Novel Double-Stranded Chains vs Two-Layer Interwoven Sheets. Subtle Coligand Effects and Related Properties for $[Co(Py_2S)_2X_2]_n$ (Py_2S = 4,4′-Dipyridyl Sulfide; X = NCS, Cl)

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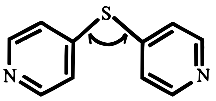
The infinite chain and sheet structures of metal-based coordination complexes have emerged as new motifs of molecular architecture due to both aesthetic considerations and potential applications as electrical conductors,[1] as molecular magnets,[2] in host−guest chemistry,[3] in crystal bending,[4] and in catalysis.[5] Their structural topologies can be designed by selecting the coordination geometry of the metals, the structure of the spacer ligands, the counterions, and the reaction conditions.[6−8] Among diverse elegant efforts to find key factors in their development, the use of a unique spacer is worthy of close attention as a rational design strategy. In particular, it has been found that the appropriate angles and flexible components of linkers play important roles in self-assembly via coordination.[9−13] Though various ligands have been used for a wide range of molecular building blocks, exploitation of 4,4′-dipyridyl sulfide (Py_2S)[14] as a bridging ligand has until recently remained unexplored. The ligand possesses a magic angle, which is essentially bent around the sulfur atom (C−S−C, ∼100°) with some flexibility in contrast to linear rigid ligands such as simple 4,4′-bipyridine analogues. We now describe dramatic changes and related thermal behaviors in structural morphology that coligand effects (NCS, Cl) can impart to cobalt(II) complexes of the interesting skeletal ligand, Py_2S.



Py_2S

The title compounds were prepared as light violet-colored crystals by slow diffusion of aqueous solutions of CoX_2 (X = NCS, Cl) into ethanolic solutions of the Py_2S ligand in mole ratios of 1:2, respectively (Scheme 1).[15] X-ray characterization[16] of **1**, $[Co(Py_2S)_2(NCS)_2{\cdot}2H_2O]_n$, and **2**, $[Co(Py_2S)_2Cl_2]_n$, has provided very similar unit structures: the local geometry of the cobalt atoms is an octahedral arrangement with two X groups in *trans* positions (N−Co−N = 176.7(2)° (**1**); Cl−Co−Cl = 179.45(9)° (**2**)) and four pyridine units in a propeller arrangement. Nevertheless, the infinite structures of **1** and **2** exhibit dramatic differences induced by simple changes of (pseudo)halides. The crystal of **1** consists of 1D infinite molecules. Py_2S spacers are linked to the cobalt(II) atom in a double-stranded bridge fashion, resulting in 20-membered ring with a small cavity (Figure 1a). The closest Co···Co intrachain distance is 10.208 Å whereas the shortest interchain Co···Co distance is 7.386 Å. This double-stranded chain is an unprecedented structure for bipyridine series complexes. In striking contrast, for **2**, each Py_2S ligand connects two cobalt(II) ions defining the edges of a 40-membered $[Co(II)]_4$ sheet. The bent angle of the sulfur atom in **2** (C−S−C = 104.4(3)°) is slightly splayed out compared with that in **1** (C−S−C = 100.1(2)°), presumably due to the different ring sizes of **1** and **2**. The most fascinating feature of **2** is the occurrence of a two-layer interwoven sheet (Figure 1b). That is, one molecular network is threaded through the centers of the 40-membered rings of another independent network with all of the cobalt(II) atoms in a coplanar sheet, thus forming a polycatenated molecular sheet with a distance (8.731 Å) between two sheets. The metal−metal separation through a Py_2S ligand is 11.077 Å. The metal−metal distance through the diagonal of the rhombus is 16.425 Å, and

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(15) $[Co(Py_2S)_2(NCS)_2{\cdot}2H_2O]_n$: An ethanol solution (20 mL) of Py_2S (188 mg, 1 mmol) was slowly diffused into an aqueous solution (10 mL) of $Co(NCS)_2$ (87 mg, 0.5 mmol). Pink crystals were formed in 1 week in 81% yield. $[Co(Py_2S)_2Cl_2]_n$: An ethanol solution (20 mL) of Py_2S (188 mg, 1 mmol) was slowly diffused into an aqueous solution (10 mL) of $CoCl_2{\cdot}6H_2O$ (137 mg, 0.5 mmol). Pink crystals were formed in 1 week in 70% yield. Elemental analysis of the two compounds gave satisfactory results.

(16) Single-crystal X-ray diffraction data were collected at 23(2) °C on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated molybdenum radiation (λ = 0.710 73 Å). Data for $[Co(Py_2S)_2(NCS)_2{\cdot}2H_2O]_n$ (light violet crystal, 0.30 × 0.22 × 0.15 mm): monoclinic $C2/c$ (No. 15); a = 16.864(4) Å, b = 10.207(4) Å, c = 17.416(3) Å, β = 112.99(2)°, Z = 4, V = 2543(1) Å^3, d_{calcd} = 1.535 g/cm^3; μ = 1.036 mm^{-1}, $2\theta_{max}$ = 49.94°, $\omega/2\theta$, $h,k,\pm l$; unique data 1639; $I > 2\sigma(I)$, final R = 0.0427, R_w = 0.1111. Data for $[Co(Py_2S)_2Cl_2]_n$ (light violet crystal, 0.40 × 0.30 × 0.20 mm): monoclinic $Pccn$ (No. 56); a = 7.433(2) Å, b = 17.461(4) Å, c = 16.424(6) Å, Z = 4, V = 2132(1) Å^3, d_{calcd} = 1.578 g/cm^3; μ = 1.266 mm^{-1}, $2\theta_{max}$ = 49.94°, $\omega/2\theta$, h,k,l; unique data 990; $I > 2\sigma(I)$, final R = 0.0403, R_w = 0.0418.

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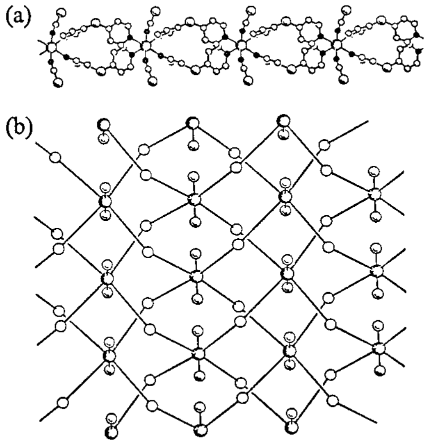
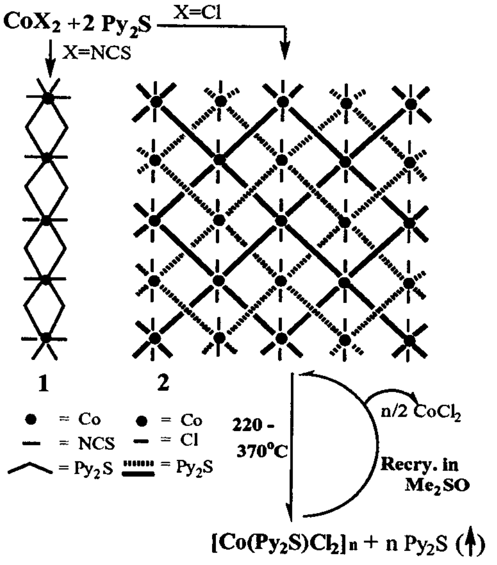


Figure 1. (a) Infinite double-stranded-chain structure of **1**. (b) Infinite two-layer interwoven sheet structure of **2**. Pyridine groups are omitted for clarity. Large circles represent Co.

Scheme 1



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thus the shortest Co···Co distance between two interpenetration networks is 8.212 Å. Compound **2** is the first integral two-layer interwoven sheet structure without any counterion or solvate.[8] The appropriate length of the Py_2S linker permits the interwoven structure, and the magic angle of the linker may afford the 2D sheet structure instead of a perpendicular interpenetration. However, for **1**, the steric effect of the isothiocyanate ligand seems to be an obstacle to forming the two-layer interwoven sheet and instead affords the double-stranded 1D infinite structure.

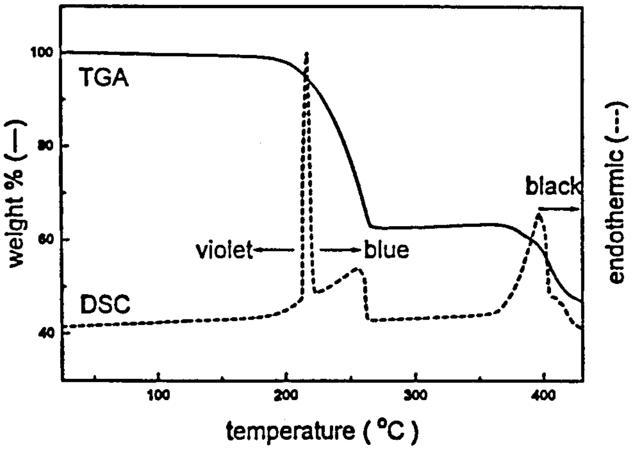

Figure 2. Overlay of TGA and DSC traces of **2**, each recorded at a heating rate of 10 °C min^{-1}.

The TGA trace of **2** (Figure 2) shows a weight loss corresponding to one Py_2S (obsd 36.8%, calcd 37.2%) in the temperature range 220−266 °C. The pyrolysis intermediate **3**, $[Co(Py_2S)Cl_2]_n$, is stable up to 371 °C (maximized at 402 °C), and further weight loss continues above 371 °C. The DSC trace of **2** (Figure 2) illustrates three endotherms at 220, 220−266, and 371−410 °C. The last endotherm is attributed to the decomposition of **3**. In contrast to the typical DSC trace of **1**,[17] the appearance of two separate endotherms at 220 and 220−266 °C for the evaporation of one Py_2S implies significant thermal behavior: the sharp peak at 220 °C suggests a prompt structural change without weight loss, and the other wide endothermic transition at 220−266 °C seems to be due to one Py_2S mass loss. This observation shows that the pyrolysis at 200−266 °C occurs in a two-step process, a ligand dissociation (eq 1) and its evaporation (eq 2). The dissociation of one Py_2S ligand collapses

$$[Co(Py_2S)_2Cl_2]_n \xrightarrow{220\ °C} [Co(Py_2S)Cl_2]_n\cdot nPy_2S \qquad (1)$$

$$[Co(Py_2S)Cl_2]_n\cdot nPy2S \xrightarrow{220-266\ °C} [Co(Py_2S)Cl_2]_n + nPy_2S\uparrow \qquad (2)$$

the interwoven sheet structure at 220 °C, subsequently followed by the evaporation of the dissociated ligand. The species $[Co(Py_2S)Cl_2]_n\cdot nPy_2S$ in the temperature range 220−266 °C seems to exist as a so-called "molecular inorganic−organic composite".[18] This unique observation reveals that the interwoven sheet structure is susceptible to the expansion of the crystal volume. Up to now, the structure of **3** could not be clearly elucidated, but the blue color of **3** suggests that the local geometry of the cobalt atom is tetrahedral.[19] When species **3** is recrystallized in Me_2SO, the compound returns to the form of its mother crystal **2** with the liberation of the remaining $CoCl_2$. This fact shows that the formation of **2** is very favorable regardless of the reaction mole ratio whereas the structure of **3** is thermodynamically unstable in solution.

In summary, the approximately 100° shape of a linker, Py_2S, is a magic angle that exhibits subtle coligand effects for the rational synthesis of metal-based coordination polymers. Though the mechanism of dramatic structural changes and thermal behaviors is manifestly unpredictable, understanding the features that can be used to direct key factors may be a clue to the development of self-assembly materials including metastable composites that exhibit desirable properties.

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Supporting Information Available: Tables giving X-ray data collection parameters, all atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for **1** and **2** (12 pages). See any current masthead page for ordering information.

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(17) TGA and DSC of **1** are typical: **1** lost weight corresponding to water molecules from 161 to 185 °C. On further heating, the compound lost weight corresponding to two Py_2S ligands at 240−328 °C.

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