Dynamic and Static Lattice Effects in Tetrachloroferrate(II) Salts: their Influence upon Mössbauer Quadrupole Splittings

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Spectroscopic data, particularly ^{57}Fe Mössbauer, and X-ray powder diffraction data are presented for a series of salts $[NR_4]_2[FeCl_4]$ and for doped materials of $[NMe_4]_2[FeCl_4]$ and $[NMe_4]_2[CoCl_4]$ in different ratios. The effect of the cation on the electronic environment of the iron is discussed in terms of direct charge effects and lattice dynamics.

The redox potentials of ferredoxins and high-potential iron proteins depend upon protein structure in ways which are only just beginning to be understood.[1] It is clear that hydrogen bonding is important, but it may also be that the potentials are affected by Coulombic effects from neighbouring positive and negative centres. If such effects are significant, they might also be detectable in Mössbauer spectroscopy. Indeed we have evidence that this is the case.[2] The current work is intended to clarify how charge effects can be detected in Mössbauer spectroscopy. Although it is well recognised that 'lattice effects' are evident in Mössbauer spectra,[3] they have not been adequately rationalized, and are often ignored. There is a mass of physical data to suggest that this is neither correct nor justifiable.[3]

We have recently shown that the ^{57}Fe Mössbauer quadrupole splitting (q.s.) in a series of tetraalkylammonium salts of $[Fe_4S_4(SBu^t)_4]^{2-}$ clusters is cation-dependent.[2] Crystallographic evidence was used to show that increasing the bulk of the alkylammonium cation increases the separation between anionic cluster and cation. This in turn reduces the lattice contribution, q_{latt}, to the q.s., and is observed as an increase in the q.s. with separation between iron and the cationic charge centres.

As part of our ongoing programme to address this question, we are attempting to establish further the nature and extent of such charge effects. One of our approaches has been to investigate simpler chemical systems containing single iron centres and a range of different symmetric and asymmetric cations. We have therefore prepared a series of tetrachloroferrate(II) salts.

There have been a number of investigations of tetrachloroferrate(II) salts,[4–16] some of which have concerned Mössbauer spectroscopy.[4,10–15] In particular, Edwards *et al.*[4] reported the Mössbauer spectra of a series of salts $Y_2[FeX_4]$ (X = halide, Y = quaternary ammonium or phosphonium ion) over a range of temperatures. All the compounds showed large q.s. values at low temperatures, indicating a distortion of the $[FeCl_4]^{2-}$ ion, which had then not previously been revealed by crystallographic studies.[4] Subsequent structural studies have shown distortion of $[FeCl_4]^{2-}$ caused by interactions with the surrounding cations. These distortions were ascribed to hydrogen bonding and direct dipolar interactions.[6,7] Changes in Mössbauer parameters with cations were observed, most evident in the temperature-dependence of the q.s. For large cations, Edwards *et al.*[4] explained the dependence in terms of a static crystal-field distortion. For the tetramethylammonium salt such a simple model failed to rationalise the data. Gibb *et al.*[10] subsequently proposed a dynamic lattice model involving vibronic admixing. This was later supported by Srivastava and Choudhary's[11] calculations on Gibb's original data and by further work of their own.[12,13]

Table 1 Iron-57 Mössbauer parameters* of $[NPr^n{}_4]_2[FeCl_4]$

T/K	i.s./mm s^{-1}	q.s./mm s^{-1}	$\Gamma_{\frac{1}{2}}$/mm s^{-1}
80	1.05	3.00	0.17
110	1.03	2.84	0.17
130	1.03	2.77	0.18
150	1.03	2.62	0.17
180	0.99	2.30	0.19
200	0.98	2.18	0.20
220	0.98	2.08	0.20
250	0.96	1.82	0.18
270	0.96	1.70	0.24
290	0.93	1.61	0.20

* Parameters are quoted within an error of ± 0.01 mm s^{-1}. I.s. = isomer shift, $\Gamma_{\frac{1}{2}}$ = half-width.

Here we report data for a series of $[FeCl_4]^{2-}$ salts, and also doped materials containing $[FeCl_4]^{2-}$ and $[CoCl_4]^{2-}$ in various ratios, and discuss the results and implications for such systems.

Results and Discussion

Temperature-dependence of the q.s. in $[FeCl_4]^{2-}$.—Table 1 shows the Mössbauer parameters of $[NPr^n{}_4]_2[FeCl_4]$ at various temperatures. The q.s. (Table 1) decreases linearly (correlation coefficient 0.99 for 10 data points) from 3.00 mm s^{-1} at 80 K to 1.61 mm s^{-1} at room temperature. There is no evidence to support any phase change, though one was observed for the tetramethylammonium salt at 239 K.[10]

Edwards *et al.*[4] realised that the temperature-dependence of the q.s. for $[NMe_4]_2[FeCl_4]$ could not be explained by a temperature-independent ligand field. For a static model the q.s. is defined as in equation (1), where $\Delta E_Q(T)$ and $\Delta E_Q(0)$ are the

$$\Delta E_Q(T) = \Delta E_Q(0)\tanh(\Delta/2kT) + \Delta E_{Q(latt)} \qquad (1)$$

Table 2 Iron-57 Mössbauer parameters of salts $Y_2[FeCl_4]$

Compound	Y	2 × Molecular mass of Y	T/K	i.s./mm s^{-1} [a]	q.s./mm s^{-1} [a]	Change in q.s./mm s^{-1}
1	$[NMe_4]^+$	148	80 (293)	1.05 (0.95)	2.68 (0.73)	1.95
2	$[NEt_4]^+$	260	80 (293)	1.06 (0.88)	2.62 (0.98)	1.64
3	$[NPr^n{}_4]^+$	372	80 (293)	1.06 (0.96)	3.00 (1.61)	1.39
4	$[NBu^n{}_4]^{+b}$	484	80 (293)	1.04 (—)	2.91 (—)	—
5	$[N(n\text{-}C_5H_{11})_4]^{+b}$	570	80 (293)	1.04 (—)	2.91 (—)	—
6	$[NMe_3(CH_2Ph)]^+$	300	80 (293)	1.04 (0.95)	2.95 (2.19)	0.76
7	$[NEt_3(CH_2Ph)]^+$	384	80 (293)	1.05 (0.93)	3.07 (2.35)	0.72
8	$[NMe_3\{(CH_2)_{18}Ph\}]^+$	776	80 (293)	1.06 (—)	2.77 (—)	—
9	$[C_5H_7S_2]^+$	262	80 (293)	1.03 (0.95)	2.92 (1.51)	1.41
10	$[C_{10}H_9S_2]^+$	386	80 (293)	1.03 (0.95)	2.91 (1.42)	1.49
11	dmbipy/2[c]	186	77 (293)	1.00 (0.88)	2.99 (2.51)	0.48

[a] Values are quoted within an error of ±0.01 mm s^{-1}. [b] Non-Lorentzian line shape. [c] dmbipy = *N,N′*-Dimethyl-4,4′-bipyridine.

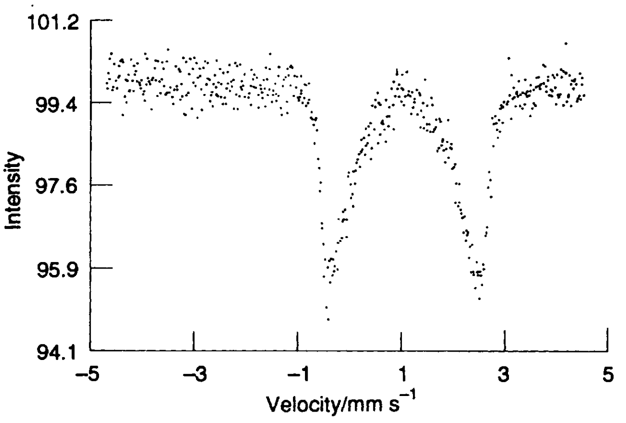

Fig. 1 Mössbauer spectrum of $[N(n\text{-}C_5H_{11})_4]_2[FeCl_4]$ **5** at 80 K

values of the q.s. at temperatures T and at zero, respectively, Δ is the subsidiary crystal-field splitting between the $d_{x^2-y^2}$ and d_{z^2} orbitals, and $\Delta E_{Q(latt)}$ is the q.s. arising from charges on the ligands and distant atoms. The relationship between ΔE_Q and T is non-linear and differs from the data for either the tetramethylammonium or the tetrapropylammonium salt. With subsequent knowledge of the phase change, Gibb *et al.*[10] used a two-phase crystal-field model to analyse the data, but this was also inadequate. They then suggested[10] the vibronic admixture of the $3d_{x^2-y^2}$ and $3d_{z^2}$ levels. This is possible when lattice vibrations of the correct symmetry are present. In the case of tetrahedral high-spin Fe^{II}, these should be of the E representation to allow admixture, the effect of which would be a reduction of the quadrupole splitting by a factor A.* Srivastava and Choudhary re-examined the data showing the linear decrease of the q.s. over the temperature range 87–237.5 K using a temperature-dependent mixing of the d_{z^2} and $d_{x^2-y^2}$ levels through interactions with lattice phonons. Good agreement was found between theory and experiment, suggesting the importance of lattice dynamics in this system. Above 239 K phase changes were observed, negating any further theoretical treatment of the data.

The introduction of orbit–lattice interaction allows the linear temperature-dependence of the q.s. to be explained. Our data for $[NPr^n{}_4]_2[FeCl_4]$ are linear over the entire temperature range investigated, suggesting that a similar dynamic lattice effect operates. The essential difference between our system and the tetramethylammonium salt lies in the difference in 'bulk' of the cations. This can be thought of as change in volume, but in this instance is perhaps best considered as a change in mass. An increase in temperature is expected to increase the vibronic interaction causing a decrease in the q.s. Implicit in the increased temperature is an increase in vibrational frequency. In this way an increase in mass (as in Me→Pr) would be expected to show the same effect upon q.s. as a decrease in temperature. This would account for the data for $[NPr^n{}_4]_2[FeCl_4]$. With these concepts in mind, a range of salts was prepared which contained cations of different masses and symmetries.

Mössbauer Spectroscopic Data.—Table 2 presents Mössbauer spectroscopic data at 80 K and room temperature and also lists the cationic masses. The isomer shift values show little variation, ranging from 0.88 to 0.96 mm s^{-1} at room temperature and 1.00 to 1.06 mm s^{-1} at 80 K. All the compounds display large q.s. values at 80 K (> 2.5 mm s^{-1}) but the effect of temperature on the q.s. of the salts differs markedly. For instance, large decreases in q.s. were observed for salts **1**–**3**, **9** and **10**; comparatively small changes were seen for **6**, **7** and **11**, and collapse of the recoil-free fraction was observed for **4**, **5** and **8**.

Compounds **4**, **5** and **8** all contain large cations with 'floppy' alkyl groups. The cations in **4** and **5** are unlikely to approximate to spheres in the crystals. The alkyl chains in these cations, each four or five carbon atoms long, will have several conformations of similar energy, not necessarily symmetrical. Compound **8** will also have cations containing differing conformations, depending on the way the C_{18} chain folds. Thus all these complexes are unlikely to form highly ordered compounds and hence poor Mössbauer recoil-free fractions would be expected.

Fig. 1 shows the spectrum of **5** at 80 K. It is apparent that the absorption line shape is non-Lorentzian, and this suggests that a number of different iron electronic environments are present. Similar line shapes were observed for **4**. These observations are supported by X-ray powder diffraction data at 298 K. For **4** and **5** broad bands in the powder diffraction patterns suggest that these compounds are amorphous. Thus the $[FeCl_4]^{2-}$ ions will be in a variety of environments and cationic fields and a range of q.s. values would be expected. Because of the amorphous nature with little long-range order, it is unsurprising that these derivatives do not exhibit room temperature Mössbauer spectra. In contrast, **1** and **2** (which were shown to be isostructural, Table 3) are highly crystalline, whereas compound **3** appears intermediate between these two extremes.

The data for compounds **4** and **5** show that it would not be fruitful to extend the series of compounds to longer chain homoleptic tetraalkylammonium salts, so we examined some heteroleptic cations to uncover other lattice effects.

Although lattice dynamics successfully describe the temperature-dependence of the q.s. for compounds **1**–**3**, the change in the absolute q.s. values between these compounds at 80 K is also important. Compounds **3**–**7** and **9**–**11** all have q.s. values within the range 2.91–3.07 mm s^{-1}. This suggests that in the presence of

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* $A = (2\cos^2\theta - 1)$, where $\cos\theta$ is the mixing coefficient of $3d_{x^2-y^2}$ and $3d_{z^2}$, as defined by Gibb *et al.*[10]

Table 3 X-Ray powder diffraction data for the compounds $[NR_4]_2[FeCl_4]$ (R = Me or Et)

$[NMe_4]_2[FeCl_4]$[a]				$[NEt_4]_2[FeCl_4]$[b]		
Intensity[c]	d_{obs}/Å	d_{calc}/Å	*hkl*	d_{obs}/Å	d_{calc}/Å	Intensity
ms	7.87	7.81	011	7.96	7.90	vs
vs	6.64	6.60	111			
vw	6.20	6.16	200			
			012			
			201	5.88	5.95	m
vw	5.34	5.32	112			
m	4.86	4.83	202	4.94	4.98	s
vs	4.53	4.52	020	4.57	4.57	ms
vvw	4.10	4.09	121			
s	3.99	3.97	203			
m	3.91	3.91	022	3.95	3.95	m
vvw	3.73	3.74	310			
		3.72	122			
mw	3.65	3.64	220			
			014	3.60	3.61	m
vw	3.56	3.55	221			
vw	3.45	3.43	114			
w	3.31	3.30	222	3.39	3.37	vs
vvw	3.23	3.22	303			
			400	3.22	3.22	w
			401	3.27	3.15	w
			214			
vvw	3.03	3.03	313			
vvw	2.99	2.98	223			
vvw	2.87	2.87	131			
			124			
			115			
vvw	2.79	2.78	205	2.82	2.82	vw
vvw	2.75	2.74	132			
vvw	2.63	2.62	323			
vvw	2.55	2.55	232			
			133			
			305	2.52	2.53	vw
			422	2.49	2.49	vw
			404			
			315	2.44	2.44	v
			233			
vvw	2.36	2.37	225			
			134	2.37	2.37	vw
			332			
			040	2.29	2.28	vw
			026	2.27	2.27	vw
vvw	2.26	2.26	164			
			234	2.25	2.25	vw
			140			
			405			
			521	2.21	2.22	vw
			325			
			430			
			107			
			415	2.18	2.18	vw
			017			
w	2.17	2.17	165			
			164			
	2.13	2.13	135			
			431			
			424			
			415			
vvw	2.08	2.08	522			
vvw	2.03	2.03	604			
			514			
			406	2.03	2.03	vvw

[a] $a = 12.31, b = 9.03, c = 15.58$ Å. [b] $a = 12.87, b = 9.14, c = 15.70$ Å. [c] s = strong, m = medium, w = weak, v = very.

large cations the lattice contribution to the field gradient is small and the q.s. is maximal. As the cations get closer to the anions in compounds **1** and **2** the lattice contribution increases and the q.s. decreases.

Compounds **9** and **10** are known[5,7] to have strong interactions between the S atoms in the cations and at least one Cl atom in the anion. This interaction, said to be responsible for 'charge-transfer pathways', is direct evidence for cationic charge influencing the structure (geometric and electronic) of the anion. We suggest that where these charge effects dominate, the temperature-dependence of q.s. deviates from a pure vibronic relationship [in the case of compound **9** the Cl··· S separations range between 3.268(2) and 3.377(2) Å].

Compounds **6** and **7** display the least temperature-dependent q.s. This can be explained in two ways. First, perhaps it reflects the inability of highly asymmetric cations to produce symmetrically correct lattice phonons for mixing of the $d_{x^2-y^2}$, d_{z^2} orbitals, as postulated by Gibb *et al.*[10] Secondly, it may simply be due to the contribution from the asymmetrical cationic field that must result in the lattice by the inclusion of these ions.

The Mössbauer parameters for compound **2** are similar to those of Edwards *et al.*[4] and are quoted here for completeness. In fact, the data can be fitted in a different way and this, with a more detailed structural investigation of the compound, will be reported later.

Doped Materials.—In an attempt to eliminate the effect of vibronic admixture from consideration of charge on the iron tetrahedral complexes, some doping experiments were undertaken involving replacement of Fe by Co in different ratios. The salts $[NMe_4]_2[FeCl_4]$[9] and $[NMe_4]_2[CoCl_4]$[5] are isostructural and isomorphous in the orthorhombic space group *Pnma* (no. 62). The cell parameters for $[NMe_4]_2[FeCl_4]$ are $a = 12.312(2), b = 9.033(2), c = 15.580(3)$ Å, and for $[NMe_4]_2[CoCl_4]$ $a = 12.276(1)$, $b = 9.001(1)$, $c = 15.539(2)$ Å. By increasing the extent to which $[FeCl_4]^{2-}$ is replaced by $[CoCl_4]^{2-}$ a decrease in cell volume should occur and is shown by the X-ray powder diffraction data obtained at 298 K (Table 4).

Mössbauer parameters for the mixed crystals are shown in Table 5. At 80 K a decrease in q.s. from 2.68 to 2.30 mm s^{-1} is seen, with a less marked decrease in the 298 K q.s. values, from 0.73 to 0.70 mm s^{-1}, with increasing cobalt concentration. Increasing cobalt concentration leads to a decrease in cell volume. The effect of this may be to decrease the cation–anion distance, causing a change in the lattice contribution to the q.s. (*i.e.* a charge effect) or to distort the $[FeCl_4]^{2-}$ tetrahedra, which would also affect the Mössbauer parameters. Structural evidence from X-ray powder diffraction shows that the materials are similar and thus evidence for distortion is weak. We interpret the change in the Mössbauer parameters as evidence of a change in the charge effect on the lattice contribution to the q.s.

The most interesting finding is that there is such a difference in the q.s. ranges at 80 and at 298 K. Of course it is possible that at low temperatures the compounds are in different crystal phases, although they are in the same crystal phase at room temperature. If we assume that the compounds are isostructural and isomorphous at both temperatures then we can exclude differences from different vibronic effects because the anion average mass only changes by 0.004% between these doped materials. Hence the q.s. differences must be due to charge effects arising from the closer approach of the anions and cations. The individual angles and distortions of the metal tetrahedra of $[NMe_4]_2[MCl_4]$ (M = Co, Ni or Zn)[5] and $[NMe_4]_2[FeCl_4]$[9] are essentially similar. Interestingly the

Table 4 X-Ray powder diffraction data for the compounds $[NMe_4]_2[Co_xFe_{1-x}Cl_4]$ (x = 0 **1**, 0.25 **12**, 0.50 **13**, 0.75 **14**, 1.00 **15**)

		d_{obs}/Å				
Intensity	*hkl*	**1**	**12**	**13**	**14**	**15**
m	011	7.87	7.91	7.91	7.91	7.74
vs	111	6.64	6.69	6.63	6.67	6.61
s	102	—	—	—	—	6.55
vw	200	6.20	6.25	6.18	6.21	6.18
vw	112	5.34	5.39	5.32	5.39	—
m	202	4.86	4.90	4.84	4.87	4.82
	211					
vs	020	4.53	4.56	4.51	4.54	4.50
vvw	300	4.13	—	—	—	—
vvw	121	4.10	—	—	—	—
s	203	3.99	4.01	3.97	4.00	3.97
m	301	3.91	3.93	3.91	3.92	3.90
vw	022	3.73	—	—	—	—
mw	122	3.65	3.66	3.64	3.66	3.64
	310					
vw	221	3.56	3.57	3.54	3.56	3.54
vw	114	3.45	3.46	—	3.45	3.42
vvw	303	3.23	—	—	—	3.21
vvw	313	3.03	3.05	3.01	3.04	—
vvw	223	2.99	—	—	—	—
vvw	131	2.88	—	2.88	2.89	2.87
	124					
	115					
vvw	205	2.79	—	—	—	—
vvw	132	2.75	—	—	—	2.73
vvw	323	2.63	—	2.62	2.64	—
vvw	232	2.55	2.56	2.55	2.56	2.54
	133					
vvw	225	2.36	—	2.35	2.36	—
vvw	164	2.26	2.27	2.28	2.26	2.25
w	165	2.17	2.18	2.17	2.15	—
	164					
vvw	135	2.13	2.14	2.13	—	2.13
	431					
	424					
	415					
vvw	522	2.09	—	2.08	2.09	2.08
	504					
	601	2.03	2.01	—	—	2.03
	514					

Table 5 Mössbauer parameters* of doped materials containing $[FeCl_4]^{2-}$ and $[CoCl_4]^{2-}$, cation = $[NMe_4]^+$

Co:Fe	*T*/K	i.s./mm s^{-1}	q.s./mm s^{-1}	$\Gamma_{\frac{1}{2}}$/mm s^{-1}
1:3	80	1.02	2.60	0.20
	293	0.94	0.72	0.24
1:1	80	1.03	2.50	0.18
	293	0.94	0.71	0.22
3:1	80	1.05	2.30	0.22
	293	0.93	0.70	0.24

* Parameters are quoted within an error of ± 0.01 mm s^{-1}.

Table 6 Elemental analyses (%)* for salts $Y_2[FeCl_4]$

Y	C	H	N
$[NMe_4]^+$	27.8 (27.6)	6.9 (7.0)	8.1 (8.0)
$[NEt_4]^+$	41.9 (41.8)	8.7 (8.9)	6.1 (6.0)
$[NPr^n{}_4]^+$	50.5 (49.7)	9.8 (9.8)	4.9 (4.7)
$[NBu^n{}_4]^+$	56.3 (56.1)	10.6 (10.8)	4.1 (3.9)
$[N(n\text{-}C_5H_{11})_4]^+$	60.5 (60.4)	11.1 (11.5)	3.5 (3.5)
$[NMe_3(CH_2Ph)]^+$	48.2 (48.4)	6.4 (6.6)	5.6 (5.6)
$[NEt_3(CH_2Ph)]^+$	53.6 (53.4)	7.6 (7.6)	4.8 (4.6)

* Calculated values in parentheses.

bond lengths and angles for the $[NMe_4]^+$ cations in these structures are less accurate, probably due to 'large vibrational effects or possible rotational disorder of the tetrahedra'.[9,11]

The anion structures are said to distort by crystal-packing forces[5,9] and not by Jahn–Teller effects. This requires some clarification. The packing forces operating are obviously those of attraction between anion and cation, and repulsions, anion–anion and cation–cation. Other interactions, such as van der Waals' interactions, will be of very minor significance. The vibronic effect is therefore significant for a given compound over a range of temperatures only when packing forces do not change dramatically (*i.e.* there is no phase change).

In the case of the doped materials studied, the packing forces change with iron content but in any given material are constant. Thus materials such as $[NMe_4]_2[Co_xFe_{1-x}Cl_4]$ (x = 0.5 or 0.25) have different absolute q.s. values at any given temperature due to the different packing forces (different distances between charged ions). However, the temperature-dependence of their q.s. data can be explained by a vibronic model.

Table 7 Elemental analyses (%)* for doped materials containing $[FeCl_4]^{2-}$ and $[CoCl_4]^{2-}$

Co:Fe	C	H	N	Co	Fe
1:3	27.6 (28.3)	6.9 (7.1)	8.1 (8.2)	4.3 (3.5)	12.1 (10.0)
1:1	27.6 (28.1)	6.9 (7.2)	8.1 (8.2)	8.5 (7.1)	8.1 (7.0)
3:1	27.6 (27.8)	6.9 (7.1)	8.1 (7.9)	12.7 (11.5)	4.0 (3.7)

* Calculated values in parentheses. Analyses were calculated for Co:Fe ratios of 1.0:3.0, 1.0:1.0 and 3.0:1.0; actual values were 1.0:3.0, 1.0:1.0 and 2.9:1.0.

Conclusion

A consideration of both vibronic interactions and cationic charge effects in a wide range of $[FeCl_4]^{2-}$ salts has allowed the Mössbauer data to be rationalized. Generally increasing cationic mass produces less temperature-dependent q.s. values. Highly symmetric cations appear to produce more temperature-dependent systems. Finally, charge effects on the q.s. appear to depend on cation size (the smaller the cation, the closer it can approach the anion and the larger the effect). The results are precisely what one would predict from the rapid decrease of a Coulombic field from the charge centre producing it.

Experimental

Elemental analyses were obtained from Medac Ltd., Brunel University, Middlesex, and Mr. C. J. Macdonald, AFRC IPSR NFL. All manipulations were performed under pure dinitrogen, and solvents were dried and degassed prior to use. The dithiolium compounds were prepared by Dr. B. W. F. Fitzsimmons and Mr. J. Higgs, University of Essex, using published procedures.[16]

Mössbauer data were recorded and fitted as described previously.[17] Mössbauer chemical shifts are referred to a natural iron foil at 298 K. X-Ray powder diffraction data were obtained with Cu-Kα radiation and with a Phillips 1710 diffractometer.

Preparation of $[NR_4]_2[FeCl_4]$.—These compounds were prepared by dissolving a 2:1 molar ratio mixture of quaternary alkylammonium chloride with anhydrous iron(II) chloride in absolute ethanol. Products were filtered off, washed with diethyl ether and dried under vacuum. In all cases a white powder was obtained in yields of 80–90%. Table 6 presents the elemental analyses for the compounds.

Preparation of Doped Materials containing $[NMe_4]_2[CoCl_4]$ *and* $[NMe_4]_2[FeCl_4]$.—The appropriate molar quantities of iron(II) chloride and cobalt(II) chloride were dissolved in absolute ethanol. To this was added the required molar quantity of $[NMe_4]Cl$ in absolute ethanol. The resulting pale blue precipitates were filtered off, washed with diethyl ether and dried under vacuum. Table 7 presents elemental analyses for the mixed crystals.

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