Synthesis, Structure, and Magnetic Properties of 1D Nickel Coordination Polymer Ni(en)(ox)·2H₂O (en = ethylenediamine; ox = oxalate)

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A new 1D oxalato bridged compound Ni(en)(ox)·2H₂O, (ox = oxalate; en = ethylenediamine) has been hydrothermally synthesized and characterized by single crystal X-ray diffraction, IR spectrum, TG analysis, and magnetic measurements. In the structure the Ni atoms are coordinated with four oxygen atoms in two oxalate ions and two nitrogen atoms in one ethylenediamine molecule. The oxalate anion acts as a bis-bidentate ligand bridging Ni atoms in *cis*-configuration. This completes the infinite zigzag neutral chain, [Ni(en)(ox)]. The interchain space is filled by water molecules that link the chains through a network of hydrogen bonds. Thermal variance of the magnetic susceptibility shows a broad maximum around 50 K characteristic of one-dimensional antiferromagnetic coupling. The theoretical fit of the data for T > 20 K led to the nearest neighbor spin interaction J = -43 K and g = 2.25. The rapid decrease in susceptibility below 20 K indicate this compound to be a likely Haldane gap candidate material with S = 1.

Key Words: Hydrothermal synthesis. Nickel oxalate. Coordination polymer. One-dimensional Heisenberg antiferromagnet, Haldane gap

Introduction

Metal oxalate complexes exhibit molecular based magnetism where the oxalate mediates magnetic exchanges by bridging paramagnetic first-row transition metal cores. Several oxalate-bridged complexes with one-dimensional structures have been synthesized and magnetically characterized. The 1D chain structures possess mainly zigzag or linear types depending on the position of capping ligands. The zigzag chains contain *cis*-configuration of two bridged oxalato ligands on metal center, whereas linear chains have *trans*-configuration.[1] The octahedral coordinate in zigzag chains can adopt one of two terminal ligand positions: monodentate or bidentate. The infinite homometallic zigzag chains with terminal monodentate ligands are found in such as Co(ox)(im)₂ (im = imidazole),[2] M(ox)(aquo)(L) (M = Cu, Co, Zn; L = purine, adenine).[3] [Zn(ox)₂(py)]·H₂O (py = pyridine)[4] and M(ox)(ampy)₂ (M = Cu, Co, Ni; ampy = 2-aminopyridine),[5] whereas examples with bidentate ligands include M₂(ox)₂(bpy)₂·2H₂O (M = Cu, Cd, Mn; bpy = 2.2'-bipyridine),[2,6] M(ox)(dpa) (M = Fe, Ni, Co; dpa = 2.2'-dipyridylamine),[7] Zn(ox)(en)·2H₂O (en = ethylenediamine)[8] and [Cu(ox)(tmem)]·4H₂O (tmem = *N,N,N',N'*-tetramethylethylenediamine).[9] Depending on orbital topology followed by the end capping ligands used in the synthesis, these compounds show ferromagnetic or antiferromagnetic couplings with various exchange coupling J values. Here we report the synthesis, structure, and magnetic properties of a new compound, Ni(en)(ox)·2H₂O, 1 which is isostructural to Zn(en)(ox)·2H₂O.[8] In the structure each Ni atom is capped by one ethylenediamine and is bridged by two oxalato ligands in a *cis*-configuration to complete the zigzag chain structure. Thermal variance of the magnetic susceptibility of 1 shows a broad maximum around 50 K characteristic of one-dimensional antiferromagnetic coupling.

Experimental Section

Materials and Methods. All chemicals used during this work were of reagent grade and used as received from commercial sources without further purification. Thermogravimetric analyses (TGA) were carried out in N₂ at a heating rate of 5 °C/min, using a high-resolution Perkin-Elmer TGA7 Thermal Analyzer. Infrared spectra were recorded on a Hartmann & Braun BOMEM FTIR spectrometer within a range of 400-4000 cm⁻¹ using the KBr pellet method. Semiquantitative analyses of the compounds were performed with JEOL JSM-5200 scanning electron microscope (SEM) equipped with a EDAX Genesis energy dispersive spectroscopy (EDS) detector. Element analyses of the compounds were carried out using ThermoQuest CE EA1110 for C, H, and N.

Synthesis of Ni(en)(ox)·2H₂O (1). Compound 1 was synthesized from a mixture of NiO (0.045 g, 0.6 mmol), oxalic acid (0.018 g, 0.2 mmol), ethylenediamine (0.013 mL, 0.2 mmol), and water (1 mL), which was sealed under vacuum in a Pyrex tube and heated to 120 °C for 2 days, followed by cooling to 30 °C at 10 °C/h. The solution pH values before and after the reaction were ~ 11 and ~ 7, respectively. The solid products were recovered by vacuum filtration and washed with water. Blue rod-shaped crystals of Ni(en)(ox)·2H₂O with unidentified dark green aggregates were found. The products were stable in air and water. The yield of the product. Ni(en)(ox)·2H₂O 1 was 21% based on nickel. The products were insoluble in common polar and non-polar solvents. EDS analysis confirmed the presence of Ni. The element analyses gave the following results: obsd (C, 20.31; H, 4.68; N, 10.89), calcd (C, 19.79; H, 4.94; N, 11.53).

Single Crystal Structure Determination. Single-crystal data were collected on a Rigaku R-AXIS RAPID diffractometer (graphite-monochromated MoKα radiation, λ = 0.71073 Å, T =

Table 1. Crystallographic details for 1.

Empirical formula	$C_4 H_{12} N_2 Ni O_6$
Formula weight	242.87
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$C2/c$
a (Å)	11.892(7)
b (Å)	8.875(7)
c (Å)	9.122(6)
β (°)	113.81(2)
V (Å^3)	880.8(10)
Z	4
ρ_{calcd} (g/cm^3)	1.831
μ (cm^{-1})	22.06
$F(000)$	504
Crystal size (mm^3)	0.35 × 0.10 × 0.08
θ range for data collection (°)	3.32 - 27.41
Index ranges	$-15 \leq h \leq 15, -11 \leq k \leq 11,$ $-10 \leq l \leq 11$
Reflections collected	4195
Independent reflections	1008 [R(int) = 0.0426]
Data / restraints / parameters	1008 / 0 / 86
GOF on F^2	1.086
R1^a [I > 2σ(I)]	0.0369
wR2^b (all data)	0.0850
Largest diff. peak and hole (e/ Å^3)	0.696 and -0.718

^{a}R1 = $\Sigma|$ F$_o$ - |F$_c$/Σ|F$_o$| (based on reflections with I > 2σ(I)). ^{b}wR2 = [Σ $w(|F_o| - |F_c|)^2/\Sigma$ w F$_o$2]$^{1/2}$, w = $1/[\sigma^2(F_o^2) - (0.031P)^2 + 3.74P]$. P = [Max(F$_o^2$,0) + 2F$_c^2$]/3.

Table 2. Bond lengths [Å] and angles [°] for 1.

Ni(1)-N(1)#1	2.069(3)	Ni(1)-N(1)	2.069(3)
Ni(1)-O(2)#1	2.0729(19)	Ni(1)-O(2)	2.0729(19)
Ni(1)-O(1)#1	2.083(2)	Ni(1)-O(1)	2.083(2)
O(1)-C(1)	1.254(4)	O(2)-C(1)#2	1.247(4)
N(1)-C(2)	1.440(8)	N(1)-C(3)	1.596(12)
C(1)-O(2)#2	1.247(4)	C(1)-C(1)#2	1.553(6)
C(2)-C(3)	0.787(10)	C(2)-C(3)#1	1.357(12)
C(2)-C(2)#1	1.493(17)	C(3)-C(2)#1	1.357(12)
C(3)-C(3)#1	1.575(19)		
N(1)#1-Ni(1)-N(1)	83.3(2)	N(1)#1-Ni(1)-O(2)#1	95.36(11)
N(1)-Ni(1)-O(2)#1	92.44(11)	N(1)#1-Ni(1)-O(2)	92.44(11)
N(1)-Ni(1)-O(2)	95.36(11)	O(2)#1-Ni(1)-O(2)	169.57(13)
N(1)#1-Ni(1)-O(1)#1	175.02(11)	N(1)-Ni(1)-O(1)#1	94.64(12)
O(2)#1-Ni(1)-O(1)#1	80.15(8)	O(2)-Ni(1)-O(1)#1	92.29(8)
N(1)#1-Ni(1)-O(1)	94.64(12)	N(1)-Ni(1)-O(1)	175.02(11)
O(2)#1-Ni(1)-O(1)	92.29(8)	O(2)-Ni(1)-O(1)	80.15(8)
O(1)#1-Ni(1)-O(1)	87.73(12)		
O(2)#2-C(1)-O(1)	126.7(3)	O(2)#2-C(1)-C(1)#2	116.4(3)
O(1)-C(1)-C(1)#2	117.0(3)	C(3)#1-C(2)-N(1)	129.7(7)
N(1)-C(2)-C(2)#1	107.1(6)	C(2)#1-C(3)-N(1)	105.8(7)
C(3)#1-C(3)-N(1)	105.9(7)		

Symmetry transformations used to generate equivalent atoms: #1 -x, y, -z + 1/2 #2 -x, -y - 1, -z.

150 K): An empirical absorption correction was applied. The structure was solved by direct methods using SHELXS97, refined on F^2 by full-matrix least squares using SHELXL97.[10,11] Hydrogen atoms on N atoms associated with the ethylenediammonium cations were placed geometrically and refined by riding. All non-hydrogen atoms were refined anisotropically. Further details of the X-ray structural analysis are given in Table 1. Selected bond distances and bond angles are listed in Table 2. The unit cell volume of isostructural Zn compound is twice as that of 1.[8] However, no reflections indicating a superstructure were detected.

Magnetic Measurement. The DC magnetic susceptibility of 1 was measured in the temperature range 5 K ≤ T ≤ 320 K using a Quantum Design MPMS XL SQUID magnetometer, at applied field strengths of 10 kOe. For the magnetic measurement loose crystals of the complex were placed into a gelatin capsule, which was placed inside a plastic straw. The diamagnetic contribution of the gelatin capsule was calibrated after the magnetic measurement of sample.

Results and Discussion

Structure of 1. The structure of 1 is built up of infinite neutral [Ni(en)(ox)] chains separated by lattice water molecules. Figure 1 shows the coordination environment around the nickel atoms. One crystallographically independent nickel atom is coordinated by four oxygen atoms in two oxalate ions and two nitrogen atoms in one ethylenediamine molecule to form a slightly distorted octahedral geometry in the range of 2.069(3) Å - 2.083(2) Å. The carbon atoms in the ethylenediamine molecule are equally disordered over two positions. The BVS calculation gives a value of 2.12 for Ni, indicating an oxidation state of +2.00.[12] One crystallographically unique oxalate ion acting as a bis-bidentate ligand bridges Ni atoms in a *cis*-configuration to complete infinite neutral chains along the c direction (Figure 2).

One crystallographically distinct water molecule that lies between the chains is bonded to nearby oxygen and nitrogen atoms in the [Ni(en)(ox)] chains through an extended network
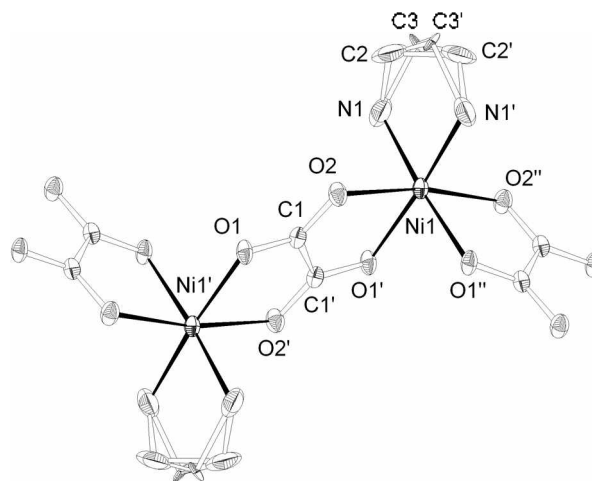
Figure 1. View of 1 showing the coordination environment of the nickel atoms (thermal ellipsoids 50%).

of O-H⋯O and N-H⋯O hydrogen bonds. Two strong hydrogen bonds are observed at O_w-H⋯O(2) and O_w-H⋯O(1) with the O⋯O distances of 2.756(4) and 2.844(4) Å, respectively. Also, two weaker H-bonds between N(1)-H⋯O_w with N⋯O distances of 3.075(5) and 3.171(5) Å are found. Out of the four H-bonds, two (O_w⋯O(1), 2.844(4) Å and O_w(1)⋯N, 3.075(5) Å) are involved in intra-chain interactions, while the others (O_w⋯O(2), 2.756(4) Å and O_w(1)⋯N, 3.171(5) Å) are responsible for inter-chain interactions in a complex arrange-
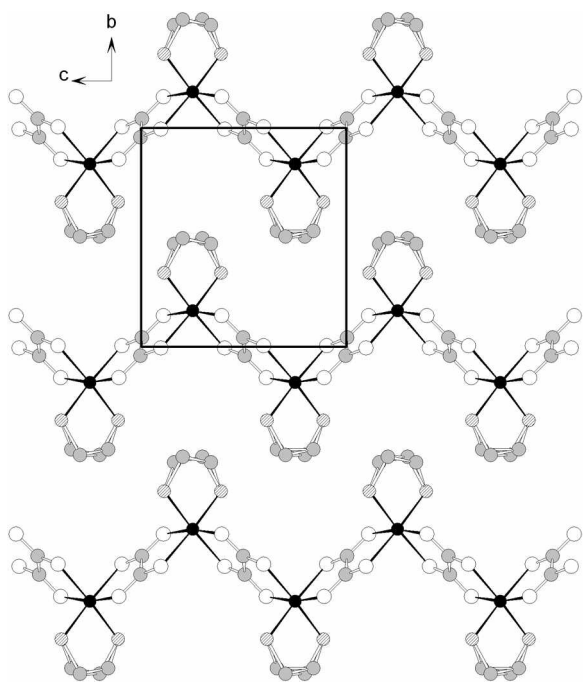
Figure 2. View of the arrangement of [Ni(en)(ox)] chains in *bc*-plane for 1. Black, empty, hatched, light gray circles are nickel, oxygen, nitrogen, and carbon atoms, respectively. Hydrogen atoms are omitted for clarity.
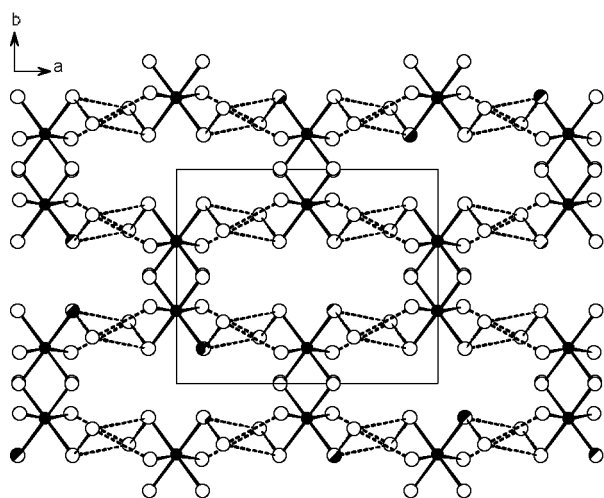
Figure 3. Hydrogen bonding interactions between lattice water molecules and oxygen/nitrogen atoms in [Ni(en)(ox)] chains. Black, empty, and hatched circles are nickel, oxygen/lattice water, and nitrogen atoms, respectively. Carbon and hydrogen atoms are omitted for clarity.

ment. This results in the formation of a 3D network structure, Figure 3. No H-bonds between the H₂O molecules are observed within the O⋯O distance of 4.0 Å.

Magnetic Properties of 1. The temperature dependence of the molar magnetic susceptibility (χ_m) and of the effective magnetic moment (μ_{eff}) for Ni(ox)(en)·2H₂O is shown in Figure 4. A magnetic moment of ～ 2.84 μ_B at room temperature is close to the theoretical spin-only value (2.828 μ_B) for *high spin* Ni^{2+} ion (S = 1). As temperature decreases, the moment decreases steadily while the susceptibility shows an increase to a broad maximum at 50 K followed by a decrease to zero. The thermal variance in susceptibility is characteristic of one-dimensional Heisenberg antiferromagnet (1D HAF). The susceptibility data have been fit using the analytical expression given by Kahn *et al.*:[13]

$$\chi = \frac{N\mu^2 g^2}{kT}\left(\frac{2+0.0194X+0.777X}{3+4.346X+3.232X^2+5.834X^3}\right)$$

with

$$X = \frac{|J|}{kT}.$$

where J is the nearest neighbor spin exchange coupling constant. The least-squares fitting (the solid line in Figure 4.) of the experimental data above 20 K yielded J = -43.0 K and g = 2.25. The agreement factor R defined by $\Sigma(\chi_{obs} - \chi_{calc})^2/\Sigma\chi_{obs}^2$ was 1.92 × 10⁻³. For the several 1D Ni complexes reported to date, the J values were estimated within the range from -12 K to -144 K, which depend on the bridging ligands, the terminal ligands and the counterions.[14] The J and g values for Ni(ox)(en)·2H₂O are comparable with those of Ni[(en)₂(NO₂)]ClO₄ (J = -47.5 K. g_a = 2.23, g_b = 2.15, g_c = 2.21).[14]

A steep decrease in the susceptibility observed below 20 K, which results in the obvious deviation from the 1D HAF model, may be explained in terms of a Haldane gap.[15] For an ideal antiferromagnetic system, the magnetic ground state is the singlet state because all the spins are aligned with opposed directions at T = 0 K. Haldane predicted that the excitation of
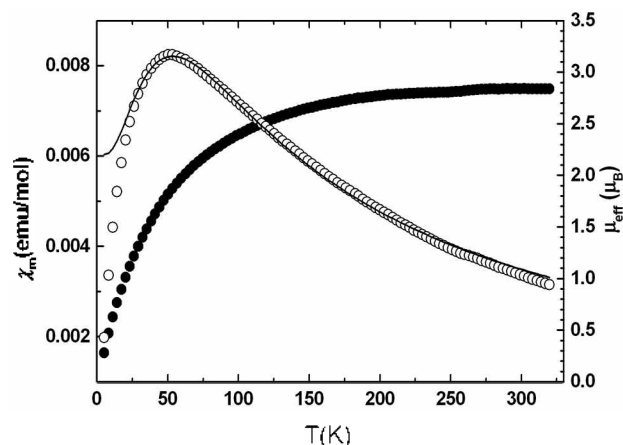
Figure 4. Thermal variation of the molar magnetic susceptibility, χ_m (○) and of the effective magnetic moment, μ_{eff} (●) for 1. Solid line represents the best fit to the 1D HAF model.

1D HAF with integer spin values might be different from that for half-integer spin values; the former has an energy gap (Haldane gap) between the non-magnetic ground state and the first excited one, while the latter has no gap. Therefore, the magnetic susceptibility approaches zero at T = 0 K in Haldane gap system, in contrast to the case of the half-integer spin. The zero susceptibility remains unchanged if the magnitude of the applied magnetic field is smaller than a critical field. Above the critical magnetic field (typically more than 10 Tesla at T = 1.5 K), a component of the first triplet excited states decreases in energy and crosses the ground state, where the magnetic susceptibility appears. Such a novel magnetism has recently been confirmed for some 1D Ni-complexes by high-field magnetic measurements.[16] The present magnetic data of 1 will provide basic knowledge for further studies.

Characterizations of 1. A simulated powder X-ray pattern based on the single-crystal structure was in excellent agreement with the X-ray powder data. The thermal decomposition of 1 occurs in several steps from room temperature to 800 °C. The first step below 100 °C corresponds to the loss of the two water molecules (weight loss: calc., 14.83%; obs., 14.59%). The dehydrated structure, $Ni(en)(C_2O_4)$, is stable up to 350 °C. Above this the evolution of ethylenediamine, CO, and CO_2 molecules occurs. Assuming that the residue at 800 °C corresponds to NiO, the overall observed weight loss of 69.66% is in good agreement with that calculated for the (69.23%). The final product after heat treatment is glassy residue, which cannot be identified by Powder-XRD.

The IR spectrum for 1 exhibits the characteristic features of the oxalate anion: $v_{as}(O\text{-}C\text{-}O)$ at 1703 and 1613 cm^{-1}, $v_s(O\text{-}C\text{-}O)$ at 1358 and 1321 cm^{-1}, and $\delta(O\text{-}C\text{-}O)$ at 810 cm^{-1}. Vibration modes for Ni-O and Ni-N are observed at 1110, 1046, and 526 cm^{-1}. Additional bands at 3496, 3427, 3321, and 3187 cm^{-1} are due to the N-H, O-H, C-H, C-C, and C-N vibrations. These values are in good agreement with those reported previously.[17]

Conclusion

During the hydrothermal investigations of NiO/ethylenediamine/oxalic acid system as a function of compositions and reaction time, a new compound $Ni(en)(ox)\cdot2H_2O$. (ox = oxalate; en = ethylenediamine) has been synthesized and characterized by single crystal X-ray diffraction, IR spectrum, element analysis, TG analysis, and magnetic measurements. In the structure the oxalate anion acts as a bis-bidentate ligand bridging Ni atoms in cis-configuration. This completes the infinite zigzag neutral chain, [Ni(en)(ox)]. The magnetic susceptibility of 1 shows a novel 1-D antiferromagnetic coupling. The steep decrease in susceptibility below 20 K indicates the existence of an energy gap between ground state and excited state, implying that this compound can be a new Haldane gap material with S = 1. Since such a novel magnetism has recently been confirmed for some 1D Ni-complexes, new nickel compounds with diverse framework structures are currently being sought.

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