



Spin crossover (SCO) iron(II) coordination polymer chain: Synthesis, structural and magnetic characterizations of $[\text{Fe}(\text{abpt})_2(\mu\text{-M}(\text{CN})_4)]$ ($\text{M} = \text{Pt}^{\text{II}}$ and Ni^{II})



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ARTICLE INFO

Article history:

Received 25 March 2013

Accepted 3 June 2013

Available online 19 June 2013

Keywords:

Iron complex

Cyanometallate

Bridging ligands

Coordination polymer

Spin crossover

ABSTRACT

New iron(II) coordination polymeric neutral chain of formula $[\text{Fe}(\text{abpt})_2(\mu\text{-M}(\text{CN})_4)]$, with $\text{M} = \text{Pt}^{\text{II}}$ (**1**), Ni^{II} (**2**) and $\text{abpt} = 4\text{-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole}$, have been synthesized and characterized by infrared spectroscopy, X-ray diffraction and magnetic measurements. The two compounds are isostructural as deduced from a Rietveld analysis of X-ray powder diffraction data of **2** simulated from the single crystal structure of **1**. The crystal packing of **1** is formed by regular chains running along the crystallographic $[-101]$ direction where the planar $[\text{Pt}(\text{CN})_4]^{2-}$ anion acts as a μ_2 -bridging ligand via two nitrogen atoms of two different *trans* cyano groups, while the two *abpt* molecules act as chelating ligands. Along the neutral chains, the $\text{Fe}\cdots\text{Pt}$ distances are imposed by the cyano groups of the $[\text{Pt}(\text{CN})_4]^{2-}$ moiety (5.027 and 5.022 Å at 294 and 150 K, respectively), leading to $\text{Fe}\cdots\text{Fe}$ intrachain distances of 10.055 and 10.045 Å at 294 and 150 K, respectively. The thermal dependence of the product of the molar magnetic susceptibility times the temperature ($\chi_m T$) for compound **1** shows a constant value close to $0.2 \text{ emu K mol}^{-1}$ in the temperature range 10–300 K in the cooling and warming scans. Above 300 K, compound **1** shows a SCO transition from the *LS* to the *HS* configuration although the transition is not fully achieved at 400 K.

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1. Introduction

Metal transition compounds exhibiting spin crossover (SCO) behavior have been widely investigated over the last decade and are still attracting intense research interest given their many potential applications in the development of novel electronic devices [1]. The applied perspectives of the SCO complexes are inherent to the potential of some pseudo-octahedral transition metal complexes to display a magnetic transition between the high spin (*HS*) and the low spin (*LS*) states through external stimuli such as temperature, pressure, magnetic field or light irradiation [2–5]. The SCO phenomenon occurs in the d^4 – d^7 transition metal complexes, but the most studied examples to date are those based on $\text{Fe}(\text{II})$ (d^6 configuration), for which a reversible paramagnetic–diamagnetic transition from the *HS* ($S = 2$, $^5T_{2g}$) to the *LS* ($S = 0$, $^1A_{1g}$) state is observed.

Up to now, numerous mononuclear compounds (mainly $\text{Fe}(\text{II})$ complexes) have been extensively studied [2–5]. In such discrete systems, the intermolecular interactions (π -stacking, hydrogen bonding and van der Waals interactions), which generate the supramolecular architecture in the solid state, play a crucial role in the transmission of the magneto-elastic cooperative interactions at the origin of the hysteretic behavior. Unfortunately, their non covalent character precludes any control on the way they extend in the solid structure, and consequently on the SCO characteristics. In order to better explore the cooperative effect between the active metal sites, an alternative approach, based on the use of suitable bridging ligands to covalently connect the metal centers, has been introduced [6]. This strategy has already resulted in the syntheses of several $\text{Fe}(\text{II})$ SCO coordination polymers exhibiting rich and fascinating structural features coupled to their magnetic behaviors. However, in contrast to the mononuclear compounds, these studies remain scarcely reported because of the limited number of potentially appropriate bridging ligands. In this context, we have extended this polymeric approach to the highly conjugated cyanocarbanion ligands involving several potentially donating nitrogen

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atoms juxtaposed in such a way that they cannot all coordinate to the same metal ion [7]. We have recently reported a detailed photocrystallographic and photomagnetic study [4] on the first SCO iron(II) molecular neutral chain $[\text{Fe}(\text{abpt})_2(\text{tcpd})]$ involving an anion as bridging ligand ($(\text{tcpd})^{2-} = [\text{C}(\text{CN})_2]_3^{2-} = 2$ -dicyanomethylene-1,1,3,3-tetracyanopropanediide anion; abpt = 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole). Continuing our investigations on such SCO polymeric materials, we have extended this study to more rigid anionic bridging ligands.

In this context, we have prepared two new SCO 1D-polymeric coordination compounds $[\text{Fe}(\text{abpt})_2(\mu\text{-M}(\text{CN})_4)] \cdot x\text{H}_2\text{O}$, with $\text{M} = \text{Pt}^{\text{II}}$ (**1**) and Ni^{II} (**2**), where the tetracyanometallate planar anions $[\text{M}(\text{CN})_4]^{2-}$ act as μ_2 -bridging ligands. The magnetic properties of a hemihydrated form of the Ni derivative (compound **2**) have been reported very recently by Trávníček et al. [8], although the crystal structure was not reported. Therefore, here we will focus on the crystal structure characterizations of both compounds (**1** and **2**) and the magnetic properties of the Pt derivative (**1**).

2. Experimental

2.1. General remarks

All reactions were carried out under aerobic conditions. The starting materials and solvents were purchased from commercial sources (analytical reagent grade) and used without further purification.

2.2. Preparations

2.2.1. Syntheses of $[\text{Fe}(\text{abpt})_2(\mu\text{-M}(\text{CN})_4)]$ ($\text{M} = \text{Pt}^{\text{II}}$ (**1**), Ni^{II} (**2**))

An ethanolic solution (10 mL) of abpt (95.3 mg, 0.4 mmol) was added progressively, under continuous stirring, to 10 mL of a 1:1 water/methanol solution containing $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (67.5 mg, 0.2 mmol) and the corresponding salt of $\text{K}_2[\text{M}(\text{CN})_4]$ ($\text{M} = \text{Pt}^{\text{II}}$ (**1**): 75.5 mg, 0.2 mmol; $\text{M} = \text{Ni}^{\text{II}}$ (**2**): 48.2 mg, 0.2 mmol). For both compounds **1** and **2**, the resulting red-orange precipitate was filtered off, washed with water and ethanol and then dried. $[\text{Fe}(\text{abpt})_2(\mu\text{-Pt}(\text{CN})_4)]$ (**1**). Yield: 130 mg, 78%. Anal. Calc. for $\text{C}_{28}\text{H}_{20}\text{N}_{16}\text{FePt}$: C, 40.4; H, 2.4; N, 26.9. Found: C, 40.2; H, 2.3; N, 27.1%. IR (cm^{-1}): 3225(br), 3179(m), 3142(m), 3079(m), 3051(m), 3019(w), 2164(m), 2132(s), 1633(s), 1609(m), 1588(s), 1568(m), 1541(w), 1521(w), 1490(m), 1461(s), 1426(s), 1402(m), 1340(w), 1301(w), 1289(w), 1276(w), 1256(m), 1167(w), 1147(m), 1116(m), 1082(s), 1057(s), 1038(s), 997(m), 907(w), 894(w), 792(s), 782(s), 755(s), 744(s), 742(s), 714(w), 693(s), 640(m), 614(m), 526(w), 509(m), 482(m), 451(m). $[\text{Fe}(\text{abpt})_2(\mu\text{-Ni}(\text{CN})_4)]$ (**2**). Yield: 103.0 mg, 74%. Anal. Calc. for $\text{C}_{28}\text{H}_{20}\text{N}_{16}\text{FeNi}$: C, 48.4; H, 2.9; N, 32.2. Found: C, 47.8; H, 2.6; N, 32.7%. IR (cm^{-1}): 3237(br), 3178(m), 3080(m), 3054(m), 3019(w), 2151(m), 2121(s), 2082(w), 1631(s), 1609(m), 1589(s), 1569(m), 1541(w), 1523(w), 1492(m), 1462(s), 1428(s), 1402(m), 1340(w), 1302(w), 1290(w), 1278(w), 1258(m), 1157(m), 1147(m), 1117(m), 1085(s), 1058(s), 1039(s), 998(m), 910(w), 895(w), 797(s), 784(s), 757(s), 745(s), 729(w), 714(w), 694(s), 641(m), 615(m), 532(w), 493(w), 468(m), 455(m).

2.2.2. Single-crystals preparation of $[\text{Fe}(\text{abpt})_2(\mu\text{-Pt}(\text{CN})_4)]$ (**1**)

Single-crystals of compound **1** were synthesized using gel diffusion technique. The gel phase was obtained by addition of tetramethoxysilane (1 mL) to an aqueous solution (9 mL) of $\text{K}_2[\text{Pt}(\text{CN})_4]$ (0.15 mmol, 56.6 mg) with stirring; the gel was formed from the resulting solution after a few hours. Then, 6 mL of a 1:1 water/ethanol solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.15 mmol, 41.7 mg) and abpt ligand (0.33 mmol, 78.6 mg) were carefully layered onto the

gel. Single-crystals of compound **1** suitable for X-ray analysis were formed within 2 weeks. The IR spectrum of the red single crystals of **1** formed within the gel is identical to that observed for the red powder of **1** (see Section 2.2.1). Attempts to prepare single crystals of nickel analogue (compound **2**) led us to only polycrystalline powder for which the IR spectrum is similar to that described above for this compound (see Section 2.2.1).

2.2.3. X-ray structure studies of $[\text{Fe}(\text{abpt})_2(\mu\text{-M}(\text{CN})_4)]$ ($\text{M} = \text{Pt}^{\text{II}}$ (**1**), Ni^{II} (**2**))

A red single crystal of **1** was placed at the top of a glass fibre with silicone grease and mounted on an Xcalibur 2 CCD Diffractometer (Oxford Diffraction) fitted with a graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Data were collected at 150 and 294 K. The crystal structures were solved by direct methods and successive Fourier difference syntheses, and were refined on F^2 by weighted anisotropic full-matrix least-square methods [9]. All non-hydrogen atoms were refined anisotropically while the hydrogen atoms were calculated and therefore included as isotropic fixed contributors to F_c . Data collection and data reduction were done with the CRYSLIS-CCD and CRYSLIS-RED programs [10,11]. All other calculations were performed with standard procedures (WINGX) [12]. Crystal data, structure refinement and collection parameters of **1** are listed in Table 1. Selected bond lengths and angles are given in Table 2. The polycrystalline powder of compound **2** (Ni(II) analogue) allowed us to perform the X-ray powder diffraction (XRPD). The room-temperature X-ray powder diffraction spectra (XRPD) were recorded on a PANalytical Empyrean X-ray powder diffractometer at 45 kV, 40 mA with a Cu-target tube. For comparison purposes, XRPD was also carried out on polycrystalline powder of compound **1**. The measured diffraction patterns were analyzed using the Rietveld method as implemented in the MAUD program [13]. As a starting point, the diffraction pattern of **1** was simulated from the single crystal data. In a second step, only selected parameters were refined in the Rietveld procedure (cell parameters, mean crystallite size, and $r.m.s.$ (root

Table 1
Crystal data and structural refinement parameters for compounds **1** and **2**.

	1	2
Temperature (K)	294	150
Empirical Formula ^a	$\text{FePtC}_{28}\text{H}_{20}\text{N}_{16}$	$\text{FeNiC}_{28}\text{H}_{20}\text{N}_{16}$
Molecular weight	831.54	695.12
Space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	8.5046(3)	8.4330(3)
<i>b</i> (Å)	9.0598(3)	8.9520(3)
<i>c</i> (Å)	10.0028(3)	10.0636(3)
α (°)	83.299(4)	83.561(3)
β (°)	65.231(3)	65.089(4)
γ (°)	89.222(3)	88.651(3)
<i>V</i> (Å ³)	694.50(4)	684.46(4)
<i>Z</i> ^a	1	1
ρ_{calc} (g cm ⁻³)	1.988	2.017
μ (cm ⁻¹)	56.07	56.89
<i>F</i> (000)	404	404
Reflections measured	7122	5531
2θ range (°)	6.00–54.00	6.04–54
Reflections unique/ <i>R</i> _{int}	3021/0.0320	2968/0.0301
Reflections with $I > 2\sigma(I)$	2870	2908
<i>N</i> _v	213	213
<i>R</i> ₁ ^b / <i>wR</i> ₂ ^c	0.0364/0.0827	0.0327/0.0773
Goodness-of-Fit (GOF) ^d	1.028	1.042
$\Delta\rho_{\text{max,min}}$ (eÅ ⁻³)	+1.668/−0.652	1.961/−0.812

^a The asymmetric unit contains 0.5 of the chemical formula.

^b $R_1 = \sum |F_o - F_c| / F_o$.

^c $wR_2 = \{ \sum [w(F_o^2 - F_c^2)]^2 / \sum [w(F_o^2)]^2 \}^{1/2}$.

^d $\text{GooF} = \{ \sum [w(F_o^2 - F_c^2)] / (N_{\text{obs}} - N_{\text{var}}) \}^{1/2}$.

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