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Research Letters in Inorganic Chemistry
Volume 2009, Article ID 243296, 4 pages
doi:10.1155/2009/243296

Research Letter

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

S. V. Vitushkina,[1] D. V. Ziolkovskiy,[1] V. A. Starodub,[2] I. A. Presniakov,[3] A. V. Sobolev,[3] M. Kajňaková,[4] A. Radvákova,[4] and A. Feher[4]

[1] *V. N. Karazin Kharkiv National University, 61077 Kharkiv, Ukraine*
[2] *Institute of Chemistry, Jan Kochanovski University, 25020 Kielce, Poland*
[3] *Department of Chemistry, Lomonosov Moscow State University, 119991 Moscow, Russia*
[4] *Centre of Low Temperature Physics, Faculty of Science, P.J. Šafárik University; IEP SAS, 04180 Košice, Slovakia*

Correspondence should be addressed to S. V. Vitushkina, vitushkina@gmail.com

Received 22 June 2009; Accepted 5 August 2009

Recommended by George Koutsantonis

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, $[Fe(C_5H_5)(CO)_2(C_3S_5\text{-}C_3S_5)Fe(C_5H_5)(CO)_2]$ (**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 olefindithiolate 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 [Cu(SP)(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 S · · · S including S_2 atoms in crystals of these complexes. Unusual structural properties for C–S–S*–C* bonds have been investigated [10]. As a consequence of this the issue of conductivity of the chain Fe–S–C=C–S–S*–C*=C*–S*–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 $C_3S_5(CH_2CH_2CN)_2$ and sodium ethylate was treated with ultrasonic waves in ethyl alcohol to prepare

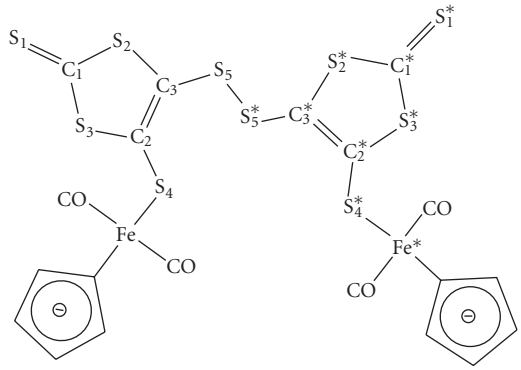

Figure 1: Schematic view of the complex (**I**).

the Na_2dmit salt. To the resulting solution the solution of $[(C_5H_5)Fe(CO)_2I]$ complex was added. After stirring, the complex (**I**) was separated from the reaction mixture with a 60% yield. In this paper, the complex (**I**) was synthesized by a method described in [12] which is a method of one-step synthesis of this complex with an 83% yield. Notably, C_6S_{10} was added to the methanolic solution of $[(C_5H_5)Fe(CO)_2]$ with stirring. The resulting mixture was brought to the boiling point and stirred about 20 hour. After cooling, the complex (**I**) was separated from the reaction mixture.

The ^{57}Fe Mössbauer spectra were recorded at different temperatures using a conventional constant-acceleration spectrometer. The radiation source ^{57}Co(Rh) was kept at the room temperature. All isomer shifts refer to the α-Fe absorber at 300 K.

In Figure 2 the spectra of ^{57}Fe atoms, obtained at different temperatures (300 K and 77 K resp.) are shown. Table 1 shows the results of the mathematical evaluation of spectra as a superposition of two quadrupole doublets, which have been described by linear combination of Gaussian and Lorentz functions.

The magnetic susceptibility and magnetization were studied using a commercial Quantum Design *MPMS* device. The temperature dependence of susceptibility was investigated in the temperature range from 2 K to 300 K in applied magnetic fields 100 mT and 1 T. The diamagnetic contribution to the susceptibility was estimated using Pascal's constants [13] and subtracted from the total susceptibility.

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].

3. Results and Discussion

In the crystals of complex (**I**) the magnetic interactions between paramagnetic centers of neighbouring molecules is practicaly impossible (shortened contacts between atoms of neighbouring molecules are missing [9]). Two $Fe(C_5H_5)(CO)_2$ groups are bound together by the ionic bridge $C_6S_{10}^{2-}$. The only symmetry element—C_2 axis—passes over the center of the disulphide S–S bridge bond, hence the point symmetry group of the molecule of the complex is C_2. Since this symmetry group has only one-dimensional irreducible representations, the double degenerated state of complex (**I**) (complex consists of two equivalent parts) has to split. This effect is fully analogical to the familiar Davydov (or exciton) splitting in crystals [16]. Resulting from the stoichiometry of the complex (**I**) we can come to the conclusion that the oxidation degree of iron is +2, with electron configuration $3d^6$. In such a case, in the absence of interactions between iron atoms in the complex, it is necessary to expect diamagnetic ground state (cyclopentadienyl-anion and CO molecules are ligands of strong field). Nevertheless, according to the magnetic measurements the complex (**I**) is paramagnetic.

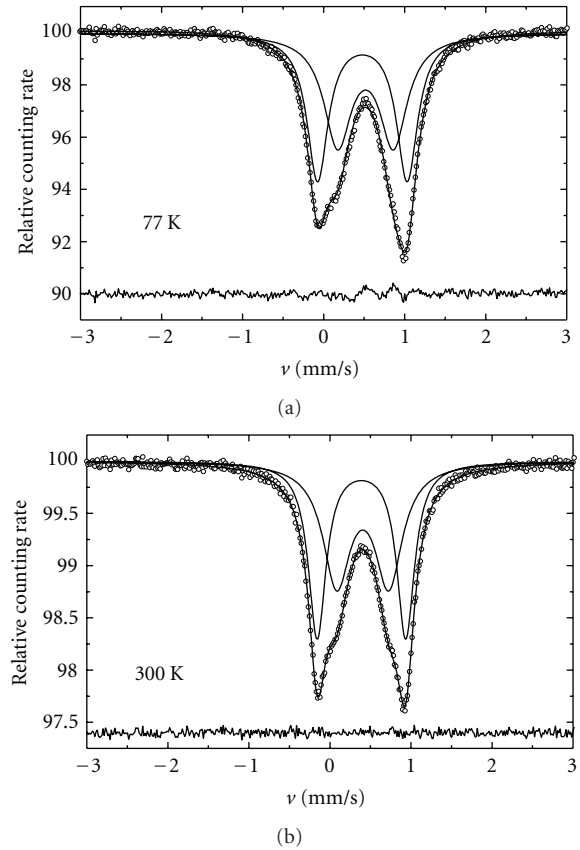

Figure 2: Mössbauer spectra of the complex (**I**) at the temperatures 77 K and 300 K.

^{57}Fe Mössbauer spectra measured at temperature 300 K and 77 K (Figure 2) correspond to the superposition of two quadrupole doublets with close values of chemical shift δ, but with apparently different values of quadrupole splitting Δ (Table 1). We point out that these values are characteristic for low-spin complexes with Fe(II) or Fe(III) [17, 18].

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 μ_B. It corresponds to two unpaired electrons per formula unit of the complex and signifies that every symmetrical moiety $[Fe(Cp)(CO)_2C_3S_5]$ has one electron. The negative value of the Wiess 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 $C_6S_{10}^{2-}$, 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 E(Fe3s) state described by the symmetric wave

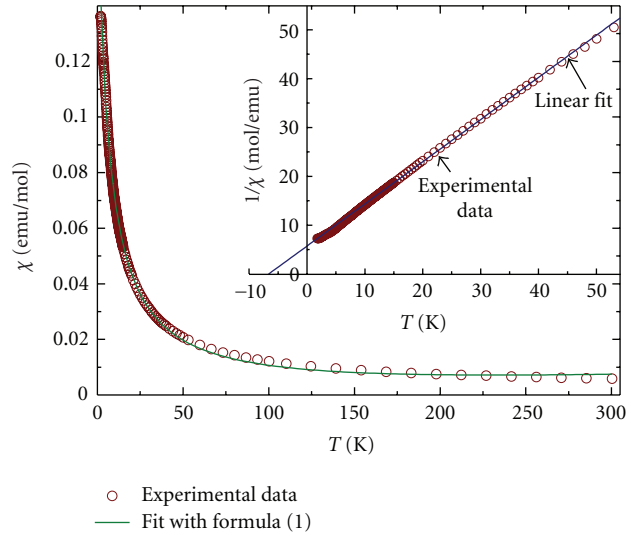

Figure 3: Temperature dependence of magnetic susceptibility of the complex (**I**), experimental data (open circles) are fitted with formula 1 (solid line). Inset shows the linear fit (solid line) to inverse susceptibility.

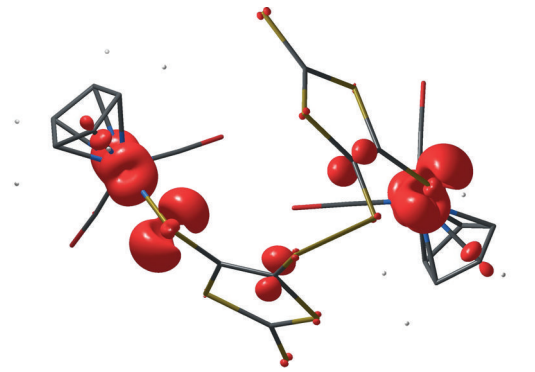

Figure 4: Spin density distribution at the molecule of the complex (**I**).

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 Fe–S_3–C_2–S_2–S_2'–C_2'–S_3'–Fe′ chain, was found.

Table 2: Values of electron bond energies of some core levels of triplet (ground) state of complex (**I**), E_{total}(LS)– E_{total} (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
FeE2$p_{3/2}$ 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]$[Fe(C_5H_5)_2]$, [b]$(Ph_4P)[Fe(NO)\{S_2C_2(CN)_2\}_2]$, [c]carbon of the carbonyl group, [d]$[Fe(CO)_5]$, [e]carbon $C_5H_5^-$, [f]$[Fe(C_5H_5)_2]$.

Acknowledgment

This work was supported by the grants of Slovak Research and Development Agency under the contracts LPP-0102-06, no. APVV-VVCE-0058-07, no. APVV-0006-07 and VEGA 1/0159/09. The financial support of U.S. Steel–DZ Energetika Košice is acknowledged.

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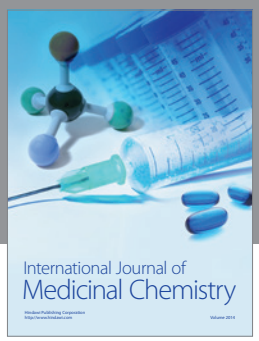

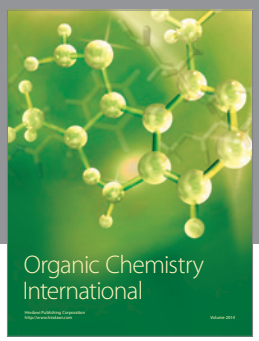

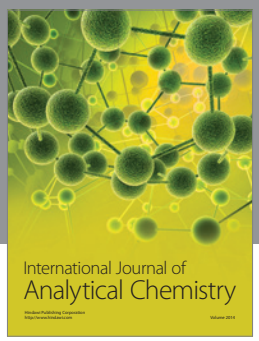

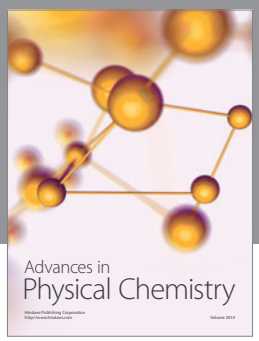

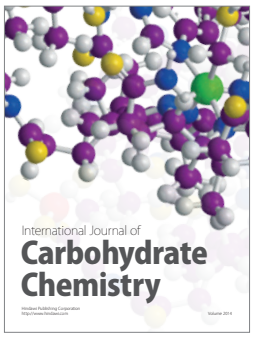

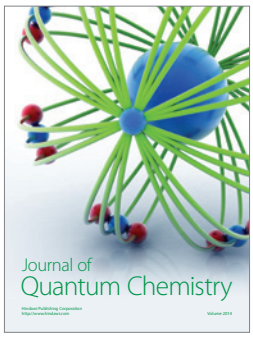

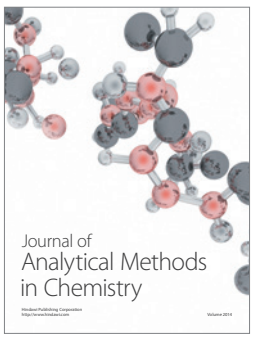

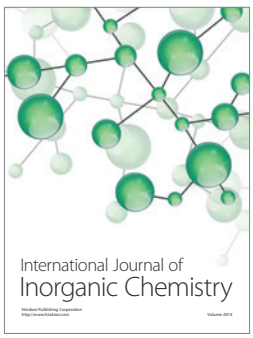

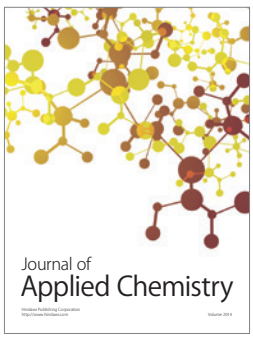

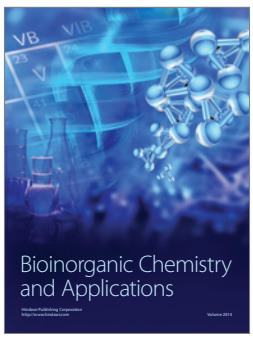

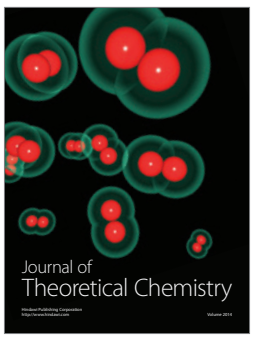

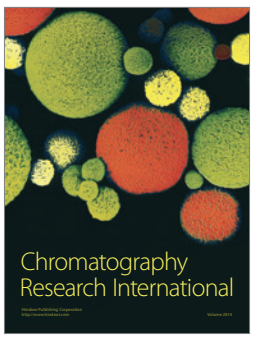

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