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Structural Studies of Transition Metal Complexes with 4,5-Bis(2-pyridylmethylsulfanyl)-4′,5′-ethylenedithiotetrathiafulvalene: Probing Their Potential for the Construction of Multifunctional Molecular Assemblies

Shi-Xia Liu,[†] Stefan Dolder,[†] Patrick Franz,[†] Antonia Neels,[‡] Helen Stoeckli-Evans,[‡] and Silvio Decurtins*,[†]

Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3,
CH-3012 Bern, Switzerland, and Institut de Chimie, Université de Neuchâtel,
Avenue Bellevaux 51, CH-2007 Neuchâtel, Switzerland

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Three divalent transition metal complexes of 4,5-bis(2-pyridylmethylsulfanyl)-4′,5′-ethylenedithiotetrathiafulvalene have been prepared and crystallographically characterized. The isostructural Co(II) and the Ni(II) complexes show octahedral geometries around the metal ions with the coordination sites occupied by the pyridyl nitrogen atoms and the thioether sulfur atoms of the ligand and cis coordination of the halide ions. Cyclic voltammetry reveals that the complexation leads to a small anodic shift in the first oxidation potential of the TTF system.

The search for molecule-based materials exhibiting multiphysical properties is one of the current challenges in molecular materials science.[1] In particular, materials based on the synergy between electrical conductivity and magnetic interactions have received much attention.[2,3] Consequently, intense investigations are devoted to the chemical modification of the donor atoms (S) of tetrathiafulvalene (TTF) series[4,5] or the attachment of functional groups to the core of the donor framework,[6,7] for enhancement of the intermolecular interactions among electron donors and acceptors (or counteranions). From a similar consideration, our strategy involves the covalent attachment of metal ion binding groups to bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) derivatives and their linkage into supramolecular systems. Thereby, some BEDT-TTF derivatives, symmetrically and asymmetrically functionalized by polypyridines or polypyrazines, have been synthesized.[8,9] Although some charge-transfer salts of TTF and its derivatives contain metal ions in an anionic part, only a few examples of the direct coordination of the metal ions to TTF derivatives were observed.[2,10−11] It is noteworthy that the coordination of metal ions to TTF derivatives might constitute an approach for the achievement of $\pi-$d interactions in such multifunctional molecular materials. As a result, we report here on the synthesis, characterization, and properties of some transition metal complexes with 4,5-bis(2-pyridylmethylsulfanyl)-4′,5′-ethylenedithiotetrathiafulvalene (**L**).

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* Author to whom correspondence should be addressed. E-mail: silvio.decurtins@iac.unibe.ch.

[†] Universität Bern.

[‡] Université de Neuchâtel.

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The ligand **L** was synthesized and structurally characterized as described in the literature.[9] Elemental analyses were performed on an EA 1110 elemental analyzer CHNS from Carlo Erba Instruments. The ^{1}H NMR spectrum was measured in THF-d_8 at 300 MHz. FT-IR data were collected at a resolution of 2 cm^{-1}. Mass spectra were recorded on a Micromass AutoSpec spectrometer.

The synthesis of $NiCl_2(L)\cdot H_2O$ (**1**) was carried out as follows. To a stirred solution of the ligand **L** (0.308 g, 0.57 mmol) in CH_3CN (25 mL) was added a solution of $NiCl_2\cdot 6H_2O$ (0.136 g, 0.57 mmol) in H_2O (1 mL). The mixture was stirred overnight at room temperature. The brown compound obtained was collected, washed with CH_3CN, and dried over P_4O_{10} under vacuum (yield, 81%). Suitable single crystals were obtained as brown needles by slow evaporation of its CH_2Cl_2 solution. Anal. Calcd for $C_{20}H_{16}N_2S_8NiCl_2\cdot H_2O$: C, 34.89; H, 2.64; N, 4.07. Found: C, 34.62; H, 2.57; N, 4.05. IR (KBr, cm^{-1}): 3431, 1601, 1569, 1483, 1438, 1386, 1270, 1193, 1156, 1103, 1057, 1019, 898, 870, 770. Mass spectrum (FAB) *m*/*z*: (relative intensity) 670 $(M - H_2O)^+$ (12), 635 $(M - H_2O - Cl)^+$ (12), 540 $(M - H_2O - NiCl_2)^+$ (9).

The synthesis of $CoBr_2(L)\cdot 2H_2O$ (**2**) was carried out as follows. To a stirred solution of the ligand **L** (0.289 g, 0.536 mmol) in CH_3CN (40 mL) was added a solution of $CoBr_2$ (0.117 g, 0.536 mmol) in CH_3CN (5 mL). The mixture was stirred overnight at room temperature. The dark-brown compound obtained was collected, washed with CH_3CN, and dried over P_4O_{10} under vacuum (yield, 51%). Recrystallization from CH_2Cl_2-THF afforded dark-red needlelike crystals suitable for X-ray crystallography. Anal. Calcd for $C_{20}H_{16}N_2S_8$-$CoBr_2\cdot 2H_2O$: C, 30.19; H, 2.53; N, 3.52. Found: C, 30.42; H, 2.10; N, 3.52. IR (KBr, cm^{-1}): 3405, 1601, 1568, 1482, 1437, 1387, 1315, 1287, 1269, 1202, 1157, 1058, 1017, 893, 870, 771. Mass spectrum (FAB) *m*/*z*: (relative intensity) 758 $(M - 2H_2O)^+$ (11), 678 $(M - 2H_2O - Br)^+$ (33), 599 $(M - 2H_2O - 2Br)^+$ (22), 540 $(M - 2H_2O - CoBr_2)^+$ (8).

The synthesis of $ZnCl_2(L)$ (**3**) was carried out as follows. To a stirred solution of the ligand **L** (0.289 g, 0.536 mmol) in CH_3CN (40 mL) was added a solution of $ZnCl_2\cdot 4H_2O$ (0.112 g, 0.536 mmol) in H_2O (1 mL). The mixture was stirred overnight at room temperature. The red-brown crystalline compound obtained was collected, washed with CH_3CN, and dried over P_4O_{10} under vacuum (yield, 60%). Anal. Calcd for $C_{20}H_{16}N_2S_8ZnCl_2$: C, 35.48; H, 2.38; N, 4.14. Found: C, 35.80; H, 2.27; N, 4.17. ^{1}H NMR: δ 3.34 (s, 4H), 4.15 (s, 4H), 7.21−7.26 (dd, $J = 7.4$ Hz, $J = 5.2$ Hz, 2H), 7.31 (d, $J = 7.7$ Hz, 2H), 7.69−7.74 (dt, $J = 1.8$ Hz, $J = 7.7$ Hz, 2H), 8.56 (d, $J = 4.4$ Hz, 2H). IR (KBr, cm^{-1}): 1605, 1568, 1487, 1441, 1323, 1211, 1162, 1066, 1022, 899, 791, 771. Mass spectrum (FAB) *m*/*z*: (relative intensity) $(M - ZnCl_2)^+$ 540 (8).

For the X-ray structure determination, the measurements were made on a Stoe Mark II image plate diffraction system[12] The structures were solved by direct methods using the program SHELXS-97[13] and refined by full matrix least squares on F^2 with SHELXL-97.[14] The hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. An empirical absorption correction was applied using DIFABS in PLATON99.[15]

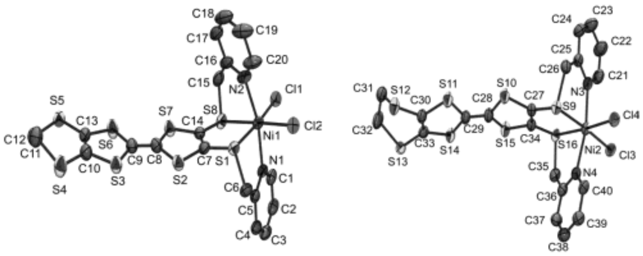

Figure 1. Molecular structure of **1**, showing both crystallographically independent molecules. Hydrogen atoms are omitted for clarity.

Reaction of ligand **L** with the halide salts of the divalent metal ions Co^{2+}, Ni^{2+}, and Zn^{2+} has given a series of stable crystalline complexes, all of which have been fully characterized. Single-crystal X-ray diffraction analysis reveals that compounds **1** and **2** are isostructural and crystallize with two crystallographically independent complex molecules and three partially disordered dichloromethane molecules per asymmetric unit (Figure 1).[16] We describe here the structure of compound **1**. Both molecules display an approximate 2-fold symmetry with the nickel ion cis-coordinated to two chloride atoms (Ni1−Cl 2.344(2), 2.375(1) Å; Ni2−Cl 2.364(2), 2.373(1) Å), bound to two trans pyridyl nitrogen atoms (Ni1−N 2.116(4), 2.127 (5) Å; Ni2−N 2.098(5), 2.099(4) Å), and to the two sulfanyl sulfur atoms (Ni1−S 2.427(2), 2.442(1) Å; Ni2−S 2.421(1), 2.425(1) Å). The TTF unit is coplanar with the $NiCl_2$ moiety. The greatest deviation from idealized octahedral geometry around the nickel ion is observed for the pyridyl nitrogen atoms, N1−Ni1−N2 165.52 (19)°; N3−Ni2−N4 167.42 (18)°.

In the crystal lattice, the molecules are linked by some unconventional C−H···Cl hydrogen bonds and also some short S···S contacts in a range of 3.64−4.09 Å. Figure 2 illustrates the crystal packing of **1**. Interestingly, the "BEDT-TTF" moieties and the metal complex units are arranged in separated columns, which are stacked along the *b*-direction.

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(16) Crystal data for **1**: brown needlelike crystal (0.40 × 0.15 × 0.05 mm^3), $M_r = 797.83$, monoclinic $P2_1/c$ with $a = 23.0117(9)$ Å, $b = 8.4975(3)$ Å, $c = 31.1483(13)$ Å, $\beta = 101.575(3)°$, $V = 5966.9(4)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.776$ g cm^{-3}. Data collection: Mo $K\alpha$ ($\lambda = 0.71073$ Å) radiation, $T = 153(2)$ K, 46348 measured with 13189 unique reflections, of which 9181($I > 2.0\sigma(I)$) were used for the structure solution. Final R1 (wR2) = 0.0615 (0.1674), GOF = 1.031 for 667 parameters. The final Fourier difference synthesis showed minimum and maximum peaks of −1.824 and +1.147 e/ Å^3. Crystal data for **2**: dark-red needlelike crystal (0.20 × 0.10 × 0.05 mm^3), $M_r = 886.97$, monoclinic $P2_1/c$ with $a = 23.4723$ (15) Å, $b = 8.6009(5)$ Å, $c = 31.359(2)$ Å, $\beta = 102.847(5)°$, $V = 6172.4(7)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.909$ g cm^{-3}. Data collection: Mo $K\alpha$ ($\lambda = 0.71073$ Å) radiation, $T = 153(2)$ K, 41280 measured with 10696 unique reflections, of which 5533($I > 2.0\sigma(I)$) were used for the structure solution. Final R1 (wR2) = 0.0804 (0.1778), GOF = 0.977 for 675 parameters. The final Fourier difference synthesis showed minimum and maximum peaks of −1.164 and +1.092 e/ Å^3.

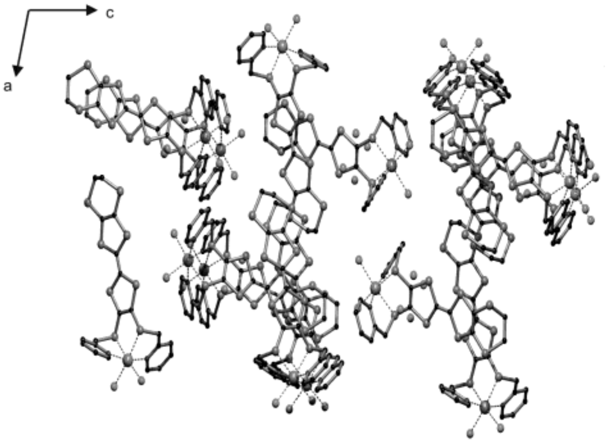

Figure 2. Projection of the crystal structure of **1** onto the *ac*-plane, showing alternating layers of organic and inorganic entities. Hydrogen atoms and solvent molecule are omitted for clarity.

Within the "BEDT-TTF columns", the shortest S···S contact, being equal to 3.64 Å, is observed in the molecule Ni(1). This crystal packing is reminiscent of what is usually observed for conducting radical salts containing organic donors and inorganic anions. Therefore, it is favorable for electrical conductivity in the oxidized state.

The compound **3** is not isostructural to **1** and **2**, as confirmed by powder X-ray diffraction measurement. The ^{1}H NMR data of the free ligand **L** and the Zn^{2+} complex were recorded in THF-d_8. The spectrum of L exhibits six sets of resonances at 8.45, 7.62, 7.29, 7.14, 4.06, and 3.34 ppm for the pyridyl, SCH_2- and $-CH_2CH_2-$, respectively.[17] Upon coordination, all the ligand proton signals except one for $-CH_2CH_2-$ move to lower field, thus indicating that all the pyridyl nitrogen atoms and the thioether sulfur atoms take part in coordination to the Zn^{2+} ion.

The electrochemical properties of compounds **L**, **1**, and **2** were investigated by cyclic voltammetry in CH_2Cl_2 (Table 1).[18] In each case, two reversible single-electron oxidation waves were observed (Table 1), corresponding to $E_{1/2(1)}$ and $E_{1/2(2)}$ of the TTF system. Upon coordination, the observed shifts are always toward more anodic potentials and affect only $E_{1/2(1)}$, whereas $E_{1/2\,(2)}$ almost remains unchanged. These observations are consistent with other metal complexed TTF systems, especially where there is a macrocyclic receptor fused to TTF, as used in cation sensing.[19] This behavior can be interpreted as being a result of the electrostatic inductive effect of the metal ion bound to the chelating ring formed by thioether and pyridyl groups, withdrawing electron density from the TTF moiety. In addition, the increased repulsive electrostatic interaction with the charged TTF moiety may lower the binding constant and eventually "push" the complexed metal ion out of the chelating ring. Moreover, **1** shows an irreversible Ni(II/I) redox process with a cathodic peak (E_{pc}) at −0.70 V vs Ag/AgCl, whereas a Ni(III/II) redox process is not observed. It seems, therefore, that ligand **L**, like acyclic ligands with soft donor atoms,[20] can stabilize Ni(I) better than Ni(III).

Table 1. Cyclic Voltammetric Data

compd	oxidation (E/V) $E_{1/2(1)}$	oxidation (E/V) $E_{1/2(2)}$	reduction (E/V) $E_{1/2}$ ($Ni^{II/I}$)
L	0.58	0.97	
1	0.63	0.95	−0.70
2	0.66	0.94	

The magnetic properties measured on a SQUID magnetometer in the temperature range 1.9−300 K revealed a paramagnetic behavior corresponding to isolated $S = 1$ and $S = {}^3/_2$ spins of the Ni(II) and Co(II) centers, respectively, which are in good agreement with their octahedral coordination spheres.

Three divalent transition metal complexes of the functionalized BEDT-TTF derivative **L** have been prepared and structurally and electrochemically characterized. The crystal structures and electrochemical properties are appropriate for their potential use as molecular building blocks for conducting and magnetic materials. A chemical and/or electrochemical partial oxidation of these complexes is under current investigation in our group.

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Supporting Information Available: X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) ^{1}H NMR spectrum of the free ligand **L**, δ (ppm; THF-d_8): 3.34 (s, 4H), 4.06 (s, 4H), 7.14−7.18 (dd, $J = 7.4$ Hz, $J = 4.8$ Hz, 2H), 7.29 (d, $J = 7.7$ Hz, 2H), 7.62−7.67 (dt, $J = 1.8$ Hz, $J = 7.7$ Hz, 2H), 8.45 (d, $J = 4.4$ Hz, 2H).

(18) Cyclic voltammetric measurements were conducted on a VA-Stand 663 electrochemical analyzer. All oxidation potentials were determined in CH_2Cl_2 under N_2 at room temperature, containing 0.1 M Bu_4NPF_6, with Ag/AgCl as reference electrode, Pt as working electrode, and glass carbon as auxiliary electrode, scan rate 100 mV s^{-1}.

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