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Mössbauer and Magnetic Studies on Solid Mixed-Ligand Iron(III) Dithiocarbamates

STANISŁAW WAJDA, KRZYSZTOF DRABENT and ANDRZEJ OŻAROWSKI

Institute of Chemistry, University of Wrocław, 14 Joliot-Curie Street, 50-383 Wrocław, Poland

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Introduction

Since Winckman and Trazzolo [1] have reported the possibility of synthesis of mixed-ligand iron(III) dithiocarbamate complexes, the presence of such complexes in solution has been many times reported [2–4]. But only Tsipis *et al.* [5] have succeeded in preparing the $Fe(dtc)_2(dtc')$ type compounds in the solid; however, their investigations concerned mainly the properties of these compounds in solution at room temperature (UV–vis spectroscopy, magnetic measurements). The results revealed that compounds of that type exhibit the thermal spin equilibrium $^6A_1(S = 5/2) \rightleftharpoons {}^2T_2(S = 1/2)$, like the iron(III) tridithiocarbamates [6].

In studies of the 'cross-over' systems the measurements of the temperature dependent magnetic susceptibility (and hence the magnetic moment) and measurements of the Mössbauer parameters (mainly of the ΔE_q quadrupole splitting) are most useful. For that reason we have undertaken the studies of the $Fe(dtc)_2(dtc')$ compounds, where dtc and dtc′ are N,N-di-ethyl-, morpholyl- and piperidyl- dithiocarbamate (further denoted as Et_2dtc, morphdtc, and pipdtc, respectively).

Experimental

The compounds under investigation were synthesized by the modified method reported by Tsipis *et al.* [5]. The crude products were recrystallized from chloroform–ethanol mixture. Their purity was stated from elemental analysis and NMR examination. Magnetic measurements were done by the Gouy method over the temperature range 80–300 K, taking the diamagnetic corrections into account. Effective magnetic moment μ_{eff} was calculated from the expression $\mu_{eff} = 2.83\ (\chi_M^{corr}\ T)^{1/2}$, where χ_M^{corr} = corrected molar susceptibility. The Mössbauer effect measurements of powders were done on a Mössbauer 2330 spectrometer (Polon, Poland). Measurements were made at 80 and 300 K. The isomer shift value was related to sodium nitroprusside (SNP). ^{57}Co in the Cr matrix, of 20 mCi activity was used as the γ-radiation source. The source and the SNP during all measurements were stored at room temperature. The spectra were processed numerically by distribution into Lorentzian curves.

The results obtained are summarized in Table I and Fig. 1–3.

Results and Discussion

The ligands selected by us could be divided into two groups. Et_2dtc and pipdtc used to form the $Fe(dtc)_3$ complexes of a similar 'cross-over' properties with the μ_{eff} which changed within the limits 2.2–4.0 BM over the examined temperature range. The morphdtc formed the compound of significantly higher μ_{eff} (see Table I). For the two first complexes the $1/2 \rightleftharpoons 5/2$ spin equilibria are discussed, and for the third complex the $3/2 \rightleftharpoons 5/2$ equilibrium is proposed, because of the magnetic properties of $Fe(morphdtc)_3\ CHCl_3$ [7].

TABLE I. The Mössbauer and Magnetic Data for the Complexes under Investigation.[a]

No.	Compound	μ_{eff}		QS[mm s^{-1}]		IS[mm s^{-1}]	
		81	295	80	300	80	300
I	$Fe(Et_2dtc)_3$	2.17	4.04	0.520	0.263	0.747	0.650
II	$Fe(Et_2dtc)_2(pipdtc)$	2.47	3.99	0.701	0.361	0.736	0.667
III	$Fe(Et_2dtc)(pipdtc)_2$	2.20	3.93	0.755	0.307	0.747	0.657
IV	$Fe(pipdtc)_3$	2.18	4.04	0.725	0.268	0.749	0.653
V	$Fe(pipdtc)_2(morphdtc)$	2.35	4.52	0.765	0.285	0.798	0.652
VI	$Fe(pipdtc)(morphdtc)_2$	2.71	4.70	0.818	0.298	0.775	0.681
VII	$Fe(morphdtc)_3$	4.55	5.45	0.539	0.283	0.745	0.676
VIII	$Fe(morphdtc)_2(Et_2dtc)$	3.21	4.99	0.857	0.362	0.792	0.666
IX	$Fe(morphdtc)(Et_2dtc)_2$	2.39	4.37	0.726	0.317	0.773	0.657

[a] IS relative to sodium nitroprusside at room temperature. QS and IS estimated error ± 0.005 mm s^{-1}. μ_{eff} in BM.

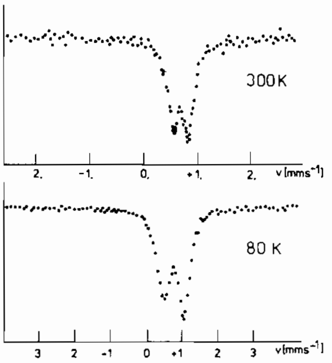

Fig. 1. The Mössbauer spectra of Fe(morphdtc)$_3$ measured at 300 and 80 K.

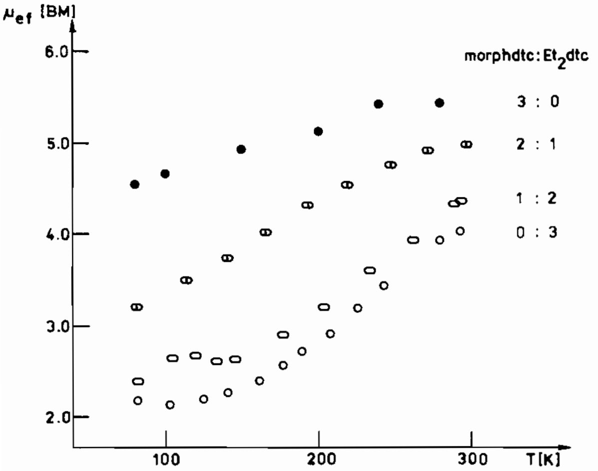

Fig. 2. Variation with temperature of magnetic moments of mixed-ligand complexes VII, VIII, IX, and I from top to bottom, respectively.

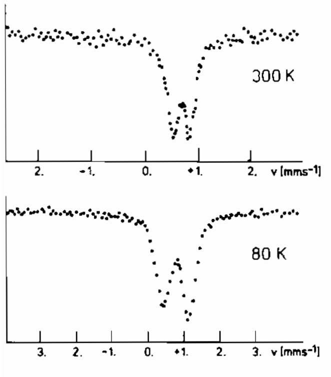

Fig. 3. The Mössbauer spectra of Fe(Et$_2$dtc)$_2$(morphdtc) (compound IX) measured at 300 and 80 K.

Rininger *et al.* [8] have confirmed the existence of such and equilibrium for iron(III) dithiocarbamate complexes upon the basis of Mössbauer spectroscopy of the Fe(morphdtc)$_3$ CH$_2$Cl$_2$ compound. The compound VII examined by us exhibits magnetic properties identical to those reported in the literature for the Fe(morphdtc)$_3$CHCl$_3$ complex [7]. However, its Mössbauer spectrum at 80 K presents one single doublet characterized by parameters given in Table I. Nevertheless, in our opinion the properties of the compound VII synthesized by us should be considered according to the model of $3/2 \rightleftharpoons 5/2$ 'crossover'. The fact that the system of two doublets due to both spin states involved in the equilibrium could not be observed in the Mössbauer spectrum is indicative of a high spin interconversion rate of those states, higher or comparable with the lifetime of the excited ^{57}Fe core ($\tau = 1.4 \times 10^{-7}$ s).

However, the main subject of our studies was the properties of the mixed-ligand iron(III) dithiocarbamates. The first suggestions reported by Tsipis *et al.* [5] indicated the considerable effect of this kind of ligands and of their mutual relations upon the properties of the obtained compounds of the Fe(dtc)$_2$(dtc$'$) type. In the case of the mixed-ligand complexes with Et$_2$dtc and pipdtc (compounds II and III) we have observed only slight influence of the change of ligands upon the magnetic properties of the obtained complexes. Their Mössbauer spectra exhibit only slight increase of the ΔE_q compared with the appropriate Fe(dtc)$_3$ complexes, what may be explained by the total symmetry lowering of the mixed-ligand systems.

The compounds where one of the ligands is morphdtc require special attention. The magnetic properties and the Mössbauer parameters of the mixed-ligand complexes containing morphdtc as dtc or dtc$'$ are drastically different from those of the appropriate Fe(dtc)$_3$ complexes. Whereas in the case of the magnetic properties the effective moments μ_{eff} in the series dtc : dtc$'$ 3 : 0, 2 : 1,1 : 2 and 0 : 3 change at room temperature almost linearly, the changes of the ΔE_q do not exhibit such a simple relation. But the quadrupole splitting value in mixed-ligand complexes exceeds that in the appropriate Fe(dtc)$_3$ complexes. In our opinion it is connected basically with the lowering of the total symmetry of the mixed-ligand complexes. The situation at 80 K is different: at that temperature magnetic properties of the compounds do not change linearly, and in the mixed-ligand compounds the Et$_2$dtc and pipdtc ligands affect the magnetic properties stronger than the morphdtc ones, independently of their mutual relations. Nevertheless, the presence even of the only one morphdtc ligand in compounds IX and V results in enhancement of the magnetic moment compared with compounds I and IV. That is reflected in the quadrupole splitting value measured at 80 K. The differences in the ΔE_q of the mixed-ligand complexes in comparison with the appropriate $Fe(dtc)_3$ values are more evident than at room temperature.

That fact may be explained by the action of two factors having the simultaneous effect on the ΔE_q value. The first one is the lowering of the total symmetry of the mixed-ligand complexes. The second is the shift (due to the presence of ligands Et_2dtc and pipdtc) of the $5/2 \rightleftharpoons 1/2$ spin equilibrium towards the low-spin state, for which the electric field gradient EFG on the iron core is different from zero. Both factors cumulate at low temperatures and therefore the observed ΔE_q value is so high. On the other hand, the Mössbauer spectra of all compounds at both temperatures have shown the single doublet characterized by the increasing ΔE_q with decreasing temperature. In the case of $Fe(dtc)_3$ complexes such a situation was explained by Frank and Abeledo [9] as being due to the very fast interconversion of the spin states, exceeding 10^{-7} s. Thus, the Mössbauer spectra of our compounds present the averaged picture of both spin states in thermal equilibrium but not the change of intensity of bands originating from both possible states as in the case of the iron(II) 'cross-over' complexes [10]. On the other hand, our results allow us to state that the properties of the $Fe(morphdtc)_3$ complex could be explained within the limits of the $3/2 \rightleftharpoons 5/2$ equilibrium, while the properties of the mixed-ligand complexes where one ligand is morphdtc (compounds V, VI, VIII, and IX) require discussion only within the frame of the classical $1/2 \rightleftharpoons 5/2$ equilibrium. Thus, the mixed-ligand complexes exhibit not the slowing down of the spin states interconversion rate, but the change of the thermal equilibrium.

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