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Polymeric Helical Motifs from the Self-Assembly of Silver Salts and Pyridazine

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Introduction

Helicity is a fundamental structural feature of great current interest in inorganic and coordination chemistry,[1,2] and much effort has been devoted in the last years to the design of metal complexes exhibiting helical architectures, which is of potential utility in some emerging fields as asymmetric catalysis[3] and nonlinear optics.[4] The induction of helicity both in oligonuclear complexes (helicates)[2] and in polymers has been attempted by using suitably tailored polydentate ligands, particularly flexible oligopyridines[2c,d] and optically active ligands.[5] However, helicity can spontaneously arise also from the peculiar self-organization of simple symmetric building blocks, as we have observed on studing the reactivity of pyridazine (pydz) with different silver salts of poorly coordinating anions.

Pyridazine and related 1,2-diazines are known to behave as exo-bidentate ligands, able to give oligomeric complexes[6] and polymeric species, usually consisting of linear chains.[7] Thanks to the coordinative versatility of the Ag(I) cations, we have isolated three unusual examples of infinite helical species, *namely* $[Ag(pydz)](NO_3)$ (**1**), $[Ag(pydz)](CF_3SO_3)$ (**2**), both 2_1 helices, and $[Ag(pydz)_2](BF_4)$ (**3**), a 4_1 helix. Several silver(I) polymeric helices have been previously reported, including two 2_1 helices assembled with chiral ligands,[5d,e] a 2_1 helical species with the bis[3-(2-pyridyl)pyrazol-1-yl]phosphinate ligand,[8] the 3_1 helix of $[Ag(2,2'\text{-biimidazole})](NO_3)$,[9] and the double helix of $[Ag(1,3\text{-bis}(4\text{-pyridyl})propane)](BF_4)$.[10]

Experimental Section

Materials. All reagents and solvents employed were commercially available high-grade purity materials (Aldrich Chemicals), used as supplied, without further purification. Elemental analyses were carried out at the Microanalytical Laboratory of this University.

Synthesis of the Compounds. Compound **1** was obtained on reacting at room temperature $AgNO_3$ with pyridazine (pydz) in water/ethanol solution. A solution of pydz (0.135 μL, 0.187 mmol) in ethanol (6 mL) was layered over a solution of the silver salt (0.032 g, 0.185 mmol) in water (5 mL), and the mixture was left in the dark for many days. Concentration by slow evaporation led to the precipitation of colorless elongated crystals of **1** in good yield. Anal. Calcd for $C_4H_4AgN_3O_3$: C, 19.22; H, 1.61; N, 16.81. Found: C, 19.42; H, 1.59; N, 16.81.

Compound **2** was obtained on reacting an ethanolic solution (4 mL) of $Ag(CF_3SO_3)$ (0.228 g, 0.89 mmol) with pydz (65 μL, 0.89 mmol) under stirring. Addition of *n*-hexane gave needle-shaped colorless crystals of **2** in 1 day. The crystals formed were filtered, washed with *n*-hexane, and air-dried. Yield of ca. 70%. Anal. Calcd for $C_5H_4AgF_3N_2O_3S$: C, 17.82; H, 1.20; N, 8.31. Found: C, 17.54; H, 1.48; N, 8.63.

On performing the above reaction with a 2-fold excess of pydz, crystals of another species were recovered, corresponding to the dinuclear species $[Ag_2(pydz)_5](CF_3SO_3)_2$, characterized by a single-crystal X-ray analysis.[11]

Compound **3** was obtained from different solvent systems (EtOH, EtOH/THF), as elongated crystals, by reacting $AgBF_4$ with pydz in molar ratios from 1:1 to 1:2. In a typical preparation on a solution of pydz (103 μL, 1.42 mmol) in THF (5 mL) we layered 1 mL of EtOH and then a solution of $AgBF_4$ (0.137 g, 0.71 mmol) in EtOH (3 mL). After few days elongated crystals of **3** were recovered. Other products, presently under investigation, were obtained in some cases together with **3**. The product was filtered and washed with ethanol. The crystals were isolated under the microscope and submitted to elemental analysis (yield of ca. 40%). Anal. Calcd for $C_8H_8AgBF_4N_4$: C, 27.07; H, 2.27; N, 15.79. Found: C, 26.98; H, 2.19; N, 15.96. The crystals of **3** very slowly decompose in the air.

Crystallography. Crystal data for compounds **1**−**3** are reported in Table 1. Colorless crystals of dimensions 0.180 × 0.025 × 0.015 (**1**), 0.256 × 0.064 × 0.032 (**2**), and 0.288 × 0.080 × 0.080 mm (**3**) were mounted under a coating of cyanoacrylic glue on a glass fiber and then tranferred on an Enraf-Nonius CAD4 diffractometer. The intensity data were collected at room temperature, using graphite-monochromatized

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[11] The compound is monoclinic, space group $C2/c$, $a = 19.797(2)$ Å, $b = 9.261(1)$ Å, $c = 17.860(2)$ Å, $\beta = 105.36(1)°$. The structure consists of dinuclear complexes, with the two metal ions triply bridged by pydz ligands and each bearing a monodentate pydz molecule. Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A., results to be published.

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Table 1. Crystallographic Data for all Compounds

	1	2	3
empirical formula	$C_4H_4AgN_3O_3$	$C_5H_4AgF_3N_2O_3S$	$C_8H_8AgBF_4N_4$
fw	249.97	337.03	354.86
space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$P4_12_12$ (No. 92)
a, Å	17.972(3)	19.006(4)	15.564(3)
b, Å	3.675(1)	5.398(3)	15.564(3)
c, Å	20.347(4)	18.737(4)	11.166(5)
β, deg	91.92(2)	93.59(2)	−
V, Å^3	1343.1(5)	1918.5(12)	2704.8(14)
Z	8	8	8
T, °C	20	20	20
λ, Å	0.71073	0.71073	0.71073
ρ_{calc}, g cm^{-3}	2.472	2.334	1.743
μ, mm^{-1}	2.957	2.353	1.523
R^a	R1 0.058, wR2^b 0.141 [$I > 1\sigma(I)$]	R1 0.034, wR2^c 0.069 [$I > 1\sigma(I)$]	R1 0.079, wR2^d 0.200 [$I > 2\sigma(I)$]

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$. [b] Weighting: $w = 1/[\sigma^2(F_o^2) + (0.019P)^2 + 44.77P]$ where $P = (F_o^2 + 2F_c^2)/3$. [c] $w = 1/[\sigma^2(F_o^2) + (0.0416P)^2]$. [d] $w = 1/[\sigma^2(F_o^2) + (0.0965P)^2 + 28.2061P]$.

Mo Kα radiation, by the ω scan method. An empirical absorption correction, based on ψ scans of suitable reflections, was applied in each case. The structures were solved by direct methods (SIR92)[12] and refined by full-matrix least-squares on F^2 (SHELX-93).[13] In compounds **1** and **2** all but the hydrogen atoms were treated anisotropically. In **3** the BF_4^- anions are heavily disordered in the large channels extending along the c axis, among the helices; indeed there are less anions than available cavities (each large enough to induce a further disorder). The final model was based on two half-disordered BF_4^- anions. Anisotropic thermal parameters were assigned to the metal atoms only. The refinement was carried out in the noncentrosymmetric space group $P4_12_12$. Within this assumption the Flack's parameter[14] has a value of 0.3(2), which is a poor indication of the absolute configuration. Indeed the high disorder of the anions, given their significant contribution to the diffraction, hampers any further insight on the absolute configuration.

The molecular drawings were produced with the SCHAKAL program.[15]

Results and Discussion

The first of these helical species, [Ag(pydz)](NO_3), **1**, was unexpectedly obtained by reacting $AgNO_3$ with pydz in H_2O/EtOH. The solid-state structure of **1** is quite unusual in that it contains two different structural motifs packed together in the same crystal. A view of the cell content down the b axis is illustrated in Figure 1. There are alternate layers containing 2_1 helical polymers (of both chiralities), **1a**, and columns of stacked dinuclear complexes, **1b**. It is noteworthy that in the projection shown in Figure 1 the two structural motifs appear to be almost identical; the differences can be observed in the lateral views given in Figure 2. A view of the helix **1a** down the 2_1 axis is shown in Figure 3 (top). The period of the helices and the translation vector in the columns are equal to b [3.675(1) Å]. In the two species the silver ions are symmetrically bridged by pydz ligands [Ag−N: 2.23(1), 2.25(1) Å in **1a**, 2.24(1), 2.27(1) Å in **1b**] and present three weak interactions with the NO_3^- anions [Ag−O: 2.62(2)−2.64(2) Å in **1a**, 2.57(1)−2.64(2) Å in **1b**]. The five-coordination (2N + 3O) of the silver ions is rather irregular, with N−Ag−N angles of 138.1(4)° in **1a** and 130.1(5)° in **1b**. The main difference on passing from **1b** to the helical **1a** consists of a concerted rotation of the pydz ligands: in the former species (lying about an inversion center) two ligands bridge a pair of metal ions and are almost coplanar (dihedral angle between the best planes of 1.7°), while in the helix two adjacent pydz ligands exhibit a relative rotation (dihedral angle of 49.3°). The Ag···Ag contact for adjacent metal ions in **1a** is 3.339(2) Å, slightly longer than the Ag···Ag separation in the dinuclear complex, 3.248(3) Å. The very existence of these two different species in the crystals of **1** is probably indicative of an open−close interconversion in solution for the dimeric species, related to the lability of the Ag−N bonds.[10] This feature suggests that the self-assembly of coordination polymers, exhibiting complex (often interwoven) architectures, can be favored by a progressive reorganization process, involving the breaking and the formation of metal−ligand bonds at the crystal−solution interface.

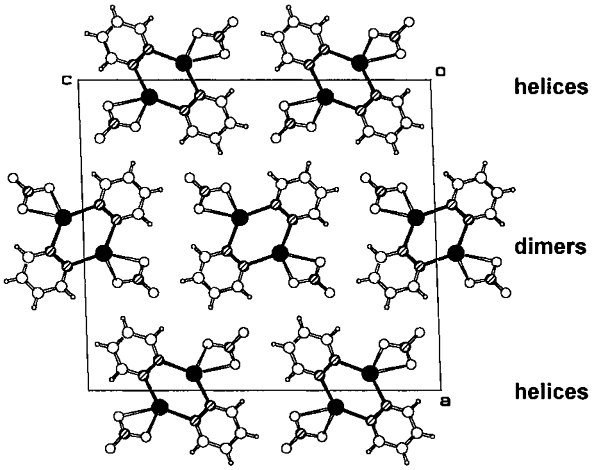

Figure 1. View of the cell content down b in compound **1**.

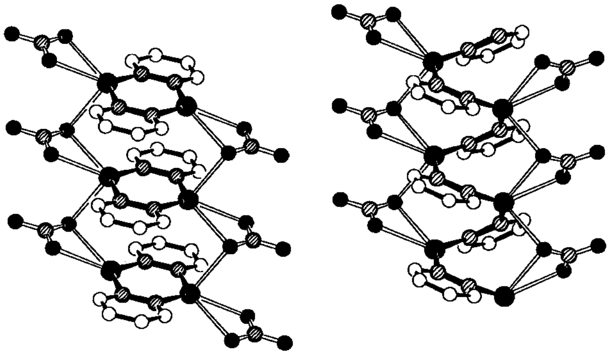

Figure 2. Comparative view of the two structural motifs present in **1**: the stacked dinuclear complexes (**1b**, left) and the infinite 2_1 helix (**1a**, right). Here and in the following figures large filled circles, small filled circles, shaded circles, and empty circles represent Ag, O, N, and C atoms, respectively.

From the reactions of silver triflate with pydz in ethanol/hexane in equimolar ratio we have obtained another helical polymer, [Ag(pydz)](CF_3SO_3), **2**. The crystal structure of **2** consists of the balanced packing of right- and left-handed 2-fold helices, with a period equal to the crystallographic b axis (5.398 Å) (see Figure 3, bottom). The silver ions are symmetrically bridged by the pydz ligands [Ag−N, 2.232(4), 2.249(4) Å; N−Ag−N, 148.2(2)°] and display a contact with an anionic oxygen atom [Ag−O, 2.422(4) Å], thus resulting in a trigonal coordination distorted toward a T-shaped geometry. The

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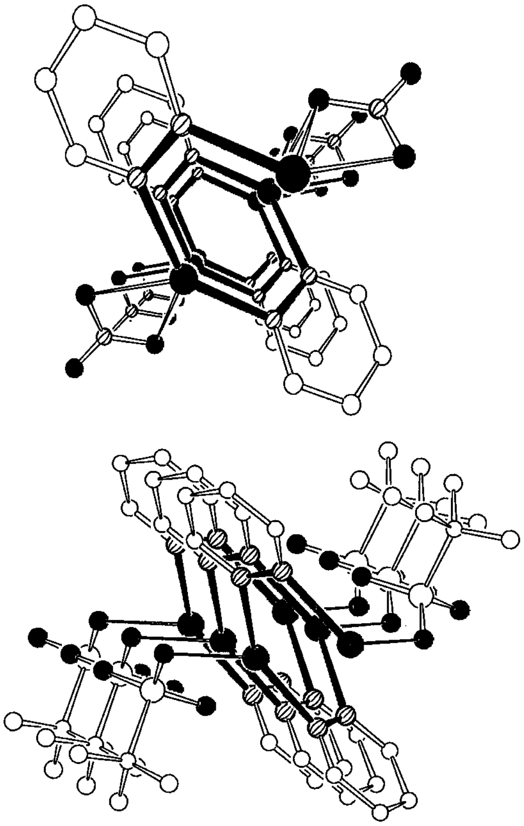

Figure 3. Views down the 2_1 axis of the helices of **1a** (top) and **2** (bottom).

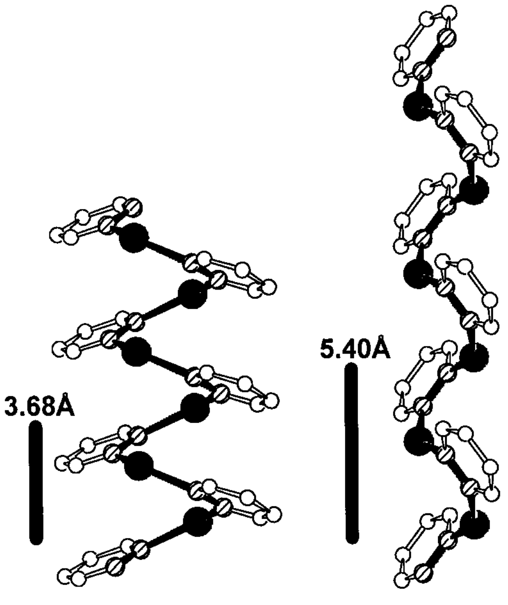

Figure 4. View of the helical backbones of **1a** (left) and **2** (right).

Ag···Ag contact for adjacent metal ions is 3.258(1) Å. The helices in **2** are more stretched than in **1a** (see Figure 4) as also indicated by the larger value of the dihedral angle between adjacent pydz ligands (65.2° vs 49.3°). This difference arises from the fact that in **1a** the nitrate anions, weakly interacting with both metals on two adjacent turns, produce a compression of the whole architecture.

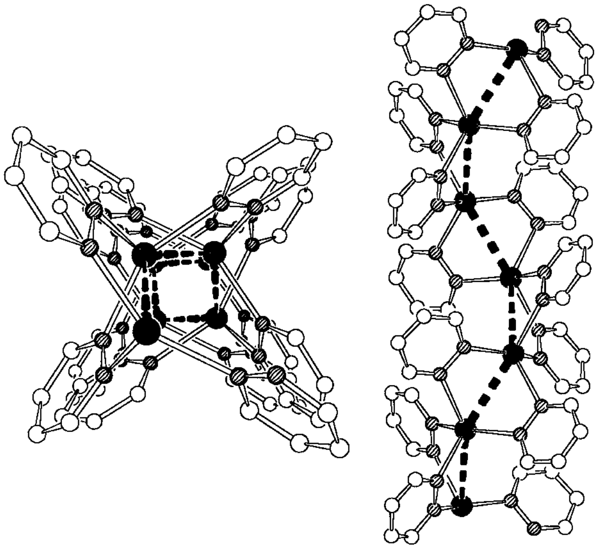

Figure 5. Two views of the 4-fold helices in **3**.

A more unusual single-stranded helical polymer has been obtained from the self-assembly of pydz ligands and $AgBF_4$. The structure of $[Ag(pydz)_2](BF_4)$, **3**, consists of parallel 4-fold single helices, running in the direction of the *c* tetragonal axis and displaying the same chirality (P, right-handed, with a period equal to *c*, 11.166 Å), as illustrated in Figure 5. In this case the adjacent silver ions [Ag···Ag contact of 3.282(1) Å] are doubly bridged by two pydz ligands, each forming an asymmetric bridge [Ag−N, short, 2.20(1), 2.26(1) Å; long, 2.42(1), 2.46(1) Å]. The four-coordination of the metal ions is of the sawhorse type, with the largest N−Ag−N angle [150.4(3)°] disposed toward the internal side of the helix. The two pydz bridges on the same Ag···Ag edge form a dihedral angle of 81.6°.

The finding of a helical structure, instead of a linear geometry, for this species is rather surprising. For instance, the bispyrazolate−copper(II) complexes are linear-chain polymers, with the metal ions disposed on a straight line and the Cu···Cu interactions doubly bridged by the ligands, to give a distorted tetrahedral coordination geometry.[16] While in **1a** and **2** a role in orienting the helicity is very probably played by the external interactions with the anions, this is not the case in **3**. Fourfold helices are rare: to our knowledge, the only previous example in coordination chemistry is a recently reported copper(II) imino nitroxide polymer, which also crystallizes in the enantiomeric space group $P4_32_12$.[17]

Further studies on this subject are in progress using substituted pydz ligands.

Supporting Information Available: Three X-ray crystallographic files, in CIF format, are available. Access information is given on any current masthead page.

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