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Heterobimetallic MOFs Containing Tetrathiocyanometallate Building Blocks: Pressure-Induced Spin Crossover in the Porous $\{Fe^{II}(pz)[Pd^{II}(SCN)_4]\}$ 3D Coordination Polymer

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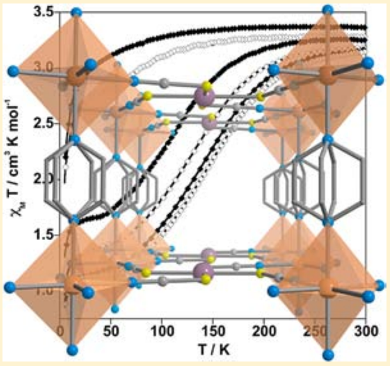
Ⓢ *Supporting Information*

ABSTRACT: Here we describe the synthesis, structure, and magnetic properties of two related coordination polymers made up of self-assembling Fe(II) ions, pyrazine (pz), and the tetrathiocyanopalladate anion. Compound $\{Fe(MeOH)_2[Pd(SCN)_4]\}\cdot pz$ (**1a**) is a two-dimensional coordination polymer where the Fe(II) ions are equatorially coordinated by the nitrogen atoms of four $[Pd(SCN)_4]^{2-}$ anions, each of which connects four Fe(II) ions, forming corrugated layers $\{Fe[Pd(SCN)_4]\}_\infty$. The coordination sphere of Fe(II) is completed by the oxygen atoms of two CH_3OH molecules. The layers stack one on top of each other in such a way that the included pz molecule establishes strong hydrogen bonds with the coordinated methanol molecules of adjacent layers. Compound $\{Fe(pz)[Pd(SCN)_4]\}$ (**2**) is a three-dimensional porous coordination polymer formed by flat $\{Fe[Pd(SCN)_4]\}_\infty$ layers pillared by the pz ligand. Thermal analysis of **1a** shows a clear desorption of the two coordinated CH_3OH molecules giving a rather stable phase (**1b**), which presumably is a polymorphic form of **2**. The magnetic properties of the three derivatives are typical of the high-spin Fe(II) compounds. However, compounds **1b** and **2**, with coordination sphere $[FeN_6]$, show thermal spin crossover behavior at pressures higher than ambient pressure (10^5 MPa).



■ INTRODUCTION

Metallosupramolecular chemisty has witnessed an impressive development during the last two decades. Self-assembly of metal ions with preferred coordination geometries and bridging ligands exhibiting desired distributions of donor atoms has afforded a huge number of predictable metal−organic frameworks, which span from discrete zero-dimensional (0D) high-nuclearity polyhedral complexes to one- (1D), two- (2D), or three-dimensional (3D) coordination polymers (CP). In this context, porous CP's have attracted much interest because of their potentially useful properties in gas storage, molecular separation, and catalysis.[1]

Implementation of porous CP's with interesting physical properties (optical,[2] magnetic,[3] charge transport,[4] etc.) has given rise to a new generation of multifunctional porous materials able to express their host−guest interactions in terms of physicochemical changes in a sensory way. A particularly well-suited approach to this end can be achieved assembling iron(II) ions and suitable bridging ligands able to induce spin crossover behavior (SCO). It is well known that SCO materials can be switched between the high-spin state and the low-spin state in a reversible, detectable, and controllable way by the action of external stimuli like temperature, pressure, light irradiation, intense magnetic field, and even analytes. This is usually accompanied by drastic changes in the magnetic properties (paramagnetism-diamagnetism), optical properties (color), and structure.[5]

The first reported porous CP featuring SCO properties is $[Fe(tvp)_2(NCS)_2]\cdot MeOH$ [tvp (also referred as bpe or dpe) is the bis(pyridyl-2-yl)ethylene]. This compound is constituted of perpendicular interpenetration of two infinite series of layers generating large square channels.[6] The influence of host−guest interactions on the spin state was investigated in detail for the closely related compound $[Fe(azpy)_2(NCS)_2]\cdot n$Solvent (L = 4,4′-azopyridine).[7] More recently this study has been extended to similar $[Fe(L)_2(NCS)_2]\cdot n$Solvent compounds where L is 2,3-bis(4′-pyridyl)-2,3-butanediol (bpbd),[8] 4′-pyridyl)-1,2-ethanediol (bped),[9] and 1,2-bis(4′-pyridyl)ethane (bpe).[10] The SCO properties of these materials can be tuned playing with the nature of the adsorbed solvents as well as conveniently decorating the walls of the pores. However, in general, the spin crossover behavior shown by these compounds is not especially cooperative, most probably due to the length and inherent flexibility of the organic ligands.

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The search for more rigid spin crossover compounds with stronger cooperative properties has afforded a new class of 3D porous CP's formulated {Fe(pz)[$M^{II}(CN)_4$]} (pz = pyrazine, M^{II} = Ni, Pd, Pt)[11] derived from the well-known Hofmann clathrates and particularly inspired in the nonporous 2D SCO CP's {Fe(py)[$M^{II}(CN)_4$]} (py = pyridine).[11,12] At variance with all previous SCO compounds, these new CPs were constituted of bridging metalloligand anions $[M^{II}(CN)_4]^{2-}$. This strategy has successfully been extended to other cyanometallate complexes such as $[M^{I}(CN)_2]^{-}$ (M^{I} = Cu, Ag, Au), $[Cr(CN)_6]^{3-}$, and $[Nb(CN)_8]_4$.[13]

The SCO compounds {Fe(pz)[$M^{II}(CN)_4$]} show strong cooperative SCO behavior characterized by a 25 K wide hysteresis loop centered at room temperature, which confer to the solid a bistable character. They form a 3D pillared-layer-type porous framework consisting of cyano-bridged Fe(II)M(II) layers and pz pillar ligands. These compounds act as true switchable molecular rotators since the rotational frequency of the pz pillars strongly depends on the spin state of the framework.[14] They adsorb various guest molecules. A bimodal reversible change of spin state at the Fe(II) sites was observed concomitantly with the uptake of guest molecules switching between the high-spin state (HS, yellow) stabilized by hydroxylic solvents, five- and six-membered aromatic molecules, and the low-spin state (LS, red-brown) stabilized by CS_2 (for M = Pt)[15] or CH_3CN (for M = Ni)[16] at 298 K. In the framework, guest molecules can interact with the pyrazine pillar ligands and the M(II) centers. In particular, the coordinatively unsaturated Pt(II) centers enhance chemisorptive uptake of dihalogen molecules involving associative oxidation of Pt(II) to Pt(IV) and reduction of the dihalogen to the corresponding halide. This happens with dramatic effects on the critical temperatures of the spin transition.[17]

Larger organic pillars such as L = azpy, bpac, and tvp have been used to get new SCO frameworks {Fe(L)[$M^{II}(CN)_4$]} with enhanced pore size able to store larger molecules such as phenazine, anthracene, or 1,3,5 trichlorophenol.[18] As a part of this investigation, we have also been investigating new alternatives to Hofmann clathrates based on substitution of the tetracyanometallate anion for new types of metalloligand building blocks with similar structural functionality. As a first step in this direction, we chose the tetrathiocyanopalladate anion $[Pd^{II}(SCN)_4]^{2-}$. To our knowledge, only a few reports deal with heterometallic complexes made up of $[M^{II}(SCN)_4]^{2-}$ (M^{II} = Pd, Pt) and in general with thiocyanometallate complexes. For example, a series of CP's of formula $[Ag^{I}_{x}Cu^{I}_{y}(SCN)_{x+y}(pyridine)]$[19] and $[Cat]_2[\{Cu(NCS)\}_3WS_4]$[20] have been reported. Similarly, some metal–organic CPs constituted of M^{I}–crown ether complexes (M^{I} = Na, K) and $[M^{II}(SCN)_4]^{2-}$ (M^{II} = Pd, Pt)[21] or $[Ir(NCS)_6]^{3-}$,[22] Mn^{II}–pyrazol,[23] or Ni^{II}–, Mn^{II}–, and Cu^{II}–imidazole building blocks linked by $[Hg(SCN)_4]^{2-}$ have been reported.[24]

Here we describe the crystal structures of the 2D-CP {Fe(MeOH)$_2$[Pd(SCN)$_4$]}·pz (**1a**) and porous 3D-CP {Fe(pz)[Pd(SCN)$_4$]} (**2**) obtained by assembling Fe(II) ions pz and $[M^{II}(SCN)_4]^{2-}$ bridging ligands. Desolvation of **1a** affords a new derivative **1b**, which seems to be a polymorphic variation of **2**. These compounds are high spin at all temperatures; however, **1b** and **2** undergo thermal-induced SCO behavior at pressures higher than 0.5 GPa.

■ EXPERIMENTAL SECTION

Materials. Pyrazine, $K_2[Pd^{II}Cl_4]$, KNCS, and $Fe(BF_4)_2{\cdot}6H_2O$ were purchased from commercial sources and used as received.

Preparation. *Synthesis of $K_2[Pd^{II}(SCN)_4]$.* This salt was synthesized as described elsewhere.[25a]

*Synthesis of **1a**.* Compound **1a** was synthesized by slow diffusion in 10 mL H-shaped vessels. A methanol–water (1:1) solution (0.5 mL) containing a mixture of $Fe(BF_4)_2{\cdot}6H_2O$ (0.03 mmol), pz (0.06 mmol), and a few crystals of ascorbic acid to prevent partial oxidation of iron(II) in iron(III) was poured in one arm of the H-shaped vessel, which was previously purged with argon. In the opposite arm a methanolic solution (0.5 mL) of $K_2[Pd^{II}(SCN)_4]$ (0.024 mmol) was poured. Then, the vessel was filled with a methanol–water (1:1) solution. Deep-red (almost black) single crystals of **1a** were formed over a period of 4 weeks. Anal. Calcd for $C_{10}H_{12}N_6O_2S_4FePd$ (**1a**): C, 22.29; H, 2.24; N, 15.60. Found: C, 22.36; H, 2.15; N, 15.44. Yield: ca. 20%. EDAX (energy-dispersive X-ray analysis) calcd for **1a**: Fe, 50%; Pd, 50%. Found: Fe, 49.8%; Pd, 50.2%.

*Preparation of **1b**.* Compound **1b** was prepared by thermal decomposition of compound **1a** at ca. 390 K. Anal. Calcd for $C_8H_4N_6S_4FePd$ (**1a**): C, 20.24; H, 0.85; N, 17.70. Found: C, 20.35; H, 0.97; N, 17.81. Yield: ca. 100%. EDAX calcd for **1b**: Fe, 50%; Pd, 50%. Found: Fe, 49.8%; Pd, 50.2%.

*Synthesis of **2**.* Compound **2** was synthesized by slow diffusion in 10 mL H-shaped vessels. An acetonitrile solution (0.5 mL) containing a mixture of $Fe(BF_4)_2{\cdot}6H_2O$ (0.06 mmol), pz (0.06 mmol), and a few crystals of ascorbic acid to prevent partial oxidation of iron(II) in iron(III) was poured in one arm of the H-shaped vessel, which was previously purged with argon. In the other arm an aqueous solution (0.5 mL) of $K_2[Pd^{II}(SCN)_4]$ (0.047 mmol) was poured, and then the vessel was filled with acetonitrile. Orange single crystals of **2** were formed after ca. 4 weeks. Anal. Calcd for $C_8H_4N_6S_4FePd$ (**2**): C, 20.24; H, 0.85; N, 17.70. Found: C, 20.19; H, 0.92; N, 17.56. Yield: ca. 10%. EDAX calcd for **1b**: Fe, 50%; Pd, 50%. Found: Fe, 49.9%; Pd, 50.1%.

Magnetic Measurements. Variable-temperature magnetic susceptibility measurements were recorded with a Quantum Design MPMS2SQUID susceptometer equipped with a 5.5 T magnet, operating at 1 T and temperatures from 1.8 to 300 K. The susceptometer was calibrated with $(NH_4)_2Mn(SO_4)_2{\cdot}12H_2O$. The hydrostatic pressure cell made of hardened beryllium bronze with silicon oil as the pressure-transmitting medium operates in the pressures range 10^5 Pa < P < 1.2 GPa (accuracy ca. ±0.025 GPa). Cylindrically shaped powder sample holders with dimensions of 1 mm in diameter and 5–7 mm in length were used. Pressure was measured using the pressure dependence of the superconducting transition temperature of a built-in pressure sensor made of high-purity tin.[26] Experimental susceptibilities were corrected for diamagnetism of the constituent atoms by use of Pascal's constants.

TGA Analysis. TGA measurements were performed on a Mettler Toledo TGA/SDTA 851e in the 300–700 K temperature range in nitrogen atmosphere with a rate of 10 K/min.

Single-Crystal X-ray Diffraction. Single-crystal X-ray data of **1a** and **2** were collected at 120 and 230 K, respectively, on a Nonius Kappa-CCD single-crystal diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). A multiscan absorption correction was performed. Structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares on F^2 using SHELXL-97.[27] Except for compound **2**, non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters.

■ RESULTS

Synthesis. Highly insoluble microcrystalline powders resulted when water solutions of $K_2[M(SCN)_4]$ (M = Pd, Pt) were added into methanolic solutions containing Fe(II)–pz (1:1). In order to obtain structural information about these precipitates, we prepared single crystals from slow diffusion of

Fe(II):pz (1:2) (in methanol) and $K_2[Pd(SCN)_4]$ (in water). Under these conditions dark-red (almost black) crystals of **1a** were exclusively obtained. In this compound, the Fe(II) ion is coordinated to two axial methanol molecules instead of coordinating the pz molecule, thereby affording a 2D CP (vide infra). To avoid this situation, the Fe(II)−pz solutions were prepared in CH_3CN, keeping the water solution of $K_2[M(SCN)_4]$. Then, single crystals of **2** were obtained. Thermogravimetric analysis shows that **1a** loses 2 molecules of MeOH in the temperature range 350−394 K with subsequent stabilization of a phase in the interval 394−598 K, which we call compound **1b** (Supporting Information Figure S1). Formation of this phase was also monitored through evolution of the unit cell parameters of single crystals of **1a** heated up to 370 K in a N_2 stream. During this process, the angles α, β, and particularly γ approached to 90°, suggesting the occurrence of a structural change from triclinic $P{-}1$ to tetragonal $P4/m$. However, we were unable to confirm this transformation since the crystals deteriorate during the process. Despite the loss of crystallinity of the resulting **1b** compound, powder X-ray diffraction (PXRD) patterns obtained from collections of single crystals of **1a**, heated in similar conditions, showed the presence of a series of peaks which do not match those of **2**, indicating that **1b** and **2** are not isostructural (Supporting Information Figure S2). Similar PXRDs were recorded from the direct precipitation method and when single crystals of **1a** were ground at room temperature, suggesting that **1b** can also be generated by means of a mechanochemical reaction.[28]

Crystal Structures. *Crystal Structure of 1a (120 K).* Compound **1a** crystallizes in the $P{-}1$ triclinic space group. Relevant crystallographic data are displayed in Table 1. A selection of significant bond distances and angles is shown in Table 2. The Fe(II) site is in an inversion center situated at the middle of a compressed octahedron defined by the $[FeN_4O_2]$ chromophore (Figure 1a, left). Equatorial Fe−N bonds [Fe−N(1) = 2.152(4) Å and Fe−N(2) = 2.131(4) Å] belong to four $[Pd(SCN)_4]^{2-}$ groups, while the axial positions are occupied by two molecules of methanol (Fe−O(1) = 2.105(3) Å). These bond lengths clearly suggest that the Fe(II) atom is in the high-spin state in agreement with the magnetic measurements. The bond angles of the $[FeN_4O_2]$ octahedron are close to 90° (deviations are in the range 0.6−1.9°). As expected, the molecule of MeOH is tilted defining an Fe−O(1)−C(3) angle of 125.2(3)°. The NCS moieties slightly deviate from linearity (ca. 4°), and the Fe−N−C(S) linkages are bent by ca. 6.7°.

Table 1. Crystal Data for 1a and 2[a]

	1a, 120 K	**2**, 230 K
empirical formula	$C_{10}H_{12}N_6O_2S_4PdFe$	$C_8H_4N_6S_4PdFe$
M_r	538.74	474.66
cryst syst	triclinic	tetragonal
space group	$P{-}1$	$P4/m$
a (Å)	7.5717(2)	8.6730(11)
b (Å)	7.7015(10)	
c (Å)	8.5073(6)	7.2010(7)
α (deg)	86.851(2)	
β (deg)	87.601(9)	
γ (deg)	69.5750(10)	
V (Å^3)	464.06(7)	541.67(11)
Z	1	1
D_c (mg cm^{-3})	1.928	1.455
$F(000)$	266	230
μ (Mo Kα) (mm^{-1})	2.216	1.881
cryst size (mm)	0.02 × 0.03 × 0.06	0.04 × 0.08 × 0.08
no. of total reflns	1278	661
no. of reflns [$I > 2\sigma(I)$]	1062	471
R_1 [$I > 2\sigma(I)$]	0.0284	0.0479
wR [$I > 2\sigma(I)$]	0.0639	0.1143
S	0.978	1.011

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (mP)^2 + nP]$, where $P = (F_o^2 + 2F_c^2)/3$; $m = 0.0494$ (**1a**) and 0.0636 (**2**); $n = 0.0000$ (**1a**) and 1.5874 (**2**).

Table 2. Selected Bond Lengths [Angstroms] and Angles [degrees] for 1a and 2

	1a, 120 K	**2**, 230 K
Fe−N(1)	2.152(4)	2.222(11)
Fe−N(2)	2.131(4)	2.115(6)
Fe−O(1)	2.105(3)	
Pd−S(1)	2.3307(11)	
Pd−S(2)	2.3384(11)	
Pd−S		2.330(2)
N(1)−Fe−N(2)	88.11(14)	
N(1)−Fe−O(1)	88.99(14)	
N(2)−Fe-O(1)	89.4(2)	
S(1)−Pd−S(2)	87.61(4)	

The Pd(II) atom lies in an inversion center defining an almost regular square planar $[PdS_4]$ chromophore (Figure 1a, right). The Pd−S bond distances and angles are Pd−S(1) = 2.3307(11) Å and Pd−S(2) = 2.3384(11) Å and S(1)−Pd−S(2) = 87.61(4)°, respectively. The Pd−S−C linkage shows significant deviation from linearity (74° on average). Furthermore, the C−N moieties are out the average plane defined by the $[PdS_4]$ unit defining angles of ca. 47° and 17.5° for S(2)−C(2)N(2) and S(1)−C(1)N(1), respectively. Each terminal N atom links a distinct Fe(II) atom in such a way that two $[FeN_4O_2]$ octahedrons are below and the other two above the $[PdS_4]$ average plane (see Supporting Information Figure S3). Each Fe(II) ion is coordinated by four $[Pd(SCN)_4]^{2-}$ groups, and each $[Pd(SCN)_4]^{2-}$ group coordinates four Fe(II), forming a corrugated 2D polymer (Figure 2a) The layers stack along the [110] direction. Two consecutive layers are separated from each other by a distance of 6.260 Å, measured from the average plane defined by the Fe(II) ions belonging to the respective layers. This space is partially filled by an uncoordinated molecule of pz per Fe(II) ion. The N atoms of the pz molecule point toward the O atoms of two methanol molecules belonging to two consecutive layers establishing a hydrogen-bond network; the O(1)···N(3) distance is 2.747(5) Å.

Crystal Structure of 2 (230 K). Compound **2** crystallizes in the $P4/m$ tetragonal space group. Relevant crystallographic data are displayed in Table 1. A selection of significant bond distances and angles is shown in Table 2. The Fe(II) atom defines an elongated $[FeN_6]$ octahedron with the axial positions occupied by the N atoms of the pz ligand [Fe−N(1) = 2.222(11) Å] and the equatorial coordination positions occupied by the N atoms of four $[Pd(SCN)_4]^{2-}$ anions [Fe−N(2) = 2.115(6) Å] related by the C_4 axis, which contains the N(1)−Fe−N(1)$^\#$ axial bonds (Figure 1b, left). The Fe−N(2)−C(2)(S) moiety is significantly less bent (2.6°) than observed for **1a**. The $[Pd(SCN)_4]^{2-}$ group defines a strictly regular square planar geometry imposed by the symmetry of the crystal

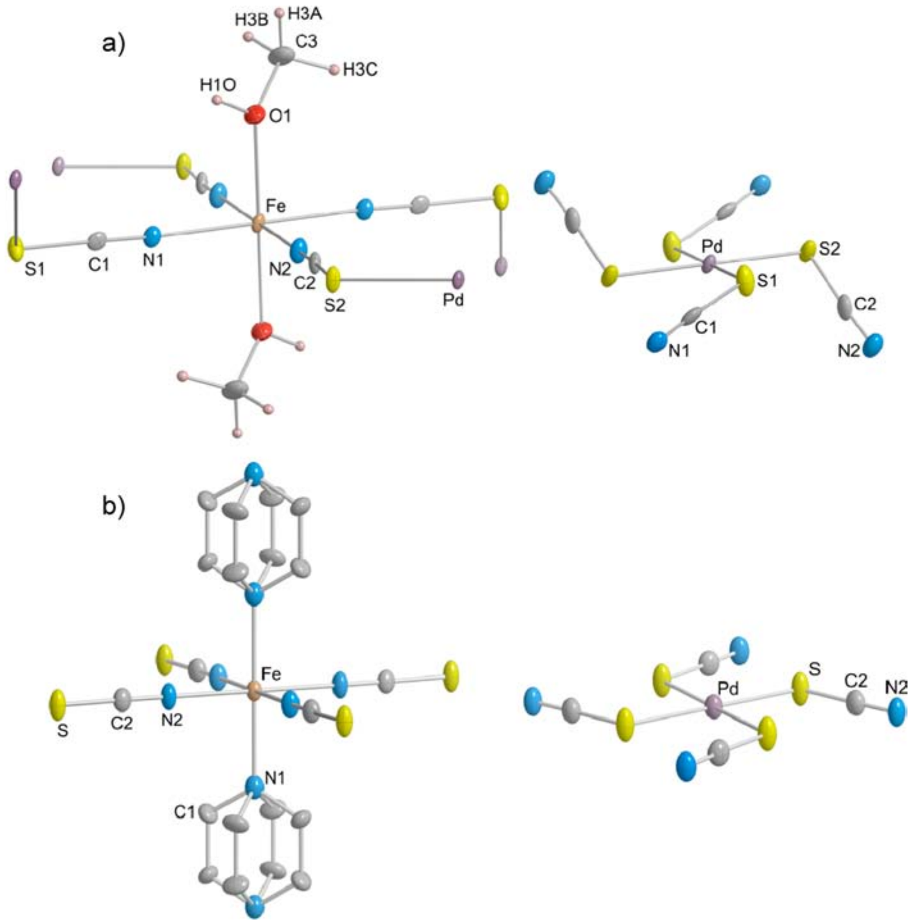

Figure 1. Fragment of the structure of **1a** (120 K) (a) and **2** (230 K) (b) with a view of the coordination sphere of the Fe(II) and Pd(II) cations with labeling and displacement ellipsoids drawn at the 60% (**1a**) and 50% (**2**) probability level.

[Pd−C bond length = 2.330(2) Å, S−Pd−S bond angle = 90°] (Figure 1b, right). Furthermore, in contrast to **1a**, the SCN groups are exactly in the same plane defined by the $[PdS_4]$ chromophore, thereby generating flat $[FePt(SCN)_4]_\infty$ layers spreading on the (110) plane. These layers are pillared by bridging pz ligands which connect the Fe(II) ions of consecutive layers along [001] direction, thus defining a 3D porous network (Figure 2b) . The separation between two consecutive layers is c = 7.2010(7) Å. Consequently, the framework defines $a \times b$ = 8.6730(11) × 8.6730(11) $Å^2$ cross-sectional square channels running along the [100] and [010] directions. The available unit cell volume, equal to 200 $Å^3$ (36.9%),[29] is apparently not occupied by solvent molecules.

Magnetic Properties. Figure 3a and 3b show the magnetic properties of **1b** and **2**, respectively, in the form of the product of $\chi_M T$ vs T at various external pressures (χ_M is the magnetic susceptibility per mole of compound, and T is the temperature). The magnetic properties of **1a** have been investigated only at atmospheric pressure since it was not expected to observe SCO behavior in the interval of pressures commonly investigated for $[FeN_6]$ chromophores. The thermal dependence of $\chi_M T$ for this compound is that of an octahedrally distorted Fe(II) ion in the S = 2 ground state (Supporting Information Figure S4). The crystal structure of **1a** confirms that this compound remains in the high-spin state at 120 K.

At 10^5 Pa (1 bar), the magnetic behavior of **1b** and **2** is that of an Fe(II) ion in the S = 2 high-spin state with noticeable orbital contribution. The $\chi_M T$ value at room temperature is 3.47 and 3.36 cm^3 K mol^{-1} for **1b** and **2**, respectively. This behavior remains essentially constant down to 100 K, then $\chi_M T$ decreases most probably due to the combined effects of spin−orbit coupling and deviation of the octahedral symmetry of the $[FeN_6]$ chromophore. At 0.44 GPa, the thermal dependence of $\chi_M T$ denotes the occurrence of an incomplete spin state change in the temperature range ca. 200−54 K for **1b**. This change involves ca. 22% of high-spin to low-spin spin state change. A similar behavior was observed for **2** at 0.28 GPa; however, because of the smaller applied pressure the spin state change is more moderate. At higher pressures the spin state transformation becomes more evident for both compounds. For example, at 0.5−0.6 GPa a transformation of ca. 52% is achieved for **1b** and **2**, while at around 0.9 GPa the residual paramagnetism at ca. 50 K indicates a transformation of ca. 75% and 64% for **1b** and **2**, respectively. As expected, the observed $T_{1/2}$ temperature increases as pressure increases, $T_{1/2}$ (0.9 GPa) = 195 (**1b**) and 147 K (**2**).

■ DISCUSSION

This work was undertaken aiming at synthesizing a new series of porous CPs able to exhibit host−guest chemistry and SCO behavior. The choice of the $[M(SCN)_4]^{2-}$ anion was inspired by our precedent results based on the Hofmann clathrates formulated $\{Fe(pz)[M(CN)_4]\}\cdot G$. It was expected to get similar 3D CPs with larger channels and enhanced structural flexibility by replacing the cyanide groups by thiocyanate groups. The solvent-accessible void for **2** has been estimated to

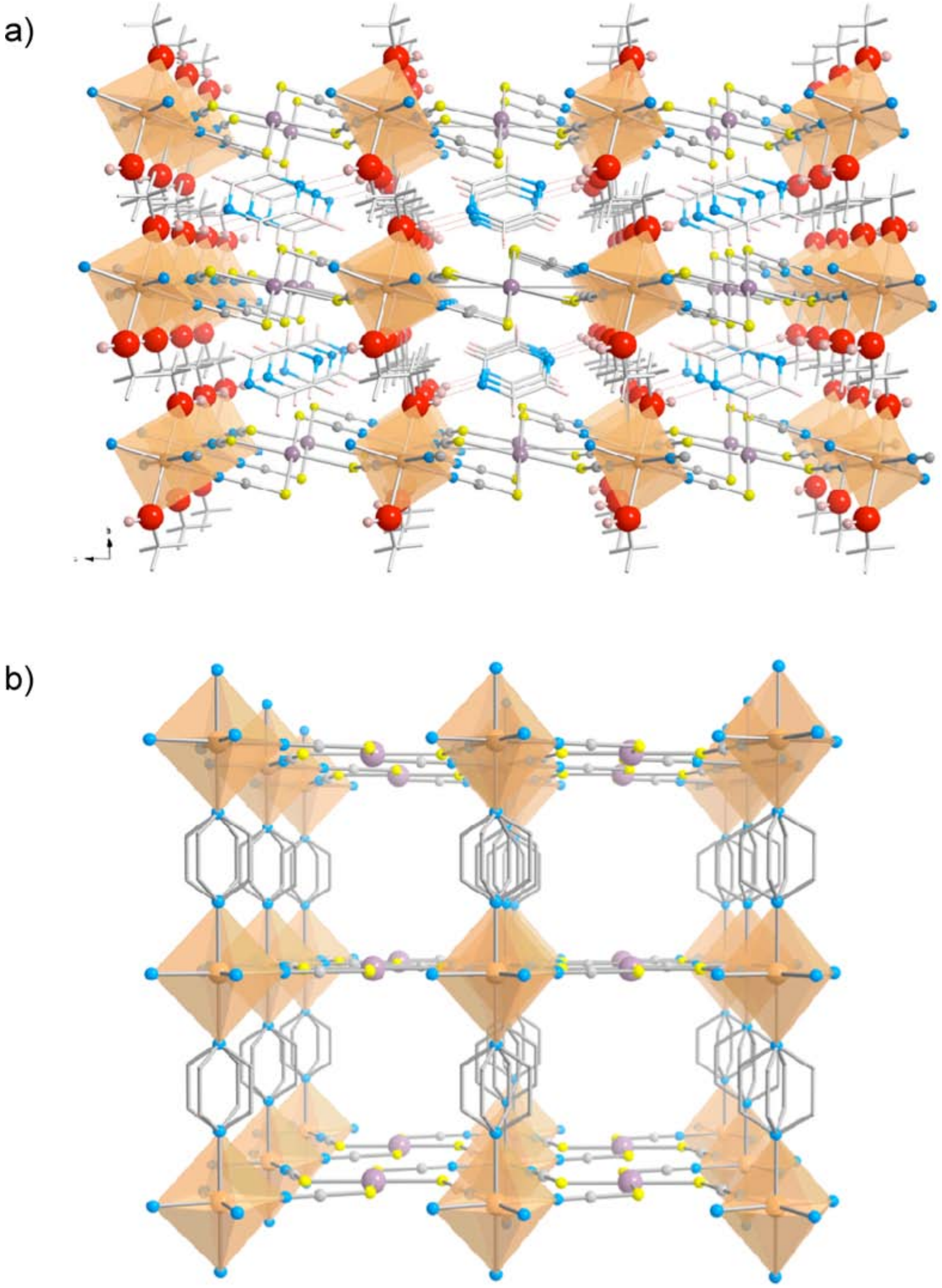

Figure 2. (a) Stacking of three consecutive layers **1a** (120 K) showing the enclathrated pz molecules. Thin red lines represent hydrogen bonds between pz and MeOH molecules. (b) Extended crystal structure **2** (230 K) displaying large channels running along the [100] and [010] directions.

be 36.9% of the unit cell volume, which is ca. 61% larger than that found for $\{Fe(pz)[M(CN)_4]\}$ in the high-spin state (M = Pt, Pd; both derivatives are strictly isostructural).[15a]

Although there are a few reports dealing with the study of 1D chain crown ether complexes of Na^+ and K^+ with $[M(SCN)_4]^{2-}$ (Pd, Pt),[21] compounds **1a** and **2** represent, to the best of our knowledge, the first bimetallic metal−organic frameworks made up of $[Pd(SCN)_4]^{2-}$ building blocks and a transition metal ion. Both compounds are clearly related to each other since **1a** can be considered, formally, as a precursor of **2**. Apparently, the coordinated solvent molecules preclude the pz molecules from coordinating the Fe(II) to form compound **2** (or a related polymorph) directly. The pz molecules remain stabilized, forming intense hydrogen bonds with the hydroxo groups of two MeOH molecules coordinated to two Fe(II) ions of consecutive layers. It is worth noting that no homologous example has been reported for the Hofmann clathrates $\{Fe(pz)[M(CN)_4]\}\cdot G$. This situation is more common for simple first-row isothiocyanato CPs with formula $\{M^{II}(L)(Solvent)_2(NCS)_2\}\cdot L$, where L is 4,4′-bipy, azpy, or tvp and M^{II} = Mn(II), Fe(II), or Co(II). In these compounds, one L ligand acts as a bridge forming $\{M^{II}(L)(Ssolvent)_2(NCS)_2\}_\infty$ chains while two trans solvent molecules (Solvent = MeOH, H_2O) and two trans NCS^- groups complete the coordination sphere

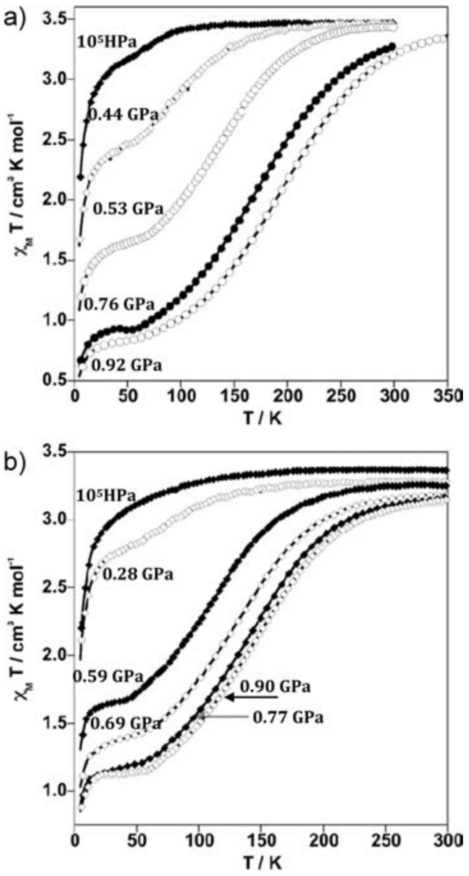

Figure 3. Thermal dependence of the $\chi_M T$ product at several pressures for **1b** (top) and **2** (bottom).

of M(II). The chains are linked to each other via strong hydrogen bonds, generated between the hydroxo group of the coordinated solvent and the N atoms of the uncoordinated L ligand, forming corrugated layers.[30] Interestingly, transformation of these self-assembled 1D CPs into $\{M^{II}(4,4'bipy)_2(NCS)_2\}$ (M = Mn(II), Fe(II), Co(II)) 2D CPs takes place through cooperative topochemical ligand substitution of the coordinated solvent molecules by the uncoordinated L ligand by means of controlled thermal decomposition in the solid state.[30c,d,f] A similar reaction was reported for transformation of the 2D SCO CP system $\{Fe^{II}(pyrimidine)_2(H_2O)_2[M^I(CN)_2]_2\}\cdot H_2O$ (M^I = Ag, Au) into the 3D framework $\{Fe^{II}(pyrimidine)[M^I(CN)_2]_2\}$. This reversible desolvation−solvation process is accompanied by remarkable reversible changes in the electronic state of the Fe(II) ion.[31]

The title compounds seem to be related to each other in the same way. Stabilization of the phase **1b** strongly suggests a concerted topochemical ligand substitution of the coordinated MeOH molecules by the uncoordinated pz molecules and probably formation of a polymorphic variant of **2**. Observation of thermal-induced SCO behavior at relatively low pressures (from 10^5 HPa to 10 GPa) strongly supports complete transformation of **1a** into a new material made up of $[FeN_6]$ coordination centers (**1b**), a fact which is in line with the conjecture of ligand substitution of MeOH by pz mentioned above. The SCO behavior of **1b** and **2** is quite similar but not identical, for example, the inflection point of the SCO curves, and hence $T_{1/2}$ are observed at slightly higher temperatures for **1b**. Furthermore, at low temperatures the residual paramagnetism is larger for **2** than for **1b**. These differences further support the hypothesis of generation of a distinct polymorph (**1b**) of **2**. This conjecture is consistent with the remarkable linkage flexibility exhibited by the Pd−NCS moiety deduced from the structures of **1a** and **2**. It is worth noting that, in this particular example, the CN-bond stretching mode characteristic of the NCS group seems to be insensitive to this flexibility. Indeed, the IR spectrum of **1a**, **1b**, and **2** features a sharp doublet absorption centered at about 2120 cm^{-1} [**1a**, 2126 and 2112 cm^{-1}; **1b**, 2127 and 2114 cm^{-1}; **2**, 2128 and 2115 cm^{-1}].

■ CONCLUSION

Here we have shown that the tetrathiocyanopaladate anion is an appropriate building block to obtain new extended 2D and 3D coordination polymers with first-row transition metal ions. Since our prime interest was to synthesize new porous CP with SCO properties, we have chosen the Fe(II) ion as a suitable component of the nodes of the resulting metal−organic framework. Self-assembly of Fe(II), pz, and $[Pd(SCN)_4]^{2-}$ has afforded the desired 3D CP with similar structural characteristics to those reported for the well-known homologous Hofmann clathrates $Fe(pz)[M(CN)_4]$ (M = Ni, Pd, Pt). In contrast, the porous compounds **2** and **1b** are HS at all temperatures at 1 bar due to the weaker ligand field generated by the NCS groups. However, they display gradual SCO properties at pressures higher than ca. 0.3 GPa. Substitution of Pd by Pt and pz by other related bismonodentate ligands affords similar CPs; this work is currently under study.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Thermal analysis (**1a**), PXRD patterns (**1a**, **1b**, and **2**), extended crystal structure of **1a** (120 K), and thermal dependence of magnetic behavior (**1a**); CIF files of **1a** (120 K) and **2** (230 K). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) See, for example: (a) Das, M. C.; Xiang, S.; Zhang, Z.; Chen, B. *Angew. Chem., Int. Ed.* **2011**, *50*, 10510. (b) Batten, S. R.; Neville, S. M.; Turner, D. R. *Coordination Polymers: Design, Analysis and Application*; RSC Publishing: Cambridge, UK, 2009. (c) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334. (d) Kitagawa, S.; Matsuda, R. *Coord. Chem. Rev.* **2007**, *251*, 2490. (e) Férey, G. *Chem. Soc. Rev.* **2008**, *37*, 191. (f) Czaja, A. U.; Trukhan, N.; Mueller, U. *Chem. Soc. Rev.* **2009**, *38*, 1284 and references therein.

(2) (a) Rocha, J.; Carlos, L. D.; Almeida Paz, F. A.; Ananias, D. *Chem. Soc. Rev.* **2011**, *40*, 926. (b) Wang, C.; Lin, W. *J. Am. Chem. Soc.* **2011**, *7*, 2034. (c) Liu, D.; Huxford, R. C.; Lin, W. *Angew. Chem., Int. Ed.*

2011, *50*, 3696. (d) Stylianou, K. C.; Heck, R.; Chong, S. Y.; Bacsa, J.; Jones, J. T. A.; Khimyak, Y. Z.; Bradshaw, D.; Rosseinsky, M. J. *J. Am. Chem. Soc.* **2010**, *132*, 4119. (e) Xie, Z.; Ma, L.; de Krafft, K. E.; Jin, A.; Lin, W. *J. Am. Chem. Soc.* **2010**, *132*, 922.

(3) (a) Maspoch, D.; Ruiz-Molina, D.; Veciana, J. *Chem. Soc. Rev.* **2007**, *36*, 770. (b) Dechambenoit, P.; Long, J. R. *Chem. Soc. Rev.* **2011**, *40*, 3249.

(4) (a) Avendano, C.; Zhang, Z.; Ota, A.; Zhao, H.; Dunbar, K. R. *Angew. Chem., Int. Ed.* **2011**, *50*, 6543. (b) Shimomura, S.; Kitagawa, S. *J. Mater. Chem.* **2011**, *21*, 5537. (c) Shimomura, S.; Yanai, N.; Matsuda, R.; Kitagawa, S. *Inorg. Chem.* **2011**, *50*, 172. (d) Shigematsu, A.; Yamada, T.; Kitagawa, H. *J. Am. Chem. Soc.* **2011**, *133*, 2034. (e) Bureekaew, S.; Higuchi, S. M.; Kawamura, T.; Tanaka, D.; Yanai, N.; Kitagawa, S. *Nat. Mater.* **2009**, *8*, 831.

(5) See for example: (a) Goodwin, H. A. *Coord. Chem. Rev.* **1976**, *18*, 293. (b) Gütlich, P. *Struct. Bonding (Berlin)* **1981**, *44*, 83. (c) König, E.; Ritter, G.; Kulshreshtha, S. K. *Chem. Rev.* **1985**, *85*, 219. (d) Hauser, A. *Comments Inorg. Chem.* **1995**, *17*, 17. (e) König, E. *Struct. Bonding (Berlin)* **1991**, *76*, 51. (f) Gütlich, P.; Hauser, A.; Spiering, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2024. (g) Sato, O. *Acc. Chem. Res.* **2003**, *36*, 692. (h) Real, J. A.; Gaspar, A. B.; Niel, V.; Muñoz, M. C. *Coord. Chem. Rev.* **2003**, *236*, 121. (i) In *Topics in Current Chemistry*; Gütlich, P.; Goodwin, H. A. Eds.; 2004, Vols. 233−235. (j) Real, J. A.; Gaspar, A. B.; Muñoz, M. C. *Dalton Trans.* **2005**, 2062. (k) Halcrow, M. A. *Polyhedron* **2007**, *26*, 3523. (l) Nihei, M.; Shiga, T.; Maeda, Y.; Oshio, H. *Coord. Chem. Rev.* **2007**, *251*, 2606. (m) Gamez, P.; Sánchez-Costa, J.; Quesada, M.; Aromí, G. *Dalton Trans.* **2009**, 7845. (n) Halcrow, M. A. *Coord. Chem. Rev.* **2009**, *253*, 2493. (o) Olguin, J.; Brooker, S. *Coord. Chem. Rev.* **2011**, *255*, 203. (p) Bousseksou, A.; Molnár, G.; Salmon, L.; Nicolazzi, W. *Chem. Soc. Rev.* **2011**, *40*, 3313.

(6) Real, J. A.; Andrés, E.; Muñoz, M. C.; Julve, M.; Granier, T.; Bousseksou, A.; Varret, F. *Science* **1995**, *268*, 265.

(7) Halder, G. J.; Kepert, C. J.; Moubaraki, B.; Murray, K. S.; Cashion, J. D. *Science* **2002**, *298*, 1762.

(8) (a) Neville, S. M.; Moubaraki, B.; Murray, K. S.; Kepert, C. J. *Angew. Chem., Int. Ed.* **2007**, *46*, 2059. (b) Neville, S. M.; Halder, G. J.; Chapman, K. W.; Duriska, M. B.; Moubaraki, B.; Murray, K. S.; Kepert, C. J. *J. Am. Chem. Soc.* **2009**, *131*, 12106.

(9) Neville, S. M.; Halder, G. J.; Chapman, K. W.; Duriska, M. B.; Southon, P. D.; Cashion, J. D.; Letard, J. F.; Moubaraki, B.; Murray, K. S.; Kepert, C. J. *J. Am. Chem. Soc.* **2008**, *130*, 2869.

(10) Halder, G. J.; Chapman, K. W.; Neville, S. M.; Moubaraki, B.; Murray, K. S.; Letard, J. F.; Kepert, C. J. *J. Am. Chem. Soc.* **2008**, *130*, 17552.

(11) Niel, V.; Martinez-Agudo, J. M.; Muñoz, M. C.; Gaspar, A. B.; Real, J. A. *Inorg. Chem.* **2001**, *40*, 3838.

(12) Kitazawa, T.; Gomi, Y.; Takahashi, M.; Takeda, M.; Enomoto, M.; Miyazaki, A.; Enoki, T. *J. Mater. Chem.* **1996**, *6*, 119.

(13) (a) Muñoz, M. C.; Real, J. A. *Coord. Chem. Rev.* **2011**, *255*, 2068. (b) Papanikolaou, D.; Margadonna, S.; Kosaka, W.; Ohkoshi, S.; Brunelli, M.; Prassides, K. *J. Am. Chem. Soc.* **2006**, *128*, 8358. (c) Ohkoshi, S.; Imoto, K.; Tsunobuchi, Y.; Takano, S.; Tokoro, H. *Nat. Chem.* **2011**, *3*, 564.

(14) Rodríguez-Velamazán, J. A.; González, M. A.; Real, J. A.; Castro, M.; Muñoz, M. C.; Gaspar, A. B.; Ohtani, R.; Ohba, M.; Yoneda, K.; Hijikata, Y.; Yanai, N.; Mizuno, M.; Ando, H.; Kitagawa, S. *J. Am. Chem. Soc.* **2012**, *134*, 5083.

(15) (a) Ohba, M.; Yoneda, K.; Agustí, G.; Muñoz, M. C.; Gaspar, A. B.; Real, J. A.; Yamasaki, M.; Ando, H.; Nakao, Y.; Sakaki, S.; Kitagawa, S. *Angew. Chem. Intl. Ed.* **2009**, *48*, 4767. (b) Boldog, I.; Gaspar, A. B.; Martínez, V.; Pardo-Ibáñez, P.; Ksenofontov, V.; Bhattacharjee, A.; Gütlich, P.; Real, J. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 6443.

(16) Neville, S. M.; Halder, G. J.; Chapman, K. W.; Duriska, M. B.; Southon, P. D.; Cashion, J. D.; Létard, J. F.; Moubaraki, B.; Murray, K. S.; Kepert, C. J. *J. Am. Chem. Soc.* **2009**, *130*, 2869.

(17) (a) Agustí, G.; Ohtani, R.; Yoneda, K.; Gaspar, A. B.; Ohba, M.; Sánchez-Royo, J. F.; Muñoz, M. C.; Kitagawa, S.; Real, J. A. *Angew. Chem., Int. Ed.* **2009**, *48*, 8944. (b) Ohtani, R.; Yoneda, K.; Furukawa, S.; Horike, N.; Kitagawa, S.; Gaspar, A. B.; Muñoz, M. C.; Real, J. A.; Ohba, M. *J. Am. Chem. Soc.* **2011**, *133*, 8600.

(18) (a) Agustí, G.; Cobo, S.; Gaspar, A. B.; Molnár, G.; Moussa, N. O.; Szilágyi, P. Á.; Pálfi, V.; Vieu, C.; Muñoz, M. C.; Real, J. A.; Bousseksou, A. *Chem. Mater.* **2008**, *20*, 6721. (b) Bartual-Murgui, C.; Ortega-Villar, N. A.; Shepherd, H. J.; Muñoz, M. C.; Salmon, L.; Molnár, G.; Bousseksou, A.; Real, J. A. *J. Mater. Chem.* **2011**, *21*, 7217. (c) Bartual-Murgui, C.; Salmon, L.; Akou, A.; Ortega-Villar, N. A.; Shepherd, H. J.; Muñoz, M. C.; Molnár, G.; Real, J. A.; Bousseksou, A. *Chem.—Eur. J.* **2012**, *18*, 507. (d) Muñoz-Lara, F. J.; Gaspar, A. B.; Muñoz, M. C.; Arai, M.; Kitagawa, S.; Ohba, M.; Real, J. A. *Chem.—Eur. J.* **2012**, *18*, 8013.

(19) Krautscheid, H.; Emig, N.; Klaasen, N.; Seringer, P. *J. Chem. Soc., Dalton Trans.* **1998**, 3071.

(20) Potvin, C.; Manoli, J.-M.; Sécheresse, F.; Marzak, S. *Inorg. Chem.* **1987**, *26*, 4370.

(21) (a) Li, D. C.; Li, Z. X.; Dou, J. M.; Wang, D. Q. *J. Inclusion Phenom. Macrocyclic Chem.* **2003**, *46*, 83. (b) Li, X.; Dou, J. M.; Liu, Y.; Zhuc, L. Y.; Zhenga, P. J. *Acta Crystallogr.* **2000**, *C56*, 1185.

(22) Ilyukhin, A. B.; Petrosyants, S. P. *Russ. J. Coord. Chem.* **2010**, *36*, 559.

(23) Machura, B.; Palion, J.; Switlicka, A.; Mrozinski, J.; Kruszynski, R. *Polyhedron* **2011**, *30*, 2499.

(24) Jian, F. F.; Xiao, H. L.; Liu, F. Q. *J. Solid State Chem.* **2006**, *179*, 3695.

(25) (a) Mawby, A.; Pringle, G. E. *J. Chem. Soc. D: Chem. Commun.* **1970**, 385. (b) Rohde, J. U.; von Malottki, B.; Preetz, W. *Z. Anorg. Allg. Chem.* **2000**, *626*, 905.

(26) Baran, M.; Dyakonov, V. P.; Gladczuk, L.; Levchenko, G. G.; Piechota, S.; Szymczak, G. *Physica C* **1995**, *241*, 383.

(27) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.

(28) Braga, D.; Grepioni, F. *Angew. Chem., Int. Ed.* **2004**, *43*, 4002.

(29) Spek, A. L. *PLATON: A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Nederlands, 2010.

(30) (a) Moliner, N.; Muñoz, M. C.; Real. *Inorg. Chem. Commun.* **1999**, *2*, 25. (b) Noro, S. I.; Kondo, M.; Ishii, T.; Kitagawa, S.; Matsuzaka, H. *J. Chem. Soc., Dalton Trans.* **1999**, 1569. (c) Lu, J.; Paliwala, T.; Lim, S. C.; Yu, C.; Nju, T.; Jacobson, A. J. *Inorg. Chem.* **1997**, *36*, 923. (d) Li, M. X.; Xie, G. H.; Gu, Y. D.; Chen, J.; Zheng, P. J. *Polyhedron* **1995**, *14*, 1235. (e) De Munno, G.; Armentano, D.; Poerio, T.; Julve, M.; Real, J. A. *J. Chem. Soc., Dalton Trans.* **1999**, 1813. (f) Wriedt, M.; Sellmer, S.; Näther, C. *Dalton Trans.* **2009**, 7975.

(31) Niel, V.; Thompson, A. L.; Muñoz, M. C.; Galet, A.; Goeta, A. E.; Real, J. A. *Angew. Chem., Int. Ed.* **2003**, *42*, 3760.