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Helicity Induction through Hydrogen Bonding and Spontaneous Resolution of a Bimetallic Nickel Complex Coordinated to an Octahedral Metalloligand

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A new bimetallic complex of nickel(II) coordinated to a molybdenum-containing metalloligand has been synthesized that forms a helical chain through hydrogen bonding and shows spontaneous resolution upon crystallization.

The creation of helical structures by self-organization is of fundamental importance in a biosphere, and this has prompted the synthesis of artificial helical structures in supramolecular chemistry.[1] Multidentate organic ligands have been used to generate helical coordination polymers, wherein the organic ligands wind around the metal centers lying on a screw axis. Helical structures having the metal centers as an integral part of the helix are not very common.[2] The construction of helical structures and their spontaneous resolution through self-assembly without using any chiral ligand or chiral auxiliary remain challenges.[2,3] In the field of coordination polymers, there are reports on the resolution of helical structures, and it has been emphasized that an efficient transfer of stereochemical information, through noncovalent interactions between neighboring homochiral helices, is a prerequisite for such a resolution.[4] Assembly of coordination compounds through hydrogen-bonding interaction in supramolecular chemistry is relatively rare.[5]

We have been interested in the assembly of bimetallic compounds using flexible metalloligands and have recently reported on polymeric sodium and cesium compounds coordinated to a molybdenum-containing metalloligand.[6] As a continuation of our studies on molybdenum-containing metalloligands, we report here on the self-organization and spontaneous chiral resolution of a heterobimetallic hydrogen-bonded helical compound, using the metalloligand $[MoO_2L]^-$ [L = (carboxymethyl)(3,5-di-*tert*-butyl-2-hydroxybenzyl)-amino acetate].

Our synthetic strategy is to design a tetradentate tribasic ligand (L) with two carboxylate donor sites, which is expected to form the metalloligand $[MoO_2L]^-$. The two

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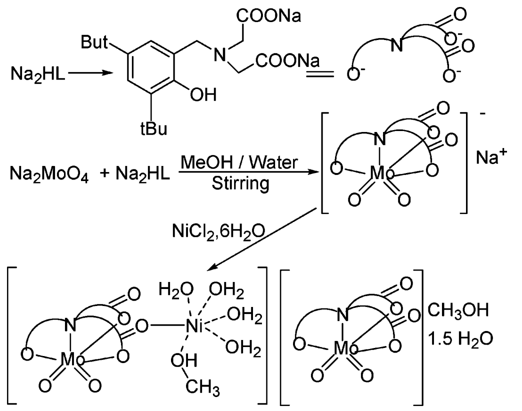
Scheme 1



carboxylate groups are expected to bind the molybdenum center in a cis fashion, and thus the resulting metalloligand is expected to act as a uninegative multidentate ligand toward transition metals. Accordingly, the ligand was synthesized by a reported porcedure,[7] and its disodium salt was reacted with $Na_2MoO_4{\cdot}2H_2O$ in aqueous methanol to generate the metalloligand in situ, which upon reaction with $NiCl_2{\cdot}6H_2O$ afforded red crystals of $[(MoO_2L)Ni(H_2O)_4(MeOH)]^+[MoO_2L]^-{\cdot}1.5H_2O{\cdot}MeOH$ (**1**; **1a** and **1b** are two enantiomorphs; Scheme 1).[8]

Compound **1** has been characterized by elemental analyses, IR, UV−visible, solid-state circular dichroism (CD) spectroscopy, thermogravimetric analysis (TGA), magnetic susceptibility measurements, and single-crystal X-ray crystallography.

Compound **1** crystallizes in the chiral monoclinic space group $P2_1$.[9] Interestingly, we were able to isolate two enantiomers, *P* or right-handed (**1a**) and *M* or left-handed (**1b**) helices, and structurally characterize them.

The observed absolute structure (Flack) parameters [−0.03(3) (**1a**) and +0.05(3) (**1b**)][10] clearly show that the coordinates correspond to the absolute structures of the molecules in the crystal. The X-ray analysis of **1** shows that, in the metalloligand, the molybdenum center is in a distorted octahedral environment and bonded by two *cis*-oxo oxygens, two carboxylate oxygens, one phenolate oxygen, and a nitrogen (Figure 1).

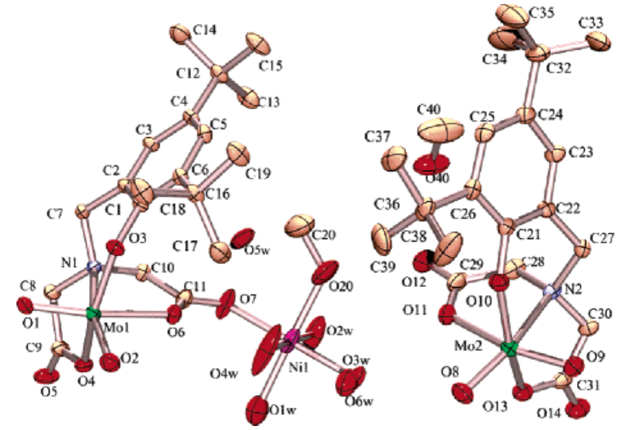


Figure 1. ORTEP view of **1a** with 30% thermal ellipsoid probability. All hydrogen atoms are omitted for clarity. Selected distance (Å) and angles (deg): Mo1−O1 1.701(3), Mo1−O4 2.075(3), Mo1−O3 1.906(3), Mo1−N1 2.334(4), Ni1−O1W 2.074(8), Ni1−O2W 2.052(5), Ni1−O3W 2.038(4), Ni1−O4W 2.023(6), Ni1−O20 2.033(9); O2−Mo1−O1 106.63(19), O2−Mo1−O3 104.97(17), O1−Mo1−O3 98.74(16), O2−Mo1−O4 94.46(17), O3−Mo1−O4 154.59(14), O1−Mo1−O6 162.24(16), O3−Mo1−O6 83.44(14), O4−Mo1−O6 80.42(13), O1−Mo1−O4 91.02(16), O4W−Ni1−O20 93.2(5), O3W−Ni1−O7 179.69(19).

The nickel(II) center in **1** adopts octahedral geometry by coordinating four aqua ligands, one methanol oxygen, and a carboxylate oxygen of the metalloligand (Figure 1). The other carboxylate oxygen, O6, of the metalloligand is hydrogen-bonded with one of the nickel(II)-bound waters, O4W. The metalloligand is bonded to the nickel(II) center as a pseudobidentate chelating ligand.

In the metalloligand, the two carboxylate groups are bonded to the molybdenum center in a cis fashion and one carboxylate oxygen, O7, is bonded to the nickel(II) centers, and the other two carboxylate oxygens, O4 and O5, are hydrogen-bonded with nickel(II)-bound waters, O2W and O3W, of the neighboring unit. The observed bond distances and angles in **1b** are almost identical with those observed in **1a** (Supporting information). Thus, because of the cis disposition of the carboxylate groups, the metalloligand acts as a pseudobidentate bridging ligand through hydrogen bonding and forms an infinite helical chain (Figure 2). The helical chain grows around a crystallographic 2_1 screw axis, with one helical pitch comprised of three metalloligands and two nickel(II) ions with pitch lengths of 11.56 Å (**1a**) and 11.69 Å (**1b**). It has been shown that cis geometry of the MoO_2F_4 metalloligand is essential for helix formation in $Zn(C_4H_4N_2)_2(H_2O)_2MoO_2F_4$.[11]

The most interesting feature of **1** is that one metalloligand is not bonded to the nickel(II) center like the other, and this free metalloligand also forms a helical chain around the 2_1 screw axis (Figure 3). The 1D chain is formed through hydrogen-bonding interactions of the lattice water, O6W, with one Mo=O oxygen, O8, and one of the carboxylate oxygens, O14, of a neighboring unit. The free water, O5W,

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(8) Synthesis of the compound: Na_2MoO_4, $2H_2O$ (0.2419 g, 1mmol), and Na_2HL (0.396 g, 1 mmol) were mixed in aqueous methanol (2:1), and the pH was adjusted to 5−6 by the addition of dilute HCl. After 6 h of stirring, $NiCl_2{\cdot}6H_2O$ (0.7131 g, 3 mmol) in water was added to the reaction mixture, and stirring was continued for a further 1 h. The final pH was found to be 3. The reaction mixture upon standing in air for 1 week afforded orange-yellow solid. The solid was washed with water, and recrystallization from methanol gave red crystals of **1** (**1a** and 1**b**) suitable for X-ray diffraction. Yield: 58%. Elem anal. (crystal of **1**). Calcd for $C_{40}H_{71}Mo_2N_2NiO_{21.50}$ (M = 1174.58 g mol^{-1}): C, 40.86; H, 6.09; N, 2.38. Found: C, 41.08; H, 5.94; N, 2.47. FTIR on a KBr disk (ν_{max} /cm^{-1}): 3416, 1623, 1388, 905, 857. UV−vis [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 373 (13 209), 260 (24 177).

(9) Crystal data for **1a**: $C_{40}H_{71}Mo_2N_2NiO_{21.50}$, M_w = 1174.58, T = 173(2) K, monoclinic, $P2_1$, a = 13.6309(11) Å, b = 11.5596(7) Å, c = 16.6061(12) Å, β = 96.355(6)°, V = 2600.5(3) Å^3, Z = 2, λ = 0.710 73 nm, R_{int} = 0.0594, R1 = 0.0519, wR2 = 0.1239 for 12 092 observed reflections [$I > 2\sigma(I)$], Flack parameter = −0.03(3). Crystal data for **1b**: $C_{40}H_{71}Mo_2N_2NiO_{21.50}$, M_w = 1174.58, T = 293(2) K, monoclinic, $P2_1$, a = 13.6989(2) Å, b = 11.691(2) Å, c = 16.783(3) Å, β = 96.635(12)°, V = 2669.8(9) Å^3, Z = 2, λ = 0.710 73 Å, R_{int} = 0.0690, R1 = 0.0502, wR2 = 0.1317 for 4944 observed reflections [$I > 2\sigma(I)$], Flack parameter = 0.05(4).

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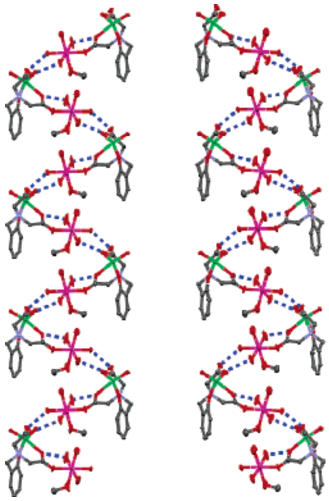

Figure 2. View of the hydrogen-bonded helical chain of cationic units in **1a** and **1b**, running along the *b* axis: *P* helix (left); *M* helix (right). All of the hydrogen atoms and the *tert*-butyl group are omitted for clarity. Color code: C, gray; Mo, green; N, turquoise; Ni, light pink; O, red.

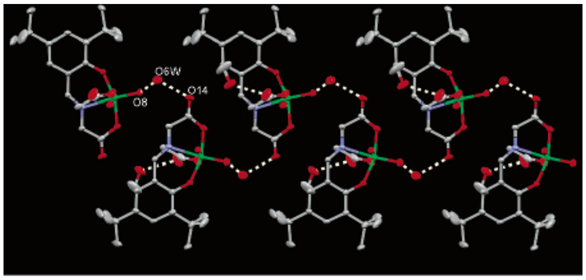

Figure 3. View of the supramolecular helical chain of the free metalloligand with lattice water O6W in **1a** along the *a* axis.

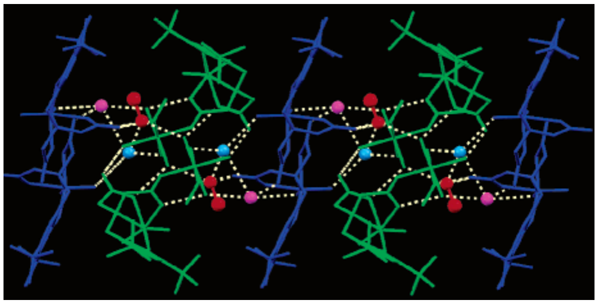

Figure 4. View of the 2D hydrogen-bonding network in **1a** along the 2_1 axis. The blue part represents the helix of the free metalloligand, and the green part represents the helix of the heterobimetallic cationic unit. Color code: O6W, pink; O5W, turquoise; methanol, red. Two helices are joined by a hydrogen bond (shown as yellow dotted lines).

is involved in hydrogen bonding with the nonbonded methanol oxygen, O40, a Mo═O oxygen, O9, of the anion, and nickel-coordinated water, O1W, of the cation. In addition, the lattice water, O6W, also binds the two helical strands through hydrogen-bonding interactions with nickel-bound waters, O3W and O4W, of the cation and forms an infinite 2D network (Figure 4). Thus, O6W plays a crucial role for the formation of the helix of the free metalloligand as well as the 2D network. Attempts to replace the free metalloligand by other anions, such as NO_3^- or SO_4^{2-}, using $Ni(NO_3)_2{\cdot}6H_2O$ and $NiSO_4{\cdot}6H_2O$ in place of $NiCl_2{\cdot}6H_2O$ have been unsuccessful.[12] Thus, the free metalloligand stabilizes the helical chain through hydrogen bonding and also satisfies the charges on the nickel(II) complex. The interstrand hydrogen-bonding interactions between the cationic and anionic helices and helix-forming hydrogen-bonding interactions are strong enough for homochiral crystal packing and spontaneous resolution of **1**.

The room-temperature magnetic moment of compound **1**, measured by the Gouy method, was found to be 3.53 μ_B, which is typical for a nickel(II) octahedral system. Hence, it is clear that at room temperature there is no interaction between the nickel(II) centers in the solid state.

The TGA of compound **1** in air showed weight loss in four steps in the temperature range 50−563 °C, which corresponds to a loss of 5.5 water molecules, two methanol molecules, and two organic ligands per formula unit (obsd loss, 69.4.%; calcd, 73.16%). The 3.76% discrepancy is due to the gain of three oxygens. The residual weight, 30.6% (calcd 30.87%), corresponds to $NiO{\cdot}2MoO_3$.

Diffuse-reflectance CD (DRCD) and transmission CD spectra of crystals of **1a** and **1b** were measured to detect the chirality of the supramolecular structure in the solid state. In the DRCD measurement, apparent CD signals were detected, which were proven to be originated from macroscopic anisotropies (linear birefringence and linear dichroism). Thus, the obtained CD signal is not true CD. Although the absorption peak was observed, the chirality signal was very weak and, hence, was not detected in both of our carefully performed solid-state CD measurements. This must reflect the fact that the 2_1 helix itself has no chirality, unlike 3_1 (3_2) and 4_1 (4_3) helices, and the chirality arises from the chiral structure of the repeating unit.

In summary, this work represents a successful example of hydrogen-bonding-directed helical-chain formation and spontaneous chiral resolution of a coordination compound containing a flexidentate metalloligand. This compound is also a potential single-source precursor for $NiO{\cdot}2MoO_3$. The effects of the solvent, pH, and temperature on crystallization are under investigation.

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Supporting Information Available: Detailed experimental procedures, crystal data, bond lengths and angles, hydrogen bonds, a TGA curve, packing diagrams, CD spectra, and X-ray crystallographic files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] Only compound **1** was formed, as confirmed by C, H, N analysis and the X-ray single-crystal unit cell determination.