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Cobalt(II) - Pyrazine-Chloride Coordination Polymers: Synthesis, Reactivity and Magnetic Properties

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The reaction of cobalt(II) chloride hexahydrate and pyrazine in a reduced amount of water under hydrothermal conditions affords [$CoCl_2$pyz]$_n$, which crystallises in an orthorhombic unit cell (a = 12.0014, b = 7.1040, c = 3.5380 Å), space group *Cmmm*. Fourier transform infrared spectroscopy confirms the coordination of pyrazine to Co(II) in an octahedral geometry. This compound is thermally stable in air up to 320 °C and may also be obtained by the single-step decomposition of [$CoCl_2$(pyz)$_2$]$_n$ at 190 °C, with an activation energy of 121 kJ mol^{-1}. [$CoCl_2$pyz]$_n$ contains Co(II) chains bridged by two chloride ions making an angle of 92.21º, leading to orthogonal (d-p) orbitals and to one-dimensional ferromagnetic chains. In contrast, in [$CoCl_2$(pyz)$_2$]$_n$ only pyrazine bridges the Co(II) ions, setting them apart, resulting in a purely paramagnetic system. Because the simple contact with pyrazine vapour or aqueous pyrazine reintroduces this molecule into [$CoCl_2$pyz]$_n$, while heating [$CoCl_2$(pyz)$_2$]$_n$ removes pyrazine affording [$CoCl_2$pyz]$_n$, the magnetic behaviour may be reversibly switched between the two states.

Introduction

It is well known that the self-assembly of Co(II) and pyrazine (pyz) under hydrothermal reaction conditions yields a number of coordination polymers.[1] A search in the Cambridge data basis reveals over three hundred coordination polymers of pyrazine and derivatives, some of which also include a second ligand. One-dimensional structures comprising linear Co-pyz chains occur, for example, in {[$Co(H_2O)_4$pyz]$(NO_3)_2\cdot 2H_2O$)}$_n$[2] and {[$Co(H_2O)_4$pyz]$(SO_4)_2\cdot H_2O$)}$_n$.[3] Two-dimensional structures are also known, where the sheets formed by the cobalt ions coordinated to four pyrazine molecules are charge-balanced by monodentate counter-ions, as in [CoX_2(pyz)$_2$]$_n$,[1,4] [Co(NCS)$_2$(pyz)$_2$]$_n$,[5] [Co(NCO)$_2$(pyz)$_2$]n[6] and [Co(NCSe)$_2$(pyz)$_2$]$_n$.[7] Apparently, there are no known three-dimensional structures of Co(II) and pyrazine only. In a number of three-dimensional structures the cobalt-pyrazine layers are interconnected by a second bidentate ligand, such as the nitrite in {[Co(NO_2)(pyz)$_2$]ClO_4}$_n$,[8] terephthalate (tp) in [Co(μ_3-tp)(μ_3-pyz)]$_n$,[9] or [Au(CN)$_2$]$^{2-}$ in {Co(pyz)[Au(CN)$_2$]$_2$}$_n$.[10]

Although the solvent determines the dimensionality of the cobalt and pyrazine frameworks the latter also depends much on the nature of the charge-balancing anion. For example, anions such as NO_3^- and SO_4^{2-} result in one-dimensional arrays.[2,3] Chelating anions may also lead to one-dimensional structures, *e.g.*, in [Co(acac)$_2$pyz]$_n$.[11] The halides and NCS$^-$ yield two-dimensional structures.[1,5]

The two distinct two-dimensional Co(II) chloride - pyrazine compounds known have the same formula [$CoCl_2$(pyz)$_2$]$_n$ and crystallize in both a tetragonal unit cell, space group *I4/mmm* (a = b = 7.12, c = 10.63),[1b] and in an orthorhombic unit cell, space group *Ccca* (a = 10.100, b = 10.672, c = 10.136 Å).[12] Here, we describe the synthesis and characterization of yet another coordination polymer prepared from cobalt(II) chloride and pyrazine formulated as [$CoCl_2$pyz]$_n$. Isostructural compounds are known for the divalent ions of Fe,[13] Mn,[14] Ni,[15] Cu[16] and Zn.[17] [$CoCl_2$pyz]$_n$ may be obtained from [$CoCl_2$(pyz)$_2$]$_n$ by thermal decomposition and may also be transformed into the latter by exposure to pyrazine. This provides an interesting way of switching reversibly the magnetic properties of the materials.

Results and Discussion

Structure

Comparing with the stoichiometric synthesis, the non-stoichiometric procedure afforded higher yield and larger and better crystallised crystals suitable for single-crystal X-ray diffraction (Figure S1). In both cases, the amount of water was critical because all attempts to obtain the [$CoCl_2$pyz]$_n$ in diluted solutions have failed, always resulting in [$CoCl_2$(pyz)$_2$]$_n$. The crystal data and structure refinement parameters for both compounds are collected in Table 1.

[$CoCl_2$pyz]$_n$ crystallized in the orthorhombic *Cmmm* space group, with an asymmetric unit (Figure 1a) containing 1/8 of Co^{2+}, 1/8 of pyz ligand and ¼ of Cl^-. Co^{2+} binds two equivalent N atoms from two pyz ligands and four equivalent Cl^- anions, forming a nearly perfect octahedron (Figure 1b). The Co-N distance is 2.154(3) Å, similar to that [2.1821(13) Å] found for [$CoCl_2$(pyz)$_2$]$_n$ (Table 2) and consistent with a previous report.[18] The Co-Cl bond length [2.4549(6) Å, Table 2] is also in the normal range, but among the longest reported.[18d,18e] The Cl^- and pyz fragments bridge the metal centres (Figures 1b, 2a) extending perpendicular to each other, leading to an infinite two-dimensional network with the shortest

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Table 1 Crystal data and structure refinement parameters for $[CoCl_2pyz]_n$ and $[CoCl_2(pyz)_2]_n$.

	$[CoCl_2pyz]_n$	$[CoCl_2(pyz)_2]_n$	$[CoCl_2(pyz)_2]_n$ *
Formula	$C_4H_4Cl_2CoN_2$	$C_8H_8Cl_2CoN_4$	$C_8H_8Cl_2CoN_4$
Formula weight (g mol^{-1})	209.92	290.01	290.01
Temperature (K)	180(2)	296(2)	180(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Tetragonal	Tetragonal
Space group	*Cmmm*	*I-4*	*I-4*
Unit cell dimensions (Å)	a = 12.0014(7)	a = 7.1489(6)	a = 7.1449(11)
	b = 7.1040(4)	b = 7.1489(6)	b = 7.1449(11)
	c = 3.5380(2)	c = 10.6653(17)	c = 10.633(2)
Volume (Å^3)	301.64(3)	545.07(11)	542.83(16)
Z	2	2	2
Density (Mg/m^3)	2.311	1.767	1.774
Crystal size (mm^3)	0.17x0.08x0.01	0.28x0.08x0.02	0.12x0.10x0.01
Theta range	3.33 to 30.67°	3.43 to 35.83°	3.44 to 28.46°
Index ranges	-17 <= h <= 17,	-11 <= h <= 11,	-9 <= h <= 6,
	-10 <= k <= 10,	-10 <= k <= 11,	-9 <= k <= 7,
	-4 <= l < = 5	-17 <= l <= 16	-8 <= l <= 13
Reflections collected	1957	5529	1015
Independent reflections	294 [*R(int)* = 0.0406]	1266 [*R(int)* = 0.0747]	663 [*R(int)* = 0.0405]
Data / restraints / parameters	294 / 0 / 18	1266 / 0 / 54	663 / 24 / 53
Goodness-of-fit on F^2	1.140	1.068	0.993
Final R indices [I>2sigma(I)]	*R1* = 0.0261,	*R1* = 0.0358,	*R1* = 0.0420,
	wR2 = 0.0634	*wR2* = 0.0763	*wR2* = 0.0696
R indices (all data)	*R1* = 0.0309,	*R1* = 0.0509,	*R1* = 0.0879,
	wR2 = 0.0654	*wR2* = 0.0832	*wR2* = 0.0834
Largest diff. peak and hole (e.Å^{-3})	0.623 and -0.576	1.120 and -0.570	0.474 and -0.429
CCDC No.	1012088	1012089	1012090

* obtained by reaction of $[CoCl_2pyz]_n$ with pyrazine.

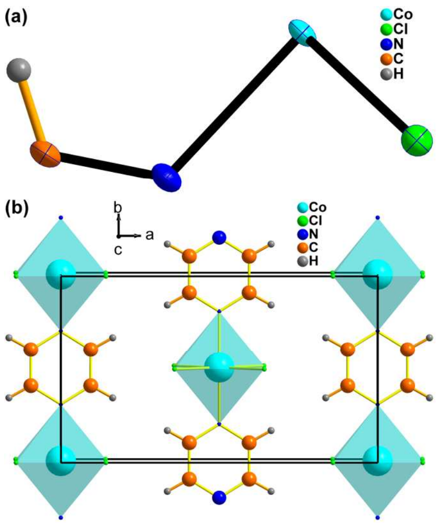

Figure 1 (a) $[CoCl_2pyz]_n$ asymmetric unit with the labelling scheme (50% probability). (b) Polyhedra view of the unit cell along the *c* axis.

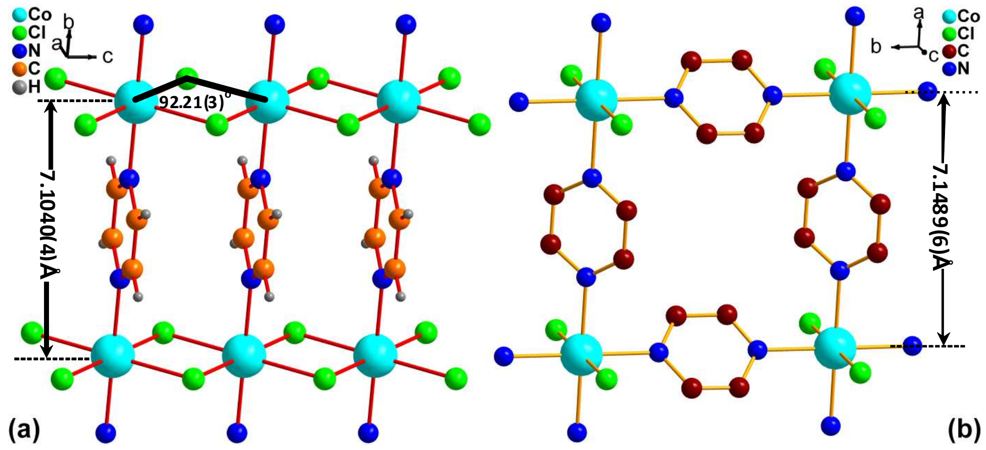

Figure 2 2D networks of (a) $[CoCl_2pyz]_n$ showing the bridging Cl^- and pyz ligands, and (b) $[CoCl_2(pyz)_2]_n$ exhibiting only bridging pyz.

Table 2 Selected bond lengths [Å] and angles [°] for $[CoCl_2pyz]_n$ and $[CoCl_2(pyz)_2]_n$.

$[CoCl_2pyz]_n$		$[CoCl_2(pyz)_2]_n$		$[CoCl_2(pyz)_2]_n$*	
Co(1)-N(1)#1	2.154(3)	Co(1)-N(1)#1	2.1821(13)	Co(1)-N(1)#1	2.183(3)
Co(1)-N(1)	2.154(3)	Co(1)-N(1)#2	2.1821(13)	Co(1)-N(1)	2.183(3)
Co(1)-Cl(1)	2.4549(6)	Co(1)-N(1)	2.1821(13)	Co(1)-N(1)#2	2.183(3)
Co(1)-Cl(1)#1	2.4549(6)	Co(1)-N(1)#3	2.1821(13)	Co(1)-N(1)#3	2.183(3)
Co(1)-Cl(1)#2	2.4549(6)	Co(1)-Cl(1)#1	2.4050(6)	Co(1)-Cl(1)#1	2.4051(14)
Co(1)-Cl(1)#3	2.4549(6)	Co(1)-Cl(1)	2.4050(6)	Co(1)-Cl(1)	2.4051(14)
N(1)#1-Co(1)-N(1)	180.0	N(1)#1-Co(1)-N(1)	90.003(3)	N(1)#1-Co(1)-N(1)	90.02(2)
N(1)#1-Co(1)-Cl(1)	90.0	N(1)#2-Co(1)-N(1)	179.1(3)	N(1)-Co(1)-N(1)#2	90.02(2)
N(1)-Co(1)-Cl(1)	90.0	N(1)-Co(1)-N(1)#3	90.004(3)	N(1)-Co(1)-N(1)#3	178.0(12)
N(1)-Co(1)-Cl(1)#1	90.0	N(1)-Co(1)-Cl(1)#1	89.55(16)	N(1)-Co(1)-Cl(1)#1	91.0(6)
Cl(1)-Co(1)-Cl(1)#1	180.0	N(1)#1-Co(1)-Cl(1)	89.55(16)	N(1)#1-Co(1)-Cl(1)	91.0(6)
N(1)-Co(1)-Cl(1)#2	90.0	N(1)#2-Co(1)-Cl(1)	90.45(16)	N(1)-Co(1)-Cl(1)	89.0(6)
Cl(1)-Co(1)-Cl(1)#2	92.21(3)	N(1)-Co(1)-Cl(1)	90.45(16)	N(1)#2-Co(1)-Cl(1)	91.0(6)
N(1)-Co(1)-Cl(1)#3	90.0	N(1)#3-Co(1)-Cl(1)	89.55(16)	N(1)#3-Co(1)-Cl(1)	89.0(6)
Cl(1)-Co(1)-Cl(1)#3	87.79(3)	Cl(1)#1-Co(1)-Cl(1)	180.0	Cl(1)#1-Co(1)-Cl(1)	180.0
Co(1)-Cl(1)-Co(1)#4	92.21(3)	C(2)-N(1)-C(1)	115.3(6)	C(2)-N(1)-C(1)	118.2(17)

Symmetry transformations used to generate equivalent atoms:
$[CoCl_2pyz]_n$: #1 -x,-y+2,-z-1; #2 x,y,z-1; #3 -x,-y+2,-z; #4 x,y,z+1.
$[CoCl_2(pyz)_2]_n$: #1 y,-x,-z; #2 -x,-y,z; #3 -y,x,-z.
$[CoCl_2(pyz)_2]_n$*: #1 y,-x,-z; #2 -y,x,-z; #3 -x,-y,z.

* obtained by reaction of $[CoCl_2pyz]_n$ with pyrazine

Co-Co distance of 3.5380(2) Å along the *c* axis and a distance of 7.1040(4) Å between Co ions, which are bridged via the pyz ligand (Figure 2a). In comparison, in $[CoCl_2(pyz)_2]_n$ only the pyz ligands interconnect Co, that is, no Cl^- bridges are present (Figure 2b).

Consider Figure 3. Thermogravimetric analysis shows that $[CoCl_2pyz]_n$ is stable up to *ca.* 350 °C exhibiting a first weight loss up to 440 ºC, equivalent to one pyrazine molecule, and a second one from 450 to 550 °C leading to the final product, Co_3O_4 (Figure S2). $[CoCl_2(pyz)_2]_n$, in turn, displays three weight losses from: (i) *ca.* 180 to 220 °C, due to loss of the first pyrazine molecule; (ii) *ca.* 350 to 410 °C due to loss of the second pyrazine molecule; and (iii) *ca.* 410 to 510 ºC leading to the final product, Co_3O_4. The DSC endothermic peak corresponding to the decomposition of $[CoCl_2(pyz)_2]_n$ into $[CoCl_2pyz]_n$ at *ca.* 180 °C allows estimating the activation energy for this process: applying the Ahrrenius equation and the Ozawa method[19] an activation energy of 121 kJ mol^{-1} was obtained.

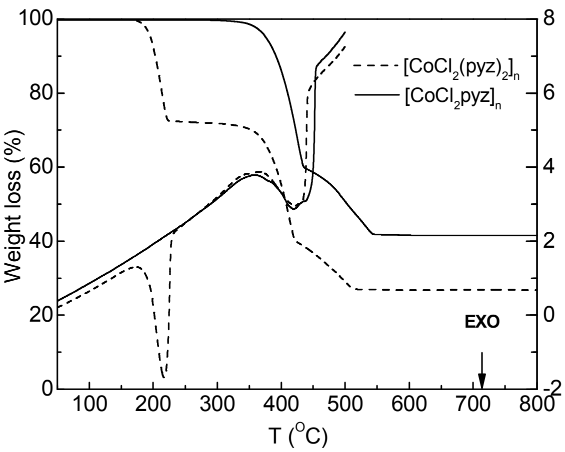

Figure 3 Thermogravimetric and differential scanning calorimetry curves of $[CoCl_2pyz]_n$ and $[CoCl_2(pyz)_2]_n$.

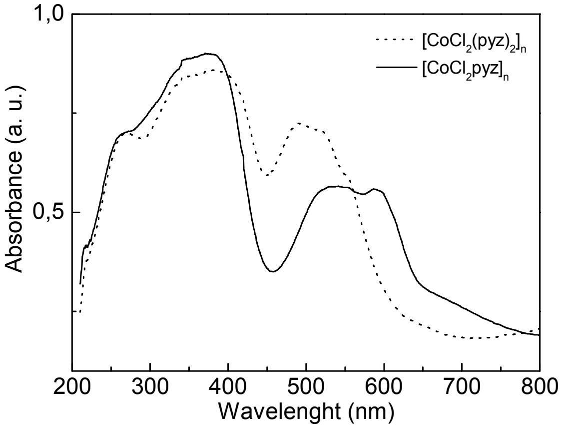

Figure 4 DRIFT electronic spectra of $[CoCl_2pyz]_n$ and $[CoCl_2(pyz)_2]_n$.

The assignment of the pyrazine infrared spectrum in the vapour and crystalline phases was previously reported,[20] while the spectrum of $[CoCl_2(pyz)_2]_n$ is also available.[1a] For the purposes of the present work, suffices to say that most $[CoCl_2pyz]_n$ and $[CoCl_2(pyz)_2]_n$ bands involving C and N atoms of the pyrazine aromatic ring (Figure S3) appear at frequencies lower than observed for vapour and crystalline pyrazine. For example: $\nu(NC)''_{as} + \nu(CC)_{as}$ modes appear at 1167 and 1154 cm^{-1} for, respectively, $[CoCl_2pyz]_n$ $[CoCl_2(pyz)_2]_n$, and at 1174 and 1179 cm^{-1} for, respectively, vapour and crystalline pyrazine; $\nu(NC)'_{as} + \delta(CH)'_{as} + \delta$ ring 1 modes appear at 1117, 1115, 1135 and 1153 cm^{-1}, respectively. These facts support the weakening of the aromatic-ring bonds upon coordination to cobalt.

Consider Figure 4. The electronic spectra of $[CoCl_2(pyz)_2]_n$ and $[CoCl_2pyz]_n$ are typical of octahedral Co(II) complexes, exhibiting three bands between 450 and 650 nm, shifted to the red in the case of $[CoCl_2pyz]_n$. The intense absorption between 250 and 400 nm is due to pyrazine that presents a set of absorption bands in this region.[21] The spectrum of $[CoCl_2(pyz)_2]_n$ was recorded from a freshly prepared compound using the procedure in ref. [1]. The spectra of $[CoCl_2pyz]_n$ given by samples prepared from both direct synthesis and from thermal decomposition of $[CoCl_2(pyz)_2]_n$ are identical. This confirms that $[CoCl_2(pyz)_2]_n$ thermally decomposes yielding $[CoCl_2pyz]_n$.

The experimental and simulated (from single-crystal data) powder X-ray diffraction patterns of $[CoCl_2pyz]_n$ show that the samples are essentially pure (Figures 5A-C). However, the reflections from the material obtained via the thermal decomposition of $[CoCl_2(pyz)_2]_n$ are relatively broad, thus confirming its poor crystallinity (suggested by SEM analysis, Figure S1). The experimental and simulated XRD patterns of $[CoCl_2(pyz)_2]_n$ are very similar also confirming sample purity (Figures 5D, E).

Reactivity

Since the thermal decomposition of $[CoCl_2(pyz)_2]_n$ led to $[CoCl_2pyz]_n$, by elimination of one pyrazine molecule, it is of interest to ascertain whether this process is reversible. For this purpose two routes for pyrazine re-insertion were considered, the reaction of: (i) an aqueous suspension of $[CoCl_2pyz]_n$ with dissolved pyrazine; (ii) solid $[CoCl_2pyz]_n$ with pyrazine vapour (from sublimation). In the first route, 17 mg of pyrazine were dissolved in 0.5 mL of distilled water to which 15.0 mg of blue $[CoCl_2pyz]_n$ (hydrothermally prepared) were added with stirring and allowed to stand for two weeks, after which 11.6 mg of orange crystals were filtered out, washed with distilled water and dried (56 % yield). The structure of $[CoCl_2(pyz)_2]_n$ was confirmed by single crystal X-ray diffraction. The data are presented in Tables 1 and 2. In the second route, 12 mg of $[CoCl_2pyz]_n$ (obtained by thermal decomposition of $[CoCl_2(pyz)_2]_n$) were placed in a sealed flask with 20 mg of pyrazine and maintained for 12 h in a boiling water bath. After washing with distilled water and drying 16.4 mg (100 % yield) of orange powder were obtained. The same procedure was used with $[CoCl_2pyz]_n$ hydrothermally prepared, but no reaction was observed.

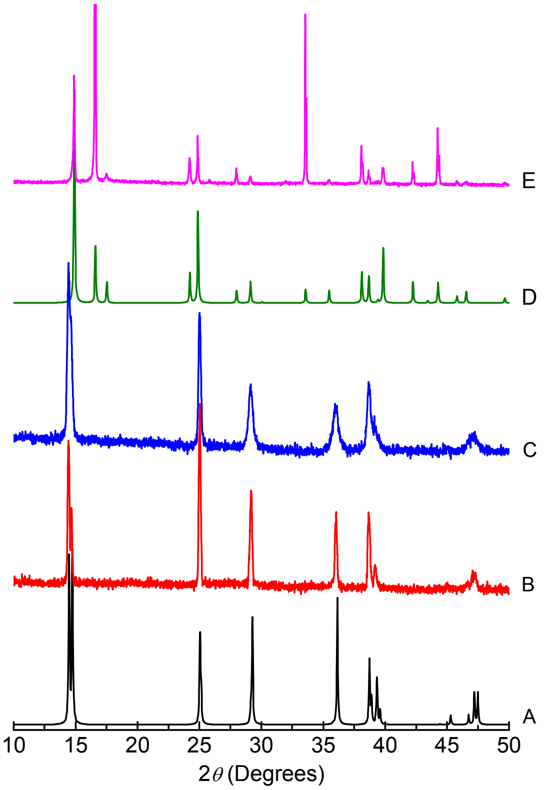

Figure 5 Powder X-ray diffraction patterns of: (A) $[CoCl_2pyz]_n$ (simulated); (B) $[CoCl_2pyz]_n$ obtained from non-stoichiometric synthesis; (C) obtained from the thermal decomposition of $[CoCl_2(pyz)_2]_n$; (D) $[CoCl_2(pyz)_2]_n$ (simulated); (E) $[CoCl_2(pyz)_2]_n$ prepared according to ref. [1].

Magnetic Properties

Figure 6 depicts the in-phase susceptibility temperature product $\chi'T$ for $[CoCl_2(pyz)_2]_n$ and $[CoCl_2pyz]_n$, after subtraction of the expected diamagnetic contribution. The temperature dependence of both compounds deviates from a simple Curie-like behaviour, showing an increase with temperature in the 50 - 100 K range. This is attributed to the influence of the crystal field, as observed in several mononuclear systems containing high-spin Co(II) ions in distorted octahedral environments. Differences between the magnetic behaviour of $[CoCl_2(pyz)_2]_n$ and $[CoCl_2pyz]_n$ are apparent at low and high temperature. While the susceptibility of $[CoCl_2(pyz)_2]_n$ is well described by spin-orbit coupling and ligand-field effects acting on magnetic isolated Co(II) ions (solid line in Fig. 6, see details in SI) the susceptibility of $[CoCl_2pyz]_n$ is higher at high and low temperature, displaying also a strong non-

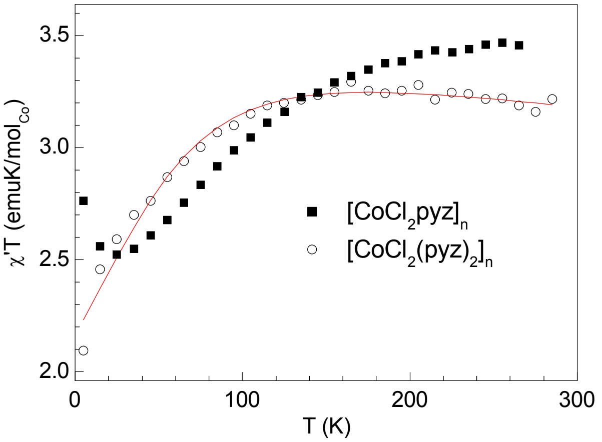

Figure 6 Temperature dependence of the in-phase magnetic susceptibility multiplied by temperature (**χ**T *vs.* T), at a frequency of 2154 Hz of [CoCl$_2$(pyz)$_2$]$_n$ and [CoCl$_2$pyz]$_n$. Solid lines are fits using the Eq. S1 Hamiltonian, obtained with programme *PHI* .[22]

monotonic behaviour with a minimum at *ca.* 30 K. At high temperatures, spin-orbit effects dominate the susceptibility, while the low-temperature 'tail' is clear evidence for ferromagnetic interactions, which become dominant below 30 K.

The sign of the interactions is ascribed to the fact that [CoCl$_2$pyz]$_n$ contains chains of Co(II) ions bridged by two chloride ions making an angle of 92.21°, leading to orthogonal (d on cobalt-p-chloride) orbitals and to ferromagnetic interactions along the chain, leading to one-dimensional ferromagnetism, according to the Goodenough arguments.[23] This simple model is successfully applied to Co(II) compounds[24] including Co(II) chains similar to the chains present in [CoCl$_2$pyz]$_n$ and where the Co-Cl-Co angles deviate even further from 90° (94.61°).[25] In these chains previously reported the susceptibility was modelled by an anisotropic exchange between effective 1/2 spins, leading to exchange parameters of *ca.* 3.9 and 1.6 cm^{-1}.

Fig. 2, helps understanding the different magnetic behaviour of [CoCl$_2$pyz]$_n$ and [CoCl$_2$(pyz)$_2$]$_n$: in the former, pyrazine isolates Co(II) into chains, blocking relevant interactions in two dimensions while allowing them in one dimension; in the latter, pyrazine is also incorporated between the Co(II) ions of the chains, isolating them and preventing their interaction in the three dimensions.

Experimental

All the reagents were used as supplied without further purification. C, H and N elemental analysis was carried out using a Truspec 630-200-200 elemental analyser with a combustion furnace temperature of 1075 °C and afterburner temperature of 850 °C. The carbon and the hydrogen contents were measured by infrared absorption and for nitrogen thermal conductivity was used.

Synthesis of [CoCl$_2$(pyz)]$_n$. A solution of 0.240 g (3 mmol) of pyrazine (Aldrich) dissolved in 1.5 mL of distilled water was added to a solution of 0.238 g (1 mmol) of CoCl$_2$.6H$_2$O (*pro analysis,* Merck) dissolved in 1 mL of distilled water. The resulting mixture was transferred to 20 mL glass vial placed inside a 30 mL Teflon-lined stainless steel container and heated in a furnace at 190 °C for 72 h, after which it was allowed to cool to room temperature. The blue crystals (0,188 g, 89% yield based on cobalt) were filtered out and washed with distilled water. This compound was also prepared by a stoichiometric procedure using 1 mmol of cobalt chloride and 0.080 g of pyrazine (1 mmol) dissolved in 1 mL of water. This resulted in blue crystals (0.104 g, 49%). Found: C, 22.18; H, 2.29; N, 13.29. Calc. for C$_4$H$_4$CoN$_2$Cl$_2$ (non-stoichiometric synthesis): C, 22.89; H, 1.92; N, 13.34%. IR (cm^{-1}): 3114 m, 3054 w, 1482 m sh, 1418 s, 1166 m, 1116 s, 1089 (shoulder), 1057 s, 789 s, 473 s.

Synthesis of [CoCl$_2$(pyz)$_2$]$_n$. For comparison purposes, this compound was prepared as previously described.[1,2]

Instrumental

Single crystal X-ray diffraction data collections were performed on a Bruker Apex II CCD diffractometer operating at 50 kV and 30 mA using Mo Ka radiation (k = 0.71073 Å) at 180 K (the dataset of [CoCl$_2$(pyz)$_2$]$_n$ was collected at 296 K). Data collection and reduction were performed using the SMART and SAINT software.[26] A multi-scan absorption correction was applied using the SADABS program.[27] The structure was solved by direct methods[28] and refined by full-matrix least squares on F^2 using the SHELXTL programme package.[29] All non-hydrogen atoms were refined anisotropically, C-bound H atoms were geometrically positioned and allowed to ride on their parent atoms and refined isotropically. PLATON is used for the cif files check. Detailed crystallographic data are given in Table 1, selected bond lengths and angles are given in Tables 2. CCDC 1012088-1012090 contain the supplementary crystallographic data and may be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article may be found in the online version, at xxxxxx.

Powder X-ray diffraction patterns were recorded on an Empyrean diffractometer with Cu-Kα radiation (k = 1.54178 Å) from 10 to 50 ° 2θ in the transmission mode. Fourier transform infrared spectra were obtained from KBr pellets using a Bruker spectrometer, model Tensor 27. Electronic spectra were recorded on a Jasco V-560 spectrophotometer with a DRIFT apparatus (Jasco, model ISV-469). Differential scanning calorimetry analysis was performed on a Shimadzu model 50 between room temperature and 500 °C using distinct heating rates in air, with a flow rate of 20 mL min^{-1} in a sealed aluminium cell. Thermogravimetric analysis was performed on a TGA-50 Shimadzu in air between room temperature and 800 °C with a heating rate of 5 °C min^{-1} using a platinum cell. Scanning electron microscopy images were obtained on a Hitachi microscopy, model SU-70 equipped with a Bruker X-ray microprobe model QUANTAX 400. The crystals were coated with carbon. AC magnetic susceptibility measurements were performed in the 5 - 270 K range and selected frequencies in the 100 to 10000 Hz range, and an amplitude of 4 Oe, in a PPMS Quantum Design system equipped with the ACMS option.

Conclusions

The Co(II)-pyrazine-chloride system provides a playground for chemically switching, in an reversible way, magnetic properties. Upon thermal decomposition, [CoCl$_2$(pyz)$_2$]$_n$ looses one pyrazine molecule and chains of Co(II) ions bridged by two chloride ions form resulting in ferromagnetic interactions along one dimension below *ca.* 30 K. Addition of a pyrazine molecule to [CoCl$_2$pyz]$_n$, in turn, sets Co(II) apart, reconstructs [CoCl$_2$(pyz)$_2$]$_n$, and leads to a paramagnetic material.

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Notes and references

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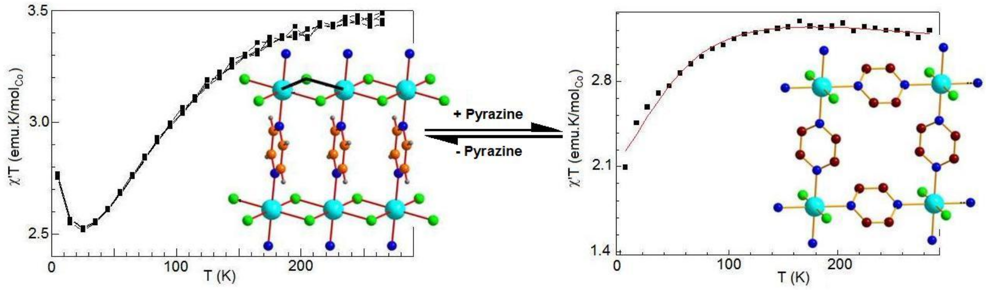

The interconversion of coordination polymers $[CoCl_2pyz]_n$ and $[CoCl_2(Pyz)_2]_n$ is prompted by reversible pyrazine insertion/removal, switching the magnetic behavior between one-dimensional ferromagnetic and purely paramagnetic states.