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Coexistence of two distinct axial ligands and their thermo-induced substitution in *trans*-[$FeL_2(NCS)_2$][$FeL_2(CH_3OH)_2$]$(NCS)_2$ (L = 4-amino-3-(*p*-chlorophenyl)-5-(2-pyridyl)-1,2,4-triazole)

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ABSTRACT

A novel iron(II) complex, *trans*-[$FeL_2(NCS)_2$][$FeL_2(CH_3OH)_2$]$(NCS)_2$ (**1**) with 4-amino-3-(*p*-chlorophenyl)-5-(2-pyridyl)-1,2,4-triazole (**L**) has been successfully synthesized and characterized. X-ray crystallography analysis shows that **1** is the first example in the mononuclear triazole-based complexes consisting of two distinct molecules: *trans*-[$FeL_2(NCS)_2$] and *trans*-[$FeL_2(CH_3OH)_2$]$(NCS)_2$ with each octahedral iron(II) center coordinated axial by two NCS^- ions in Fe1 but two MeOH molecules in Fe2. Moreover, **1** can lose two MeOH molecules at 220 °C to form *trans*-[$FeL_2(NCS)_2$] (**2**) which can be transformed to **1** when recrystallizing **2** in methanol. Both **1** and **2** are high-spin species in the range of 1.8–300 K.

Over the past four decades, substituted 1,2,4-triazoles have attracted considerable attention in coordination chemistry due to their rich and versatile coordination modes [1,2]. Moreover, triazole derivatives are known to often induce temperature-mediated spin-crossover (SCO) in iron(II) complexes [3–10]. Among them, the mononuclear complexes *trans*-[$Fe(Trz)_2(NCS)_2$] (Trz = 1,2,4-triazole derivative) are one of most interesting systems. For example, complex *trans*-[$Fe(ABPT)_2(NCS)_2$] (ABPT = 4-amino-3,5-bis(2-pyridyl)-1,2,4-triazole) exhibits SCO properties associated with intriguing polymorph behavior (red polymorph A, $T_{1/2} = 180$ K [11]; orange polymorph B, High-spin [12]; polymorph C, partial SCO at 86 K [13]; polymorph D, partial SCO at 162 K [13] and revealing a long-lived photoinduced metastable state through NCS^- linkage isomerization accompanied with a SCO [14]). In addition, complex *trans*-[$Fe(MBPT)_2(NCS)_2$] shows an abrupt SCO with $T_{1/2} = 231$ K, in contrast to its homologous one *cis*-[$Fe(mMBPT)_2(NCS)_2$] still staying in a high-spin state [MBPT (or *m*MBPT) = 4-*p*(or *m*)-methylphenyl-3,5-bis(2-pyridyl)-1,2,4-triazole] [5].

Rich magnetic properties of the *trans*-[$Fe(Trz)_2(NCS)_2$] complexes prompted us to widen further the range of used ligands from symmetrical [15–19] to asymmetrical 3,5-disubstituted 1,2,4-triazole [20–24]. Here we present the synthesis of a new asymmetrical triazole, 4-amino-3-(*p*-chlorophenyl)-5-(2-pyridyl)-1,2,4-triazole (**L**) and its iron(II) complex, *trans*-[$FeL_2(NCS)_2$][$FeL_2(CH_3OH)_2$]$(NCS)_2$ (**1**). Complex **1** represents the first example in any mononuclear triazole-based complexes consisting of two unique molecules: *trans*-[$FeL_2(NCS)_2$] and *trans*-[$FeL_2(CH_3OH)_2$]$(NCS)_2$ with each octahedral iron(II) center coordinated axial by two NCS^- ions in Fe1 but two MeOH molecules in Fe2. Notable, when heated at 220 °C, complex **1** can be converted to another new complex, *trans*-[$FeL_2(NCS)_2$] (**2**) accompanied with loss of two coordinated methanol molecules. In turn, when recrystallized in methanol, **2** can be transformed to **1**. In addition, both **1** and **2** are high-spin species in the range of 1.8–300 K.

Ligand **L** was solvothermally synthesized by anhydrous hydrazine and 1,4-dichloro-1-(2-pyridyl)-4-(*p*-chlorophenyl)-2,3-diaza-1,3-butadiene (**II**) in a yield of 46.6% [25]. Compound **II** can be prepared by treating N-(*p*-chlorophenylcarbonyl)-N′-(2-pyridylcarbonyl)hydrazine (**I**) [23] with thionyl chloride in anhydrous toluene (Scheme S1). Ligand **L** reacting with iron(II) and KSCN in molar ratio of 2:1:2 under an argon atmosphere produces complex **1** in a yield of 73.8% [26].

The X-ray structure analysis indicates that **L** crystallizes in the monoclinic space group *C*2/*c* (Table 1), and consists of one *p*-chlorophenyl ring, one pyridyl group and one triazole ring (Fig. 1). These rings almost share a common plane because the 1,2,4-triazole ring is oriented at dihedral angles of 8.6(3)° and 5.7(3)° with the pyridyl ring and the *p*-chlorophenyl ring, respectively. These values are similar to those [3.28(10)° and 6.13(9)°] found in ABPT [27]. The intermolecular N5 – H5A···N2(N3)[a] hydrogen bonds link the **L** molecules to form a 1D chain along *b* axis (Fig. S1), which are further connected by some intermolecular edge-to-face C – H···π and N5 – H5A···π interactions (Table S1) and a face-to-face π···π stacking interaction between

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Table 1
Crystal data and structure refinement for **L** and **1**.

Compounds	L	1
Empirical formula	$C_{13}H_{10}N_5Cl$	$C_{58}H_{48}Cl_4Fe_2N_{24}O_2S_4$
Formula weight	271.71	1494.94
Crystal system	Monoclinic	Triclinic
Space group	*C*2/*c*	*P*-1
a (Å)	28.68 (7)	11.356 (4)
b (Å)	6.041 (16)	12.581 (4)
c (Å)	14.68 (4)	13.511 (4)
α (°)	90.00	104.277 (4)
β (°)	103.90 (3)	106.390 (4)
γ (°)	90.00	105.604 (4)
V ($Å^3$)	2470 (11)	1671.4 (9)
Z	8	1
D_c (g cm^{-3})	1.462	1.485
μ (mm^{-1})	0.302	0.781
F (000)	1120	764
Crystal size (mm^3)	0.16 × 0.12 × 0.10	0.20 × 0.16 × 0.08
θ range (°)	1.46–25.00	1.79–25.00
Reflections collected	8203	11977
Independent reflections	2175 [$R_{int}=0.0757$]	5820 [$R_{int}=0.0337$]
Reflections observed [$I>2\sigma(I)$]	1436	3651
Data/restraints/parameters	2175/3/178	5820/6/439
Goodness-of-fit on F^2	1.071	0.943
Final *R* indices ($I>2\sigma(I)$)	0.0682/0.1834	0.0444/0.1034
R indices (all data)	0.1027/0.1985	0.0892/0.1175
Largest difference peak and hole (e$Å^{-3}$)	0.801 and −0.280	0.264 and −0.254

p-chlorophenyl and triazole ring (the centroid–centroid distance = 3.817(3) Å and dihedral angle = 5.7(3)°) to form a 2D network in the *bc* plane (Fig. S2).

Complex **1** crystallizes in the triclinic space group *P*-1 (Table 1), and its asymmetric unit contains two crystallographically distinct mononuclear Fe(II) centers, *trans*-$[FeL_2(NCS)_2]$ (Fe1 site) and *trans*-$[FeL_2(CH_3OH)_2]^{2+}$ cation (Fe2 site), together with two non-coordinated NCS^- anions (Fig. 2). The Fe1 site adopts one distorted $[FeN_6]$ octahedron surrounded by four nitrogen atoms from two **L** ligands in the equatorial plane and two NCS^- in the axial positions. While the Fe2 site is coordinated by four nitrogen atoms from two **L** ligands in the basal plane and two oxygen atoms from two *trans*-disposed CH_3OH molecules to form another distorted $[FeN_4O_2]$ octahedral geometry. To the best of our knowledge, the simultaneous presence of two *trans*-positions NCS^- and CH_3OH in a mononuclear complex with triazole is unprecedented. The only example of triazole-based complex with *trans*-coordinated NCS^- and CH_3OH was reported by Tong et al. in a dinuclear cobalt(II) complex, $[Co_2(bpt)_2(NCS)_2(MeOH)_2]$ (bpt = 3,5-bis(2-pyridyl)-1,2,4-triazolato) [28]. Each **L** in **1** coordinates to iron(II) via N1 of pyridyl and N2 of the triazole, similar to these observed in the related complexes [5,11]. The average Fe1–N bond length is 2.157(3) Å (Table S2), which falls in the typical range of an Fe(II)–N bond in a high spin state. The spin-state assignment made on the basis of Fe(II)–N bond distance is related with the octahedral distortion parameter (Σ), a parameter commonly used for the quantification of the angular deviation of octahedron from an ideal octahedral geometry [29]. A smaller Σ value is generally associated with a stronger ligand field and, therefore, a low spin state of the metal ion, while the opposite suggests a high spin state [29,30]. In the present case, the Σ value is 82.8°, suggesting that the Fe1 center is in a high spin state at 293 K (vide post). The bond lengths in Fe2 center are 2.222(3) Å, 2.117(3) Å and 2.114(3) Å for Fe2–N7, Fe2–N8 and Fe2–O1, respectively, which are similar to the characteristic values of the $[FeN_4O_2]$ core in a high spin state [31]. A distortion from the $[FeN_4O_2]$ octahedron was also induced from the inequivalence of the bond lengths. Calculation of the octahedral distortion parameter, Σ = 64.8°, showed that the distortion of Fe2 center is smaller than that of Fe1. In addition, the $Fe-N_{trz}$ bond lengths are always shorter thanFe–N_{py} ones in two Fe(II) centers, consistent with

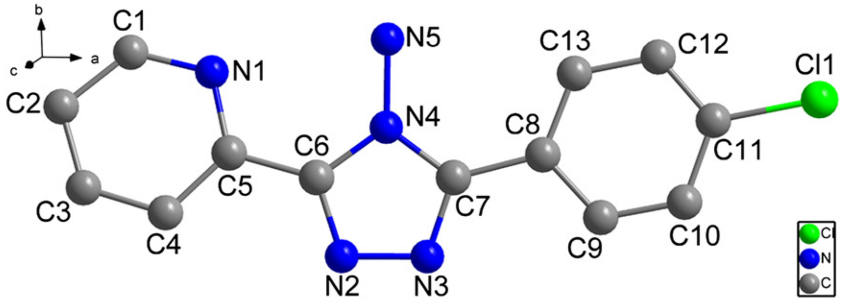


Fig. 1. Projection of the structure of L with the atomic labeling system. Hydrogen atoms are omitted for clarity.

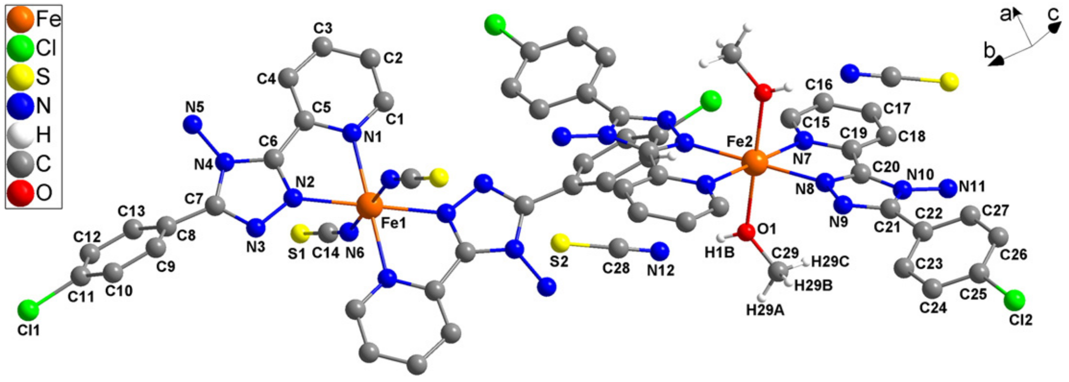


Fig. 2. Projection of the structure of **1** with the atomic labeling system. Hydrogen atoms except CH_3OH are omitted for clarity.

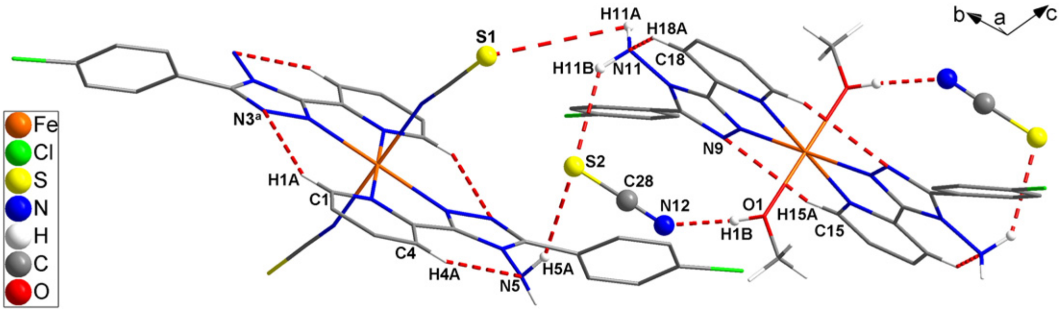


Fig. 3. The hydrogen bonding interactions involving NCS^- in **1**.

those observed in the analogous Fe(II) complexes [2,5,32–34]. The pyridine–triazole moiety of **L** in **1** is nearly perfectly planar because the dihedral angles are 4.2(2)° for Fe1 site and 3.2(2)° for Fe2 center, showing that on coordination, the pyridyl–triazole twist angle becomes smaller than that in the free **L** ligand. However, the dihedral angles (49.3(3)° for Fe1 and 32.5(4)° for Fe2) between the triazole and the *p*-chlorophenyl ring are much larger than those in the free **L** ligand. It is noticeable that in complex **1** there are four linear NCS^- groups [$\angle N6-C14-S1 = 178.4(3)^\circ$ and $\angle N12-C28-S2 = 178.0(4)^\circ$], two of which do not take part in coordination. The non-coordinated NCS^- group, nearer to the Fe2 center, acts not only as a counter ion but also as an important bridge to link the *trans*-$[FeL_2(NCS)_2]$ and *trans*-$[FeL_2(CH_3OH)_2]^{2+}$ cations by the intermolecular $O1-H1B\cdots N12$ and $N-H\cdots S2$ hydrogen bonds (Fig. 3 and Table S3). Finally, the molecules of **1** are further connected by intermolecular $N11-H11A\cdots S1^d$ hydrogen bonds and edge-to-face $C29-H29A\cdots\pi^c$ interactions to form a compact 3D supramolecular structure (Fig. S3).

The unusual structural feature of **1** encouraged us to further investigate the possible exchange interactions of axial ligands between the *trans*-disposed CH_3OH molecules and the non-coordinated NCS^- group on Fe2 site, which will be helpful to understand the competing coordination of axial ligands in an octahedral complex in the process of crystallization of **1**. When **1** was heated at 220 °C under an argon atmosphere, it can lose completely two coordinated CH_3OH molecules to produce a new complex, *trans*-$[FeL_2(NCS)_2]$ (**2**) [35], which was demonstrated by TGA, IR, elemental analysis and powder X-ray diffraction (Fig. S4). TGA of **1** (Fig. 4) shows that the weight loss of 5.21% between 30 and 220 °C is due to the loss of two coordinated CH_3OH molecules (calculated, 4.29%), associated with an exothermic peak at 218 °C in the DSC curve. As shown in Fig. 5, the IR spectrum of **1** shows two strong bands at 2077 and 2057 cm^{-1}, attributable to $C{\equiv}N$ stretching vibrations of the *trans*-coordinated [5] and non-coordinated NCS^- groups, respectively [36]. Two medium bands at 3284 and 3184 cm^{-1} are mainly due to $N-H$ stretching vibrations of $-NH_2$ groups. Two weak bands at 2973 and 2796 cm^{-1} can be assigned to $C-H$ stretching vibrations of $-CH_3$ groups of the coordinated CH_3OH molecules. In contrast, the IR spectrum of **2** (Fig. 5) exhibits only a strong band at 2077 cm^{-1} due to $C{\equiv}N$ stretching vibrations of the *trans*-coordinated NCS^- groups. Furthermore, lack of any bands in the region of 2700–3100 cm^{-1} in **2** also reveals that the non-coordinated NCS^- ions of **1** have replaced completely the coordinated CH_3OH molecules under the intense heat conditions. It is worthwhile to note that **1** can be obtained again when recrystallizing the powder of **2** in methanol solution and its unit cell has been re-measured by single crystal X-ray diffraction [35]. So complexes **1** and **2** can be transformed each other in a specific condition shown in Scheme 1.

Unfortunately, the magnetic property study (Fig. S5) revealed that **1** was not SCO active but kept in a high-spin state in the entire observed temperature range, and this behavior can be interpreted by Curie–Weiss law, $\chi_m = C/(T-\theta)$, with a Curie value of 7.09 and Weiss constant of $-0.11(5)$ K. This result is in good agreement with the X-ray crystallography analysis. Similarly, **2** is also a high-spin species in the range of 1.8–300 K with $C = 3.16$ and $\theta = -1.2(2)$ K (Fig. S5).

In conclusion, a new ligand, 4-amino-3-(*p*-chlorophenyl)-5-(2-pyridyl)-1,2,4- triazole (**L**) and its iron(II) complex, *trans*-$[FeL_2(NCS)_2]$ $[FeL_2(CH_3OH)_2](NCS)_2$ (**1**), have been successfully synthesized and characterized by FT-IR, ^1H NMR, ESI-MS, TGA, elemental analysis and single crystal X-ray crystallography. The structural analysis indicates that **1** is a rare example of coexistence of two *trans*-coordinated NCS^-

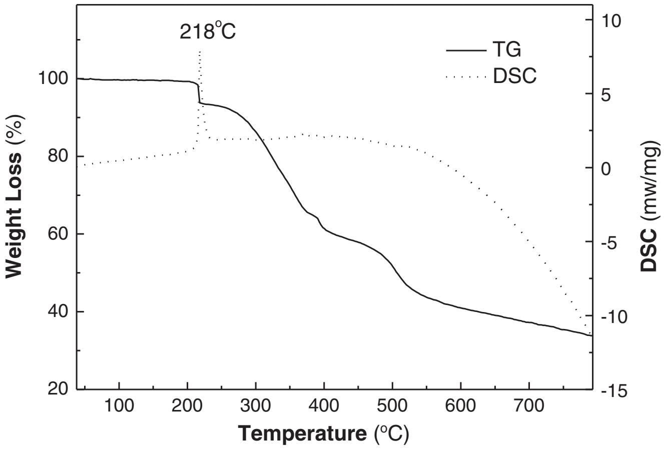


Fig. 4. TGA/DSC curves of **1**.

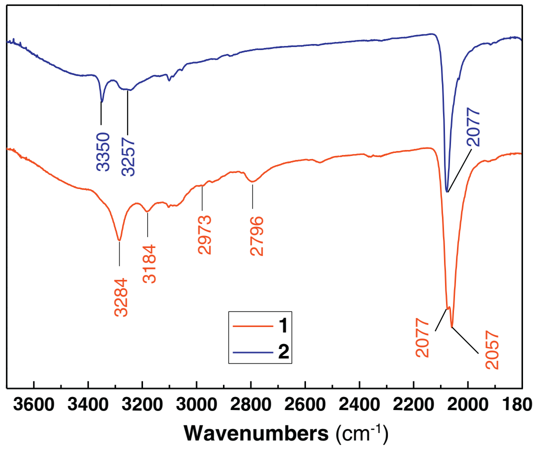
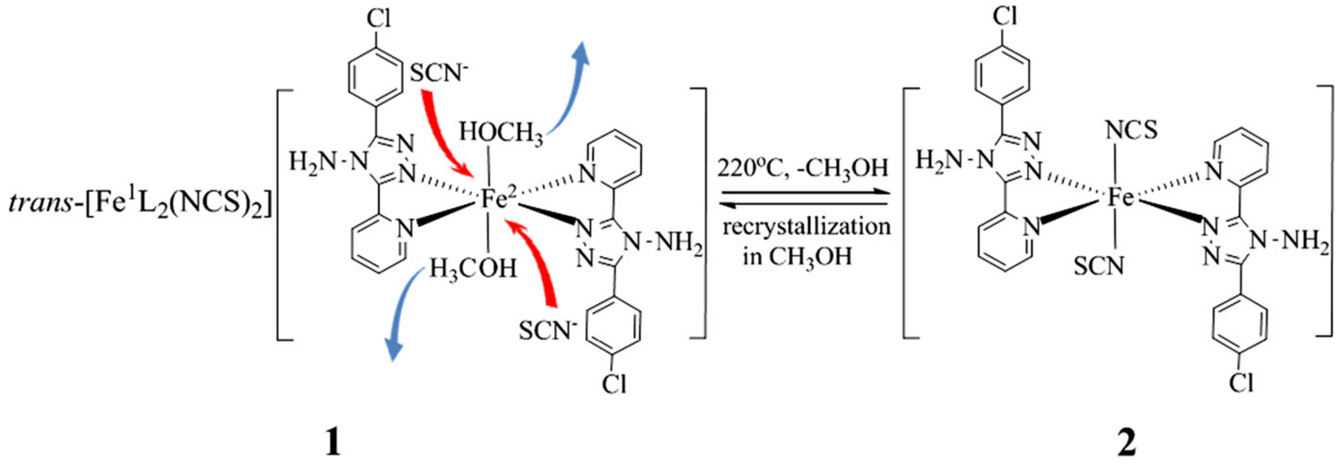


Fig. 5. IR spectra of **1** and **2** in the region of characteristic bands of NCS^-, $-NH_2$ and CH_3OH (3600–1800 cm^{-1}).



Scheme 1. The transformation of **1** and **2**.

anions and CH_3OH molecules in a mononuclear triazole-based octahedral complex. An interesting substitution of axial ligand NCS^- for CH_3OH in **1** occurs at 220 °C. Complexes **1** and **2** keep in high-spin states in the range of 1.8–300 K.

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Appendix A. Supplementary data

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 901929 (**L**) and 901930 (**1**). Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or email: deposit@ccdc.cam.ac.uk). Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2012.11.022.

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[25] Synthesis of **L**: N-(*p*-chlorophenylcarbonyl)-N′-(2-pyridylcarbonyl)hydrazine (**I**) was prepared as the procedure reported earlier [20]. Thionyl chloride (3 mL, 40 mmol) in anhydrous toluene (10 mL) was added dropwise to a stirring solution of **I** (2.2 g, 8 mmol) in anhydrous toluene (30 mL). The solution was refluxed for 12 h at 120 °C and the solvent was removed under reduced pressure. The precipitate was filtered and the resulting solid was recrystallized from anhydrous toluene to give 1,4-dichloro-1-(2-pyridyl)-4-(*p*-chlorophenyl)-2,3-diaza-1,3-butadiene (**II**) as white solids (1.8 g, 71.7%), m.p. 146–148 °C. 4-Amino-3-(*p*-chlorophenyl)-5-(2-pyridyl)-1,2,4-triazole (**L**) was prepared by condensation of **II** (1.872 g, 6.0 mmol) with anhydrous hydrazine (2 mL, 63.0 mmol) in a 25 mL capacity Teflon-lined stainless-steel reactor at 120 °C for 12 h (Scheme S1), yield of 0.76 g (recryst. from ethanol, 46.6%), and m.p. of 212–213 °C. Single crystals of the **L** suitable for X-ray diffraction study were obtained from

anhydrous ethanol upon slow evaporation at ambient temperature. Anal. Calcd for $C_{13}H_{10}N_5Cl$ (%): C, 57.47; H, 3.71; N, 25.78. Found (%): C, 57.65; H, 3.76; N, 25.62. FT-IR: 3283 (m), 3191 (m), 1615 (m), 1594 (s), 1467 (s), 1093 (s), 1012 (m), 966 (m), 834 (vs), 787 (m), 727 (m), 693 (m) cm^{-1}. ^1H NMR δ: 6.44 (2H, br), 7.39 (1H, t), 7.46 (2H, d), 7.87 (1H, d), 8.20 (2H, d), 8.35 (1H, d), 8.63 (1H, s). ESI-MS: $m/z=272.3$.

[26] Synthesis of **1**: A solution of KSCN (0.039 g, 0.4 mmol) in anhydrous MeOH (2 mL) was added in a solution of $FeSO_4{\cdot}7H_2O$ (0.056 g, 0.2 mmol) in MeOH (2 mL). The mixture was stirred for 30 min, then filtered. The K_2SO_4 precipitate was washed with 2 mL of anhydrous MeOH. The methanolic fractions containing $Fe(SCN)_2$ were collected and then were poured into a methanol solution of the corresponding ligand (0.108 g, 0.4 mmol). The resulting orange solution was stirred for 2 h during which time an orange precipitate formed. The precipitate was filtered and washed with H_2O and dried in vacuo to give 0.11 g (73.8%) of the complex. The orange single crystals suitable for X-ray diffraction were obtained by evaporation from a methanol solution. Anal. Calcd for $C_{58}H_{48}Cl_4Fe_2N_{24}O_2S_4$ (%): C, 46.60; H, 3.24; N, 22.49; S, 8.58%. Found: C, 46.48; H, 3.31; N, 22.37; S, 8.43%. FT-IR: 3421 (br, m), 3284 (m), 3184 (w), 2973 (w), 2796 (w), 2077 (vs), 2057 (vs), 1604 (m), 1485 (m), 1469 (m), 1297 (m), 1157 (m), 1093 (m), 1014 (m), 984 (m), 834 (m), 796 (m), 698 (w) cm^{-1}. ESI-MS: $m/z=272.2$, 656.5.

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[35] Synthesis of **2**: After **1** (0.075 g, 0.5 mmol) was heated at 220 °C under an argon atmosphere for 0.5 h, **2** was obtained quantitatively as an orange powder, 0.070 g (97.8%). Anal. Calcd for $C_{28}H_{20}Cl_2FeN_{12}S_2$ (%): C, 47.01; H, 2.82; N, 23.49; S, 8.96%. Found: C, 47.25; H, 3.02; N, 23.23; S, 8.63%. FT-IR: 3350 (m), 3257 (w), 2077 (vs), 1629 (m), 1478 (m), 1467 (m), 1291 (m), 1252 (m), 1093 (m), 1014 (m), 977 (m), 835 (m), 796 (m), 692 (w) cm^{-1}. When recrystallizing the powder of **2** in methanol, complex **1** was obtained in a yield of 89% and its unit cell has been measured by single crystal X-ray diffraction as $a=11.2515(9)$ Å, $b=12.5804(10)$ Å, $c=13.3776(10)$ Å, $\alpha=104.0210(10)°$, $\beta=107.1340(10)°$, $\gamma=105.4930(10)°$, $V=1634.4(2)$ $Å^3$, and $Z=1$.

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