Synthesis and magnetic properties of a 1-D helical chain derived from a Nickel-Sodium Schiff base complex

APOORVA UPADHYAY^a, CHINMOY DAS^a, SHAIK NAGUL MEERA^a,
STUART K LANGLEY^b, KEITH S MURRAY^b and MAHESWARAN SHANMUGAM^{a,*}

^aDepartment of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai,
Maharashtra 400 076, India

^bSchool of Chemistry, University of Monash, Clayton, Victoria 3800, Australia
e-mail: eswar@chem.iitb.ac.in

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Abstract. The reaction of the deprotonated form of the Schiff base ligand; (E)-2-methoxy-6-((phenylimino)methyl)phenol (L) with nickel chloride hydrate results in the formation of the 1-dimensional coordination polymer; $\text{Na}[\text{Ni}(\text{L})_2(\text{OMe})(\text{MeOH})]_n$ (**1**). The structure was determined via single crystal X-ray diffraction measurements. A careful analysis of the complex shows that the polymer exists as a helical structure, where the helicity is brought about by the presence of an alkali metal ion which is observed for the first time. Moreover the helical structure in **1** is maintained predominantly through covalent bond rather than supramolecular interactions. Direct current magnetic susceptibility measurement suggests that complex **1** obeys the Curie law. The fitting of magnetic data using the PHI software package yields parameters of $S = 1$, $g = 2.26$ and $D = +4.51$ (or $D = -7.24 \text{ cm}^{-1}$) for **1**.

Keywords. Nickel; Schiff base; magnetism; Helical chain.

1. Introduction

Helicity and chirality are the two most important features in biological process and are intimately associated with each other. In biological systems, L-amino acids and D-ribose molecules are the building blocks for the construction of α -helical polypeptides and DNA, respectively.^{1–3} However, mimicking the biological system through coordination chemistry, particularly at the supramolecular level remains a demanding challenge for chemists as it is often difficult to predict the chirality and the helical nature of the product.^{4–11} Much attention has, however, still been drawn towards helical and chiral coordination complexes due to their fascinating structures, and the numerous potential applications such as molecular recognition, non-linear optical materials, asymmetric catalysis and enantiomorph separation.^{12–26} The ligand design is essential for the formulation of helical structures; with the use of enantiopure ligands along with specific transition metal ions allowing one to isolate the desired structures.^{17,27–29} Usually the chirality is transferred from the enantiopure ligand to the resultant helix, leading to the isolation of either right- (Δ) or left-handed (Λ) helical structures.^{30–36} Precedents are known for the use of

achiral ligands with transition metal ions which will result in a racemic mixture of left and right handed helical structures or with small enantiomeric excess.^{37–41} Single stranded helical structures are the most commonly observed form compared to double and triple stranded structures, either with enantiopure or achiral ligands. The secondary structure of helical complexes is determined by weak metal-ligand covalent interactions, halide ions such as iodide and supramolecular interactions such as hydrogen bonding and $\pi - \pi$ stacking.^{42–47} It is well established in the literature of the formation of homometallic helical structures with transition metal ions such as Ag(I), Fe(III), Ni(II), Cu(II).^{33,40,48–55} To the best of our knowledge, however, mixed metal ion helical structures have not been reported. In this line of interest we have reported the crystal structure of a helical complex containing octahedral Ni(II) ions with a Schiff base ligand, where the secondary structure was induced by an alkali metal ion and we have investigated its magnetic properties.

2. Experimental

Unless otherwise mentioned, all the reactions were carried out under aerobic condition. All the chemicals were purchased from commercially available sources

*For correspondence

(Alfa Aesar). The Schiff base ligand was synthesized as previously reported.^{56,57} The elemental analyses (CHN) were carried out on a Thermoquest microanalyser. Infrared spectra were collected for the solid samples using KBr pellets on a Perkin-Elmer FT-IR spectrometer between 400–4000 cm^{-1} range. Single crystal data were collected on a Rigaku Saturn CCD diffractometer ($\text{MoK}\alpha$, $\lambda = 0.71073 \text{ \AA}$). The selected crystal was mounted on the tip of a glass pin using mineral oil and placed in the cold flow produced with an Oxford Cryocooling device. Complete hemispheres of data were collected by using ω -scans (0.3° , 16 s per frame). Integrated intensities were obtained with Rigaku Crystal Clear-SM Expert 2.1 software and they were corrected for absorption effects. Structure solution and refinement were performed with the SHELX-package. The structures were solved by direct methods and completed by iterative cycles of ΔF syntheses and full-matrix least-squares refinement against F^2 . The magnetic measurement was carried out on a MPMS SQUID magnetometer equipped with 7.0 Tesla magnet. The magnetic data were fitted using PHI software.⁵⁸

2.1 Synthesis of complex 1

The Schiff base ligand (E)-2-methoxy-6-((phenylimino)methyl)phenol (HL) (1 g, 4.4 mmol) was dissolved in ethanol after which NaOH (1.1762 g, 4.4 mmol) was added and the resulting orange solution was stirred for ten minutes. Into this an ethanol solution of nickel chloride (0.5235 g, 2.2 mmol) was then added dropwise. The colour of the solution slowly changed from orange to light green and the reaction mixture was stirred for 18 h at room temperature. After completion of the reaction, ethanol was evaporated under reduced pressure. Purification was performed by washing the crude mixture with water and cold pentane. The purified sample was recrystallized from MeOH and crystals suitable for X-ray diffraction were obtained after 4 days at low temperature (5°C). Yield: 1.2 g (90%). IR (KBr pellet): 1608 cm^{-1} ($\nu_{\text{C=N}}$). Elemental analysis (%): exp: C = 58.94, H = 5.09, N = 4.96; Calcd: 59.11, H = 5.60, N = 4.45.

3. Results and Discussion

The reaction of the deprotonated ligand (L) and the nickel salt resulted in green single crystals (scheme 1). Single crystal X-ray diffraction measurements revealed that the complex is a 1-dimensional (1-D) coordination polymer of molecular formula $\text{Na}[\text{Ni}(\text{L})_2(\text{OMe})(\text{MeOH})]_n$ (**1**) (figure 1). It is found that complex **1**,

Scheme 1. General synthetic procedure followed for the isolation of complex **1**.

crystallizes in monoclinic space group $C2/c$ and the crystallographic parameters are given in table 1. The asymmetric unit consists of a Ni(II), Na(I), two Schiff base, methoxy and methanol ligands. The divalent nickel ion displays a distorted octahedral geometry and is coordinated by the two deprotonated Schiff base ligands. Two phenolate oxygen- and two imine nitrogen-atoms make up four of the coordination sites. The final two sites are accomplished by a methoxy group (O61) and a methanol solvent molecule (O51). The assignment of methanol and methoxy ligand is based on the bond length parameters (as it is difficult to find out the fourier peak for the hydrogen in X-ray) where the later coordinated ligand possesses slightly longer bond length (2.168 $\text{\AA}$) than the former (2.156 $\text{\AA}$). The average Ni1-O and Ni1-N bond distances are found to be 2.0735 $\text{\AA}$ and 2.074 $\text{\AA}$ respectively, consistent with that of other Ni(II) complexes.^{59,60} The Na(I) ion present in six coordinate environment, which is stabilized by covalent interactions provided by the Schiff base methoxy and phenolate groups, as well as the methoxide and methanol ligands, with an average Na1-O bond length of 2.8055 $\text{\AA}$. The phenoxy groups of L, the methanol (O51) and the methoxide ligands (O61) provides a linkage between the Ni(II) and the sodium ion with the (Ni1-O51-Na1) angle being 109.3° and (Ni1-O11-Na1) angle being 106.9° . In the crystal structure, the Na^+ ion resides in a special position, which is responsible for the 1-D extended structure. Analysis of the crystal structure of complex **1** reveals that it exists as a single stranded helical structure (figure 1). Also, by considering the overall metal arrangement, sodium and nickel ion are arranged in a zigzag manner. Existence of both zigzag nature and helical structure is very rare. Helical structures with Schiff base ligands like L are unusual. However, single stranded helical structures are common with other ditopic ligands, either through covalent or supramolecular interactions.^{61–65} Furthermore, there is not only precedent for single stranded helical complexes, but also for double or even triple stranded helical structures with specifically designed flexible Schiff base ligands or with flexible

Figure 1. a) Ball and stick representation of crystal structure of complex **1** (left) B) space filling model of crystal structure of **1** (middle). C) Thermal ellipsoid structure of repeating unit found in complex **1**. Hydrogen atoms are omitted for clarity. Colour code: Magenta = Ni(II); Yellow = Na; Red = O; Blue = N; grey = C.

amide functionalities.^{63,66–71} Supramolecular interactions offered by these functionalities are the essential ingredients that are indispensable for the unusual double-helical or triple helical structures.^{61,72–77}

The most common single stranded helical structures are induced predominantly by ligand design and through metal-ligand covalent interactions, hydrogen bonding, π – π stacking and argentophilic interactions. Recently, an iodine assisted helical structure has also been reported.⁷⁸ To our surprise, both intra and intermolecular supramolecular interactions such as hydrogen bonding or π – π interactions are absent in the packing arrangement of **1**, an uncommon outcome. Moreover the Schiff base ligand employed in the reaction does not possess any flexible spacer which is often responsible for the helical nature of many complexes.^{39,79–82} These scenarios clearly emphasize

that the helical nature of the complex **1** is purely due to metal-covalent interactions and the alkali ion present in the crystal lattice plays a significant role. To the best of our knowledge, alkali metal ion induced helicity is observed for the first time as opposed to other cases where homometallic transition metal complexes stimulate the helicity in the structure.

It is well understood that when achiral ligands are used for the design of helical structures, the resultant complex is isolated as a racemic mixture i.e., a 50:50 mixture of left and right handed helical structures. As expected for **1**, it is found that 1-D helical chains of left and right handed configurations arrange in an alternate manner. From the crystal packing diagram (figure 2), we can clearly see the helical chains are arranged along the b-axis and there are no significant intermolecular interactions between the chains (closest Ni(II)–Ni(II)

Table 1. Crystallographic parameters for complex **1**.

	1
Formula	C ₃₀ H ₃₁ N ₂ Na ₁ NiO ₆
Size	0.570 × 0.560 × 0.130
System	Monoclinic
Space group	C2/c
<i>a</i> [Å]	28.669(6)
<i>b</i> [Å]	12.460(3)
<i>c</i> [Å]	16.680(3)
β [°]	110.61(3)
<i>V</i> [Å ³]	5576.9(19)
<i>Z</i>	8
ρ_{calcd} [g/cm ⁻³]	1.420
$2\theta_{\text{max}}$	52.74
Radiation	MoK α
λ [Å]	0.71073
<i>T</i> [K]	100(2)
Reflns	34401
Ind. Reflns	5535
Reflns with $>2\sigma(I)$	5053
<i>R</i> 1	0.0524
<i>wR</i> 2	0.1774

distance 9.27 Å). Moreover, the enantiomers of **1** are not direct mirror images of one another, one isomer (either left or right handed) is however, translated into space along the *c*-axis with mirror reflection leading to a close packing arrangement that in turn results in

the non-availability of voids in the structure (figure 3). Unlike the situation here, there are several reports where the helical chain arrangement leads to a large void space, which is used for accommodating solvent molecules.^{83–89}

Although several characterization methods have been reported, magnetic properties for these helical structures are very scarce in the literature.^{8,71,90–96} Direct current magnetic susceptibility measurements were performed on a polycrystalline sample of **1**, with an applied magnetic field of 0.5 Tesla, between 2–300 K (figure 4). The room temperature $\chi_M T$ value of 1.285 cm³ K mol⁻¹ is slightly higher than the spin only value of 1.0 cm³ K mol⁻¹ with an average *g*-value of 2.0. The $\chi_M T$ value remains constant from room temperature down to 15.0 K. This temperature independent behaviour emphasizes that the Ni(II) ion behaves as a simple paramagnet (figure 5), which is conceivable due to the closest Ni(II)-Ni(II) distance within the chain being 7.68 Å. However, the $\chi_M T$ value drops steeply, below 15.0 K, which could be due to the magnetic anisotropy, Zeeman depopulation effect and/or antiferromagnetic intermolecular interactions. The later contribution is unlikely due to the longer Ni(II) distance found between the chains of 9.28 Å and the absence of any solvate molecules in the crystal lattice which are often responsible for intermolecular antiferromagnetic interactions through dipolar interactions.

Figure 2. Packing diagram of complex **1**.

Figure 3. Space filling models of Λ which is reflected and translated in space (glide plane) leads to Δ isomers of **1** and its crystal packing shows that there are no void space available to accommodate solvent molecules.

In order to extract the Spin Hamiltonian (SH) parameters, the magnetic data was fitted using the PHI software package. An excellent fit of the experimental data (figure 4) resulted in the following parameters; $S = 1$, $g = 2.26$, $D = +4.51 \text{ cm}^{-1}$. The fitting however is insensitive to sign of D and a fit can also be obtained with $S = 1$, $g = 2.26$, $D = -7.24 \text{ cm}^{-1}$. In order to determine whether easy plane or easy axis anisotropy operates in **1**, further spectroscopic measurements such as EPR, single crystal measurement (to extract χ_x , χ_y , and χ_z) and MCD are required. These studies are currently

Figure 4. Temperature dependent $\chi_M T$ versus T plot of polycrystalline sample of **1** measured at the indicated external field. The red solid line represents the best fit obtained and the SH parameters obtained are listed.

under progress. Therefore, complex **1** possesses an $S = 1$ ground state with a g value of 2.26, similar to that of previously reported Ni(II) complexes.^{97–100}

4. Conclusion

We have reported a novel single stranded helical chain consisting of Ni(II) and Na(I) ions,

Figure 5. Temperature dependent χ_M versus T plot of polycrystalline sample of **1** measured at 0.5 Tesla (open star). The solid purple line represents the best fit obtained using the parameters discussed in the main text. Inverse susceptibility versus temperature (open circle) plot of complex **1** emphasize the paramagnetic nature of Ni(II) in **1**. Solid line represents a linear fit (red line) between 300 K to 2.0 K which goes closer to the origin (intercept = 0.3).

with the Schiff base ligand (E)-2-methoxy-6-((phenylimino)methyl)phenol). The structure of the complex was determined via X-ray diffraction measurements. The crystal lattice contains both left and right handed helical structures with equal probability; hence the resultant structure is racemic in nature. The involvement of sodium ion in determining the secondary structure of **1** is observed for the first time. Investigation of the magnetic properties of **1** reveals that the intramolecular super-exchange interactions are negligible, implying that the nickel ion behaves like a simple paramagnet. The SH parameters obtained by fitting the magnetic data ($S = 1$, $g = 2.26$ and $D = + 4.51 \text{ cm}^{-1}$ (or $D = - 7.24 \text{ cm}^{-1}$)) clearly suggest that the Ni(II) ion possess significant anisotropy. To determine the D value quantitatively, further spectroscopic investigations are required which will be carried out and communicated in near future.

Supplementary Information

The cif file for the complex **1** is given in the ESI. CCDC number: 999644. Supplementary information is available at www.ias.ac.in/chemsci.

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