[Fe(SCN)₂(bipy)₂]·2(S₈): A Two-Dimensional Coordination

Polymer Intercalating the S₈ Molecules

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Abstract

A new coordination polymer compound [Fe(SCN)₂(bipy)₂]·2(S₈) (**1**) (bipy = 4,4'-bipyridine) has been synthesized by the reaction of the bifunctional ligand bipy, Fe(SCN)₂ and sulfur powder under hydrothermal conditions. The compound has been characterized by single and powder X-ray diffraction analysis, infrared spectroscopy and elemental analysis. Compound **1** features a two-dimensional layered structure with neutral S₈ molecules confined in between layers. The magnetic property studies of **1** indicated antiferromagnetic interactions.

Keywords: coordination polymer; S₈ molecules; Iron(II); layered structure; magnetic properties

Elemental sulfur shows a variety of allotropes such as rings and chains [1], among which the most stable one at ambient conditions is S₈ (α -sulfur), a crown-shaped cyclic molecule [2-4]. In the field of crystal engineering, a variety of crystalline compounds containing the neutral chalcogen S₈ [5-25], Se₈ [26] or Te₈ [27] rings have been isolated. The ring-like S₈ molecule with lone pair of electrons on each S can function as a Lewis base with weak capability of coordination, thus normally it is not a good ligand for metal ions. As a result, the compounds with S₈ coordinated to the metal ions are rare [5-9]. While the majority of compounds containing S₈ molecules are those in which the S₈ cocrystallized with other molecules [10-24]. The typical cocrystallized species are discrete molecules such as SbI₃ [20], AsI₃ [10], CoS₈(CO)₆ [12] and C₆₀ [24]. In rare cases, the bulky S₈ rings may act as guest molecules being encapsulated in between the layers or the cavities of open-frameworks, which are only exemplified by Cs₂Sn₃S₇·0.5(S₈) [25] and S₈@zeolite A [28].

On the other hand, the use of elemental sulfur as an alternative feedstock has produced many functional composites and polymeric materials [29-31]. For instance, the carbon-sulphur cathode for lithium-sulphur batteries has attracted increasing interest due to the high theoretical capacity of 1675 mAh g⁻¹ and low cost. Encapsulating sulfur in porous hosts is important for the enhanced cycling life of the resultant Li-S battery [31]. A variety of porous carbon materials have proven to be good confined hosts for sulfur [32-34]. Porous coordination polymers (PCPs), whose pore or cage sizes can be systematically tuned, might act as a new type of promising matrix for encapsulating S₈ rings. Indeed, the incorporations of sulfur into the PCP matrix such as MIL-100-Cr [35] and HKUST-1 [36] have been realized by post-syntheses with sulfur sublimed impregnation. In this communication, we report on the synthesis, crystal structure and characterizations of the first crystalline coordination

polymer *in-situ* encapsulating the S₈ as guest molecules, namely [Fe(SCN)₂(bipy)₂]₂·2(S₈) (**1**). Its magnetic properties were also investigated.

<Fig. 1 inserted here>

The compound **1** was solvothermally synthesized by the reaction of a mixture of Fe(SCN)₂, bipy, S (α -sulfur) and N,N-Dimethylformamide (DMF) at 120 °C for 3 days [37]. Single-crystal X-ray analysis revealed [38] that compound **1** crystallizes in the monoclinic space group of *C2/c*. The asymmetry unit consists of half a Fe (II) atom, two halves 4,4-bipy, one SCN[−] and one S₈ rings (Fig. 1a). As shown in Fig. 1b, each Fe(II) is hexa-coordinated by four N atoms from four 4,4-bipy and two N atoms from two SCN[−] anions in an octahedral coordination sphere (Fig. 1b). The distances of Fe–N from 4,4-bipy and SCN[−] are 2.2347(18) and 2.089(2) Å, respectively, which are within the normal ranges observed in other Fe(II) coordination polymers [39]. Interconnections of Fe and 4,4-bipy along the [1 0 1] direction and *b* axis, respectively, result in a two-dimensional (2D) (4, 4) network of [Fe(SCN)₂(bipy)₂]_{*n*} extended along the (1 0 -1) plane, where the SCN[−] act as terminal ligands coordinated to the Fe atoms and open windows with the size of $\sim 11.59 \times 11.59 \text{ Å}^2$ (including atomic radii of Fe) are evidenced (Fig. 1c). The crown-like S₈ rings exhibit the S–S distances in a range of 2.0352(13) Å and 2.0516(16) Å. As shown in Fig. 1c and 1d, a pair of S₈ rings reside above or below each open window of the 2D (4,4) net. The adjacent layers are stacked in an *ABC* sequence and the S₈ rings are located at the interlayer spaces, Fig. 1d. One set of the 4,4-bipy (N2, C2–C6) from the [Fe(SCN)₂(bipy)₂]_{*n*} layer forms weak C–H[⋯]S hydrogen bonds with the S₈ rings up and down (C5–H5A[⋯]S2 (3.703(3) Å, 162.5°), leading to a supramolecular 2D architecture, Fig. S1. The similar (4,4) nets of 2D layer with different ligands or metals have been observed in [Fe(pyraz)₂(NCS)₂] [pyz = pyrazine] [39], [Fe(N₃)₂(4,4-bipy)] [40],

[Fe(btx)₂(SCN)₂]·0.5EtOH·CH₃CN [btx = 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene] [41], [Cu(Br₂BDC)₂]·(HTEA)₂ (Br₂BDC = 2,5-dibromoterephthalate, TEA = triethylamine) [42], Fe(4-bpdh)₂(SCN)₂ (4-bpdh = 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene) [43], M(1,2-bis(1,2,4-triazol-4-yl)ethane)₂(NCS)₂ (M(II) = Fe, Co) [44], {[Cu₆(pybz)₈(OH)₂]· I₅⁻ · I₇⁻} (pybz = 4-pyridyl benzoate) [45], and [Co^{II}₃(lac)₂(pybz)₂]·3DMF (pybz = 4-pyridyl benzoate, lac = D- and L-lactate) [46].

However, none of them encapsulates S₈ as guest molecules. To the best of knowledge, compound **1** represents the first example of crystalline coordination polymer with *in-situ* confined S₈ rings.

The phase purity of the product was confirmed by powder X-ray diffraction analysis (PXRD) and elemental analysis. The experimental PXRD pattern of the title compound is in accordance with the simulated one from the single-crystal X-ray structure, Fig. S2, demonstrating the phase purity of **1**.

FT-IR analysis was carried out to identify the functional groups presented in **1** and the spectrum is shown in Fig. 2. Compared with the standard 4,4-bipy spectrum, four absorption peak observed in the region about 3000 cm⁻¹ (2989 cm⁻¹, 2887 cm⁻¹, 3202 cm⁻¹, 3302 cm⁻¹) can be attributed to C-H stretching vibration on the ring of 4,4-bipyridine; while the four peaks presented at 1500 cm⁻¹ (1683 cm⁻¹, 1544 cm⁻¹, 1500 cm⁻¹, 1405 cm⁻¹) turn out to be the pyridine ring breathing bands of 4,4-bipy. The three peaks appeared at 873 cm⁻¹, 817cm⁻¹ and 693cm⁻¹ can be regarded as the vibration of C-H in C=C. The functional -N=C=S group gives a medium sharp peak at 2063cm⁻¹, while the S₈ gives a weak peak at 437cm⁻¹, which are similar with that of Cs₂Sn₃S₇·(S₈)_{0.5} [25]. The peak appearing at 3443 cm⁻¹ and 3526 cm⁻¹ may be the stretching vibration of H in S···H. The sharp peak observed at 3643 cm⁻¹ ascribes to the stretching vibration of O-H, which may come from the absorbed water in the

process of experiment.

<Fig. 2 inserted here>

Thermogravimetric analysis (TGA) for **1** was performed on a pure powder sample (~ 10 mg) in N₂ atmosphere from 30 to 450 °C. The TG curve indicates two steps of weight loss. The first stage of weight loss is 35.0% in the temperature range of 175~315 °C, and the second weight loss takes place from 352 to 422 °C, losing about total weight of 18.1%. All the weight losses correspond to the losses of S₈ and the decomposition of 4, 4-bipy and SCN⁻. After decomposition of compound **1** at high temperature, the residue corresponds to Fe₂S, Fe_{0.95}S_{1.05} and C₃N₄ according to the PXRD analysis, Fig. S3.

<Fig. 3 inserted here>

The magnetic properties of compound **1** were investigated over the temperature range of 2-300 K under the field of 1 kOe. The curves of $x_m T$ and $1/x_m$ versus T are shown in Fig. 4. At 300 K, the value of $x_m T$ is 3.623 cm³ K mol⁻¹, which is typical for isolated high spin Fe(II) ions in the octahedral coordination environment. As the temperature decreases, the value decreases gradually and reaches a minimum value of 1.3362 cm³ K mol⁻¹ at 2 K, indicating the presence of antiferromagnetic interaction (AF) between the paramagnetic centers. The AF interaction is further suggested by the negative Weiss constant $\theta = -4.706$ K, obtained from the fitting result of Curie–Weiss law ($x_m = C/(T-\theta)$) in the temperature range of 2-300 K. Similar magnetic behavior was also observed in other cases, such as that in sheet-like [Fe(btx)₂(SCN)₂] $\cdot$ 0.5EtOH $\cdot$ CH₃CN [41] and [Fe(brte)₂(SCN)₂] [brte = (1,2-bis(1,2,4-triazol-4-yl)ethane) [44].

<Fig. 4 inserted here>

In summary, we have presented a new coordination polymer, namely

[Fe(SCN)₂(bipy)₂](S₈)₂, which was solvothermally synthesized and structurally and thermally characterized. The compound represents the first example of crystalline coordination polymer *in-situ* encapsulating ring-like neutral S₈ molecules.

Acknowledgements

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Appendix A. Supplementary data

CCDC 1483160 contains the supplementary crystallographic data for **1**. The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. More table, PXRD pattern and TG curve of **1** are available as electronic supplementary information in the online version, at doi: [xx.xxxx/j.inoche, 2016.xxxx.xx](https://doi.org/10.1039/C6XX00000X)

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- [37] Synthesis of **1**. A mixture of $\text{Fe}(\text{SCN})_2$ (51.0 mg, 0.3 mmol), bipy (26.0 mg, 0.17 mmol), S (26.0 mg, 0.81 mmol) and 1 mL of DMF was sealed in a thick-wall Pyrex at 120 °C for 3 days. The reaction mixture was slowly cooled to room temperature over 2 days, and the dark-red block-like crystals were obtained; Yield based on S: 26.2 mg, 52.0%. Elemental analysis, calcd. (%): C 26.55, H 1.71, N 8.50; found: C 26.49, H 1.62, N 8.43.
- [38] The intensity data were collected on a Rigaku Mercury CCD diffractometer for **1** with graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the *SHELX2014* program package. Crystal data for **1**: $\text{C}_{22}\text{H}_{16}\text{FeN}_6\text{S}_{18}$, $M = 997.35$, $0.25 \times 0.20 \times 0.15 \text{ mm}^3$, monoclinic, $C2/c$, $a = 21.251(6)$, $b = 11.591(3)$, $c = 16.459(5) \text{ \AA}$, $\beta = 105.750(2)^\circ$, $V = 3901.9(19) \text{ \AA}^3$, $Z = 4$, $D_c = 1.698 \text{ g/cm}^3$, $\mu = 1.378 \text{ mm}^{-1}$, $F(000) = 2016$, $GOF = 1.011$. Data collection ($2.020 < \theta < 27.483^\circ$) gave the final $R_1 = 0.0405$, $wR_2 = 0.1115$ and all data $R_1 = 0.0474$, $wR_2 = 0.1173$ for 3930 observed reflections with $I > 2\sigma(I)$ out of 4460 unique reflections ($R_{\text{int}} = 0.0216$).
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Figure Captions

Fig. 1 (a) The crystallographically asymmetry unit of **1**; (b) the coordination environment of Fe in compound **1**. (c) View of a layer of $[\text{Fe}(\text{SCN})_2(\text{bipy})_2] \cdot 2(\text{S}_8)$ along the $[10\text{-}1]$ direction. (d) View of the packing diagram of **1** along the b axis. Hydrogen atoms are omitted for clarity except for H5A forming hydrogen bond.

Fig. 2 FT-IR spectrum of **1**.

Fig. 3 TG curve of **1**.

Fig. 4 $x_m T$ and $1/x_m$ vs T curves for **1** in the temperature range of 2-300 K.

Figure(s)

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