line area of the two peaks is still evident at 90 K, although they are symmetric at 1.8 K, as was shown first by Wignall [11]. The origin of this asymmetry is well explained by Thrane and Trumpy [12], in terms of combined spin–spin interaction and the Goldanskii–Karyagin effect.

The dihydrate, $FeCl_3 \cdot 2H_2O$ shows similar values of 0.509 mm s^{-1} for δ and 0.799 mm s^{-1} for Δ, indicating again the presence of a D_{4h} *trans*-configuration. An additional doublet in this case, however, shows the presence of Fe(III) in another form (in this case the value of 0.409 mm s^{-1} for δ, coupled with 0.240 mm s^{-1} for Δ) suggesting [13] that this part of the compound is $FeCl_4^-$, tetrahedral but distorted. This is to be compared with other values for

TABLE I. Mössbauer Parameters for the Hydrates $FeCl_3 \cdot nH_2O$ Measured at 90 K. *Note that These Tetrahedra Are all Distorted.

n	δ mm s^{-1}	Δ mm s^{-1}	Assignment	δ mm s^{-1}	Δ mm s^{-1}	Assignment	Compound
6	0.580	0.871	*tr*- $[FeCl_2(OH_2)_4]^+$				$FeCl_2(OH_2)_4Cl \cdot 2H_2O$
2	0.509	0.799	*tr*- $[FeCl_2(OH_2)_4]^+$	0.409	0.240*	$[FeCl_4]^-$	$FeCl_2(OH_2)_4FeCl_4$
2½	0.585	0.302	*cis*-$[FeCl_2(OH_2)_4]^+$	0.380	0.380*	$[FeCl_4]^-$	$FeCl_2(OH_2)_4FeCl_4 \cdot H_2O$
3½	0.575	0.256	*cis*-$[FeCl_2(OH_2)_4]^+$	0.354	0.308*	$[FeCl_4]^-$	$FeCl_2(OH_2)_4FeCl_4 \cdot 3H_2O$

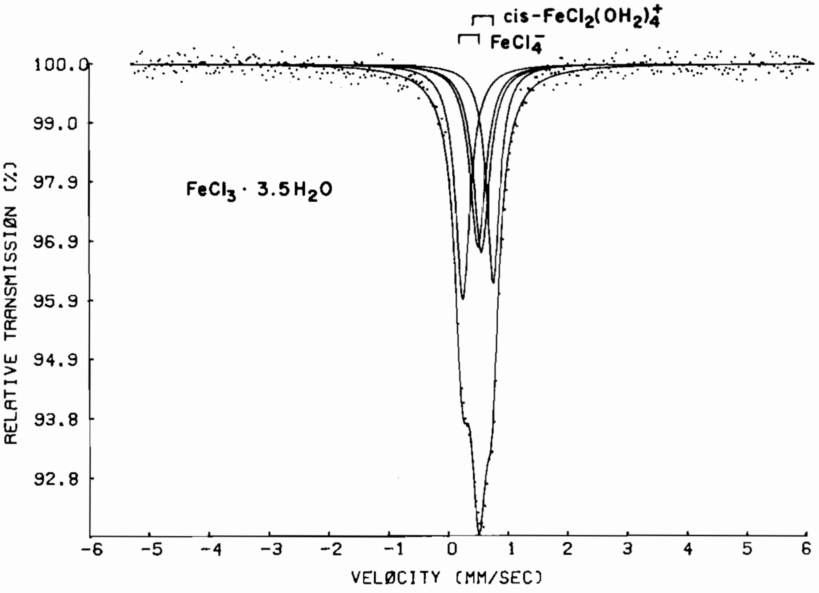

Fig. 3. Mössbauer spectra measured at 90 K for $FeCl_3 \cdot 3½H_2O$.

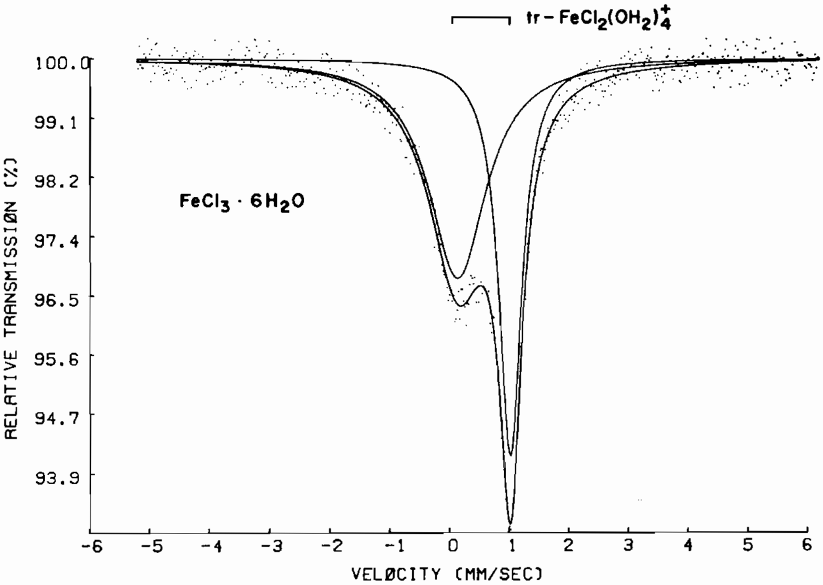

Fig. 4. Mössbauer spectra measured at 90 K for $FeCl_3 \cdot 6H_2O$.

TABLE II. Configuration of Several Compounds $[FeCl_2(OH_2)_4]X \cdot nH_2O$, Where X is a Large Anion, $SbCl_6^-$ for $FeCl_4^-$.

Compound	Formulation	n	Configuration
$FeCl_3.SbCl_5 \cdot 8H_2O$	$[FeCl_2(OH_2)_4]SbCl_6 \cdot 4H_2O$	4	*trans*
$FeCl_3.6H_2O$	$[FeCl_2(OH_2)_4][FeCl_4] \cdot 2H_2O$	2	*trans* [4]
$FeCl_3 \cdot 2H_2O$	$[FeCl_2(OH_2)_4][FeCl_4]$	0	*trans* [5]
$FeCl_3 \cdot 2½H_2O$	$[FeCl_2(OH_2)_4][FeCl_4] \cdot H_2O$	1	*cis* [6]
$FeCl_3 \cdot 3½H_2O$	$[FeCl_2(OH_2)_4][FeCl_4] \cdot 3H_2O$	3	*cis*

the quadrupole splitting of 0.30 and 0.2 mm s^{-1} for $NaFeCl_4$ and $(Ph_4As)FeCl_4$ respectively, which are both known to be tetrahedral [14, 15]. A Δ value of 0.45 mm s^{-1} is found for the tetrahedral $LiFeCl_4$ [16]. Given no other influence, this seems to indicate a rough inverse correlation of Δ with the sizes of the four cations: Li^+, Na^+, *trans*-$[FeCl_2(OH_2)_4]^+$ and Ph_4As^+ with Δ values of 0.45, 0.30, 0.240 and 0.2 mm s^{-1}, respectively. The most reasonable configuration for the dihydrate, then, is *trans*-$[FeCl_2(OH_2)_4][FeCl_4]$. Again, the *trans*-configuration is in keeping with conclusions made earlier [5] from infrared measurements.

The two intermediate hydrates (n = 2½, 3½) seem to show somewhat different spectra. Each gives a doublet whose isomer shift is characteristic [13] of the tetrahedral $FeCl_4^-$, where the doublet indicates a distortion of the tetrahedron. The Δ values for the $FeCl_2(OH_2)_4^+$ doublet are rather small, 0.25S mm s^{-1} for the 3½ hydrate and 0.302 mm s^{-1} for the 2½ hydrate. These values indicate greater likelihood of a *cis*-configuration.

The crystal structure of the 2½ hydrate has been recently published [6] and shows an unambiguous *cis*-configuration. The lattice also contains a distorted tetrahedron of $FeCl_4^-$ and a single water molecule. The distorted tetrahedral configuration was also borne out by the present Mössbauer data. The quadrupole splitting value of 0.380 mm s^{-1} seems rather high and suggests an influence of the crystal packing. This is borne out on examination of the crystal structure. The crystal shows a layered structure, with one plane consisting of $FeCl_4^-$ anions and an equal number of lattice water molecules, while the alternate planes each consist of $FeCl_2(OH_2)_4^+$ cations. The distinctly lower value of 0.302 mm s^{-1} for the other doublet is clearly indicative of the *cis*-configuration for the $FeCl_2(OH_2)_4^+$, in agreement with the crystallographic results.

The data for the 3½ hydrate seem unambiguous. The hexacoordinate iron is identified by its isomer shift value of 0.575 mm s^{-1}, while the value of 0.256 mm s^{-1} for the quadrupole splitting is clearly not consistent with the *trans*-configuration, and is well within the range expectable for the *cis*-$FeCl_2(OH_2)_4^+$. The tetrahedral $FeCl_4^-$ likewise is distinct and unambiguously identified. The Δ value of 0.308 mm s^{-1} suggests that the crystal packing is less asymmetric in this compound, although unfortunately nothing is known about its crystallography.

The reasons for the transformation through this series from *trans* to *cis* and back again, as one goes from the hexahydrate to the dihydrate, are at present obscure. The effect of the availability of lattice water for binding or hydration of the anion seems significant. Szymanski shows [6] the lattice water to be hydrogen bonded to two chlorine atoms of the $FeCl_4^-$, thus contributing to the distortion of the $FeCl_4^-$ anion, although these two chlorines subtend 110.6° at the iron atom. These water molecules seem not to interact strongly with the octahedra.

It is interesting to regard all these hydrates as being derived from a $[FeCl_2(OH_2)_4]^+$ cation, where the anion can be $SbCl_6^-$, Cl^- or $FeCl_4^-$, and to consider then that the number of water molecules associated with each $[FeCl_2(OH_2)_4]^+$ is the deciding factor, as is shown in Table II.

One sees that the $[FeCl_2(OH_2)_4]^+$ cations which are in a *trans*-configuration are all associated with *even* numbers of lattice water molecules, while the *odd* numbers seem to go along with a *cis*-configuration. Whether this observation represents a cause or an effect is at present difficult to say.

Acknowledgements

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References

1 H. W. B. Roozeboom, *Z. Phys. Chem., 10,* 477 (1892).
2 F. A. Forward and I. H. Warren, *Met. Rev., 5,* 137 (1960).

3 J. E. Dutrizac and R. J. C. MacDonald, *Min. Sic. Eng.*, *6*, 59 (1974).

4 M. D. Lind, *J. Chem. Phys.*, *47*, 990 (1967).

5 M. T. Kossar-Nechan and J. Roziere, *C.R. Acad. Sci. Paris*, *C279*, 461 (1974).

6 J. T. Szymanski, *Acta Cryst.*, *B35*, 1958 (1979).

7 G. Brauer, 'Handbook of Preparative Inorganic Chemistry', Academic Press, New York.

8 C. E. Violet and D. M. Pipcorn, *J. Appl. Phys.*, *42*, 4339 (1971).

9 Based on a program by D. W. Carson (Mineral Sciences Division, Energy, Mines and Resources Canada, Internal Report M5 70-102), (1970).

10 J. Danon, 'Chemical Applications of Mössbauer Spectroscopy'. V. I. Goldanskii and R. H. Herber, eds., Academic Press, New York (1968) pp. 246–247.

11 J. W. G. Wignall, *J. Chem. Phys.*, *44*, 2462 (1966).

12 N. Thrane and G. Trumpy, *Phys. Rev.*, *B1*, 153 (1970).

13 C. A. Clausen and M. L. Good, *Moss. Effect Methods*, *4*, 187 (1968).

14 G. K. Wertheim and R. H. Herber, *J. Chem. Phys.*, *36*, 2497 (1962).

15 E. R. Jones, M. E. Hendricks, S. L. Flinklea and L. Cathey, *J. Chem. Phys.*, *52*, 1922 (1970).

16 K. Tempelhoff, H. H. Emons and W. Meisel, *A. Allgem. Chem.*, *372*, 1 (1970).