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Structural and Bonding Properties of Bis(*N*,*N*-dimethyldithiocarbamato)iron(III) Diiodide and Bis(*N*,*N*-diethyldithiocarbamato)iron(III) Triiodide from Iron and Iodine Mössbauer Spectroscopy

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The bonding and magnetic properties of the complexes $Fe(Me_2dtc)_2I_2$ and $Fe(Et_2dtc)_2I_3$ were studied by ^{57}Fe and ^{129}I Mössbauer spectroscopy. For the first complex, ^{57}Fe spectra from 4.2 to 1.36 K and in magnetic fields up to 7.5 T demonstrate the occurrence of antiferromagnetically coupled dimers and a magnetic ordering transition below 1.6 K. The ^{129}I results indicate the presence of I_2 as bridging unit. In contrast, the second complex behaves as a single paramagnetic iron(III) monomer as shown by low-temperature magnetically perturbed ^{57}Fe spectra. The presence of an I_3^- unit with one of the terminal iodines bonded to iron in the $Fe(Et_2dtc)_2$ group is inferred from the ^{129}I spectra.

Introduction

In aprotic solvents molecular iodine reacts with iron(III) dithiocarbamates of the $Fe(R_2dtc)_3$ or $Fe(R_2dtc)_2I$ series to yield a variety of products.[2] An interesting feature of this reaction is the effect of the alkyl substituent in the $(R_2dtc)^-$ ligand on the composition of the obtained products as evidenced by the following representative examples: $Fe(Me_2dtc)_2I_2$, $Fe(Et_2dtc_2)_2I_3$, $Fe(i\text{-}Pr_2dtc)_3I_3$ and $Fe(Et_2dtc)_3I_5$. The last two compounds have been proved to be iron(IV) complexes containing the $Fe(R_2dtc)_3^+$ ion.[2,3]

We focus our attention in this paper on the first two compounds. Room-temperature Mössbauer measurements[2] give isomer shift values that indicate the presence of iron(III) and quadrupole splittings that though significantly higher than the corresponding iodobis compounds,[4,5] suggest an $S = {}^3/_2$ ground state. This assignment has been verified by magnetic susceptibility measurements at our laboratory which give magnetic moments of 3.80 and 4.00 μ_B for $Fe(Me_2dtc)_2I_2$ and $Fe(Et_2dtc)_2I_3$, respectively, in accord with a $S = {}^3/_2$ system.

We report here detailed ^{57}Fe and ^{129}I Mössbauer measurements on the two complexes $Fe(Me_2dtc)_2I_2$ and $Fe(Et_2dtc)_2I_3$ at low temperatures and the information that can be extracted on iodine bonding, possible structures, and intermolecular magnetic interactions in these molecules.

Experimental Section

The $Fe(Me_2dtc)_2I_2$ complex was prepared by reacting 1 g of $Fe(Me_2dtc)_3$ in 50 mL of CH_2Cl_2 with 0.610 g of iodine in 20 mL of CH_2Cl_2. After the addition of 50 mL of hexane, the mixture was left for 3 h. Crystals were formed which were collected, washed with hexane, and recrystallized from a methylene chloride–hexane mixture. **The $Fe(Et_2dtc)_2I_3$** complex was prepared similarly by reacting 1 g of $Fe(Et_2dtc)_3$ with 0.750 g of iodine. The purity of the complexes was confirmed by elemental analyses, as well as by their infrared and Mössbauer spectra. The ^{129}I-labeled complexes were obtained by the same procedure using $^{129}I_2$. The latter was extracted in methylene chloride after oxidation with H_2O_2 of an aqueous solution of Na ^{129}I acidified with H_2SO_4. The ^{129}I labeled complexes were identified by their ^{57}Fe Mössbauer spectra.

Mössbauer spectra were obtained with a conventional constant acceleration spectrometer. A ZnTe source enriched in ^{66}Zn and ^{128}Te and irradiated in the NRC Demokritos reactor was used for the ^{129}I measurements. A ^{57}Co (Rh) source was used for the ^{57}Fe measurements. Spectra were recorded in the temperature range of 1.4–300 K and in external fields up to 7.5 T.

Table I. Isomer Shifts (IS) and Quadrupole Splittings (ΔE_Q) for ^{57}Fe in the Studied and Related Complexes at 4.2 K

compd	IS,[a] mm s^{-1}	ΔE_Q, mm s^{-1}
$Fe(Me_2dtc)_2I_2$	0.47 (1)	3.23 (1)
$Fe(Et_2dtc)_2I_3$	0.46 (1)	3.80 (1)
$Fe(Me_2dtc)_2I$[b]	0.49	2.93
$Fe(Et_2dtc)_2I$[c]	0.52 (1)	2.85 (1)

[a] Relative to Fe metal at room temperature. [b] Reference 3. [c] Reference 6.

Results and Discussion

(A) **^{57}Fe Measurements.** The ^{57}Fe Mössbauer spectra of both complexes consist of a quadrupole doublet which is independent of temperature down to 2 K. The parameters of these spectra are shown in Table I together with results of the corresponding simple iodine bis(dithiocarbamates) for comparison. Below 2 K the spectra of the two complexes develop in different ways. A symmetric quadrupole doublet persists down to 1.6 K for the $Fe(Me_2dtc)_2I_2$ complex. Below this temperature magnetic hyperfine splitting appears in a narrow temperature range, and it is clearly developed at 1.36 K, indicating a magnetic transition (Figure 1a). The spectra of the $Fe(Et_2dtc)_2I_3$, on the other hand, display an asymmetric broadening at 1.6 K without any clear evidence for magnetic hyperfine interaction down to 1.36 K (Figure 2b).

Application of a transverse magnetic field of 0.9 T reveals further differences in the magnetic properties of these two compounds. An asymmetric broadening typical of a diamagnet appears at 4.2 K in the $Fe(Me_2dtc)_2I_2$ molecule (Figure 1c) while a "triplet–doublet" pattern is clearly displayed by the $Fe(Et_2dtc)_2I_3$ complex (Figure 2c). A positive quadrupole coupling constant is consistent with both patterns. At 1.36 K the hyperfine pattern of $Fe(Me_2dtc)_2I_2$ in an applied transverse field of 0.9 T shows slightly smaller overall splitting and significantly broader lines than at zero field (Figure 1a,b). In contrast, the application of a magnetic field on $Fe(Et_2dtc)_2I_3$ at 1.36 K results in well-defined hyperfine magnetic splitting typical of a paramagnetic species (Figure 2a). These results suggest an antiferromagnetic coupling arising from dimer formation in the $Fe(Me_2dtc)_2I_2$ complex and a paramagnetic monomeric character for $Fe(Et_2dtc)_2I_3$. In the former case the lack of magnetic hyperfine splitting at 4.2 K and 0.9 T is expected from an $S = 0$ ground state formed by two spin ${}^3/_2$ ions coupled antiferromagnetically. The broadening of the lines at 1.36 K also can be attributed to decoupling of the magnetic dimers by the applied field and consequent distribution of the orientation of the hyperfine fields. Very similar results have been reported previously for the closely related compound $Fe(Me_2dtc)_2I$.[4]

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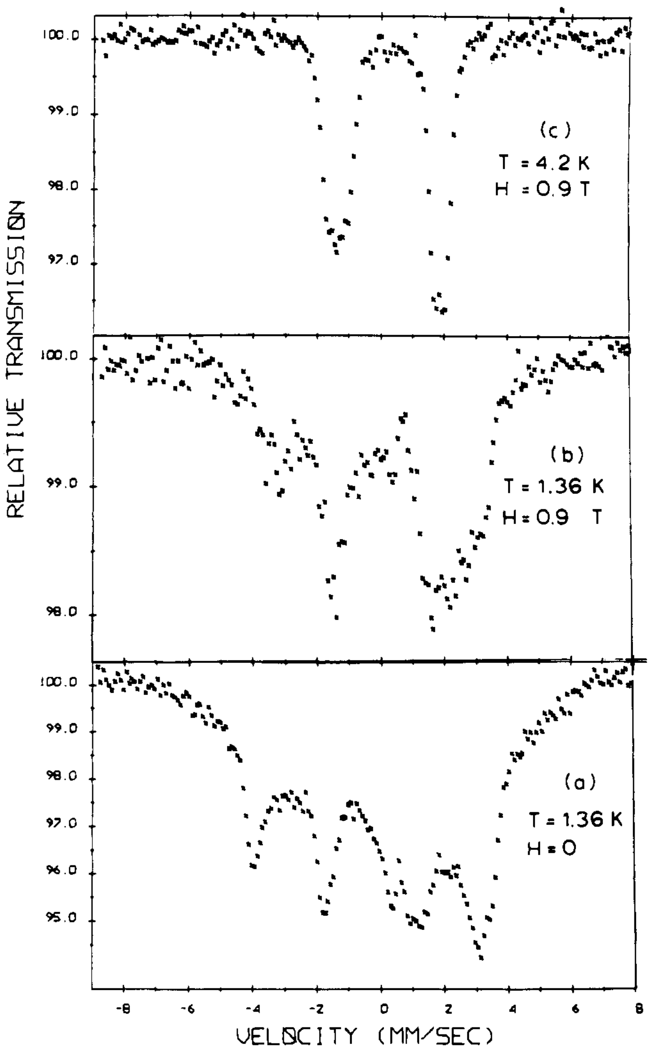

Figure 1. ^{57}Fe Mössbauer spectra of $Fe(Me_2dtc)_2I_2$.

Further evidence for the magnetic properties of the two complexes is provided by the variation of the hyperfine field H_{hf} with the externally applied field. The hyperfine field is related to the effective magnetic field H_{eff} acting on the ^{57}Fe nucleus by eq 1. As demonstrated in several previous investigations of iron bis(dithiocarbamates),[6] the dominant contribution to the hyperfine field arises from the contact interaction, shown in eq 2, where the constant A has a value of 220 kOe per unit spin.

$$\vec{H}_{eff} = \vec{H}_{hf} + \vec{H}_{appl} \qquad (1)$$

$$\vec{H}_{eff} = A\langle \vec{S} \rangle \qquad (2)$$

Values of H_{eff} have been obtained from magnetically perturbed spectra at 4.2 K and in externally applied fields up to 7.5 T. The values were calculated from the line positions with the assumption of an angle $\theta = 90°$ of H_{eff} in the EFG system. This assumption is found to be correct at low applied fields where the direction of H_{eff} is determined by anisotropy in the electronic spin Hamiltonian resulting in spectra with narrow lines. With these values, H_{hf} is calculated from (1), taking into account that its direction is opposite to H_{appl}. The results are plotted in Figure 3. For comparison we have plotted in the same figure the variation of the average value of the spin induced by an external field, given by a Brillouin function for $S = {}^3/_2$. It is seen that the values for $Fe(Me_2dtc)_2I_2$ are systematically lower than this function, indicating the presence of intramolecular antiferromagnetic coupling. The hyperfine field for $Fe(Et_2dtc)_2I_3$ on the other hand is slightly higher than predicted by the Brillouin function. It is worth noting, however, that normalization to the Brillouin function of the value of H_{hf} at $H_{appl} = 7.5$ T gives a saturation value of ~300 kOe, which is close to that expected for a spin $^3/_2$ system from (2).

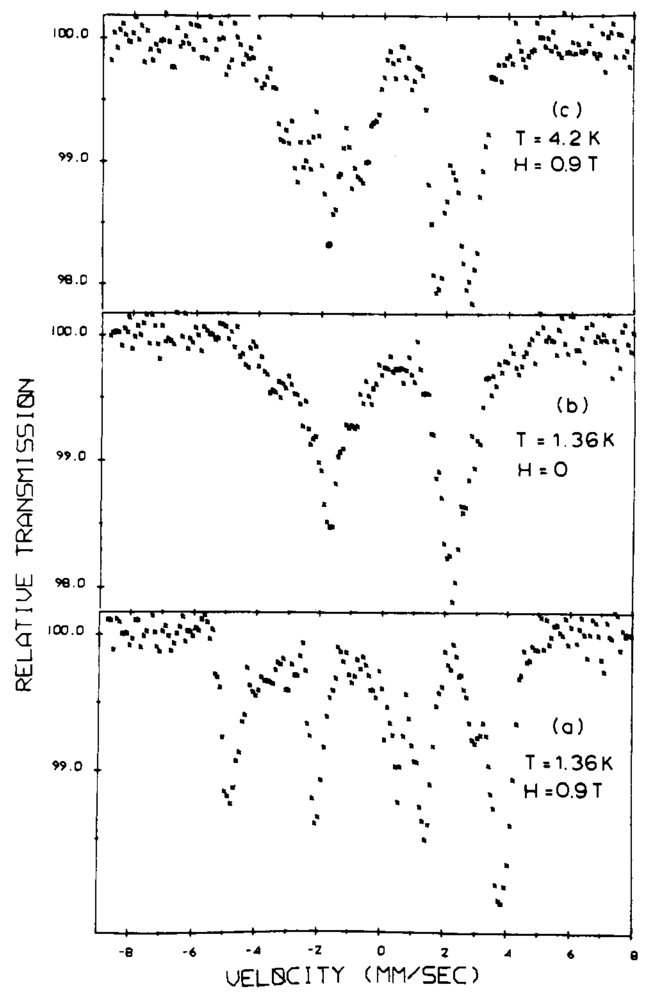

Figure 2. ^{57}Fe Mössbauer spectra of $Fe(Et_2dtc)_2I_3$.

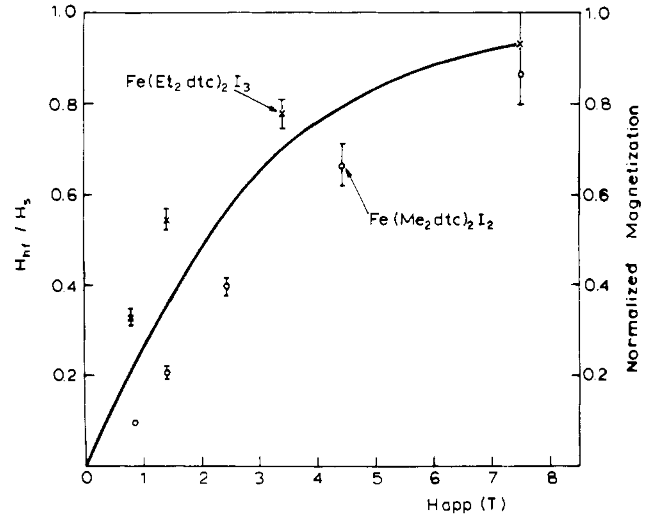

Figure 3. Variation of the hyperfine field H_{hf} at 4.2 K with the applied magnetic field H_{appl}. The solid line is a plot of the Brillouin function $B_{3/2}(H/T)$. The hyperfine fields H_{hf} are normalized to the value of H_{hf} of $Fe(Et_2dtc)_2I_3$ at $H_{appl} = 7.5$ T.

In summary, the ^{57}Fe Mössbauer results indicate the presence of magnetic dimerization in the $Fe(Me_2dtc)_2I_2$ complex while the $Fe(Et_2dtc)_2I_3$ behaves like a simple paramagnetic iron(III) monomer.

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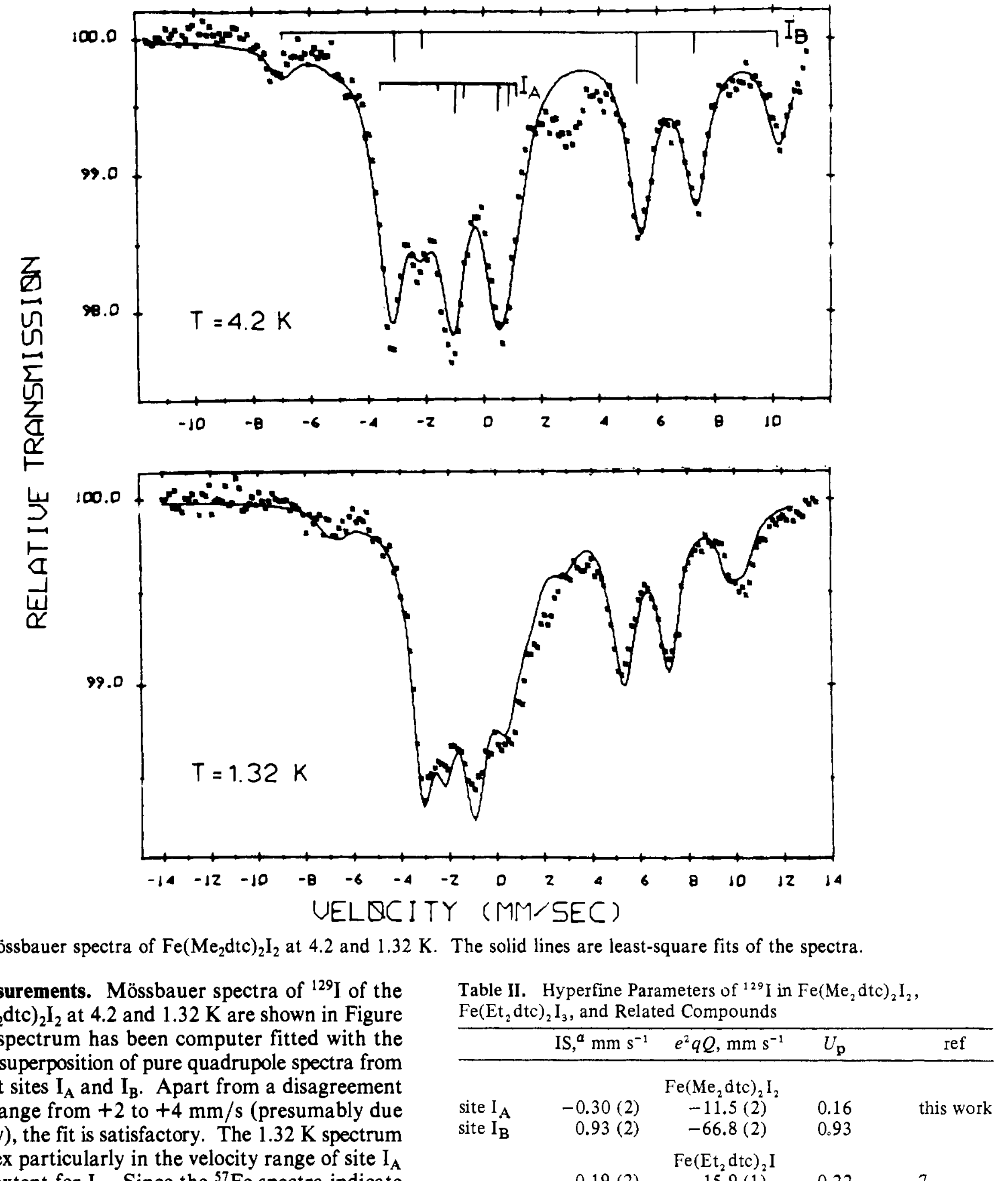

Figure 4. ^{129}I Mössbauer spectra of $Fe(Me_2dtc)_2I_2$ at 4.2 and 1.32 K. The solid lines are least-square fits of the spectra.

(B) ^{129}I Measurements. Mössbauer spectra of ^{129}I of the complex $Fe(Me_2dtc)_2I_2$ at 4.2 and 1.32 K are shown in Figure 4. The 4.2 K spectrum has been computer fitted with the assumption of a superposition of pure quadrupole spectra from two inequivalent sites I_A and I_B. Apart from a disagreement in the velocity range from +2 to +4 mm/s (presumably due to some impurity), the fit is satisfactory. The 1.32 K spectrum becomes complex particularly in the velocity range of site I_A and to a lesser extent for I_B. Since the ^{57}Fe spectra indicate the presence of magnetic order at 1.36 K, this broadening of the ^{129}I lines may be attributed to transferred hyperfine interactions. A computer fit of the 1.32 K spectrum, including magnetic hyperfine interactions and constraining the quadrupole splitting and the isomer shift parameters to the values determined by the 4.2 K spectrum, yielded the values of effective hyperfine fields at the ^{129}I nuclei $H_{eff}(I_A) = 53$ kOe and $H_{eff}(I_B) = 6$ kOe. Due to the overlapping of the two components the angles θ and ϕ, determining the orientation of H_{eff} in the EFG system cannot be determined reliably. The results of these fits are listed in Table II. The hyperfine parameters of related complexes reported in previous investigations are also listed in this table for comparison.

Inspection of the data of Table II immediately shows that the hyperfine parameters of site I_A are similar to those of the simple iron bis(dithiocarbamato) iodides[7] while those of site I_B are very close to corresponding parameters of molecular iodine.[8] The essential identity of the parameters for I_B with I_2 strongly suggests the presence of a molecular iodine moiety weakly bonded to two $Fe(Me_2dtc)_2I$ units as required by

Table II. Hyperfine Parameters of ^{129}I in $Fe(Me_2dtc)_2I_2$, $Fe(Et_2dtc)_2I_3$, and Related Compounds

	IS,[a] mm s^{-1}	e^2qQ, mm s^{-1}	U_p	ref
		$Fe(Me_2dtc)_2I_2$		
site I_A	−0.30 (2)	−11.5 (2)	0.16	this work
site I_B	0.93 (2)	−66.8 (2)	0.93	
		$Fe(Et_2dtc)_2I$		
	−0.19 (2)	−15.9 (1)	0.22	7
I_2	0.93 (5)	−69.8 (6)	0.97	8[b]
		$Fe(Et_2dtc)_2I_3$		
site I_A	−0.30 (4)	−16 (1)	0.22	this work
site I_B	0.55 (8)	−47 (1)	0.65	
site I_C	1.39 (6)	−79 (1)	1.10	
		CsI_3		
site I_A	0.01 (4)	−25.7 (3)	0.36	11
site I_B	0.49 (4)	−45.8 (4)	0.64	
site I_C	1.40 (4)	−78.8 (6)	1.10	

[a] Relative to ZnTe source at 4.2 K. [b] Mean values from the two independent works listed in ref 8.

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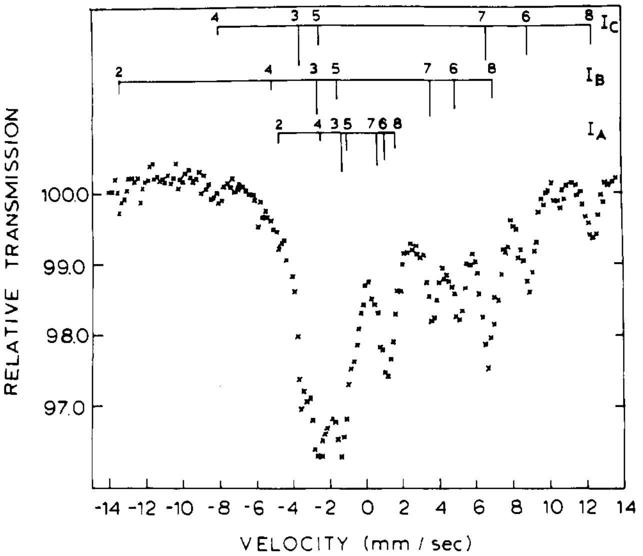

Figure 5. ^{129}I Mössbauer spectra of $Fe(Et_2dtc)_2I_3$ at 4.2 K. The stick diagrams correspond to the three iodine sites discussed in the text.

stoichiometry. The presence of a weak magnetic field on the I_B site in the magnetically ordered state suggests that the I_2 is at least partly responsible as a bridging unit for the formation of antiferromagnetically coupled dimers. These conclusions are consistent also with a recent crystal structure determination of another derivative of this series, $Fe((pyrr)dtc)_2I_2$[9] (pyrr = pyrrolidine), where it is found that an iodine molecule is located on a crystallographic center of symmetry. The iodine atoms interact weakly with two complexed iodine atoms at distances of 3.516 (3) Å to form a loose "dimeric" association of the type $(dtc)_2FeI\cdots I\text{–}I\cdots Fe(dtc)_2$. It is also worth noting that the Fe–I distance in this structure is 2.652 (3) Å, somewhat longer than the corresponding distance in $Fe(Et_2dtc)_2I$ which is 2.59 (1) Å. The observed increase of both isomer shift and e^2qQ for the apex iodine in passing from $Fe(Me_2dtc)_2I_2$ to $Fe(Et_2dtc)_2I$ (Table II), implying a greater depletion of the p shell of I in the latter compound, is consistent with the difference in bond lengths.

The spectrum of ^{129}I in $Fe(Et_2dtc)_2I_3$ at 4.2 K is shown in Figure 5. It is seen that this spectrum is considerably more complicated than that of $Fe(Me_2dtc)_2I_2$, indicating the presence of at least three inequivalent sites. Approximate values of isomer shift and quadrupole splittings with the assumption of superposition of three components can be obtained from line positions and are listed in Table II. In accordance with results of previous studies of compounds containing an I_3 unit, axial symmetry was assumed in this calculation ($\eta = 0$).[10] The stick spectra calculated for these parameters are shown in Figure 5, and it is seen that they reproduce satisfactorily the main features of the spectrum. The chemical character of the three sites may be deduced by comparison with parameters for CsI_3 which are also included in Table II.[11] The close similarity of parameters for sites I_B and I_C suggests that I_B must be assigned to a terminal iodine and I_C to a central iodine in an I_3^- unit. For the central iodine the isomer shift and quadrupole splitting are close to those of neutral iodine, indicating that the charge in the I_3^- unit resides on the terminal iodines. In the case of $Fe(Et_2dtc)_2I_3$, the second terminal iodine may be associated with site I_A, which is complexed to the $Fe(Et_2dtc)_2$ group as indicated by comparison of the hyperfine parameters to those of $Fe(Et_2dtc)_2I$. The significant difference in the parameters of site I_A for CsI_3 and $Fe(Et_2dtc)_2I_3$ indicates that the terminal iodine close to the metal ion is more charged in the latter complex.

The bonding character of the iodine groups in the compounds studied here can be discussed with reference to the correlation given by de Waard[11] between the isomer shift and the parameter U_p, which is related to the occupation number of states in the p shell by eq 3 where $e^2q_{at}Q_{129} = -71.81$ mm

$$U_p = \frac{e^2qQ_{129}}{e^2q_{at}Q_{129}} = -U_z + \frac{U_x + U_y}{2} \qquad (3)$$

s^{-1} for atomic ^{129}I. For pure unhybridized σ bonds eq 4 is obtained where $b = 0.66$ and $\delta_0 = -0.54$ mm s^{-1}. Values of

$$\delta - \delta_0 = bU_p \qquad (4)$$

U_p of the studied compounds are included in Table II. Inspection of the values of Table II shows that eq 4 is followed very well by both complexes of this study, leading to the conclusion that for all iodine atoms the bonding is of pure unhybridized σ type.

Summarizing, by combined ^{57}Fe and ^{129}I Mössbauer measurements on the molecular complexes $Fe(Me_2dtc)_2I_2$ and $Fe(Et_2dtc)_2I_3$, we have demonstrated that (a) the first complex contains a molecular iodine (I_2) unit mediating the formation of weakly coupled dimers with antiferromagnetic interaction and (b) the second complex is a paramagnetic monomer containing an I_3^- unit with one of the terminal iodines bonded to the metal ion of the $Fe(Et_2dtc)_2$ group.

Registry No. $Fe(Me_2dtc)_2I_2$, 79933-21-4; $Fe(Et_2dtc)_2I_3$, 62171-16-8; $Fe(Me_2dtc)_3$, 14484-64-1.

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