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Synthesis of a BEDT-TTF Bipyridine Organic Donor and the First Fe^{II} Coordination Complex with a Redox-Active Ligand

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The synthesis of the new ligand, BEDT-TTF-bipy [4,5-ethylenedithio-4′,5′-(4′-methyl-2,2′-dipyrid-4-ylethylenedithio)-tetrathiafulvalene] is reported. The first Fe^{II} coordination complex, namely $[Fe(NCS)_2(BEDT\text{-}TTF\text{-}bipy)_2]\cdot CHCl_3$, with this redox-active ligand is obtained. Magnetic measurements and Mössbauer spectroscopy revealed the coexistence of high-spin and low-spin Fe^{II} species with a ratio of 40:60 in this compound.

Introduction

Charge transfer (CT) complexes based on organic donors such as TTF (tetrathiafulvalene) and its derivatives have been intensively studied.[1] Considerable efforts are currently devoted to the synthesis and investigations of new molecule-based materials involving interplay and synergy between multiple physical properties, such as electrical conductivity or superconductivity and magnetic effects, optical and magnetic properties or spin crossover.[2] Construction of such materials appears to be a challenging target for synthetic chemists who are faced with the difficult control of the self-assembly of molecular building blocks. This is indeed a crucial step to obtain a supramolecular compound that has the desired structure, stability and physical properties. Some significant achievements have been obtained in different directions: (i) light-induced magnetization[3] observed in a Prussian blue derivative, namely $K_{0.2}Co_{1.4}[Fe(CN)_6]\cdot 6.9H_2O$,[3c,3d] which exhibits a reversible photoinduced magnetization as a result of oxidation state changes for the metal ions from [Co^{III}, $S = 0$ and Fe^{II}, $S = 0$] to [Co^{II}, $S = 3/2$ and Fe^{III}, $S = 1/2$]; (ii) synergy between spin-crossover and magnetic interactions:[4] $[Fe(mnt)_2(rad)]$ [mnt = maleonitriledithiolate; rad = 2-(*para*-*N*-methylpyridinio)-4,4,5,5-tetramethylimidazolin-1-oxyl] exhibits a spin crossover between $S_{Fe} = 5/2$ at high temperature and $S_{Fe} = 1/2$ at low temperature and also an antiferromagnetic (AF) interaction at low temperature between the radical unit and Fe^{III}; (iii) electrical conductivity and magnetic interactions:[5–7] conducting materials incorporating localized spins are currently a subject of intense investigations and many compounds of this kind were obtained and characterized, such as $(BEDT\text{-}TTF)_3[MnCr(C_2O_4)_3]$ [BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene (or ET)],[6a] $(BETS)_2FeCl_4$ [BETS = bis(ethylenedithio)tetraselenafulvalene],[6b] $(C1\text{-}TET\text{-}TTF)_2FeX_4$ [X = Cl, Br; C1-TET-TTF = 4,5-bis(methylthio)-4′,5′-ethylenedithiotetrathiafulvalene].[2a]

Only two examples of hybrids with a combination of a spin cross-over property and electrical conductivity have been reported so far, namely $Fe(abpt)_2(TCNQ)_2$[8] and $[Fe(sal_2\text{-}trien)][Ni(dmit)_2]$.[9] However, in both cases no conductivity was observed. In order to enhance interactions between the two subsystems, a strategy consisting of the covalent linkage of paramagnetic transition-metal ions to redox-active ligands has been addressed.[7] However, to the best of our knowledge, there is no example of such a system with TTF derivatives as ligands. As a first attempt in this direction, we report here a detailed study on the synthesis and characterizations of the new ligand BEDT-TTF-bipy as well as its Fe^{II} complex, namely $[Fe(NCS)_2(BEDT\text{-}TTF\text{-}bipy)_2]\cdot CHCl_3$.

Results and Discussion

Synthesis

The synthesis of ligand **6** was performed as shown in Scheme 1 by a phosphate-mediated cross-coupling method between chalcogenones **4** and **5**. The former was prepared by transchalcogenation of the corresponding thione **3**, the synthesis of which was based on the thermal depolymerization of oligomer **1** on heating, followed by Diels–Alder re-

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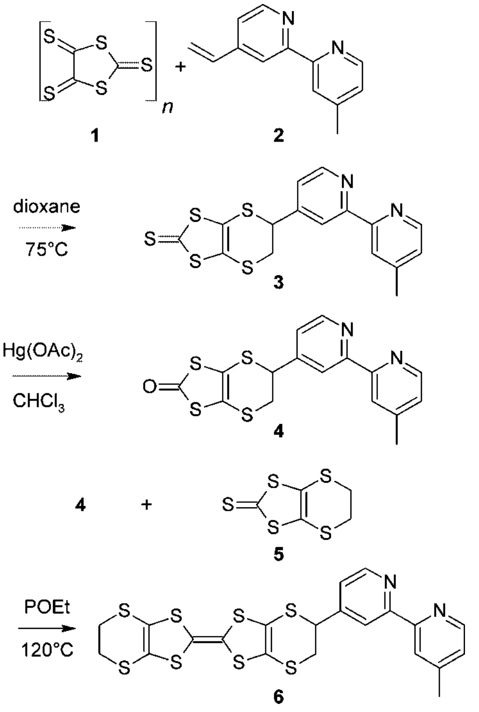
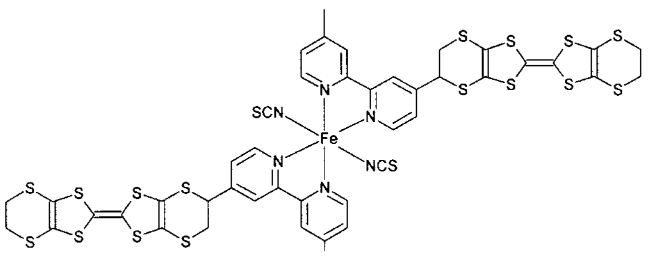
action with 4-methyl-4′-vinyl-2,2′-bipyridine (**2**). All compounds were easily purified by chromatographic separation or precipitation and have been fully characterized. Compound **7** (Scheme 2) was obtained by allowing $Fe(NCS)_2$ to react with **6** in chloroform.



Scheme 1. Synthesis of BEDT-TTF-bipy (**6**).



Scheme 2. One of the possible isomers of the Fe^{II} complex **7**.

Single-Crystal Structure of Compound 4

An ORTEP plot of molecule **4** with the atomic numbering scheme is shown in Figure 1.

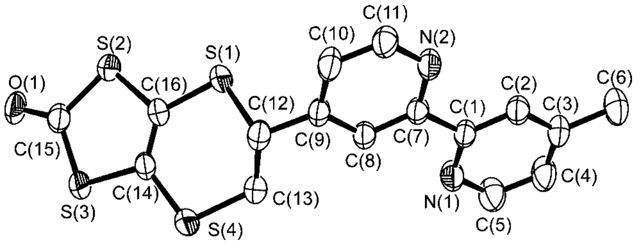


Figure 1. ORTEP (50% probability ellipsoids) structure of compound **4**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: S1–C16 1.754(2), S2–C16 1.745(2), S2–C15 1.765(3), S3–C14 1.748(2), S3–C15 1.765(3), S4–C14 1.747(3), S1–C12 1.839(3), S4–C13 1.808(3), O1–C15 1.207(3).

Molecule **4** contains an essentially planar moiety, comprising atoms C(14), C(15), C(16), O(1) and all four sulfur atoms; this plane forms an angle of 126.5° with the mean plane calculated from the C(7)–C(8)–C(9)–C(10)–C(11)–N(2) atoms belonging to the pyridyl ring. All atoms of the bipyridyl moiety lie almost perfectly within one plane with atoms N1 and N2 situated in *anti* orientation. As expected, S(1)–C(12) and S(4)–C(13) are typical single bonds, while the other C–S bonds are considerably shorter than that of a single C–S bond, indicating some delocalized π-bonding through the interaction of the sulfur d-orbitals with the C=C and C=O π-bonds. These C–S bond-length differences have been found in other analogous compounds.[10]

Single Crystal Structure of Compound 6

Although the quality of the crystal of compound **6** was poor, it was possible to determine its crystal structure. An ORTEP plot of the molecule with the atomic numbering scheme is shown in Figure 2. Compared to compound **4**, the nitrogen atoms of the bipyridyl moiety also lie in an *anti* position, but an angle of 11.8(11)° is observed between the two pyridyl rings. The mean plane calculated from the pyridyl ring [C(11)–C(12)–C(13)–C(14)–C(15)–N(1)] directly bonded to the BEDT-TTF moiety, forms an angle of 75.2(5)° (see Figure 3) with the almost planar TTF skeleton [S(3)–S(4)–C(5)–C(6)–S(5)–S(6)]. As usual, a boat conformation is observed for the ET molecule. One can notice that the S(7)–C(9) and S(8)–C(10) bonds are significantly shorter than the corresponding ones [S(1)–C(12) and S(4)–C(13)] observed in compound **4** (see Figures 1 and 2).

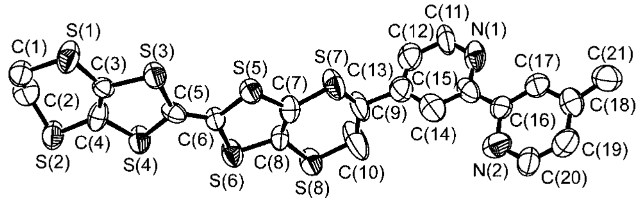


Figure 2. ORTEP structure of **6** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: S6–C8 1.723(16), S6–C6 1.734(15), S3–C5 1.720(17), S3–C3 1.787(16), S8–C8 1.731(17), S8–C10 1.78(2), S4–C5 1.753(16), S4–C4 1.76(2), S5–C6 1.731(16), S5–C7 1.762(19), C5–C6 1.42(2), C8–C7 1.38(3), C4–C3 1.32(3), S7–C9 1.72(3), S7–C7 1.729(18).

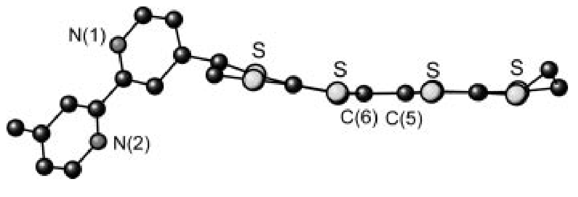


Figure 3. View of compound **6** showing the angle of 75.2(5)° between the TTF skeleton and the $N(1)C_5$ pyridyl ring.

TGA of Compound 7

The detection of the temperature dependence of weight loss of $[Fe(NCS)_2(BEDT\text{-}TTF\text{-}bipy)_2]\cdot CHCl_3$ was carried out on a powdered sample between 25 and 150 °C, where the compound starts to decompose. In total, a weight loss of 8.1% is observed within the range 25–65 °C. The gas analysis by means of mass spectrometry coupled to TGA revealed the presence of chloroform only. The calculated weight loss for one molecule of $CHCl_3$ is equal to 8.5%.

Electrochemical Measurements of Compound 7

The solution redox properties of the new donor ligand **6** and of the target compound **7** were investigated by cyclic voltammetry (CV), in dichloromethane. Table 1 gives these results and those obtained for BEDT-TTF (ET) under the same conditions. In each case, two typical reversible single-electron redox couples are observed, corresponding to respective formations of the monocation followed by the dication. No difference is observed between ET and donor **6** redox potentials, showing that the methylbipyridyl group has no effect on the redox potentials. The first potential of compound **7** remains unaffected while the second potential decreases.

Table 1. Cyclic voltammetric data[a].

Compound	$E_1^{1/2}$ [V]	$E_2^{1/2}$ [V]	$E(Fe^{2+}/Fe^{3+})$ [mV]	$\Delta E = E_2^{1/2} - E_1^{1/2}$ [mV]
ET	0.52	0.94		420
6	0.55	0.95		400
7	0.55	0.86	1100	310

[a] All oxidation potentials were determined under N_2 in CH_2Cl_2 vs. ESC at room temperature. Measurements have been performed at a scan rate of 100 mV·s^{-1} using 0.1 M $(Bu_4N)PF_6$ as the electrolyte and Pt as the working electrode.

UV/Vis Spectra of Compound 7

The room-temperature UV/Vis absorption spectra of BEDT-TTF-bipy and $[Fe(NCS)_2(BEDT\text{-}TTF\text{-}bipy)_2]$ in DMF solution are shown in Figure 4. The spectra mainly reveal that upon complexation, an intense broad band appears at around 19000 cm^{-1}. This band is characteristic of the Fe–bipyridine metal-to-ligand charge transfer (MLCT).[11,12] The presence of this MLCT band reflects the formation of the complex $[Fe(NCS)_2(BEDT\text{-}TTF\text{-}bipy)_2]$. The intense absorption band observed at energies > 25000 cm^{-1} corresponds to the tail of the intra-ligand charge transfer π-π*.[13,14]

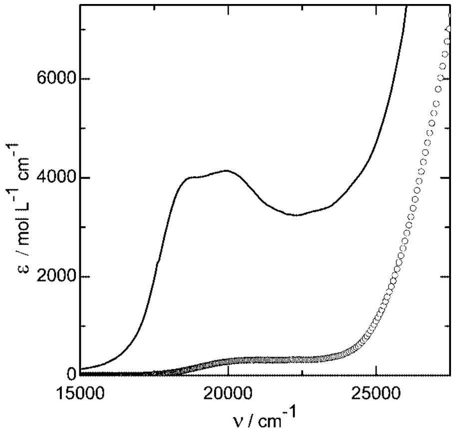


Figure 4. Absorption spectra of **6** (circles) and $[Fe(NCS)_2(BEDT\text{-}TTF\text{-}bipy)_2]$ (——) in dimethylformamide solution.

Magnetic Susceptibility of Compound 7

The thermal dependence of the $\chi_M T$ product of $[Fe(NCS)_2(BEDT\text{-}TTF\text{-}bipy)_2]\cdot CHCl_3$ is represented in Figure 5. At room temperature, $\chi_M T$ is equal to 1.65 cm^3·K·mol^{-1} and the value remains almost constant down to 60 K where it starts to decrease. The room-temperature value is, on the one hand, much lower than the expected value for a high-spin (HS) Fe^{II} species ($\chi_M T \approx$ 3.7 cm^3·K·mol^{-1})[15] and, on the other hand, much higher than the expected value for a purely low-spin (LS) Fe^{II} species ($\chi_M T \approx$ 0.1 cm^3·K·mol^{-1}).[16] We may therefore conclude that both HS and LS Fe^{II} species are mixed together, the ratio being close to 40:60. It may also be the result of the presence of *cis*/*trans* configurations in the complex, but this could not be answered conclusively. The lowering of $\chi_M T$ at low temperatures can be due to the zero-field splitting of Fe^{II}[17] and intermolecular antiferromagnetic interactions between the metal centres.

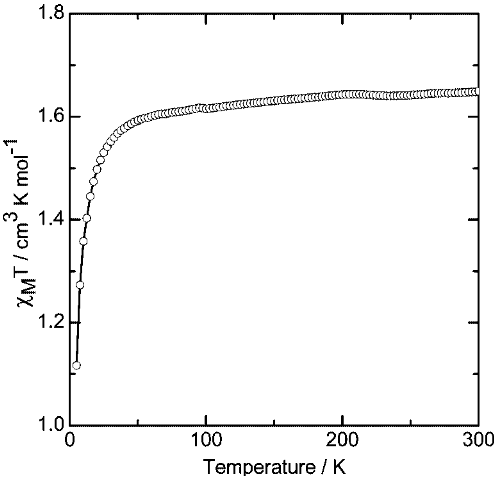


Figure 5. Thermal variation of $\chi_M T$ for a powdered sample of $[Fe(NCS)_2(BEDT\text{-}TTF\text{-}bipy)_2]\cdot CHCl_3$.

Mössbauer Spectroscopy of Compound 7

The Mössbauer spectrum of $[Fe(NCS)_2(BEDT\text{-}TTF\text{-}bipy)_2]\cdot CHCl_3$ at 80 K is shown in Figure 6. The spectrum shows unambiguously the presence of two spin states for Fe^{II}: a high-spin state, characterized by a doublet with quadrupole splitting ΔE_Q = 2.70(1) and an isomer shift *IS* = 1.000(6) mm·s^{-1} and a low-spin state, characterized by a second quadrupolar doublet with quadrupole splitting ΔE_Q = 0.369(2) and an isomer shift *IS* = 0.367(1) mm·s^{-1}. These Mössbauer parameters are in good agreement with those observed in the literature for high-spin and low-spin Fe^{II} compounds.[18] On the basis of equal Debye–Waller factors (f) for HS and LS Fe^{II}, the ratios A_{HS}/A_{TOT} and A_{LS}/A_{TOT} result in 0.25(1) and 0.75(1), respectively. However, this parameter for the resonating nuclei can differ distinctly for HS and LS Fe^{II},[19] whereby the determined LS area (A_{LS}) overestimates the LS molar fraction if $f_{HS} = f_{LS}$ is assumed. Consequently, an HS Fe^{II} fraction in the order of 0.3–0.4 can be estimated in fairly good agreement between the magnetic and the Mössbauer measurements.

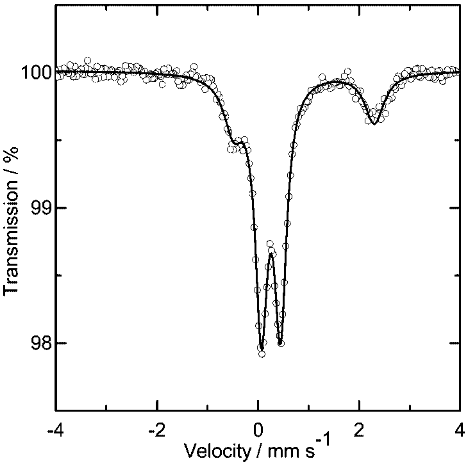


Figure 6. Mössbauer spectrum of [Fe(NCS)$_2$(BEDT-TTF-bipy)$_2$]·CHCl$_3$ at 80 K. The spectrum is characterized by two quadruple doublet characteristics of high-spin and low-spin states of Fe^{II}, respectively.

Conclusions

We reported in this contribution a detailed synthesis and structure of a new ligand, namely BEDT-TTF-bipy as well as the first Fe^{II} coordination complex, namely [Fe(NCS)$_2$-(BEDT-TTF-bipy)$_2$]·CHCl$_3$ with this redox-active ligand. Although it was not possible to obtain single crystals of this complex, the use of different techniques (TGA, elemental analysis, cyclic voltammetry, magnetic measurements, UV and Mössbauer spectroscopy) allowed us to fully characterize this material. Magnetic measurements and Mössbauer spectroscopy showed a mixture of high-spin and low-spin Fe^{II} species with a ratio of 40:60 in this complex. Moreover, one of the reasons for the lack of crystallization might be the existence of several possible isomers for this compound. In order to limit the number of isomers, work is underway to prepare the corresponding ligand with a terminal C=C double bond [C(9)–C(10) in Figure 2].

Experimental Section

General: X-ray data for compound **4** were collected at 253 K with a Stoe Image Plate Diffraction System,[20] while for compound **6** data were collected at room temperature with an Enraf–Nonius four-circle diffractometer equipped with a CCD camera (CDFIX centre of Université de Rennes 1). Both sets of data were collected using an Mo-K_α graphite-monochromated radiation source (λ = 0.71073 Å). The room-temperature UV/Vis absorption spectra were obtained with a BIO-TEK Instruments UVIKON-XL spectrophotometer. The magnetic susceptibility χ_M was recorded with a Quantum Design MPMS SQUID magnetometer operating in the 2–300 K temperature range at a field of 1 T. The experimental data have been corrected from the diamagnetism of the sample holder and the intrinsic diamagnetism of the materials evaluated with Pascal's tables. Mössbauer measurements were obtained on a constant-acceleration spectrometer with a 50 mCi source of ^{57}Co (Rh matrix). The isomer shift values (*IS*) are given with respect to metallic iron at room temperature. The absorber was a sample of microcrystalline powder enclosed in a 2 cm diameter cylindrical plastic sample holder, the size of which was determined to optimize the absorption. The 80 K spectrum was obtained by using an MD306 Oxford cryostat, the thermal scanning being monitored by an Oxford ITC4 servocontrol device (±0.1 K). Fitting parameters for all spectra were obtained by using a least-squares computer program. The standard deviations of statistical origin of the Mössbauer parameters are given in parentheses. Cyclic voltammetry measurements were conducted with an EDAC EA161 Potentiostat. Thermogravimetric analysis was performed with a SETARAM LABSYS DTA-TG/DSC apparatus coupled to a Pfeiffer Omnistar mass spectrometer.

Synthesis: All reagents were of analytical grade and used as received. All reactions were carried out under argon, using freshly distilled and degassed solvents. The [C$_3$S$_5$]$_x$ oligomer **1**[21] and 4-methyl-4′-vinyl-2,2′-bipyridine (**2**)[22] were prepared according to literature procedures.

4,5-[(4′-Methyl-2,2′-dipyrid-4-yl)ethylenedithio]-1,3-dithiole-2-thione (3): A mixture of oligomer **1** (1 g) and compound **2** (1 g, 5.1 mmol) in dioxane (20 mL) was heated to 75 °C and stirred for 1.5 h. The resulting mixture was filtered hot and the precipitate was further washed with dichloromethane (3 × 25 mL) to completely extract the product. The filtrate and combined washings were treated with activated charcoal. After filtration, the solvent was evaporated under vacuum to give a yellow oil that was purified by chromatography on silica gel with dichloromethane/ethyl acetate (1:1) to afford a yellow powder (1.44 g, 72 %). $C_{16}H_{12}N_2S_5·0.3C_4H_8O_2$ (419.05): calcd. C 49.30, H 3.46, N 6.69; found C 49.50, H 3.16, N 6.64.

4,5-(4′-Methyl-2,2′-dipyrid-4-ylethylenedithio)-1,3-dithiol-2-one (4): To a solution of **3** (0.4 g, 1 mmol) in chloroform (55 mL) and acetic acid (7 mL), was added Hg(OAc)$_2$ (0.935 g, 2.9 mmol). The mixture was stirred at room temperature for 45 min. During this period, the suspension changed colour from yellow to white. The resulting white precipitate was filtered off using Celite and washed thoroughly with CHCl$_3$. The filtrate and combined washings were neutralized with a saturated Na$_2$CO$_3$ aqueous solution and then extracted with water (3 × 40 mL). After drying with Na$_2$SO$_4$, the combined organic phases were concentrated under vacuum. The resulting oily product was solidified upon the addition of diethyl ether to give **4** as a pale yellow powder (0.28 g, 73 %). $C_{16}H_{12}N_2OS_4·0.2C_4H_{10}O$ (391.36): calcd. C 51.56, H 3.60, N 7.16; found C 50.70, H 3.57, N 6.90.

4,5-Ethylenedithio-4′,5′-(4′-methyl-2,2′-dipyrid-4-ylethylenedithio)-tetrathiafulvalene (6): A suspension of 4,5-ethylenedithio-1,3-dithiole-2-thione (**5**)[23] (0.26 g, 1.16 mmol) and compound **4** (0.3 g, 0.54 mmol) in triethyl phosphite (5 mL) under nitrogen was heated to 120 °C and stirred for 2 h. After cooling to room temperature, a red precipitate had formed, which was filtered off and washed with diethyl ether to afford analytically pure **6** as a red powder

(0.19 g, 44%). $C_{21}H_{16}N_2S_8\cdot0.5H_2O$ (561.89): calcd. C 44.89, H 2.85, N 4.99; found C 44.88, H 2.90, N 4.57.

$[Fe(NCS)_2(BEDT\text{-}TTF\text{-}bipy)_2]\cdot CHCl_3$ (7): A mixture of $FeSO_4\cdot7H_2O$ (25.2 mg, 0.09 mmol), KNCS (17.6 mg, 0.18 mmol) and a pinch of ascorbic acid in 3 mL of freshly distilled methanol was stirred at room temperature for 30 min. After filtration, the resulting colourless solution of $Fe(NCS)_2$ was added dropwise to a solution of compound **6** (100 mg, 0.18 mmol) in distilled chloroform (22 mL). A red-brown precipitate formed immediately, which was filtered off and washed with MeOH and $CHCl_3$ to give the desired Fe^{II} complex as a dark-purple powder (87 mg, 75%). $C_{44}H_{32}FeN_6S_{18}\cdot CHCl_3$ (1397.17): calcd. C 38.68, H 2.38; N 6.01, S 41.31; Fe 4.00; found C 38.97, H 2.45, N 6.46, S 39.95, Fe 4.42.

X-ray Crystallography. 4: A pale-yellow, rod-like crystal of compound **4** ($0.42\times0.15\times0.11$ mm) was obtained by slow concentration of a solution of compound **4** in a mixture of CH_2Cl_2 and ethyl acetate. The intensity data were collected at 253 K. This compound crystallized in the $P\bar{1}$ triclinic space group with the following parameters: $a = 5.6428(7)$ Å, $b = 10.1851(13)$ Å, $c = 15.158(2)$ Å, $\alpha = 105.847(15)°$, $\beta = 94.448(16)°$, $\gamma = 103.526(15)°$, $V = 805.5(2)$ Å^3, $Z = 2$, $\mu = 0.594$ mm^{-1}, 2911 unique for 5724 collected reflections, $R_1 = 0.0392$, $wR_2 = 0.1039$. **6:** Compound **6** was dissolved in a mixture of CH_2Cl_2 and ethyl acetate and heated in an ultrasonic bath. The resulting solution was filtered and a few drops of methanol were added to the solution. After slow concentration, a few crystals of **6** of very low quality were obtained. The intensity data were collected at room temperature. This compound crystallized in the monoclinic space group $P2_1/c$ with the following parameters: $a = 6.8420(4)$ Å, $b = 17.6760(11)$ Å, $c = 19.2560(14)$ Å, $\beta = 96.146(2)°$, $V = 2315.4(3)$ Å^3, $Z = 4$, $\mu = 0.785$ mm^{-1}, 4026 unique for 13627 collected reflections, $R_1 = 0.1949$, $wR_2 = 0.4551$. All structures were solved by direct methods using the program SHELXS-97.[24] The refinement and all further calculations were carried out using SHELXL-97.[25] H-atom positions were calculated as a riding model. Non-H atoms were refined anisotropically, using weighted full-matrix least squares on F^2. CCDC-287337 and -600718 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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