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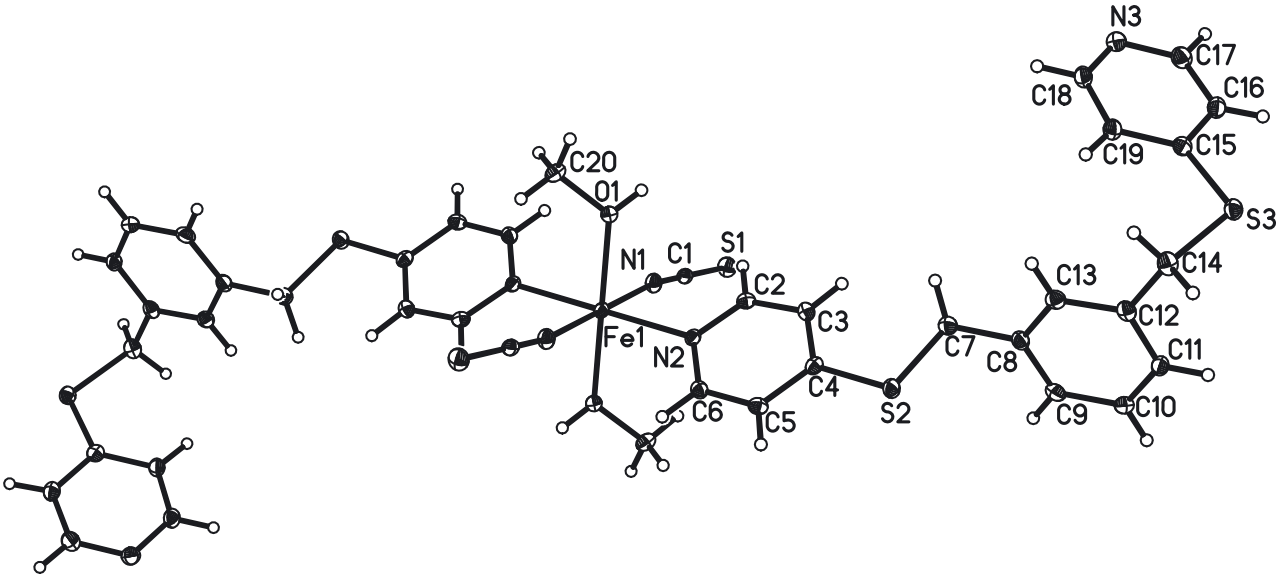
# The crystal structure of di(thiocyanato-κ$^1$N)-bis(methanol)-di(1,3-bis((pyridin-4-ylthio)methyl) benzene)-iron(II), $C_{40}H_{40}FeN_6O_2S_6$

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**Abstract**

$C_{40}H_{40}FeN_6O_2S_6$, monoclinic, $P2_1/n$ (no. 14), $a$ = 9.0820(3) Å, $b$ = 17.1717(6) Å, $c$ = 13.0782(5) Å, $\beta$ = 99.022(4)°, $V$ = 2014.36 Å$^3$, $Z$ = 2, $R_{gt}(F)$ = 0.0348, $wR_{ref}(F^2)$ = 0.0844, T = 293 K.

**CCDC no.:** 2442646

The molecular structure is shown in the Figure and Table 1 contains crystallographic data.

**Table 1:** Data collection and handling.

| | |
|---|---|
| Crystal: | Brown block |
| Size: | 0.15 × 0.11 × 0.09 mm |
| Wavelength: | Mo *K*α radiation (0.71073 Å) |
| $\mu$: | 0.73 mm$^{-1}$ |
| Diffractometer, scan mode: | Bruker APEX II, $\varphi$ and $\omega$ scans |
| $\theta_{max}$, completeness: | 25.0°, 100 % |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$, $R_{int}$: | 6580, 3532, 0.022 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\sigma(I_{obs})$, 2,976 |
| $N(param)_{refined}$: | 251 |
| Programs: | Bruker,[2] SHELX[3,4] |

## 1 Source of materials

The ligand 1,3-bis((pyridin-4-ylthio)methyl)benzene (L$^1$) was prepared by following the reported literature method.[1] A solution of ligand L$^1$ (6.28 mg, 0.2 mmol) in methanol (5 mL) was added dropwise under stirring to a methanolic solution (10 mL) containing $FeCl_2$ (12.7 mg, 0.10 mmol) and KSCN (19.4 mg, 0.2 mmol). The formed solution was stirred for 1–2 min followed by filtering and the filterate was allowed to slowly evaporate in air at room temperature. Block brown crystals appeared after about one week, which were collected and air-dried. Yield: 46.9 mg (53.1 %).

## 2 Experimental details

Coordinates of hydrogen atoms bonded to the C atoms were refined with constraints or restraints. Their $U_{iso}$ values were

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set to 1.2 $U_{eq}$ or 1.5 $U_{eq}$ of the parent atoms. For the H atom of the coordinated methanol molecule, it was refined isotropically with fixed U values, and the DFIX command was used to rationalize the bond parameter.

## 3 Comment

In recent years, due to the various important potential applications in magnetic devices, spin crossover (SCO) complexes[5,6] with distinctive characteristic of the controlled switching between high spin state (HS) and low spin state (LS), have always been an important research topic in molecule magnetism field. As has been displayed in many previous reports, iron(II) ions with $d^6$ electron configurations could switch between paramagnetic HS and dimagnetic LS through external stimuli such as temperature, pressure, light, electricity, or light radiation.[7–10] Here, we report the structure of a new Fe(II) complex based on a semi-rigid V-shaped bidentate ligand 1,3-bis((pyridin-4-ylthio)methyl)benzene ($L^1$).

As presented in the figure, the title neutral Fe(II) complex $[Fe(L^1)_2(CH_3OH)_2(NCS)_2]$ crystallizes in the monoclinic space group $P21/n$. The Fe(II) ion in title complex is involved in a hexa-coordinated octahedron surrounding, in which the six coordinate sites with mutual trans positions were occupied by two N atoms of 1,3-bis((pyridin-4-ylthio)methyl) benzene acting as terminal monodentate ligand, the O atoms of the two methanol molecules and the two N atoms of the thiocyanato ions, respectively. The Fe–$N_L1$, Fe–$N_{NCS}$ and Fe–$O_{methanol}$ bond lengths are 2.1886(19), 2.130(2) and 2.1348(16) Å, respectively, showing the slightly distorted octahedral coordination sphere of the central Fe(II) ion and implying the high spin state nature of the Fe(II) ion in this complex. The Fe–NC bond angle is 171.1(2)°, indicating the almost linear configuration of these three atoms. Under the help of the intermolecular O–H···N hydrogen bond interactions between the O atom of the methanol molecule and the uncoordinated N atom of the ligand $L^1$, the title complex could be further linked into two-dimensional supramolecular network structure.

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## References

1. Xu, Z. J.; Meng, S.; Cao, T.; Xin, Y.; Wang, C. Y.; Hao, H. G.; Yang, L.; Zhou, Z.; Zhang, D. P. Substituent Group Tuned Structural Dimensionalities and Magnetic Properties of V-Shaped Bis-Pyridyl Ligands Based Fe(II) Coordination Polymers. *J. Mol. Struct.* **2024**, *1296*, 136866.
2. Bruker. Apex2, Saint–Plus, Xprep; Bruker AXS Inc.: Madison, Wisconsin, USA, 2004.
3. Sheldrick, G. M. Shelxt – Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr.* **2015**, *A71*, 3–8.
4. Sheldrick, G. M. Crystal Structure Refinement with Shelxl. *Acta Crystallogr.* **2015**, *C71*, 3–8.
5. Diaz–Torres, R.; Boonprab, T.; Gómez–Coca, S.; Ruiz, E.; Harding, P.; Harding, D. J. Structural and Theoretical Insights into Solvent Effects in an Iron(III) SCO Complex. *Inorg. Chem. Front.* **2022**, *9*, 5317–5326.
6. Qin, C. Y.; Zhao, S. Z.; Wu, H. Y.; Li, Y. H.; Wang, Z. K.; Wang, Z.; Wang, S. The Dynamic Interplay between Intramolecular and Intermolecular Interactions in Mononuclear Manganese (III) SCO Complexes. *Dalton Trans*. **2021**, *50*, 5899–5910.
7. Chen, X. Q.; Cai, Y. D.; Jiang, W.; Peng, G.; Feng, J. K.; Liu, J. L.; Tong, M. L.; Bao, X. A Multi-Stimuli-Responsive Fe(II) SCO Complex Based on an Acylhydrazone Ligand. *Inorg. Chem.* **2019**, *58*, 999–1002.
8. Kumar, K. S.; Salitros, I.; Heinrich, B.; Fuhr, O.; Ruben, M. A Charge Neutral Iron(II) Complex with an above Room Temperature Spin Crossover (SCO) and Hysteresis Loop. *J. Mater. Chem. C* **2015**, *3*, 11635–11644.
9. Luo, Y. H.; Nihei, M.; Wen, G. J.; Sun, B. W.; Oshio, H. Ambient-temperature Spin-State Switching Achieved by Protonation of the Amino Group in $[Fe(H_2Bpz_2)_2$ (bipy–$NH_2)]$. *Inorg. Chem.* **2016**, *55*, 8147–8152.
10. Shepherd, H. J.; Rosa, P.; Vendier, L.; Casati, N.; Létard, J. F.; Bousseksou, A.; Guionneau, P.; Moln'ar, G. High-pressure Spin-Crossover in a Dinuclear Fe(II) Complex. *Phys. Chem. Chem. Phys.* **2012**, *14*, 5265–5271.