Studies on Mixed Metal(II)–Iron(II) Chloride Systems. Part 3.[1] Mössbauer and *X*-Ray Powder Diffraction Data on $M_xFe_{1-x}Cl_2{\cdot}yH_2O$ (M = Mn, Co, or Ni; $x = 0.5$ or 0.75; $y = 4$ or 6)

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The iron-57 Mössbauer spectra of the phases $M_xFe_{1-x}Cl_2{\cdot}yH_2O$ (M = Mn, Co, or Ni; $x = 0.5$ or 0.75; $y = 4$ or 6) are discussed. The temperature dependence of the quadrupole splitting in the manganese material with $x = 0.5$ is fitted, to derive the crystal-field splittings; the other phases show similar Mössbauer parameters after ageing for three months, which allows development of the hexahydrate phase ($y = 6$). A different ground state is found to fit the data of the manganese material compared with iron(II) chloride tetrahydrate, and these results are discussed in terms of the increased lattice spacings found in the parent $MCl_2{\cdot}yH_2O$ crystals.

In Mössbauer studies on iron(II) chloride hydrates, the results have been explained [2–14] on the basis of the known crystal structure [15,16] of $FeCl_2{\cdot}4H_2O$. The quadrupole coupling constant, e^2qQ, was found to be positive,[4,7,17] with the principal axis of the electric field gradient tensor being due to the Fe–Cl bonds of the *trans*-octahedral $FeCl_2(OH_2)_4$ unit.[7]

We have reported Mössbauer data for the $M_xFe_{1-x}Cl_2{\cdot}4H_2O$ (M = Mn, Co, or Ni; $x = 0$—0.75) systems.[18] Phases having more than 50% $CoCl_2$ were found to contain a site with a quadrupole splitting of 2.65 mm s^{-1} at 298 K, compared with values of 3.00 and 1.55 mm s^{-1} in other samples having <50% $CoCl_2$; the intermediate splitting was noted as being due to an $FeCl_2{\cdot}4H_2O$ or $FeCl_2{\cdot}6H_2O$ species, but was not further discussed due to lack of a definite assignment.

The detailed temperature dependence of the manganese phase reported previously is evaluated here, and its similarity with the previously undiscussed cobalt and nickel phases reported.

Experimental

The preparation and Mössbauer spectroscopic details were as given in a previous paper.[18] The materials are very air-sensitive and were handled in a nitrogen atmosphere. The materials were aged in an atmosphere of nitrogen that was not dry.

Analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, University of Manchester, and the results are given in Table 1, together with the calculated values for the given compositions.

X-Ray powder diffraction data were obtained using a Philips 11.64 cm powder camera and Cu-K_α radiation. The results, illustrated by those found for the cobalt material and its pure cobalt analogue, are displayed in Table 2.

Table 1. Analytical results for $M_{0.75}Fe_{0.25}Cl_2{\cdot}yH_2O$ (M = Co or Ni; $y = 4$ or 6), freshly prepared and after ageing for three months. Calculated results are also presented in parentheses, using the formulae quoted

		M (%)	Fe (%)	Cl (%)
Fresh	$Co_{0.75}Fe_{0.25}Cl_2{\cdot}4H_2O$	21.80	6.40	35.10
		(21.95)	(6.95)	(35.30)
	$Ni_{0.75}Fe_{0.25}Cl_2{\cdot}4H_2O$	21.75	6.35	35.10
		(21.90)	(6.95)	(35.30)
Aged	$Co_{0.75}Fe_{0.25}Cl_2{\cdot}6H_2O$	18.65	5.80	29.80
		(18.65)	(5.90)	(29.95)
	$Ni_{0.75}Fe_{0.25}Cl_2{\cdot}6H_2O$	18.55	5.85	29.90
		(18.60)	(5.90)	(29.95)

Results and Discussion

The cobalt- and nickel-iron(II) chloride hydrates, containing more than 50% Co or Ni, showed two sites in their Mössbauer spectra (Table 3); one, with quadrupole splitting 1.55 (Co) and 1.61 (Ni) mm s^{-1} at 298 K, was fully discussed previously,[18] and formulated as having a *trans*-octahedral $FeCl_2(OH_2)_4$ origin. The other, splitting 2.58 (Ni) and 2.65 (Co) mm s^{-1} at 298 K, is found to be the only site when the samples are aged for three months at ambient temperature; this site for the Fe–Ni material has a splitting of 2.61(1) mm s^{-1} at 298 K (Figure 1) and 3.20(1) mm s^{-1} at 80 K.

These results are similar to those we have previously reported for the iron–manganese chloride hydrate system (2.63 mm s^{-1} at 298 K, 3.29 mm s^{-1} at 80 K). However, the Fe–Co and Fe–Ni materials which were previously regarded as predominantly isostructural with $FeCl_2{\cdot}4H_2O$, were found to have gained water during ageing. Chemical analysis and *X*-ray crystallography show that they can be formulated as $MCl_2{\cdot}6H_2O$, isostructural with $CoCl_2{\cdot}6H_2O$ (Table 2) while the manganese material remains in the $MCl_2{\cdot}4H_2O$ system.

Thus, materials originally isostructural with $FeCl_2{\cdot}4H_2O$ are finally isostructural with $CoCl_2{\cdot}6H_2O$, and the extra water allows the $FeCl_2(OH_2)_4$ units to sit in a larger hole in the lattice of the cobalt or nickel host. The axially symmetric $CoCl_2{\cdot}6H_2O$ and $FeCl_2{\cdot}4H_2O$ crystals have nearest metal–metal distances of 6.26 and 5.54 Å respectively; although the extra water molecules in the hexahydrates might be expected to modify the hydrogen bonding between the octahedra, it would appear that they are arranged in such a way that no pressure effects are generated in the Fe^{2+} environment. The less regular manganese chloride tetrahydrate crystal structure shows distances of 5.58, 5.78, and 6.17 Å, but the lack of axial symmetry in this *cis*-chloride parent will provide larger holes than indicated by these metal–metal separations. This will allow the iron(II) chloride tetrahydrate octahedra to retain the natural *trans*-chloride configuration previously proposed [18] with less distortion than in the parent $FeCl_2{\cdot}4H_2O$ phase.

The detailed quadrupole splitting *versus* temperature data

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Table 2. *X*-Ray diffraction powder data[a] for the cobalt material after three months

	$CoCl_2{\cdot}6H_2O$			$Co_{0.75}Fe_{0.25}Cl_2{\cdot}6H_2O$		
hkl	$d_{calc.}$[b]/ Å	$d_{obs.}$/ Å	Intensity	Intensity	$d_{obs.}$/ Å	$d_{calc.}$[c]/ Å
001	5.64	5.57	vs	vs	5.69	5.62
110	5.49	5.47	vs	vs	5.59	5.53
$20\bar{1}$	4.970	4.99	m	ms	5.01	5.02
$11\bar{1}$	4.826	4.80	vs	vs	4.87	4.876
020	3.530	3.52	ms	s	3.57	3.570
$31\bar{1}$	3.097	3.11	w	m	3.14	3.126
021	2.993	2.98	m	ms	3.01	3.014
$11\bar{2}$	2.942	2.93	vs	vs	2.96	2.954
002	2.822	2.81	vvw	m	2.82	2.812
220	2.747	2.75	vs	vs	2.78	2.764
310	2.696	2.71	vs	vs	2.74	2.738
$40\bar{1}$	2.548	2.56	ms	s	2.59	2.575
$22\bar{2}$	2.413	2.41	vs	vs	2.44	2.438
$20\bar{3}$ 022	2.207 2.204	2.209	vs	vs	2.222	2.218 2.209
$40\bar{3}$	2.074	2.078	w	m	2.101	2.100
$42\bar{2}$	2.032	2.043	vw	m	2.054	2.057
$11\bar{3}$ $51\bar{2}$	1.996 1.975	1.987	ms	s	2.006	1.998 1.997
202	1.946	1.947	vw	vvw	1.965	1.957
132	1.903	1.903	ms	s	1.924	1.919
$22\bar{3}$	1.871	1.868	m	m	1.890	1.889
040	1.765	1.768	m	m	1.784	1.785
222	1.704	1.710	m	m	1.725	1.720
$20\bar{4}$	1.618	1.616	m	m	1.621	1.622
$24\bar{2}$	1.557	1.556	m	m	1.572	1.574

[a] *d*/Å = interlayer spacing. [b] The $CoCl_2{\cdot}6H_2O$ phase is fitted to the lattice parameters given in ref. 21 (a = 10.34, b = 7.06, c = 6.67 Å, β = 122.20°). [c] This $Co_{0.75}Fe_{0.25}Cl_2{\cdot}6H_2O$ phase is fitted to a cell (a = 10.44, b = 7.14, c = 6.72 Å, β = 123.20°) based on that of $CoCl_2{\cdot}6H_2O$, but as the cell constants and β may be varied to fit these data, this fitting will not necessarily be the best.

Table 3. ^{57}Fe Mössbauer parameters for high-spin iron(II) halides

Compound	*T*/K	δ/mm s^{-1}	Δ/mm s^{-1}	Γ/mm s^{-1}
$Co_{0.75}Fe_{0.25}Cl_2{\cdot}yH_2O$	298	1.21(1) 1.21(1)	1.55(4) 2.65(1)	0.11(1) 0.23(1)
$Ni_{0.75}Fe_{0.25}Cl_2{\cdot}yH_2O$	298	1.188(8) 1.205(2)	1.61(2) 2.58(1)	0.10(1) 0.13(1)
$Co_{0.75}Fe_{0.25}Cl_2{\cdot}6H_2O$ *	298	1.20(2)	2.64(1)	0.23(1)
	80	1.29(2)	3.14(1)	0.23(2)
$Ni_{0.75}Fe_{0.25}Cl_2{\cdot}6H_2O$ *	298	1.20(1)	2.61(1)	0.14(1)
	80	1.33(1)	3.20(1)	0.15(1)

* After three months.

for the manganese phase[18] can be used to give an approximate value for the *d* splittings; since the isomer shift decreases linearly with temperature rise, a structural change is unlikely, and the decrease of quadrupole splitting can be attributed to the population of excited electronic states. Since there are no data below 80 K, a full treatment is impossible, and so a simplified model is used that ignores spin-orbit coupling and treats the covalency as an adjustable parameter. Equation (1)[19] uses the contributions $F_q{}^n$ of the n different d orbitals to the axial field gradient, and $F_\eta{}^n$ to the assymmetry parameter, for orbitals of energy ε_n above the ground state; A is a set of constants that also includes the covalency, and the individual contributions F^n are then multiplied by the Boltzmann contributions and summed.

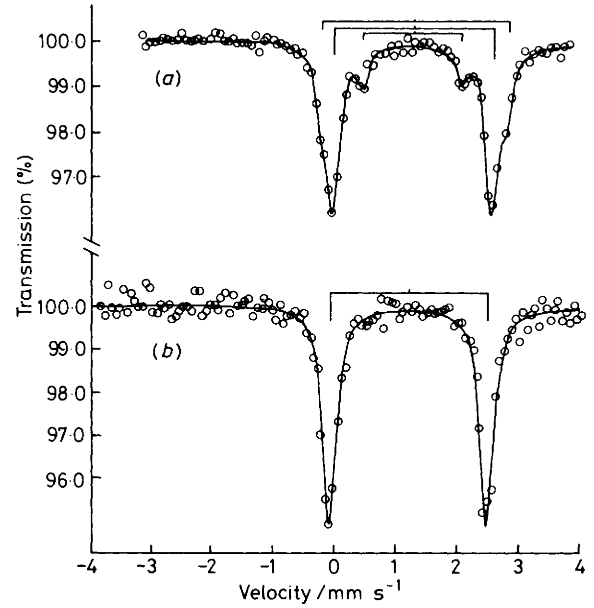

Figure 1. ^{57}Fe Mössbauer spectra of $Ni_{0.75}Fe_{0.25}Cl_2{\cdot}yH_2O$ at 298 K: (*a*) as prepared, sometimes containing the outer doublet derived from $FeCl_2{\cdot}4H_2O$, and (*b*) after ageing for three months, when only a single site spectrum is observed

The exact equation used depends upon the model used; all must have a singlet ground state, but using the $d_{x^2-y^2}$ ground state proposed by Ingalls[19,20] for $FeCl_2{\cdot}4H_2O$ does not give a good fit at higher temperatures (Figure 2, dotted line). A doublet excited state gives a worse fit at all temperatures, and the best model appears to be that obtained with equation (2) for the d_{xy}, d_{yz}, d_{xz} orbital set. This leads to ε_1, the energy of the first higher orbital, = 420±20 cm^{-1} and ε_2, that of the second higher orbital, = 780±80 cm^{-1} as the best fit.

While this crude calculation ignores higher order effects such as mixing of states, it is noticeable that all models lead to a first excited state energy of *ca.* 500 cm^{-1}, which must be compared with the value of 750 cm^{-1} obtained for $FeCl_2{\cdot}4H_2O$,[19] which showed a much smaller temperature dependence.

The 50% iron–cobalt and iron–nickel materials, whose parents are known to contain *trans*-octahedral chlorides,[21,22] must therefore also permit the iron centres to attain a less-distorted environment than found in $FeCl_2{\cdot}4H_2O$, to give the similar values of quadrupole splitting and reduced *d*-orbital separations observed here.

The iron hexahydrate solid phase that was investigated by Deszi *et al.*[22] showed a splitting of 1.7 mm s^{-1} at 93 K; an iron chloride nonahydrate, containing hexa-aquairon(II) ions, was postulated to have a splitting of 3.6 mm s^{-1} at 80 K[23] and was confirmed to be present in frozen solutions at low pH.[24]

$$q(T) = \frac{A[\{\sum_n F_q{}^n \exp(-\varepsilon_n/kT)\}^2 + \frac{1}{3}\{\sum_n F_\eta{}^n \exp(-\varepsilon_n/kT)\}^2]^{\frac{1}{2}}}{\sum_n \exp(-\varepsilon_n/kT)} \quad (1)$$

$$q(T) = \frac{A\{1 + \exp(-2\varepsilon_1/kT) + \exp(-2\varepsilon_2/kT) - \exp(-\varepsilon_1/kT) - \exp(-\varepsilon_2/kT) - \exp[-(\varepsilon_1 + \varepsilon_2)/kT]\}^{\frac{1}{2}}}{1 + \exp(-\varepsilon_1/kT) + \exp(-\varepsilon_2/kT)} \quad (2)$$

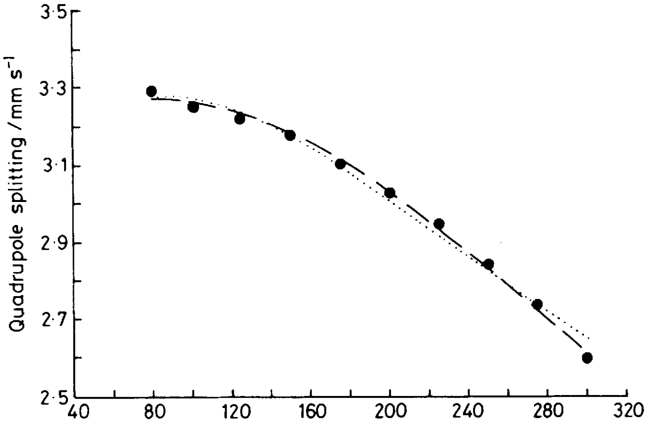

Figure 2. Quadrupole splitting of $Mn_{0.5}Fe_{0.5}Cl_2{\cdot}4H_2O$ as a function of temperature. The data points were reported in ref. 18; the dashed line is the best fit, using orbitals d_{xy} as the ground state, and d_{xz} and d_{yz} as the excited states. The alternative ground state $d_{x^2-y^2}$ found in $FeCl_2{\cdot}4H_2O$ gives the best fit shown by the dotted line, which is a poorer description of the higher temperature values whose spin-orbital coupling will be less important

Thus, the intermediate splitting considered cannot originate from either of these two phases.

The cobalt phase, with longer metal–metal distances, still shows a larger linewidth after ageing, which may be attributed to the presence of local inhomogeneities caused by some subtly altered distortion which must occur. We propose that the manganese tetrahydrate and cobalt and nickel hexahydrate phases provide sufficient room for $FeCl_2(OH_2)_4$ units to exist unstrained by external forces. All these $M_xFe_{1-x}Cl_2{\cdot}yH_2O$ ($x = 0.5$ or 0.75; $y = 4$ or 6) materials revert to the respective $MCl_2{\cdot}yH_2O$ (M = Mn, Co, or Ni) structure but allow the $FeCl_2(OH_2)_4$ octahedra to attain very similar electronic environments that differ from the pure iron phase.

These findings are in keeping with this unstrained iron site being close to a tetragonally distorted octahedron; conversely, packing forces in the parent $FeCl_2{\cdot}4H_2O$ structure cause a rhombic distortion, required to explain the temperature dependence of the quadrupole splitting.[19]

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