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Heterotopic Helicand for Designing Heterometallic Helicates

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A new diazine tetratopic helicand, H_4L, is obtained from 3-formylsalicylic acid and hydrazine. The reaction between H_4L and cobalt(II) perchlorate, iron(III) perchlorate, and sodium carbonate leads to triple-stranded tetranuclear anionic helicates, $[L_3Co^{II}_2Fe^{III}_2]^{2-}$, which are connected through Na ions, resulting in chiral coordination polymers, $[{}^{1}_{\infty}L_3Na_2Fe_2Co_2(H_2O)_4(EtOH)_2]\cdot 3H_2O$.

Metallosupramolecular chemistry deals with the design of highly organized architectures (catenanes, rotaxanes, knots, grids, ladders, racks, molecular squares and boxes, cubes, helicates, etc.), based upon metal-ion-directed self-assembly processes.[1] Two components are necessary in every synthetic approach leading to inorganic supramolecular architectures: the suitably designed organic ligand and the metal ion. In the language of supramolecular chemistry, the ligand is a programmed species, that is, a molecule with binding sites in a correct arrangement, whose encoded information is read by the metal ions according to their coordination algorithm.[2] The synthesis of metallohelicates, by twisting multidentate organic ligands (helicands), through interaction with the appropriate metal ions, played a key role in the development of supramolecular chemistry.[2] The helicands are linear strands with repeating complexation sites separated by suitable spacers.[3] The majority of self-assembled linear multistranded helicates are binuclear, with some examples of trinuclear analogues, while those with four or more metal centers remain rare.[4] Several families of organic molecules were designed for the assembly of double- and triple-stranded homo- and heterometallic helicates, which have been recently reviewed in excellent papers.[5] One of these families consists of bis-Schiff bases derived from hydrazine (diazine ligands). Such ligands are easily obtained by reacting formylpyridines or formylphenols with hydrazine and provide chelating sites connected by a $=N-N=$ single bond.[6] Self-assembly processes leading to metallic helicates, assisted by two different metal ions, have been reported as well.[7] In such cases, the ligands must be programmed to interact selectively with the different metal ions. For example, 3d and 4f metal ions can simultaneously assemble with an organic ligand containing a soft unit, coded to interact with a soft d transition-metal ion, and a hard unit, coded to interact with a hard rare-earth metal ion.[7]

The diazine derivative of *o*-hydroxybenzaldehyde is a ditopic helicand that generates binuclear triple-stranded helicates.[6c] The nuclearity of the helicate can be increased through additional coordination sites at the above-mentioned helicand. This is possible by using a potential bicompartmental precursor, for example, 3-formylsalicylic acid, which leads, by reacting with hydrazine, to a tetratopic helicand, H_4L (Scheme S1 in the Supporting Information).

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Here we report on a novel coordination polymer, $[{}^{1}_{\infty}L_3Na_2Fe_2Co_2(H_2O)_4(EtOH)_2]\cdot 3H_2O$ (**1**), built up from tetranuclear helicates connected by Na ions. The anionic helicate results from the self-assembly process involving the heterotopic helicand and Co^{II} and Fe^{III} ions. The organic ligand is easily obtained by reacting 3-formylsalicylic acid with hydrazine.[8] This new tetratopic helicand offers two different types of binding domains: one with only O donor atoms and the other one with N and O donor atoms. The phenoxo O atoms belong to the two chelating moieties. Each phenoxo O atom will act as a bridge between two metal ions. The different coordination sites make the ligand appropriate for interaction with different metal ions. Moreover, the O atoms from the carboxylato groups allow the propagation of the helical motif through subsequent coordination to a third metal ion.

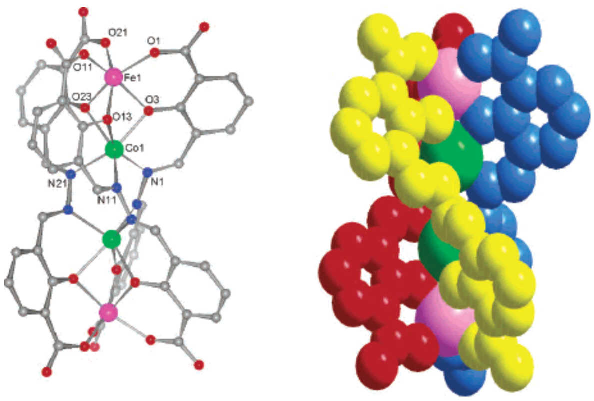
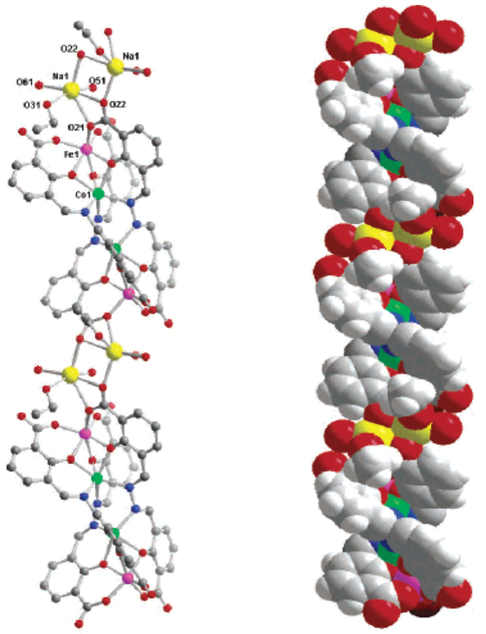


Figure 1. View of the anionic triple-stranded helicate along with the atom-labeling scheme (left). Selected metal−ligand distances (Å): Co1−O3 = 2.041(5), Co1−O23 = 2.074(4), Co1−N1 = 2.095(6), Co1−N11 = 2.105(6), Co1−N21 = 2.133(6), Co1−O13 = 2.166(4), Fe1−O11 = 1.945(5), Fe1−O21 = 1.978(5), Fe1−O1 = 1.987(5), Fe1−O13 = 2.028(4), Fe1−O23 = 2.032(4), Fe1−O3 = 2.049(5). Space-filling representation of the triple helical structure (right).



(a) (b)

Figure 2. (a) Perspective view of the coordination polymer **1** (M chirality). Selected metal ligand distances (Å): Na1−O22A = 2.337(6), Na1−O51 = 2.392(8), Na1−O61 = 2.393(7), Na1−O21 = 2.481(5), Na1−O22 = 2.602(6), Na1−O31 = 2.457(7). (b) Space-filling representation of the chiral coordination polymer.

The heterotrimetallic coordination polymer **1** results from the reaction between the organic ligand, $Co(ClO_4)_2$, and $Fe(ClO_4)_3$ in the presence of Na_2CO_3. The Fe−Co ratio was confirmed by elemental chemical analysis as well as by mass spectrometry (fast atom bombardment, FAB).[9] The crystal structure of **1** has been solved[10] and consists of tetranuclear triple-stranded dianionic helicates connected through Na ions. In each anionic entity $[L_3Co^{II}_2Fe^{III}_2]^{2-}$, the three ligands are twisted along the central N−N single bonds (Figure 1). Two Co^{II} and two Fe^{III} ions are accommodated into the resulting triple helicate architecture. The metal ions display different coordination environments: the Co^{II} ions are coordinated by the inner pockets of the helicand, while the Fe^{III} ions are coordinated by the peripheral ones. The Co chromophore, $[CoN_3O_3]$, displays a distorted octahedral stereochemistry, with the N atoms disposed in the facial position. The Co−N and Co−O distances are in the ranges 2.095(6)−2.133(6) and 2.041(5)−2.166(4) Å, respectively. The Fe ions, with a distorted trigonal-prismatic geometry, are coordinated by six O atoms: three from the carboxylato groups and three from the phenoxo bridges, with distances varying between 1.945(5) and 2.049(5) Å. The metric parameters of the metal centers are in agreement with their oxidation states, that is, Co^{II}[11] and Fe^{III}.[12] The distances between the metal ions within the tetranuclear helicate are Co1···Co1a = 3.620(2) Å and Co1···Fe1 = 2.9265(11) Å. The oxidation states of the metal ions (four paramagnetic centers) have been further confirmed through the magnetic measurements (vide infra). Homochiral $[L_3Co^{II}_2Fe^{III}_2]^{2-}$ anions are connected by pairs of Na ions, resulting in a chiral 1-D coordination polymer (Figure 2). Each site of the tetranuclear anion interacts with two Na ions through one carboxylato group. The bridging mode of the

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(8) To a stirred solution of 3-formylsalicylic acid (0.332 g, 2 mmol) in absolute methanol (10 mL) was added dropwise hydrazine hydrate (0.050 g, 1 mmol). After a few minutes, an orange precipitate appeared, which was isolated by filtration, washed with methanol, and dried in air. Yield: 90%. ^1H NMR (400 MHz, DMSO-d_6, 298 K): δ 8.97 (1H, s), 8.16 (1H, dd, J = 7.8 and 1.7 Hz), 7.96 (1H, dd, J = 7.8 and 1.7 Hz), 8.16 (1H, t, J = 7.8 Hz). Elem anal. Calcd: C, 58.54; H, 3.68; N, 8.53. Found: C, 57.67; H, 3.71; N, 8.47. FAB-MS: found m/z 329.119 $[LH]^+$; calcd m/z 329.293.

(9) To a stirred suspension of H_4L (0.3 mmol) in EtOH−H_2O (1:1, 40 mL) was added an aqueous solution (10 mL) of $Na_2CO_3\cdot 10H_2O$ (0.6 mmol). The formed clear light-yellow solution was reacted with a mixture of $Fe(ClO_4)_3\cdot 6H_2O$ (0.2 mmol) and $Co(ClO_4)_2\cdot 6H_2O$ (0.2 mmol) in EtOH−H_2O (1:1, 10 mL). The resulting red solution was allowed to evaporate slowly, and red squarelike crystals formed after 1 week, which were isolated by filtration, washed with ethanol, and dried in air. Yield: 42%. IR data (KBr, cm^{-1}): 3451br, 1605vs, 1555vs, 1460s, 1432s, 1382m, 1341s, 1228m, 1082w, 879w, 764m. Elem anal. Calcd: C, 42.55; H, 3.41; N, 5.73; Co, 7.77; Fe, 7.63; Na, 3.14. Found: C, 41.40; H, 2.90; N, 6.04; Co, 8.47; Fe, 8.02; Na, 3.30. FAB-MS: found m/z 1248.747 $[L_3Fe_2Co_2Na_2 + H]^+$; calcd m/z 1249.278.

(10) Crystallographic analysis of **1**: $C_{52}H_{34}Co_2Fe_2N_6Na_2O_{26}$, M = 1434.39 g mol^{-1}, monoclinic, space group $C2/c$, a = 21.896 Å, b = 17.306 Å, c = 17.538 Å, β = 123.16°, V = 5563.6 Å^3, Z = 2, T = 293 K, D_c = 1.712 g cm^{-3}, μ = 1.209 mm^{-1}, R1 = 0.0743, wR2 = 0.1143, GOF = 1.104. CCDC reference number for **1**: 298054.

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carboxylato group is quite unusual, connecting one Fe and two Na ions. The Na ions are hexacoordinated by three carboxylato O atoms, two aqua ligands, and one ethanol molecule. The Na−O distances vary between 2.337(6) and 2.602(6) Å. The space group is centrosymmetric, so chains with opposite chiralities are present in the crystal.

Compound **1** contains different paramagnetic metal ions, and its magnetic properties have been investigated. The room-temperature value of the $\chi_M T$ product gives information on the spin states of the different metal ions. Indeed, at 300 K, this value (12.58 emu mol^{-1} K) is indicative of the presence of two high-spin Fe^{III} ($t_{2g}{}^3e_g{}^2$, $S = {}^5/_2$) and two high-spin Co^{II} ($t_{2g}{}^5e_g{}^2$, $S = {}^3/_2$) ions (the expected uncorrelated value is around 14 emu mol^{-1} K taking into account the orbital contribution to g_{Co}). Upon cooling, it decreases slowly, as is often observed when octahedral Co^{II} is present. Below 100 K, the decrease of $\chi_M T$ becomes faster and faster, reaching a value of 1.42 emu mol^{-1} K at 7 K, where it exhibits a minimum. At lower temperatures, the $\chi_M T$ curve increases until a value equal to 2.51 emu mol^{-1} K at 2.5 K. The magnetic structure of compound **1** is composed of tetranuclear units isolated by diamagnetic Na$^+$ ion pairs. Within the tetranuclear unit, two different exchange pathways are evidenced. The first one, associated with the exchange constant J_1, involves the Fe^{III} and Co^{II} ions that are connected by three phenoxo bridges. Because the exchange interaction is dominated by the overlap between the e_g orbitals, an antiferromagnetic coupling is expected. The antiferromagnetic interaction between the Co^{II} and Fe^{III} ions is confirmed by the low value of the $\chi_M T$ product reached at low temperature. A weaker antiferromagnetic interaction, labeled J_2, is expected between the two central Co^{II} ions through the three $\mu_{1,2}$-diazino bridges.[13] A quantitative analysis of the magnetic interactions present in the tetranuclear unit cannot neglect the orbital contribution of Co^{II} ions. An acceptable simplified treatment considers only the ground doublet of the $^4T_{1g}$ state split by spin−orbit coupling and low-symmetry components of the ligand field. To not overparametrize the problem, we have assumed Ising-type anisotropy of $S_{eff} = {}^1/_2$, leading to the spin Hamiltonian

$$H_{ex} = J_1^z(S^z_{Fe1}S^z_{Co1} + S^z_{Fe1'}S^z_{Co1'}) - J_2^z(S^z_{Co1}S^z_{Co1'})$$

where the apex indicates the symmetry-related atoms inside the tetranuclear unit. The interaction with the magnetic field has been considered to be isotropic for Fe^{III}, while we have assumed $g_x = g_y = 0$ for the $S_{eff} = {}^1/_2$ of Co^{II}. Such a simplified treatment is valid only in the low-temperature region where the experimental $\chi_M T$ below 50 K has been successfully reproduced with $J_1^z = -44.5$ cm^{-1}, $J_2^z = -2.8$ cm^{-1}, and g_z(Co) = 7.6. This last value is in good agreement with that expected for octahedral Co^{II} spins with easy-axis anisotropy.[14] However, below 8 K an increase of $\chi_M T$ is observed that is not reproduced by our model. A possible explanation for this behavior can be found in the fact that the {Fe^{III}−Co^{II}} pairs connected by $\mu_{1,2}$-diazino bridges are related by a binary axis. Therefore, the easy axes of each Co ion are, in general, pointing in different directions. In similar cases of antiferromagnetically interacting anisotropic centers with noncollinear easy axes, a sort of weak ferromagnetism in the paramagnetic phase has been observed.[15] The M vs H curve, measured with a VSM magnetometer between 1.7 and 10 K up to ±120 kOe (inset of Figure 3), does not depend on the field sweeping rate and is qualitatively in agreement with such a picture. A first hint of saturation is observed at low fields, but around 60 kOe, the curve shows an inflection point, suggesting that a weak antiferromagnetic interaction is overcome by applying the field. This interaction is probably the one mediated by the diazino bridges because the Zeeman energy at this field is too weak to compete with the interaction mediated by phenoxo bridges. In fact, the features rapidly disappear on increasing temperature. Moreover, the M value even at 120 kOe is still very far from the parallel alignment of all of the spins. In this picture, the hint of saturation at low field is attributed to the noncompensated component typical of canted antiferromagnets. Efforts to obtain larger crystals to perform single-crystal magnetic measurements are in progress. The potential of the new helicand deserves to be further exploited: it can generate homo- and heterometallic helicates with unique structural features and interesting magnetic properties.

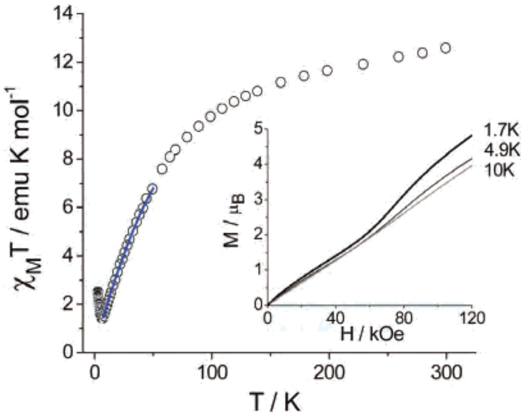

Figure 3. Plot of $\chi_M T$ vs T for compound **1** measured at 10 kOe down to 50 K and at 1 kOe at lower temperatures, with the solid line representing the calculated values (see the text). In the inset, the magnetization curves measured with a sweeping rate of 150 Oe s^{-1} at three temperatures are reported.

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Supporting Information Available: X-ray crystallographic data in CIF format, temperature dependence of $1/\chi_M$ (Figure S1), and structure of a tetratopic helicand, H_4L (Scheme S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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