

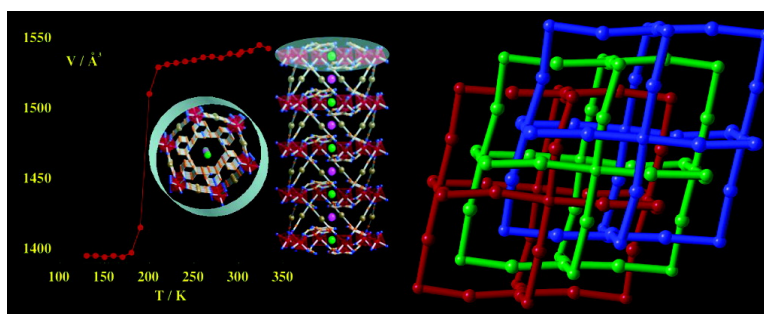
Communication

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Synergy between Spin Crossover and Metallophilicity in Triple Interpenetrated 3D Nets with the NbO Structure Type

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Functional crystalline materials with switch properties and memory transduction have considerable interest in view of their potential technological applications.¹ In this respect, the development of rational synthetic routes by self-assembly have afforded an important number of coordination polymers with specific topologies.² Besides their construction principles, a particular attractive goal has been the synthesis of zeolite-like porous networks of potential ability in catalysis, absorption, and host-guest chemistry.³ Incorporation of mechanically, electronically, or optically active building blocks as essential structural components in the construction of such functional materials is further implementation scarcely investigated.⁴ In this context, the use of spin-crossover (SCO) building blocks is a suitable strategy as they change reversibly from the low-spin (LS) to the high-spin (HS) state accompanied by drastic structural modifications and color changes in response to stimuli such as variation of temperature or pressure and light irradiation.⁵

Hofmann-like clathrate compounds containing iron(II) ions have afforded a number of two-dimensional (2D)^{6,7} and 3D⁷ polymeric SCO networks $\{\text{Fe}(\text{L})_x[\text{M}^{\text{II}}(\text{CN})_4]\cdot\text{G}\}$ [L = pyridine ($x = 2$), pyrazine ($x = 1$, G = 2·H₂O), M^{II} = Ni, Pd, Pt] whose magnetic and chromatic properties change abruptly and display thermal- and pressure-induced hysteresis at temperatures close to room temperature.⁸ The assembly of $[\text{M}^{\text{I}}(\text{CN})_2]^-$ groups (M^I = Cu, Ag, Au), Fe(II), and *trans*-bispyridylethylene, 4,4'-bipyridine,⁸ or pyrimidine (pmd) has resulted in new 2D and double or triple interpenetrated porous 3D SCO polymers with interesting architectures and properties.⁹ Continuing this research, we herein report the synthesis of $[\text{Fe}(\text{3CNpy})_2[\text{Ag}(\text{CN})_2]_2]\cdot 2/3\text{H}_2\text{O}$ (**1**) (3CNpy = 3-cyanopyridine),¹⁰ a system made up of triple interpenetrated 3D SCO networks with tunable metallophilic interactions.

The crystal structure has been solved for the HS (240 K) and the LS (145 K) forms.¹¹ **1** adopts the trigonal *P*-3 space group irrespective of the spin state. The iron atom lies at the inversion center of an elongated octahedron. The equatorial bond lengths defined by the nitrogen atoms of four $[\text{Ag}(\text{CN})_2]^-$ groups [Fe–N(1) = 2.133(8), 1.951(3) Å and Fe–N(2) = 2.133(9), 1.953(3) Å for the HS and LS states, respectively] are shorter than those of the axial positions occupied by the 3CNpy ligands [Fe–N(3) = 2.203(8) Å (HS), 1.988(3) Å (LS)]. The average change of the equatorial and axial bond distances upon spin change is 0.181 and 0.215 Å, respectively. The quasi-linear bisonodentate $[\text{Ag}(\text{CN})_2]^-$ bridges and the iron atoms assemble to form $\{\text{Fe}[\text{Ag}(\text{CN})_2]_2\}_\infty$ 4-connected 3D networks, which corresponds to an expanded version of the prototypal NbO net decorated by the 3CNpy groups (Figure 1a).¹² The much larger intraframework spaces are occupied by two other identical but independent

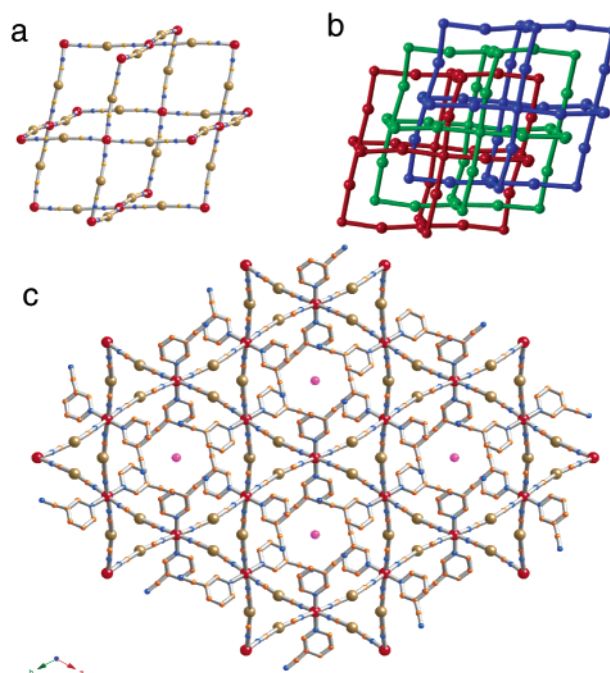


Figure 1. Fragment of a NbO net (a), interpenetration of three networks (b) (3CNpy groups are omitted for clarity), and perspective view along the *c*-axis of the framework (c) [code: red (Fe), brown (Ag), orange (C), pink (H₂O)].

networks, which interpenetrate the first and each other (Figure 1b). The closest approach between nets corresponds to Ag⁺⋯Ag contacts, which define triangular Ag arrangements. The Ag⁺⋯Ag distance, 3.256(2) Å (HS), indicates the occurrence of argentophilic interactions.¹³ The HS→LS spin change increases significantly the homoatomic interactions. The Ag⁺⋯Ag distance, 3.1593(6) Å, decreases by 0.0967 Å in the LS form.

Along the *c*-axis, the nets display cross-sectional trigonal channels where the homoatomic interactions take place. The vertices and edges being defined by the iron atoms and the $[\text{Ag}(\text{CN})_2]^-$ groups, respectively (Figure 1c). Each vertex is shared by an equivalent trigonal motif defining hexagonal shaped voids. The relative orientation of the $[\text{FeN}_6]$ sites imparts handedness to the trigonal channels so that right- and left-handed channels alternate around the hexagonal voids. The 3CNpy ligands fill partially these voids defining hexagonal channels (diameter ca. 7.5 Å) where water molecules are located.

Variation of the unit cell volume with temperature, expressed per iron atom, shows an abrupt change, $\Delta V_{\text{SCO}} = 45.05 \text{ \AA}^3$, in the surroundings of the SCO (210–170 K, vide infra), which corresponds to 91.7% of the total volume variation $\Delta V_T = 49.1 \text{ \AA}^3$ ($\Delta V_T - \Delta V_{\text{SCO}} = 4.05 \text{ \AA}^3$ corresponds to thermal dilation/contraction)

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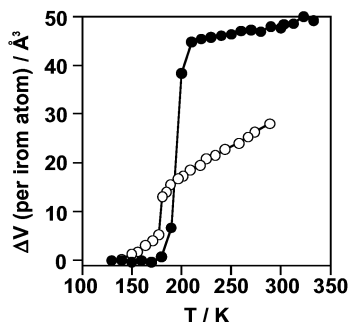


Figure 2. Thermal dependence of the unit-cell volume change per iron atom for the title compound (●) and for [Fe(phen)₂(NCS)₂] (○).

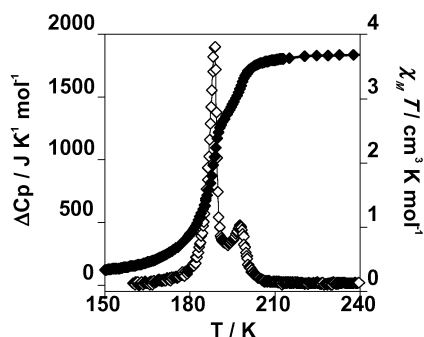


Figure 3. χ_{MT} (■) and ΔC_p (□) vs T plots.

(Figure 2). Typical ΔV_{SCO} values are in the range 15–30 Å³ for most mononuclear and polynuclear SCO iron(II) compounds. Therefore, in the present case there is a considerable excess of volume change that cannot be accounted for in terms of SCO. To emphasize this singularity, the relative variation of the unit cell volume per iron atom measured for the classical [Fe(phen)₂(NCS)₂] SCO compound ($\Delta V_{SCO} = 22$ Å³, value extrapolated to 100% of SCO) has been also included in Figure 2.¹⁴ Further, it should be mentioned that for the related polymeric {Fe(pmd)(H₂O)-[M^I(CN)₂]₂}·H₂O (M^I = Ag or Au) SCO compounds, where metallophilic interactions are operative, ΔV_{SCO} is 24.86 Å³ (Ag) and 16.06 Å³ (Au).^{9c} Then, considering 25 Å³ as a reasonable value for ΔV_{SCO} , the remaining volume change, ca. 20.5 Å³, can be attributed to the increase/decrease of the trinuclear metallophilic interactions operating among the three interlocked independent 3D nets. Consequently, the SCO and the change in intensity of the metallophilic interactions take place simultaneously in the three interpenetrated networks.

The SCO has been investigated from the thermal dependence of the χ_{MT} product (χ_M = molar magnetic susceptibility and T = temperature) and of the molar anomalous heat capacity ΔC_p . χ_{MT} decreases abruptly in two steps from 222 K down to 150 K ($T_c \approx 187$ K). The χ_{MT} values at 300 and 50 K indicate that the SCO is complete. The magnetic behavior in the warming and cooling modes show the occurrence of a narrow hysteresis loop ca. 2 K wide involving the steepest part of the conversion. The ΔC_p vs T curve shows the occurrence of two peaks, one at 198 K and another much more intense at $T_c \approx 188.6$ K (warming mode). These values agree rather well with those observed from the χ_{MT} vs T plot (Figure 3).

The overall enthalpy (ΔH) and entropy (ΔS) variations 13.0 ± 0.4 kJ mol⁻¹ and $\Delta S = 69 \pm 3$ J K⁻¹ mol⁻¹, respectively, are large with respect to the cooperative nature of the transition and likely reflect the coupling between SCO and metallophilicity.

The results reported here show, for the first time, the synergetic interplay between SCO and metallophilic interactions between triple interpenetrated 3D nets. Such a cooperative combination of different dynamic events may be of fundamental significance for the generation of new switchable, multiproperty materials.

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Supporting Information Available: X-ray crystallographic files (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org/instruct/jacsat.pdf>.

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- (10) To a methanolic solution containing Fe(BF₄)₂·6H₂O (0.125 mmol, 42.2 mg) and 3CNpy (0.25 mmol, 26 mg) in 20 mL was added a water solution of K[Ag(CN)₂] (0.25 mmol, 49.75 mg). The resulting solution was stirred for 10 min and left at room temperature to evaporate under an argon stream. Orange-yellow crystals were separated one week later. Yield ca. 40%. Anal. Calcd for C₁₆H_{9.33}N₈Ag₂O_{0.66}Fe: C, 32.22; H, 1.57; N, 18.79. Found: C 31.71, H 1.63, N 18.50.
- (11) Crystal structure of **1** HS (LS): trigonal, space group *P*-3 (No. 147) with $a = 15.7070(9)$ (15.2900(9)) Å, $c = 7.2040(3)$ (6.9050(3)) Å, $V = 1539.18(14)$ (1398.01(13)) Å³, $Z = 1$, $d_{\text{calc}} = 1.929$ (2.123) g cm⁻³, $T = 240(2)$ (145(2)) K, and $\mu(\text{Mo K}\alpha) = 2.608$ (2.871) mm⁻¹, $3.84 < \theta < 27.49^\circ$ ($4.07 < \theta < 27.47^\circ$), $R(R_w) = 0.0879(0.2393)$ (0.0333(0.0629)) for 1426 (1504) independent reflections out of a total of 2305 (2077) reflections with $I > 2\sigma(I)$ and 75 (95) parameters, and $R(R_w) = 0.1382$ (0.2725) (0.0637(0.0693)) for all the data. The goodness-of-fit on F^2 is 1.017 (0.961), and the residual electron density (min/max) is $-0.929/1.305$ ($-0.616/0.655$) e Å⁻³.
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