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Structure and Magnetic Properties of the Radical Cation Salt of a TTF-based Ni^{II} Complex

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*Chemical oxidation of a TTF-based Ni^{II}complex with I_2 produces the corresponding radical cation salt **1**, $[Ni_2Cl_2(L)_2](I_3)_2(I_5)_2(I_2)(H_2O)_2(C_4H_8O)_3$, (L=4,5-bis(2-pyridylmethylsulfanyl)-4',5'-ethylenedithiotetrathiafulvalene). The results of magnetic susceptibility measurements show the occurrence of intramolecular magnetic exchange interactions in **1**. The lack of close S···S contacts, confirmed by crystal structure analysis, results in an insulating behavior.*
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1. INTRODUCTION

One of the current objectives in the field of conducting molecular materials derived from tetrathiafulvalene (TTF) is to try to correlate within the same solid two distinct physical properties such as magnetic and conducting properties, seeking to establish in this case a coupling between the conduction electrons and the magnetic spin moments[1,2]. Numerous research groups are involved in this area[3]. In addition to co-assembling organic donors and paramagnetic metal anions, another strategy for constructing dual-property materials is the direct coordination of paramagnetic metal ions to organic radicals through an intervening coordination function such as pyridine-type heterocycles[4] or phosphine substituents[5], both well-known for their chelating ability toward various transition metal complexes. Although a large number of inorganic/organic hybrid materials contain metal ions in an anionic part, only a few examples of the direct coordination of the paramagnetic metal ions to TTF derivatives have been reported[6,7]. It is noteworthy that the coordination of metal ions to TTF derivatives might constitute an approach for the achievement of π-d interactions in such multifunctional molecular materials. As a result, we

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report here on the synthesis, characterization, and properties of the radical cation salt of a Ni^{II} chloride complex of 4,5-bis(2-pyridylmethylsulfanyl)-4',5'-ethylenedithiotetrathiafulvalene (**L**).

2. EXPERIMENTAL PART

10 ml of a 10 mM clear solution of I_2 in CH_2Cl_2 was introduced into a glass tube and layered successively with 4ml pure CH_2Cl_2 and 4ml of pure THF as a buffer zone. Then 10 ml of a 1.2 mM solution of Ni(**L**)Cl_2[7] in CH_2Cl_2 was added very gently to avoid possible mixing. The glass tube was sealed and left in the dark at room temperature for four days. Black single crystals were isolated at the interface between the two solutions. Anal. Calc. for $C_{40}H_{32}N_4S_{16}Ni_2Cl_4(I_3)_2(I_5)_2(I_2)\cdot C_4H_8O\cdot 2H_2O$: C,14.43; H, 1.21; N, 1.53. Found: C, 14.52; H, 0.92; N, 1.42. IR (KBr, cm^{-1}): 3431, 1668, 1661, 1568, 1481, 1439, 1385, 1268, 1156, 1057, 1019.

3. RESULTS AND DISCUSSION

Based on the neutral Ni(**L**)Cl_2 compound[7], we aimed to obtain corresponding TTF radical cation salts by electrocrystallization with a range of suitable anions as well as by chemical oxidation. Consequently, chemical oxidation with I_2 by slow layer diffusion produces the crystalline dimeric Ni^{II} compound **1,** as shown in Figure 1, formulated as $[Ni_2Cl_2(L)_2](I_3)_2(I_5)_2(I_2)(H_2O)_2(C_4H_8O)_3$. Crystal structure analysis (monoclinic, *C*2/c) reveals that the bond lengths around the Ni atom in **1** are very close to those found in the neutral complex Ni(**L**)Cl_2.

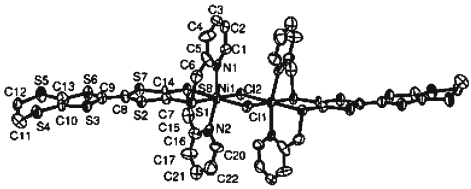

Fig. 1. ORTEP plot (50% probability ellipsoids) showing the Ni^{II} coordination sphere of **1**. Anions, solvents and hydrogen atoms are omitted for clarity. The two halfs of the molecule are related by an inversion center.

The ionicity of the donor **L** can be estimated from the C=C bond length [1.41(3) Å in **1**] of the TTF unit, being slightly larger than in the neutral complex [1.334(8) Å]. Thus, it can be inferred that the TTF core in **1** is essentially fully oxidized according to the correlation between the oxidation

states of TTF derivatives and bond lengths of central C=C bonds[8]. In order to get further experimental information about the electronic distribution within the donor moieties, we have performed Raman microscope measurements on single crystals of **1**. From the linear relationship found in other TTF salts[9] between the the C=C stretching frequencies ν_2, ν_3 and the degree of ionicity (ρ), one can estimate ρ for the two **L** moieties in compound **1**. Thus, if the two doublets centered at 1467 and 1422 cm^{-1} are assigned to ν_2 and ν_3 modes, respectively, one can estimate by interpolation a ρ value of 1. These results are also consistent with the stoichiometry of **1** and the fact that the oxidized compound **1** is black in color, while its neutral complex is brown. However, due to a bulky coordination sphere, there are no close S•••S contacts observed in this oxidized ionic salt (Figure 2), which results in an insulating behavior.

Magnetic susceptibility measurements of **1** (Figure 3) reveal, as expected, the occurrence of intramolecular magnetic exchange interactions. Essentially, there is a ferromagnetic coupling between the Ni^{II} spins (S = 1) mediated through the μ-dichloro bridge and a weaker antiferromagnetic coupling to the pendant radical sites. Of course, zero-field splitting for the Ni^{II} ions will be significant at lower temperatures, too.

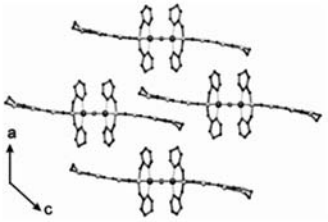

Fig. 2. *ac* projection of the crystal structure of **1**. Anions, solvents and hydrogen atoms are omitted for clarity.

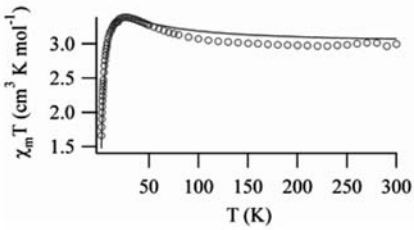

Fig. 3. Magnetic susceptibility in form of $\chi_m T$ *vs* T plot for compound **1**. The solid line shows a simulation of the intramolecular magnetic interactions.

4. CONCLUSIONS

A new radical cation salt of a TTF-based Ni^{II} complex, **1**, has been prepared by chemical oxidation with I_2, and also structurally characterized. The preliminary results of magnetic susceptibility measurements show the occurrence of intramolecular magnetic exchange interactions in **1**. A full paper about these results will be ready for publication in due course.

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