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Synthesis, crystal structure, and magnetic properties of a phenoxo-bridged dinuclear nickel(II) complex

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A new dinuclear nickel complex, $[\text{Ni}_2^{\text{II}}(\text{H}_{1.5}\text{L})_2](\text{ClO}_4) \cdot 2\text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ (**1**) ($\text{H}_3\text{L} = 1,3\text{-bis}(\text{salicylamino})\text{-2-propanol}$), was synthesized and characterized by single-crystal X-ray diffraction, IR spectra, elemental analysis, and magnetic measurements. In contrast to commonly observed alcoholic oxygen bridges in previously reported dinuclear complexes, single-crystal X-ray studies reveal that the H_3L is highly distorted and links two Ni^{II} through the phenoxo oxygens of the ligands forming a $[\text{Ni}_2\text{O}_2]$ core. The remarkable distortion of the ligand brings the two non-bridging phenol groups from different ligands close to share one hydrogen, keeping charge neutrality of the complex. Magnetic studies indicate that an overall antiferromagnetic interaction is operative between the metal centers.

Keywords: Dinickel(II) complex; Crystal structure; Magnetic properties; Schiff base

1. Introduction

Schiff bases are important in coordination chemistry. As a class of the Schiff bases extensively used, the tetradentate N_2O_2 donor set, including salen-type ligands, have been particularly popular. Furthermore, salen-type ligands have attracted much attention in potential applications. For example, one application comes from the fact that salen ligands (L) coordinate to a metal center (M), forming a “metalloligand” (ML), which is suitable for the development of cooperative multi-metal complexation systems [1]. Other applications are development of catalysts [2], the design of single-molecule and single-chain magnets [3, 4], and the construction of salen-based infinite coordination polymers [5]. Therefore, many research groups have been devoted to synthesis and characterization of complexes with salen-type ligands and their reduced analogs, due to their applications in the above-mentioned fields.

Among many salen-type ligands that have been investigated, $\text{N,N}'\text{-bis}(\text{salicylidene})\text{-1,3-diaminopropan-2-ol}$ is a representative example of acyclic compartmental salen-type N_2O_3 dinucleating ligands whose bridging groups bind metal ions in close proximity and a wide variety of complexes were prepared. However, there are relatively

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few complexes containing nickel(II) among them [6–11]. A dinuclear Ni₂ active site in urease can hydrolyze urea [12] and nickel(II) containing complexes can also be used to design new molecular magnetic materials [13]. We are exploring the possibility of obtaining nickel complexes through self-assembly between this multinucleating ligand and nickel(II). Herein, we describe the synthesis, crystal structure, and magnetic properties of the dinuclear nickel compound [Ni₂^{II}(H_{1.5}L)₂](ClO₄)·2CH₃OH·H₂O (**1**) (H₃L = 1,3-*bis*(salicylamino)-2-propanol).

2. Experimental

2.1. Materials and synthesis

All chemicals were commercially obtained without purification. H₃L, 1,3-*bis*(salicylamino)-2-propanol, was obtained by applying a previously reported synthetic method [14].

2.2. Physical measurements

Elemental analyses (C, H, and N) were performed with a VarioEL element analyzer. IR measurements were performed on a VERTEX 70 Fourier transform infrared spectrophotometer using the reflectance technique (4000–300 cm⁻¹). Samples were prepared as KBr discs. Magnetic susceptibility measurements were performed from 2 to 300 K using a Quantum Design MPMS XL-7 SQUID magnetometer equipped with a 7 T magnet. The diamagnetic corrections for the compounds were estimated using Pascal's constants, and magnetic data were corrected for diamagnetic contributions of the sample holder.

2.3. X-ray crystal structure determination

Suitable single crystal with dimensions 0.15 × 0.12 × 0.08 mm³ for **1** was selected for single-crystal X-ray diffraction analysis. Crystallographic data were collected at 173 K on a Bruker Apex II CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Data processing was accomplished with the SAINT program. The structure was solved by direct methods and refined on *F*² by full-matrix least squares using SHELXTL97 [15]. Crystallographic and refinement details of **1** are listed in table 1. Selected bond lengths and angles are summarized in table 2.

3. Results and discussion

3.1. Preparation of [Ni₂^{II}(H_{1.5}L)₂](ClO₄)·2CH₃OH·H₂O (**1**)

H₃L (0.046 g, 0.15 mmol) was dissolved in methanol (10 mL) and solid Ni(ClO₄)₂·6H₂O (0.1089 g, 0.3 mmol) was added to this solution; the mixture was stirred for 1 h at room temperature to afford a blue solution, then the reaction mixture was left unperturbed to

Table 1. Crystallographic data and structure refinement for **1**.

Empirical formula	C ₃₆ H ₅₁ ClN ₄ Ni ₂ O ₁₃
Formula weight	900.68
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2(1)/ <i>c</i>
Unit cell dimensions (Å, °)	
<i>a</i>	16.0071(6)
<i>b</i>	14.0891(5)
<i>c</i>	18.4322(6)
β	114.0560(10)
Volume (Å ³), <i>Z</i>	3795.9(2), 4
Calculated density (g cm ⁻³)	1.576
Absorption coefficient (mm ⁻¹)	1.134
<i>F</i> (000)	1888
Reflections collected/unique	21735/7489 [<i>R</i> (int) = 0.0284]
Completeness to $\theta = 26.03$ (%)	99.8
Data/restraints/parameters	7489/0/527
Goodness-of-fit on <i>F</i> ²	1.092
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0415, <i>wR</i> ₂ = 0.1058
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0505, <i>wR</i> ₂ = 0.1135
Largest difference peak and hole (e Å ⁻³)	1.496 and -1.466

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Ni(1)–O(1)	2.0125(19)
Ni(1)–O(5)	2.050(2)
Ni(1)–N(3)	2.078(3)
Ni(1)–N(4)	2.089(2)
Ni(1)–O(4)	2.107(2)
Ni(1)–O(6)	2.143(2)
Ni(2)–O(5)	2.0258(19)
Ni(2)–O(1)	2.033(2)
Ni(2)–N(1)	2.081(2)
Ni(2)–N(2)	2.088(2)
Ni(2)–O(3)	2.1075(19)
Ni(2)–O(2)	2.1506(19)
Ni(1)··Ni(2)	3.0966(5)
O(1)–Ni(1)–O(5)	79.26(8)
O(1)–Ni(1)–N(3)	98.49(9)
O(5)–Ni(1)–N(4)	91.70(9)
N(3)–Ni(1)–N(4)	90.52(10)
O(5)–Ni(2)–O(1)	79.34(8)
O(1)–Ni(2)–N(1)	89.66(9)
O(5)–Ni(2)–N(2)	101.73(9)
N(1)–Ni(2)–N(2)	89.57(10)
Ni(1)–O(1)–Ni(2)	99.89(8)
Ni(1)–O(5)–Ni(2)	98.89(8)

allow slow evaporation of the solvent. Blue single crystals, suitable for X-ray diffraction analysis, formed after 1 week, were collected by filtration, washed with cold methanol, and dried in air. Yield: 23.2 mg (34.3%, based on the ligand). Elemental analysis (%) calcd for C₃₆H₅₁ClN₄Ni₂O₁₃: C, 48.00; H, 5.70; N, 6.22. Found: C, 47.86; H, 5.51; N, 5.83. IR (KBr, cm⁻¹): 3551(w), 3291(m), 3073(w), 2944(w), 2927(w), 2872(w), 2838(w), 2672(w), 2588(m), 2169(w), 2018(w), 1707(w), 1595(m), 1569(w), 1484(s), 1456(m),

1447(s), 1353(w), 1321(w), 1285(s), 1192(w), 1154(w), 1096(s), 1045(s), 1007(s), 976(m), 918(m), 898(m), 877(m), 807(w), 779(s), 756(s), 727(w), 622(m), 590(m), 574(w), 550(w), 520(w), 468(w), 459(w), 437(w).

CAUTION: Although we have experienced no problems in working with perchlorate salts, they are potentially explosive and should be prepared and handled in small amounts, and with great care.

3.2. Description of the structure of $[\text{Ni}_2^{\text{II}}(\text{H}_{1.5}\text{L})_2](\text{ClO}_4) \cdot 2\text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ (**1**)

The reaction of nickel(II) perchlorate with 1,3-*bis*(salicylamino)-2-propanol (H_3L) in methanol produces the dinuclear compound $[\text{Ni}_2^{\text{II}}(\text{H}_{1.5}\text{L})_2](\text{ClO}_4) \cdot 2\text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ (**1**), whose molecular structure determined by single-crystal X-ray diffraction is depicted in figure 1. Complex **1** crystallizes in the monoclinic $P2(1)/c$ space group. The molecular structure of **1** consists of $[\text{Ni}_2^{\text{II}}(\text{H}_{1.5}\text{L})_2]^+$, one perchlorate, two solvated methanols, and one water molecule. The structure shows a dimeric unit where the two nickels are bridged by two deprotonated phenol oxygens (O1 and O5) from two H_3L , forming a Ni_2O_2 core. The two remaining phenol oxygens (O3 and O4) from the two ligands are coordinated to Ni2 and Ni1, respectively, as previously observed in a dinuclear zinc compound [16]. The Ni1–Ni2 separation and Ni1–O1–Ni2, Ni1–O5–Ni2 angles are $3.0966(5)^\circ\text{\AA}$ and $99.89(8)^\circ$, $98.89(8)^\circ$, respectively. Each nickel has a N_2O_4 donor set in six-coordination with two ligands. For Ni1, the equatorial plane is provided by O1O5N3N4, whereas for Ni2, it is O1O5N1N2. The average deviations of the constituent atoms from their least squares planes in the two cases are 0.0313 and 0.0724\AA . For both metal centers, the axial positions are occupied by a phenol oxygen (O4 for Ni1 and O3 for Ni2) and an alcohol oxygen (O6 for Ni1 and O2 for Ni2). The dihedral angle between these two equatorial planes is 15.3° .

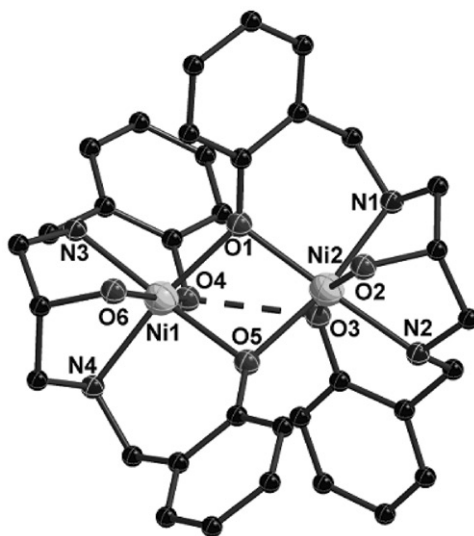
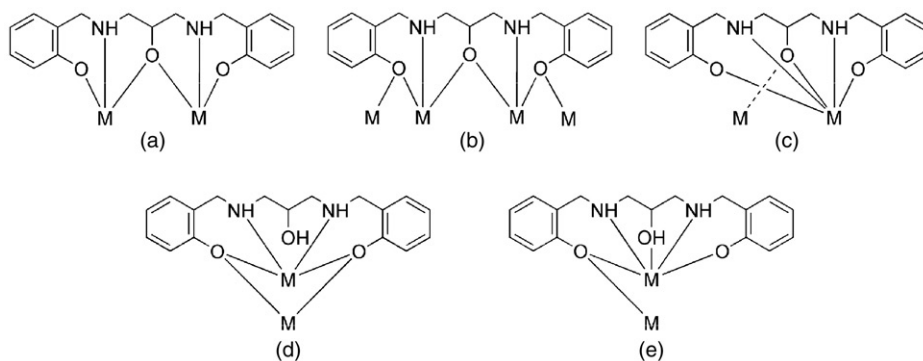


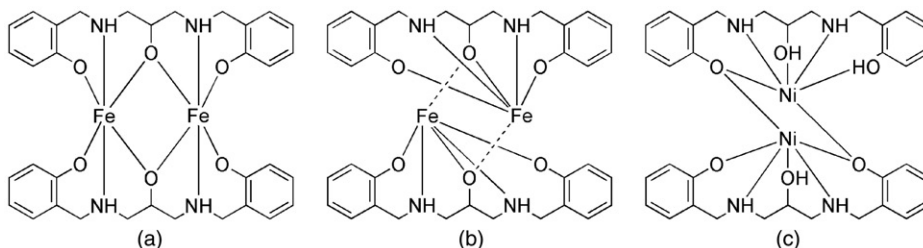
Figure 1. Molecular structure of **1**. The ClO_4^- , non-coordinated solvent and hydrogens have been omitted for clarity.

Alcohol oxygens O2 and O6 in **1** remain protonated, but coordinate to nickel. In most previously reported compounds, the alcohol oxygen coordinates to metal ions upon deprotonating [14, 16–22], while in several complexes the alcohol oxygen does not coordinate at all [23–26]. Five different binding modes have been observed for H₃L as shown in scheme 1, but the binding (scheme 1(e)) in **1** is different from those of previously reported compounds. In general, deprotonated phenol oxygens or alcohol oxygens readily bridge metal centers to form [M₂O₂], and three different types of dinuclear complexes can be observed (scheme 2). Two metal centers are bridged by alcohol oxygens as shown in scheme 2(a) and (b), while in scheme 2(c) two metal ions are linked through phenol oxygens. Other bridging modes can be found in azido- [27] and hydroxo-bridged [28] nickel(II) complexes. The special coordination mode (scheme 2c) makes the ligands highly distorted so that two phenols from two ligands are close (O3···O4 distance of 2.4672(32) Å) and share one hydrogen, thus keeping charge neutrality of the complex.

Examination of the crystal packing reveals that molecules of **1** are in contact through hydrogen bonds (O2···O13···O4), generating an infinite supramolecular 1-D chain along the crystallographic *c* axis as shown in figure 2. However, no obvious π - π stacking interactions between the aromatic rings in the 1-D chain are detected. The hydrogen bonds and angles of **1** are provided in table 3.



Scheme 1. The crystallographically established coordination modes of H₃L.



Scheme 2. Three different types of dinuclear complexes containing H₃L.

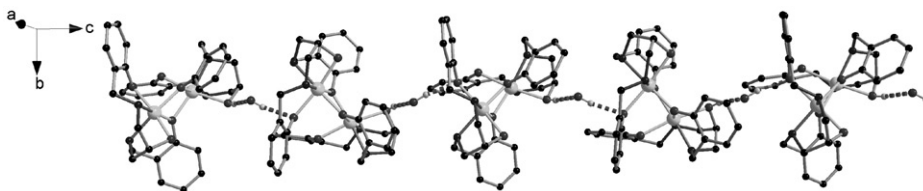


Figure 2. Hydrogen bond interactions in the crystal packing of **1** showing the 1-D chain.

Table 3. Hydrogen-bonding interactions in **1**.

D–H···A	$d(\text{D–H})$	$d(\text{H···A})$	$d(\text{D···A})$	$\angle(\text{DHA})$
O13–H13A···O4#1	0.81(6)	1.90(6)	2.706(3)	169(6)
O2–H2H···O13	0.85(5)	1.79(5)	2.633(3)	169(5)

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

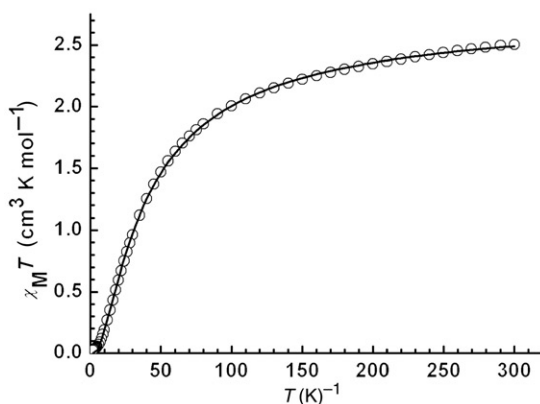


Figure 3. Temperature dependence of the $\chi_M T$ product at 1000 Oe for **1**. Solid line is the best fit obtained with the model described in the text.

3.3. Magnetic properties

Variable-temperature magnetic susceptibility measurements were carried out on microcrystalline samples of **1** in a 1 kOe dc field from 2 to 300 K. The temperature dependence of $\chi_M T$ is shown in figure 3, where χ_M is the molar magnetic susceptibility per Ni_2 unit. The $\chi_M T$ value at 300 K is $2.50 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, lower than the theoretical $\chi_M T$ value ($2.65 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) for two isolated nickel(II) centers with local spins $S_1 = S_2 = 1$ and $g = 2.3$. Upon further cooling, $\chi_M T$ decreases gradually reaching a minimum of $0.025 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2 K; the decline is sharp below ~ 75 K. The profile is indicative of the existence of antiferromagnetic interaction between the nickel centers, similar to those of previously reported nickel complexes [29]. To fit and interpret the magnetic susceptibility data of **1**, we consider that the exchange coupling of magnetic centers in the dinuclear compound can be modeled using spin Hamiltonian that includes the effect of the nickel ion zero-field-splitting term: $\hat{H} = -2J\hat{S}_1\hat{S}_2 - D(\hat{S}_{1z}^2 + \hat{S}_{2z}^2)$ with

the introduction of a Weiss term, θ , to account for intermolecular interactions and J as the total exchange parameter between nickel(II) ions. The theoretical expression derived from this Hamiltonian is shown in equation (1), where all the parameters have their usual meanings.

$$\chi = \frac{2N\beta^2 g^2}{kT} \frac{4 \exp(A) + \exp(B) + \exp(D)}{2 \exp(A) + 2 \exp(B) + \exp(C) + 2 \exp(D) + \exp(E) + \exp(F)}, \quad (1)$$

where

$$A = (6J + 2D)/kT; \quad B = (6J + D)/kT; \quad C = [(3J + D) - (6J^2 - 2DJ + D^2)^{1/2}]/kT;$$

$$D = (2J + D)/kT; \quad E = (2J + 2D)/kT; \quad F = [(3J + D) - (9J^2 - 2DJ + D^2)^{1/2}]/kT.$$

The best fit has been obtained for $g=2.3$, $J=-6.27 \text{ cm}^{-1}$, $D=-3.16 \text{ cm}^{-1}$, $\theta=-19.22 \text{ K}$, and $R^2=0.99977$. The negative value of J indicates that an overall antiferromagnetic interaction between nickel(II) ions is operative.

4. Conclusions

We have described the synthesis, structure, and magnetic properties of a dinuclear $[\text{Ni}_2^{\text{II}}(\text{H}_{1.5}\text{L})_2](\text{ClO}_4) \cdot 2\text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ complex using a salen-type Schiff base. The magnetic properties indicate that antiferromagnetic coupling exists between two paramagnetic nickel(II) sites bridged by two phenol oxygens of the Schiff-base ligand.

Supplementary material

CCDC-806576 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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