

Research Letter

Exchange Interaction in Complex Bis[(1,3-Dithiole-2-Thione-4,5-Dithiolato)-di-(Carbonyl)-Cyclopentadienyl Iron(II)]

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The splitting of the quasidegenerate electronic states in dinuclear bis[(1,3-dithiole-2-thione-4,5-dithiolato)-di-(carbonyl)-cyclopentadienyliron (II)] complex with the bridging, S–S coupled, dimerized sulfur-rich dithiolate ligands, $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2(\text{C}_3\text{S}_5-\text{C}_3\text{S}_5)\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2]$ (**I**) was found by the means of Mössbauer spectroscopy and by the measurement of the temperature dependence of magnetic susceptibility in a wide temperature range from 2 K to 300 K. The experimental results were confirmed by the calculations of the singlet and triplet states of the complex, as well as of the distribution of spin density within the bounds of the DFT method in the B3LYP/6-31(dp)G basis. In the more stable triplet state, the spin density is significantly delocalized, which is a characteristic of olefinedithiolate complexes.

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1. Introduction

During the last decade the chemistry of 1,3-dithiole-2-thione-4,5-dithiole complexes (dmit complexes) was developing rapidly. The interest was motivated above all by the possibility of preparation of molecular metals, superconductors, and magnetically ordered structures based on them [1–3]. Mixed-ligand complexes, containing in addition to dmit also heterocycle amine molecules, have perspective application as materials for non-linear optics [4] and dye-sensitized solar cells [5–7]. Moreover, the complex $[\text{Cu}(\text{SP})(\text{mnt})]$ (SP = (–)sparteine (6R, 11S), mnt—maleonitriledithiolate) with a distorted tetrahedral geometry has been studied as a model of blue copper protein [8].

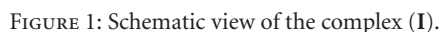
In previous paper [9] the mixed-ligand complex bis [(1,3-dithiole-2-thione-4,5-dithiolato)-di(carbonyl)-cyclopentadienyliron (II)] (**I**) and its crystal structure has been described (Figure 1).

The ability of dmit to form complexes having the properties of molecular metals and/or superconductors is explained by the existence of shortened intermolecular

contacts $\text{S} \cdots \text{S}$ including S_2 atoms in crystals of these complexes. Unusual structural properties for $\text{C}-\text{S}-\text{S}^*-\text{C}^*$ bonds have been investigated [10]. As a consequence of this the issue of conductivity of the chain $\text{Fe}-\text{S}-\text{C}=\text{C}-\text{S}-\text{S}^*-\text{C}^*=\text{C}-\text{S}^*-\text{Fe}^*$ for complex (**I**) (the stars mark the atoms of complex which are connected with the rotation axis C_2) arises. The higher the conductivity of the chain is, the stronger are the exchange interactions between paramagnetic atoms of iron in complex (**I**). Due to this, we performed a study of the complex by means of Mössbauer spectroscopy which is very sensitive to the changes of energy [11] and by the measurement of the temperature dependence of magnetic susceptibility in a wide temperature range from 2 K to 300 K.

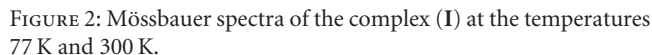
2. Experimental

The authors in [9] have prepared complex (**I**) in two steps. At first the mixture of $\text{C}_3\text{S}_5(\text{CH}_2\text{CH}_2\text{CN})_2$ and sodium ethylate was treated with ultrasonic waves in ethyl alcohol to prepare



Quantum chemical calculations of the triplet and singlet states of complex (I) were performed by the RODFT method in the B3LYP/6-31(dp)G basis using structural data from [9]. The advantage of the DFT methods is that they methods allow, in principle, to calculate accurately the spin state splitting. The calculated trends are roughly independent on the choice of the density functional and are consistent with the experimental data [14, 15].

In the crystals of complex (I) the magnetic interactions between paramagnetic centers of neighbouring molecules is practically impossible (shortened contacts



As we know, quadrupole splitting is a result of three contributions: the asymmetry of the crystal lattice (this

TABLE 1: Basic parameters of the Mössbauer spectra of complex (I). Symbols: δ -value of isomer shift; Δ -value of quadrupole splitting; $\Gamma_{1/2}$ -halfwidth of the line; $S\%$ -relative probability of the effect.

T, K	Center	δ mm/s	Δ mm/s	$\Gamma_{1/2}$ mm/s	$S\%$
300	Fe	0.39(1)	1.09(1)	0.26(1)	48.8(1)
	Fe*	0.40(1)	0.64(1)	0.41(1)	51.2(1)
77	Fe	0.46(1)	1.11(1)	0.31(1)	50.8(1)
	Fe*	0.50(1)	0.69(1)	0.41(1)	49.2(1)

contribution is absent in cubic crystals), the presence of so-called imbalanced electrons in d-suborbital, and the asymmetry of the electron distribution in internal orbitals [18]. With regard to the features of the complex (I) crystal structure (which may be classified as a molecular crystal), the first contribution should be negligible and the second one (for ion with configuration d^6 in strong fields) is equal zero. Thus the main contribution to the gradient of electric field on ^{57}Fe atoms is determined by the asymmetry (polarization) of internal electron orbitals. This contribution is practically temperature independent what was confirmed by experiments (Table 1).

The temperature dependence of the magnetic susceptibility is shown in Figure 3. It is like dependence for paramagnets, but it still cannot be described by the Curie-Weiss law. In the entire temperature range it can be described by an empirical formula:

$$\chi = \chi_0 + \chi' T + \frac{C}{T - \Theta}, \quad (1)$$

with parameters $\chi_0 = -2.83 \cdot 10^{-3}$ emu/mol, $\chi' = 2 \cdot 10^{-5}$ emu/mol, $C = 1.214$ emu·K/mol, $\Theta = -6.5$ K and with the correlation coefficient $R = 0.9982\%$. The value of the effective magnetic moment was estimated from the Curie constant as $3.13 \mu_B$. It corresponds to two unpaired electrons per formula unit of the complex and signifies that every symmetrical moiety $[\text{Fe}(\text{Cp})(\text{CO})_2\text{C}_3\text{S}_5]$ has one electron. The negative value of the Weiss constant Θ indicates the presence of antiferromagnetic interactions in the system.

If for magnetism of complex (I) only the Fe(II) ions were responsible, the complex would be either diamagnetic (spin-coupled state of Fe(II)), or would have four unpaired electrons (two on each Fe(II) ion). Therefore, the presence of two unpaired electrons means that the stable state of complex (I) is a triplet state with delocalized spin density.

The results of the quantum chemistry calculations, presented in Table 2, agree well with experimental data. According to the calculations the triplet state of the complex is more stable than the singlet state at 1.56 eV (150 kJ/mol). The spin density distribution in the complex molecule (Figure 4) from which it can be seen that the spin density is localized mainly on iron atoms, sulfur S_4 atoms, and carbon atoms C_3 of dithiolate ion $\text{C}_6\text{S}_{10}^{2-}$, serving as a bridge in the binuclear complex.

The energy splitting of core levels, which gives main contribution to the electric field gradient on iron atoms, is practically absent or very weak. For example, the energy of the $\text{E}(\text{Fe}3s)$ state described by the symmetric wave

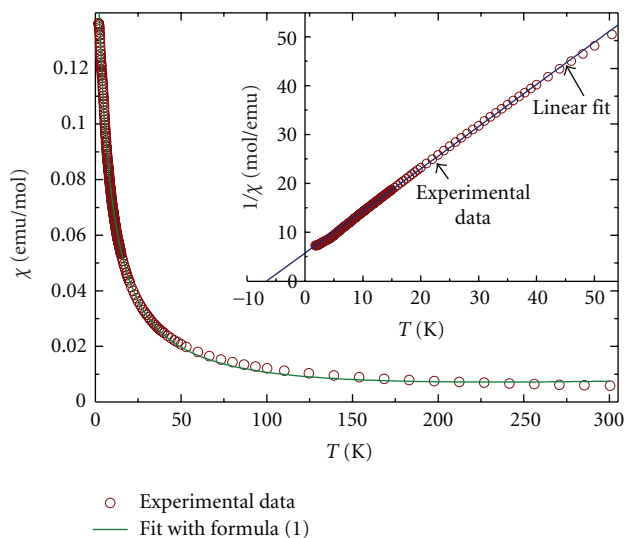


FIGURE 3: Temperature dependence of magnetic susceptibility of the complex (I), experimental data (open circles) are fitted with formula 1 (solid line). Inset shows the linear fit (solid line) to inverse susceptibility.

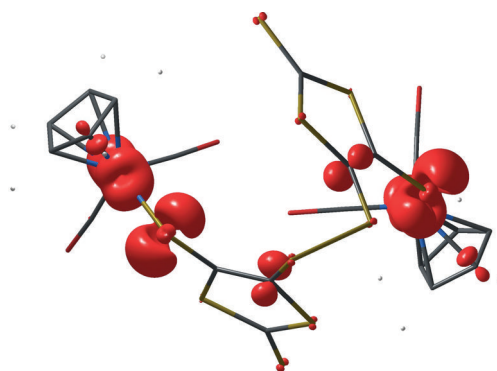


FIGURE 4: Spin density distribution at the molecule of the complex (I).

function (irreducible representation A of group C_2) is only by 0.0027 eV more stable than the state with symmetry B (Table 2). More symmetrical orbitals—orbitals transformed by the irreducible representation A of C_2 group—give lower contribution to the gradient and orbitals with B symmetry give a larger one. The existence of two doublets in the Mössbauer spectra of complex (I) can be explained in such a way that they originate from two different electronic states with practically the same value of the isomer shift but with different symmetry. The doublet with quadrupole splitting 0.64 mm/s originates from the states with A symmetry and the doublet with $\Delta = 1.09$ mm/s from the states with B symmetry.

Thus, as a result of the performed study, an unusual effect of the splitting of electron states of the binuclear low symmetry complex, caused by a notable electron conductivity of the $\text{Fe}-\text{S}_3-\text{C}_2-\text{S}_2-\text{S}'_2-\text{C}'_2-\text{S}'_3-\text{Fe}'$ chain, was found.

TABLE 2: Values of electron bond energies of some core levels of triplet (ground) state of complex (I), $E_{\text{total}}(\text{LS}) - E_{\text{total}}(\text{HS}) = 0.0574$ in hartree (a. u), LS: low spin state, HS: high spin state.

Calcul.	Exper. [19]
FeE1s 256.1007 (A), 256.1007 (B)	—
FeE2s 30.0389 (A), 30.0389 (B)	31.037
FeE3s 3.4522 (A); 3.4521 (B)	3.351
FeE2p _{3/2} 25.9199 (A); 25.9199 (B);	25.999 ^a
FeE3p 2.1989 (B); FeE3p 2.1989 (B)	1.944
ES1s 88.9466 (B); 88.9466 (A)	—
ES2s 7.9441 (B); 7.9441 (A)	—
ES2p 5.9715 (A); 5.9715 (B)	5.979 ^b
O1s 19.2317 (B); 19.2317 (A)	19.535
C1s 10.3257(A) ^c 10.3257(B) ^c	10.620 ^d
C1s 10.3006(B) ^e 10.3006(A) ^e	10.499 ^f

^a[Fe(C₅H₅)₂], ^b(Ph₄P)[Fe(NO){S₂C₂(CN)₂}₂], ^ccarbon of the carbonyl group, ^d[Fe(CO)₅], ^ecarbon C₅H₅[−], ^f[Fe(C₅H₅)₂].

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