

[Ni₂O(L-Asp)(H₂O)₂]₂·4H₂O: A Homochiral 1D Helical Chain Hybrid Compound with Extended Ni–O–Ni Bonding

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The increasing demand for materials for enantioselective catalysis and separation¹ and the interest in fundamental aspects of chirality and molecular recognition² have stimulated extensive research in the area of chiral coordination polymers.³ In this field, the main synthetic strategy to induce chirality and prepare an enantiomerically pure bulk material has been the use of optically pure chiral multidentate ligands. Chiral ligands naturally occurring in a pure enantiomeric form and their derivatives have received significant attention⁴ since, while lacking the predictability of network topology recently achieved with “designer” synthetic ligands,⁵ they are readily available and do not require complex synthesis and chiral resolution procedures. In particular, natural amino acids are well-known to form coordination polymers with transition metals (TM),⁶ although the main focus of the extensive studies on amino acid coordination chemistry has been on their biologically relevant molecular complexes. Recently, a “second wave” of new coordination polymers with natural amino acids has been discovered,⁷ indicating the richness of this field. The vast majority of chiral coordination polymers are based on mononuclear metal centers. Numerous examples of remarkable structural and physical properties resulting from condensation of metal polyhedra into oligomeric units or extended arrays in hybrid frameworks with achiral ligands⁸ motivated us to investigate chiral amino acid–TM systems under the synthesis conditions favoring the hydrolysis of cations and the formation of M–O–M bonding, i.e., elevated pH and mild hydrothermal conditions.⁹

Here we present a new nickel aspartate oxide, [Ni₂O(L-Asp)(H₂O)₂]₂·4H₂O (**1**) (Figure 1) which is, to our knowledge, the first example of a chiral one-dimensional compound with an extended helical TM–O–TM subnetwork synthesized as an optically pure product. Its racemic analogue, [Ni₂O(D,L-Asp)(H₂O)₂]₂·2H₂O (**2**), is also described.

Compound **1** was synthesized hydrothermally in a 23-mL Teflon-lined autoclave by heating a mixture of a 2 M solution of NiCl₂, a 2 M solution of (Et₃NH)(L-H₂Asp), and Et₃N (molar ratio NiCl₂:H₂Asp:Et₃N, 1:0.5:1.25) at 150 °C for 2 days. The final pH of the mixture was 5.0. The product was obtained as a single-phase, blue-green powder in 55% yield based on nickel. Elemental analysis: calcd/found: Ni, 31.51/31.97; C, 12.89/12.84; N, 3.76/3.66, H, 4.60/3.90%. Optical rotation of a solution of **1** in 2 M HCl was the same as that of a reference solution of the corresponding amounts of NiCl₂·6H₂O and L-H₂Asp in 2 M HCl. A reaction starting with a racemic (Et₃NH)(D,L-H₂Asp) solution led to conglomerate crystallization of L-**1** and D-**1**. Needlelike single crystals of **2** formed as a mixture with **1** from the same reagents (molar ratio NiCl₂:L-H₂Asp:Et₃N, 1:0.5:1) heated at 170 °C for 7 days. The structure analysis¹⁰ indicated that **2** crystallizes in the centrosymmetric space group *I*4₁/*a*, which implies that thermal racemization of aspartic acid had occurred. This was confirmed by the absence of optical activity in **2**.

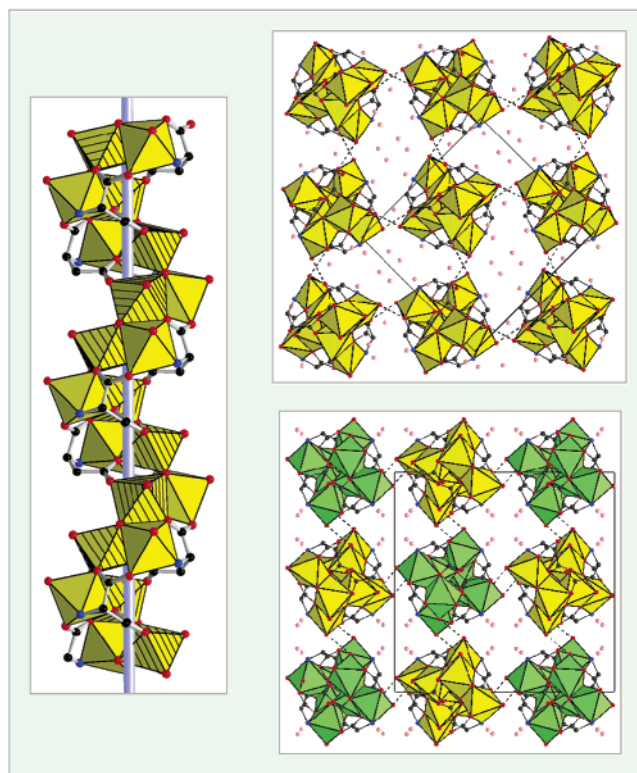


Figure 1. (Left) [Ni₂O(L-Asp)(H₂O)₂]₂ helix. Hatched octahedra: Ni(1)-O₅(H₂O); non-hatched octahedra: Ni(2)O₄N(H₂O). (Right) packing of helices in **1** (top) and **2** (bottom). Helices of opposite handedness in **2** are distinguished in color.

The crystal structure of **2** consists of one-dimensional [Ni₂O(Asp)(H₂O)₂]₂ helices of opposite handedness (Figure 1) formed by two independent nickel octahedra and one independent aspartate ligand. The nickel octahedra are linked into an extended chain via a novel pattern of edge- and corner sharing. The main structural motif of the chain is a trimeric unit Ni₃O₁₀N(H₂O)₃ where one Ni(2)O₄N(H₂O) octahedron shares its two 60° adjacent edges with two Ni(1)O₅(H₂O) octahedra (Figure 2a). The trimers link to each other via Ni(1)O₅(H₂O) octahedra so that in the resulting chain, each Ni(1)O₅(H₂O) octahedron shares its *trans*-corners with two Ni(1)O₅(H₂O) octahedra and skew edges with two Ni(2)O₄N(H₂O) octahedra (Figure 1). The helical twist of the chain originates from the asymmetric arrangement of the edges which each trimeric unit shares with Ni(2)O₄N(H₂O) octahedra from adjacent trimers (Figure 2a). The choice of these edges is probably imposed, in turn, by the steric requirements of the aspartate ligands. Each aspartate ligand coordinates to five nickel atoms (Figure 2b): three Ni(1) and one Ni(2) in a monodentate mode through carboxylic groups, and to one Ni(2) in a chelating tridentate mode through the amino group and one oxygen from each carboxylic group. The latter local

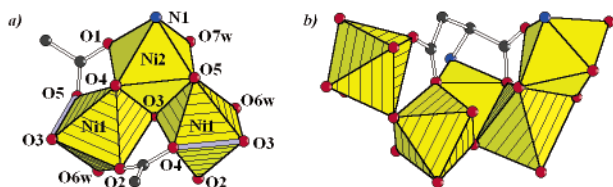


Figure 2. (a) Trimeric building unit in **2**. $d(\text{Ni}(1)\text{--Ni}(2)) = 3.066(2), 3.166(2), d(\text{Ni}(1)\text{--Ni}(1)) = 3.527(2)$ Å; highlighted in blue are the edges shared with $\text{Ni}(2)\text{O}_4\text{N}(\text{H}_2\text{O})$ octahedra from adjacent trimers; (b) coordination of aspartate ligand in **2**.

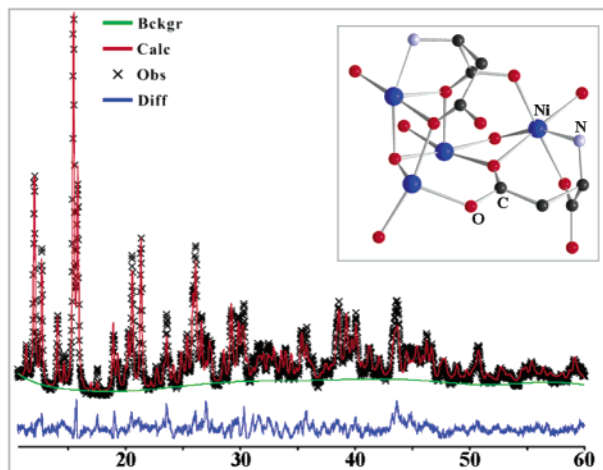


Figure 3. Observed, calculated, and difference powder diffraction profiles for the final Rietveld refinement of **1**. (Insert) helix fragment from compound **2** used in structure solution of **1**.

tridentate chelating coordination geometry is typical in transition metal–aspartate complexes and occurs, in particular, in the polymeric chain compound $[\text{NiAsp}(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$.^{6a} Aspartate coordination to a total of five metal centers is, to our knowledge, unprecedented.

The crystal structure of compound **1** was determined from X-ray powder diffraction data.¹¹ Its powder pattern was indexed in an orthorhombic unit cell with a large asymmetric unit containing 36 non-hydrogen atoms, and our attempts to solve the structure by direct methods using several software packages were not successful. The similarities of the composition, morphology (needle-shaped crystals easily split into fibers), and *c*-axis dimensions between the compounds **1** and **2** along with the difference in their optical activity suggested that compound **1** could be a structural analogue of **2** containing only right-handed helices. The structure of **1** was solved using FOX software¹² that is based on global optimization in real space and takes advantage of the available chemical and structural information. We have selected a helix fragment from the structure **2** containing two complete aspartate ligands and one complete and three incomplete nickel octahedra (Figure 3). The fragment was allowed a slight flexibility (± 0.2 Å for bond lengths and $\pm 2^\circ$ for bond and torsion angles) to adjust to the minor differences in the repeating unit dimensions between **1** and **2**. This semirigid fragment and eight guest water molecules were randomly placed and oriented in the unit cell, and global optimization using parallel tempering was carried out with integrated R_w factor and “anti-bump” cost functions. In the resulting solution, all nickel atoms had a complete octahedral coordination, and the connectivity between the octahedra was identical to that in compound **2**. This solution was used as a starting model for Rietveld refinement that converged to $R_p = 0.044$ (Figure 3).

Magnetic measurements showed that at $T > 30$ K, the susceptibility of **1** follows Curie–Weiss law with $\theta = 13.5$ K, and $\mu_{\text{eff}} = 2.75 \mu_B$ which is close to the spin-only value for $S = 1$ ($\mu_{\text{eff}} = 2.83 \mu_B$). Below 12 K, two transitions are observed with different magnetization behavior as a function of temperature in FC and ZFC regimes at fields below 200 G. A detailed study of magnetic properties of **1** will be reported elsewhere.

In summary, the new nickel aspartate obtained in this work demonstrates the potential of hydrolysis-favoring synthesis conditions for the preparation of novel, structurally complex, chiral compounds with extended M–O–M bonding from “ordinary”, well-investigated ligands such as natural amino acids.

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Supporting Information Available: Synthesis details, IR spectra, crystal data (CIF format) and details of structure solution and refinement (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- Crystal data for **2**: $[\text{Ni}_2\text{O}(\text{d,l-C}_4\text{H}_7\text{NO}_4)(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, $M_r = 336.57$, space group $I4_1/a$, $a = 19.130(5)$ Å, $c = 11.379(4)$ Å, $V = 4164(2)$ Å³, $Z = 16$, $T = 298$ K, $\mu(\text{Mo K}\alpha) = 3.65$ mm⁻¹. Single-crystal data were collected on a Siemens SMART/CCD diffractometer (2510 reflections total, 1515 unique, $R_{\text{int}} = 0.073$). The final refinement converged to $R_1 = 0.061$, $wR_2 = 0.126$ for 743 reflections with $I > 2\sigma(I)$ and 145 parameters.
- Crystal data for **1**: $[\text{Ni}_2\text{O}(\text{l-C}_4\text{H}_7\text{NO}_4)(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$, $M_r = 372.56$, space group $P2_12_12_1$, $a = 13.932(1)$ Å, $b = 14.657(1)$ Å, $c = 12.193(1)$ Å, $V = 2489.9(4)$ Å³, $Z = 8$, $T = 298$ K, $\mu(\text{Cu K}\alpha) = 4.30$ mm⁻¹. X-ray powder diffraction data were collected on a Scintag XDS 2000 diffractometer in a θ – θ geometry using Cu K α radiation. The data were measured over 2θ range of 6.5 – 60° in 0.02° steps for 62 h. The structure was solved with FOX 1.2.¹² A constrained Rietveld refinement using GSAS¹³ converged to $\chi^2 = 10.8$, $R_p = 0.044$, $R_{wp} = 0.056$, $R_{\text{Bragg}}(F^2) = 0.278$ for 869 reflections (436 unique) and 102 structural parameters.
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