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Investigations on Fe(II)-Solvates with N,N-Dimethylformamide and N,N-Dimethylthioformamide

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XPS electron binding energies, ^{57}Fe Mössbauer parameters, and magnetic properties of solvates of Fe(II)-chloride -bromide, -iodide and -perchlorate with N,N-dimethylformamide (DMF) and N,N-dimethylthioformamide (DMTF) are reported. The crystal structure of both perchlorate complexes are given and the bond lengths are discussed in connection with the bond length variation rules. $Fe(DMF)_6(ClO_4)_2$ shows a two doublet Mössbauer spectrum with a temperature-dependent relative intensity ratio which, in accordance with the results of the X-ray diffraction experiments, is interpreted by highly rotary mobilities of the perchlorate ions. The Fe(2p) and Fe(3p) binding energies were found to be intimately correlated with the observed Mössbauer isomer shifts.

Introduction

The donor properties of N,N-dimethylformamide (DMF) and N,N-dimethylthioformamide (DMTF) towards Fe(II) ions have been described previously [1]. DMF and DMTF differ with regard to their coordinating atoms, which are in the complexes with Fe(II)chloride, -bromide, -iodide, and -perchlorate the oxygen and sulfur atoms, respectively.

The influence of the ligands DMF and DMTF as well as of the anions Cl^-, Br^-, I^-, and ClO_4^- on the electron charge density at the nuclear sites of Fe can be studied by observing the isomer shift of the Mössbauer spectra. Furthermore, information concerning the symmetry of the local environment of the Mössbauer atom can be obtained from studies of the quadrupole interaction [2]. Results from Mössbauer as well as from electronic absorption spectroscopy [1, 3] revealed octahedral symmetry for the perchlorate complexes. More detailed information can be expected from X-ray diffraction studies on single crystals.

In the case of $Fe(DMF)_6(ClO_4)_2$ Mössbauer experiments yielded a two doublet spectrum, the intensity ratio of the two components depending upon the temperature [3] which may be attributed to two different local symmetries at the iron sites. Similar results were already obtained by Deszi *et al.* [4] for $Fe(H_2O)_6(ClO_4)_2$ and by Latorre *et al.* [5] for Fe(N,N-dicyclohexylthiourea)$_6$(ClO_4)$_2$. Several series of Mössbauer experiments, where finally an external magnetic field was applied, led to the conclusion that a sign reversal of the electric field gradient (EFG) causes the change of the hyperfine pattern.

In order to obtain further information on structural aspects and charge distribution with respect to the effects by the oxygen and sulfur donor atoms respectively, results from the following investigations are reported here: ^{57}Fe Mössbauer spectroscopy, X-ray photoelectron spectroscopy (XPS), and magnetic measurements for all compounds under observation. Additionally X-ray diffraction experiments down to T = 130 K are reported in the case of the perchlorate complexes.

Since XPS-electron binding energies are related to the screening of the nuclear charge and the Mössbauer isomer shift is a function of the electron

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charge density at the nucleus, possible correlations [6] between XPS-electron binding energies and Mössbauer isomer shifts were studied.

Experimental

The preparation of the complexes Fe(DMF)$_6$-(ClO$_4$)$_2$, Fe(DMTF)$_6$(ClO$_4$)$_2$, Fe(DMF)$_2$Cl$_2$, Fe-(DMTF)$_2$Cl$_2$, Fe(DMF)Br$_2$, Fe(DMTF)$_2$Br$_2$, Fe(DMF)$_3$I$_2$ has been described previously [1]. Fresh samples of the compounds were used for the investigations.

The X-ray diffraction investigations were performed on single crystals with a diameter of about 0.17 mm, using a Philips Four Circle single Crystal Diffractometer PW 1100 with graphite monochromated Mo-Kα radiation. For the low temperature experiments a gaseous nitrogen flow cryostat was used. The minimum temperature which could be achieved was 130 K.

For the Mössbauer experiments a conventional constant acceleration type spectrometer, covering a temperature range from liquid helium to room temperature, was available. The source used was ^{57}Co diffused into a rhodium matrix with approximately 20 mCi (supplied by the Radiochemical Centre, Amersham). The data were analysed by applying a least squares fit procedure assuming a superposition of Lorentzian lines [7]. The isomer shift values reported are given relative to the standard reference material sodium nitroprusside. The experimental error for all the hyperfine parameters deduced from Mössbauer spectra was ±0.01 mm/s.

The XPS-experiments were carried out with a GCA McPherson ESCA 50 photo electron spectrometer using a Mg-Kα source (1253.6 eV). Because of the high sublimation rate of the compounds in a vacuum a special sample holder was used, constructed to hold the sample at liquid nitrogen temperature [8].

The magnetic measurements were performed with an extraction magnetometer in fields up to 72 kOe and at temperatures from 4.2 K to 120 K.

Results

Crystal Structure of the Perchlorate Complexes

Both Fe(DMF)$_6$(ClO$_4$)$_2$ and Fe(DMTF)$_6$(ClO$_4$)$_2$ were found to be of monoclinic symmetry. The lattice parameters are given in Table I.

The unit cell of the DMF-compound was found to contain four formula units and one of the DMTF-compounds two. Intensity data were collected using $\theta/2\theta$ scans up to $\theta = 25°$. Of 6074 unique reflections for the DMF compound and 3207 for the DMTF compound, 1434 and 1069 respectively had $I \geqslant 2\sigma(I)$ and were considered as significant for the following treatment. Lorentz and polarisation corrections were applied; because of the small absorption coefficient ($\mu R = 0.08$) no corrections were made for absorption. Systematic absences indicated space groups $P2_1/b$ and $P2_1/n$, respectively. The refinement of both structures lead to final values of R_F ($R_F = (\Sigma|F_0 - |F_c||)/\Sigma F_0$) of about 0.10, due to rather high temperature coefficients.

TABLE I. Parameters of the Elementary Cell of Fe(DMF)$_6$-(ClO$_4$)$_2$ and Fe(DMTF)$_6$(ClO$_4$)$_2$.

	Fe(DMF)$_6$(ClO$_4$)$_2$	Fe(DMTF)$_6$(ClO$_4$)$_2$
a	1482.5(1) pm	1261.6(2) pm
b	2094.1(5) pm	1957.7(7) pm
c	1107.5(1) pm	744.1(1) pm
γ	91.64(1)°	95.79(2)°

In Fe(DMF)$_6$(ClO$_4$)$_2$ Fe(II)-ions occupy the special positions 0 0 0 and ½ 0 0 and are octahedrally surrounded by the DMF molecules. The ClO$_4^-$-ions are found in the remaining spaces (Fig. 1). The mean value for the Fe–O distances is 213 pm, which is an good agreement with values obtained for similar compounds [9–11]. O–Fe–O angles are 180° and between 85° and 95° respectively, since Fe(II)-ions occupy inversion centres. The average Cl–O distances are 135 pm and somewhat shorter than given in the literature for similar compounds (144 pm). At room temperature the oxygen atoms in the perchlorate tetrahedrons cannot be located strictly. The uncertainty of their positions decreases markedly when lowering the temperature. This suggests increasing mobilities of the oxygen atoms with increasing temperature (perchlorate rotation).

The structure of Fe(DMTF)$_6$(ClO$_4$)$_2$ is similar (Fig. 2). The Fe(II)-ions occupy the special position

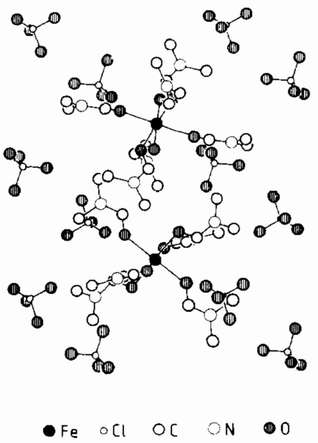


Fig. 1. Crystal structure of Fe(DMF)$_6$(ClO$_4$)$_2$.

TABLE II. Hyperfine Parameters Deduced from the Mössbauer Spectra.

Substance	T [K] ± 0.2	ΔE_Q[a] [mm/s] ± 0.01	IS[b] [mm/s] ± 0.01	Γ [mm/s] ± 0.01
$Fe(DMF)_2Cl_2$	80	3.20	1.32	0.18
	4.2	3.36	1.56	0.16
$Fe(DMF)Br_2$	80	3.15	1.48	0.17
	4.2	3.28	1.55	0.16
$Fe(DMF)_3I_2$	80	3.77	0.91	0.25
$Fe(DMTF)_2Cl_2$	80	3.11	1.20	0.16
	4.2	3.14	1.27	0.14
$Fe(DMTF)_2Br_2$	80	3.24	1.14	0.14
	4.2	3.31	1.22	0.12
$Fe(DMTF)_2I_2$	80	3.45	1.13	0.17
$Fe(DMTF)_6(ClO_4)_2$	80	3.33	1.26	0.17
	4.2	3.39	1.46	0.16

$Fe(DMF)_6(ClO_4)_2$

T [K] ± 0.2	ΔE_{Q1} [mm/s] ± 0.01	ΔE_{Q2} [mm/s] ± 0.01	IS_1 [mm/s] ± 0.01	IS_2 [mm/s] ± 0.01	Γ [mm/s] ± 0.01	I_1/I_2[c]
200	1.47	1.12	1.55	1.56	0.12	0.562
120	1.77	1.42	1.59	1.60	0.12	0.724
80	2.17	1.64	1.60	1.62	0.12	0.786
50	2.50	1.84	1.61	1.63	0.12	0.923
4.2	2.56	2.02	1.61	1.63	0.12	1.000

[a] ΔE_Q: quadrupole splitting. [b] IS: isomer shift rel. sodiumnitroprusside. [c] I_1/I_2: intensity ratio of the two doublets.

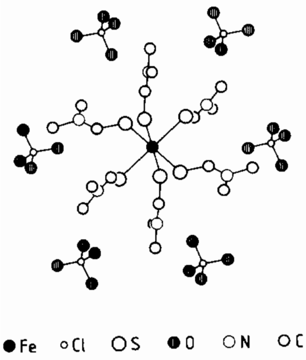


Fig. 2. Crystal structure of $Fe(DMTF)_6(ClO_4)_2$.

0 0 0 on inversion centres and they are octahedrally surrounded by the sulfur atoms of the DMTF ligands. The mean value of Fe–S distances is 254 pm, the S–Fe–S angles are 180° and between 86° and 94° respectively. The mean value of the Cl–O distances is 141.3 pm, which is close to the value found in DMF adducts with diacetoxy-2,4,6-trinitro,2,4,6-triazaheptane and NaI [10, 12]. The uncertainty of the position of the perchlorate oxygen atoms in this compound is distinctly smaller than in the DMF compound, indicating no rotation of the perchlorate group in $Fe(DMTF)_6(ClO_4)_2$.

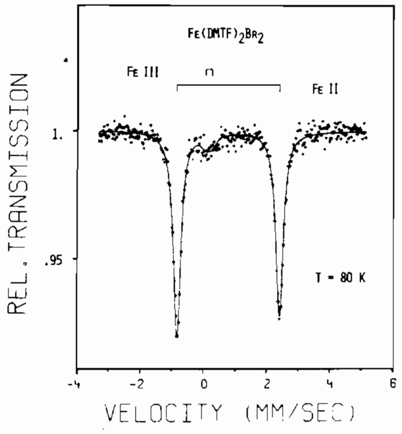


Fig. 3. Mössbauer spectrum of $Fe(DMTF)_2Br_2$ recorded at T = 80 K; +++ = experimental points, solid line = computer fit described in the text. The bars on top of the spectrum indicate the line positions.

Mössbauer Spectra

With the exception of $Fe(DMF)_6(ClO_4)_2$, quadrupole split doublets were obtained for the temperature range under investigation. Sometimes an unequal line intensity was found indicating a certain degree of preferred orientation of the crystallites in the absorber. In some cases small amounts (less than

TABLE III. Electron Binding Energies (eV) from the XPS Studies.

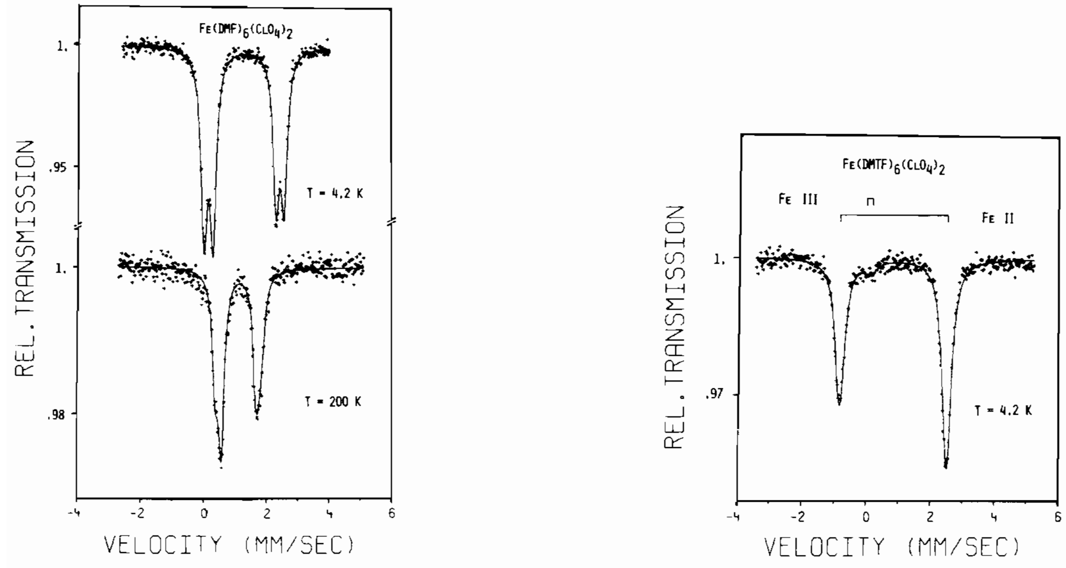
	Fe		Halogen		N	O	C
	2p	3p			1s	1s	1s
$Fe(DMTF)_6(ClO_4)_2$	713.1	52.1	2s 273.6	2p 197.8	399.6	529.9	283.6
$Fe(DMF)_6(ClO_4)_2$	716.6	55.7	2s 268.9	2p 198.1	399.1		283.4
$Fe(DMTF)_2Cl_2$	708.4	55.4	2s 273.4	2p 198.1	399.1		283.4
$Fe(DMF)_2Cl_2$	709.5	56.5	2s 268.9	2p 198.5	399.0	529.7	284.1
$Fe(DMTF)_2Br_2$	707.3	54.4	3d 70.2	3p 482.6	399.3		285.2
$Fe(DMF)_2Br_2$	713.8	59.1	3d 70.9	3p 483.5	399.1	530.2	285.5
$Fe(DMTF)_2I_2$	703.9	50.2	3d 615.7	4d 55.6	399.4		282.9

2%) of Fe(III) were observed which could be distinguished spectrally from Fe(II) because of small quadrupole splitting and more negative isomer shift. As a typical example the spectrum of $Fe(DMTF)_2Br_2$ is shown in Fig. 3.

The hyperfine parameters deduced from the spectra by applying the fitting procedure described above are given in Table II.

The observed shift of the total spectrum with temperature is attributed to the average square velocity of the oscillating atoms, *i.e.* to the second order Doppler effect as well as to the lattice contraction by lowering the temperature. The quadrupole splitting generally was found to be only weakly temperature-dependent: the 4.2 K values never exceed the 80 K values by more than 2%. The DMF complexes exhibit a slightly higher quadrupole splitting and a more positive isomer shift compared to those of the DMTF complexes. Within one ligand-series the quadrupole splitting increases from Cl^- to I^-. The isomer shift increases from Cl^- to I^- in the DMF complexes, whereas it decreases in the same sequence in the DMTF complexes.

The Mössbauer spectra of $Fe(DMF)_6(ClO_4)_2$ exhibit a four line pattern (two quadrupole doublets showing a relatively low splitting), with a temper-



(a)

(b)

Fig. 4. a) Mössbauer spectrum of $Fe(DMF)_6(ClO_4)_2$ recorded at 4.2 K (upper) and at 200 K (lower); b) Mössbauer spectrum of $Fe(DMTF)_6(ClO_4)_2$ recorded at 4.2 K.

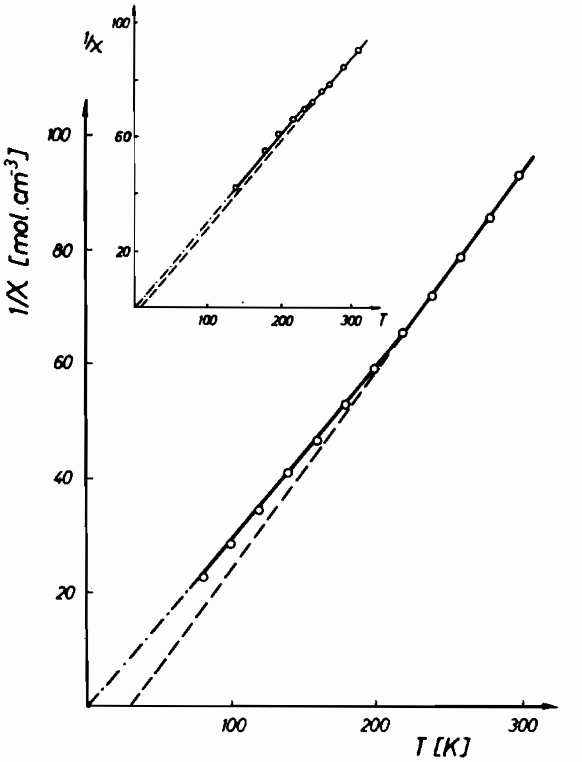


Fig. 5. Inverse magnetic susceptibility as a function of temperature of $Fe(DMTF)_6(ClO_4)_2$; Insert: Inverse magnetic susceptibility as a function of temperature of $Fe(H_2O)_6(ClO_4)_2$.

ature-dependent intensity ratio which was found to be nearly 1:1 at T = 4.2 K and 35:65 at T = 200 K (the highest measuring temperature possible because of the low melting point (~400 K)). In Fig. 4 two of those spectra can be compared with the pattern of $Fe(DMTF)_6(ClO_4)_2$.

XPS-Measurements

The electron binding energies deduced from the XPS spectra are summarized in Table III.

The Fe(2p) and Fe(3p) electron binding energies of the DMF complexes exceed those of the corresponding DMTF complexes, with the exception of the chlorides. The inverse statement is valid for the corresponding halogen levels. The differences in the electron levels between the DMF and DMTF complexes for a given anion is approximately the same for Fe(2p) and Fe(3p). The differences in halogen (2s) and (3p) levels for the pairs $Fe(DMF)_6(ClO_4)_2$/$Fe(DMTF)_6(ClO_4)_2$ and $Fe(DMF)_2Cl_2$/$Fe(DMTF)_2Cl_2$, respectively may be taken as an indication for strong mutual interrelationships between the electrons in the cationic coordination centre and those in the anionic coordination centre or the monoatomic anions respectively. Stronger electron bonding at the cation results in weaker electron bonding at the anion, and *vice versa*. The electron binding energies of the nitrogen atoms are not significantly changed over the whole series. A small difference between the DMF and DMTF species has been found only for the perchlorate complexes (see Table III).

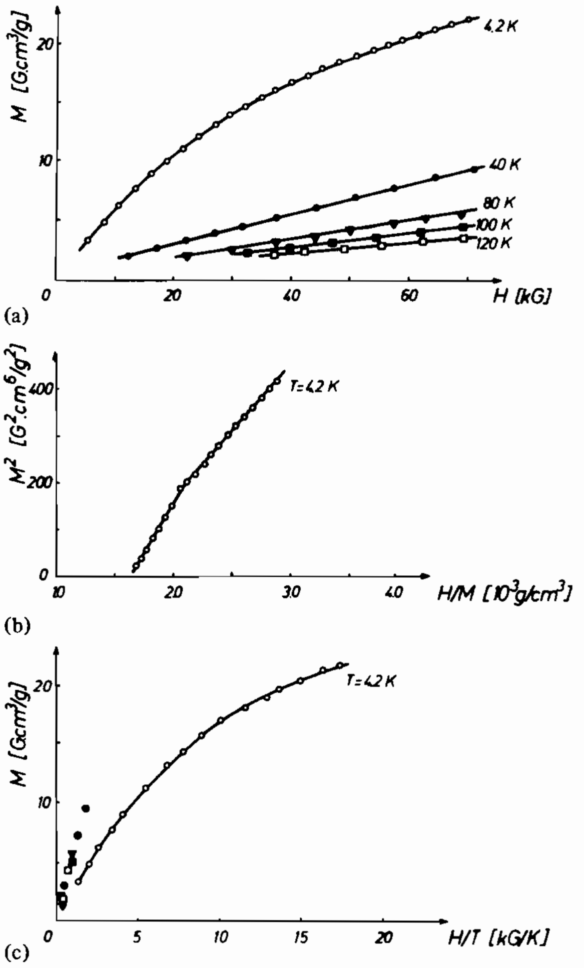


Fig. 6. Magnetization as a function of temperature and magnetic field of $Fe(DMF)_6(ClO_4)_2$: a) M *vs.* H for different temperatures; b) M_2 *vs.* H/M at T = 4.2 K; c) M *vs.* H/T for different temperatures; ○... T = 4.2 K, ●... T = 40K, ▼... T = 80 K, ■... T = 100 K, □... T = 120 K.

Magnetic Measurements

With the exception of $Fe(DMF)_6(ClO_4)_2$ all compounds under consideration follow Curie's law between liquid nitrogen and room temperature [1]. For $Fe(DMF)_6(ClO_4)_2$ a kink in the inverse susceptibility *vs.* temperature curve was found at about 200 K (Fig. 5). For reason of comparison the inverse susceptibility of $Fe(H_2O)_6(ClO_4)_2$ which gives similar temperature effects is shown as an insert in Fig. 5.

The dependence of the magnetisation M upon both the applied magnetic field H and the temperature is shown in different ways in Figs. 6a–c.

Discussion

Structural Features and Quadrupole Interaction in the Perchlorate Complexes

Single crystal X-ray diffraction investigations on $Fe(DMF)_6(ClO_4)_2$ and on $Fe(DMTF)_6(ClO_4)_2$ confirmed that iron is octahedrally coordinated, as has been suggested from the electronic absorption spectra [1,3]. The differences in bond lengths within the compounds under consideration are in accordance with the bond length variation rules [13, 14]. Thus, in the crystalline DMF complex the O–C bond is longer and the C_1–N bond shorter than in gaseous DMF [7], the O–C distance of 120 pm in free DMF is shorter than in the complex (124 pm), and the C_1–N distance in free DMF of 134 pm is longer than in the complex (131 pm). The distances between the N-atom and the methyl C-atom are longer in the complex compound, namely 147 pm in $Fe(DMF)_6(ClO_4)_2$ as compared to 146 pm in gaseous DMF. The bond angles are only slightly changed. The same trends are known for the DMF adducts with 1,7-diacetoxyl-2,4,6-trinitro-2,4,6-triazaheptane [8] and NaI [9], respectively.

No bond length parameters are available for gaseous DMTF, but information on bond lengths may be deduced from those in the DMTF–CuCN adduct [10], where DMTF is expected to be more weakly bonded than in the complex under consideration. Whereas in both adducts the S–C distances are nearly the same, the C_1–N bond is shorter and the distance between the nitrogen atom and the methyl groups longer in the iron complex than in the CuCN complex.

The main difference between DMF and DMTF perchlorate complexes is the greater mobility of the ClO_4^- groups for rotation in the DMF compound. The smaller mobilities observed in the DMTF compound may be related to the somewhat greater acidities of the hydrogen atoms of the methyl groups near the perchlorate ions in the DMTF complex and hence to somewhat stronger donor-acceptor interactions between the perchlorate oxygen atoms and the ligands. This should correspond to a shift in the charge transfer absorption bands between the iron d-levels and the unoccupied π^* orbitals of the ligand. Consequently a rearrangement in the charge distribution at the ligands should occur, which is reflected in the observed change in colour (light green to white) when cooling the substance with liquid nitrogen. We expect further information from low temperature optical spectroscopy investigations which are in progress.

The unexpected behaviour of the DMF-complex is also evidenced in the Mössbauer spectra (Fig. 4a,b). According to the physical principles of the quadrupole interaction the electric quadrupole splitting ΔE_Q is regarded as being due to the interaction between the nuclear quadrupole moment eQ and the electric field gradient (EFG) tensor [2].

A non-zero EFG is considered to arise essentially from two sources:

i) an aspherical charge distribution of electrons in the valence orbitals and

ii) an aspherical charge distribution in the ligand sphere and/or the lattice surrounding with symmetry lower than cubic.

The quadrupole energy in compounds with a dominating crystal field contribution depends generally upon temperature, since the lowest unoccupied orbitals are allowed to be thermally populated. On the other hand non-cubic distributed charges on atoms and/or ligands around the Mössbauer nucleus (iron-coordination centre) should give rise to another EFG contribution which is assumed to depend only weakly upon temperature.

The small temperature dependence of the quadrupole splitting of all compounds under investigation, with the exception of $Fe(DMF)_6(ClO_4)_2$, indicates a dominant ligand/lattice contribution to the total EFG. In the latter case the valence contribution is supposed to be predominant, originating from an asymmetrical 3d orbital population. This population reacts sensitively upon the charge density distribution in the ligand orbitals which in turn are influenced by the perchlorate rotation described above. This rotation gives rise to two individual states, which is confirmed by the occurrence of two quadrupole patterns (Fig. 4a, Table II):

i) A donor-acceptor interaction between the perchlorate oxygen atoms and the neighbouring hydrogen atoms leads to a redistribution of the charge density of the whole system. In this way the electric field gradient at the iron site is enhanced (outer doublet in Fig. 4a) whereas the total charge density, as observed by the isomer shift, remains almost unchanged.

ii) In the case of a rotation of the perchlorate ions the charge distribution in the ligands remains unchanged. Consequently the EFG is no longer enlarged in $Fe(DMF)_6(ClO_4)_2$ leading to the inner doublet in Fig. 4a.

As can be seen from Fig. 4a and Table II the relative intensity ratio of the two quadrupole patterns shows only weak temperature dependence, indicating a ‘phase transition’ which is unusually ‘gradual’. On the other hand the X-ray diffraction experiments yield no indication for a crystallographic phase transition. Similar results have been reported by Deszi *et al.* [4] for $Fe(H_2O)_6(ClO_4)_2$ and by Latorre *et al.* [5] for $Fe(N,N\text{-dicyclohexylthiourea})_6(ClO_4)_2$. In those cases the transition is complete, from a narrow quadrupole doublet at higher temperatures to one with a wider splitting at lower temperatures. The transition region (*i.e.* the temperature range for the coexistence of the two components) increases from

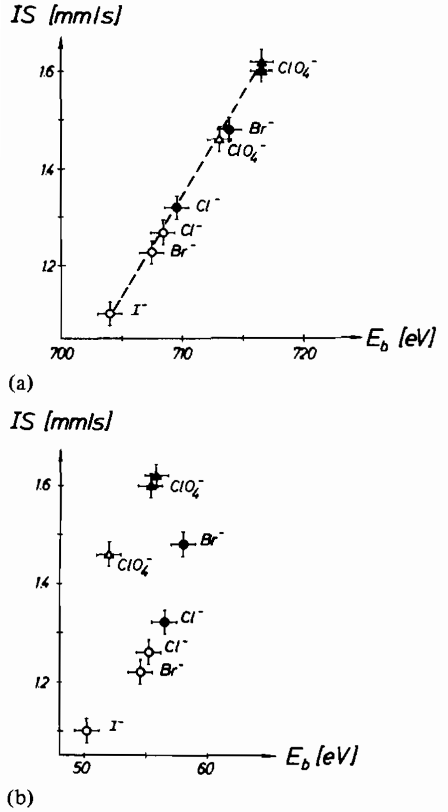


Fig. 7. Mössbauer isomer shifts *vs.* XPS electron binding energies for a) Fe(2p) levels, ●, ▲... DMF complexes; b) Fe(3p) levels, ○, △... DMF complexes. The two points displayed for Fe(DMF)$_6$(ClO$_4$)$_2$ correspond to the two Mössbauer subspectra in Fig. 4a.

15 K for the former complex to about 100 K for the latter. The fact that for the compound under investigation both components are present within the temperature range from 4.2 K up to room temperature means that the transition region is extraordinarily broad. We suggest that the different degree of the mobility of the perchlorate group accounts for these results. Increasing mobility is related to decreasing strength of the interaction between the perchlorate groups and the ligands in the sequence aqua-, thiourea-, and DMF-complex.

Correlation between Mössbauer Isomer Shift and XPS Electron Binding Energy

In this section the discussion will be extended to include all compounds under investigation.

The Mössbauer isomer shift is interpreted as being due to a Coulomb interaction beteen the nuclear and the surrounding electronic charge. An increase of the isomer shift indicates reduction of s-electron charge density at the Mössbauer nucleus. By the presence of d-electrons this charge density is lowered by screening effects.

The XPS-electron binding energies are sensitive towards the screening of the nuclear potential by other electrons, especially by those which have a charge density close to the nucleus. Therefore, a correlation between Mössbauer isomer shifts and XPS-electron binding energies has been suggested [6]. This has been found experimentally for the compounds under consideration in the case of the Fe(2p) and the Fe(3p) levels (Figs. 7a and 7b).

According to electrostatic considerations the effects of the outer electrons of the atom and the surrounding crystal should be taken into account. The coordination in the ClO$_4^-$-complexes is different from that in the halide complexes. In the case of the less screened Fe(3p) electrons this leads to relatively low Fe(3p)-electron binding energies compared with their strong positive isomer shift values (see Fig. 7b). Consequently the ClO$_4^-$-complexes no longer scale with the halide complexes, contrary to the Fe(2p) electron binding energies,where also the ClO$_4^-$ can be included in the functional dependence (see Fig. 7a). This may be explained by the fact that in the case of the Fe(2p) electrons mainly the core properties are observed and consequently the isomer shift and the electron binding energy values are more strongly correlated.

The isomer shift values (Table I) indicate that at the iron nucleii the s-electron density is smaller in the DMF complexes than in DMTF complexes, with the exception of the Cl$^-$ complexes. This is also concluded from the XPS-values for both measured Fe levels (Figs. 7a and 7b).

Within the series of DMF complexes the isomer shift increases from chloride to iodide, and within the series of the DMTF complexes from iodide to chloride. Changes in isomer shift may be related to differences in size of the unit cells [15] (the isomer shift increases as the s-electron density decreases with rising lattice constants). This explains the trend of the isomer shifts and the XPS-electron binding energies in the case of the DMF complexes when compared with the covalent radii of the corresponding anion. The inverse behaviour within the DMTF series may be attributed to the different properties of oxygen and sulfur ligand atoms. The former ligand atom is considered as a hard donor and the latter as a soft donor [16]. This means that in the latter case a strong dπ--pπ back donation to the DMTF ligands makes the latter to act actually as electron acceptors; Fe should 'see' a greater number of s-like electrons in the chloro complexes than in the iodo complexes.

Magnetic Properties

In a homogeneous paramagnet the susceptibility χ is considered to depend on temperature according to Curie's law, *i.e.* the plot of the magnetization M *vs.* the field H should yield a straight line for a given temperature. Moreover, the plots of M *vs.* H at different temperatures have to scale in a M *vs.* H/T diagram, in a M^2 *vs.* H/M diagram (Arrott-plot) again straight lines are expected for a given temperature. Deviations from linearity are commonly correlated with the onset of magnetic order [17, 18].

The halide complexes generally exhibit a Curie-like behaviour at temperatures above ~20 K. At lower temperatures slight deviations were found [3]. In the case of the perchlorate complexes this behaviour is more pronounced, which for the DMF complex is demonstrated in Fig. 6a–c.

The following results point to the onset of short range magnetic order at low temperatures induced by the applied magnetic field (superparamagnetism [18]):

i) the M *vs.* H plot at 4.2 K exhibits a distinct curvature contrary to the plots at elevated temperatures (Fig. 6a);

ii) the M^2 *vs.* H/M curve at 4.2 K shows a kink (Fig. 6b), whereas at higher temperatures straight lines are obtained [3];

iii) the M *vs.* H/T curves scale with the exception of that one for 4.2 K (Fig. 6c).

These facts lead us to the suggestion that at low temperatures ($T \lesssim 20$ K) and above a certain value of the magnetic field ($H > 20$ kG) superparamagnetism is induced by the action of the external field. Since the Mössbauer experiments were carried out in zero applied field this effect is not apparent in the spectra which were recorded at liquid helium temperature.

Summary and Conclusion

The main results obtained on $Fe(DMF)_nX_2$ and $Fe(DMTF)_nX_2$ (X = Cl, Br, I, ClO_4) may be summarized in the following way:

i) Experimental evidence has been found for a close correlation between XPS electron binding energies and Mössbauer effect isomer shifts, as has been proposed by Wertheim [6];

ii) An uncommon sequence of the electron-pulling properties of the halides in the DMTF-complexes was observed (the opposite direction in the sequence of the Mössbauer isomer shifts of the halide compounds between DMF and DMTF complexes reflects the strong $d\pi$–$p\pi$ interaction in the DMTF case);

iii) The structural features found for DMF and DMTF perchlorates are in agreement with expectations of the so-called bond length variation rules [13, 14].

iv) In the case of $Fe(DMF)_6(ClO_4)_2$ the small differences in the X-ray pattern at different temperatures and the differences of the Mössbauer spectra appear to be due to a temperature-dependent rotary mobility of the ClO_4^- groups. This leads to the temperature-dependent interactions between the oxygen atoms in the perchlorate ions and the neighbouring hydrogen atoms, which are much weaker in the DMF complexes than in the DMTF complexes. No indication for a crystal structure phase transition was found when lowering the temperature down to 130 K. Although the static aspects of order remain nearly unchanged, one might be tempted to talk about an extremely gradual 'transition' between 'states' of different dynamic aspects of order. We wish to draw attention to the fact that even the static aspects of order appear dynamically maintained [19]. We shall therefore continue investigations on the dynamic aspects of order for the systems under consideration.

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