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A New Half-Salamo-Based Homo-Trinuclear Nickel(II) Complex: Crystal Structure, Hirshfeld Surface Analysis, and Fluorescence Properties

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Abstract: A new homo-trinuclear Ni(II) half-salamo-based complex $[Ni_3(L)_2(\mu - OAc)_2(OAc)_2(CH_3OH)_2] \cdot 2CH_3OH$ was synthesized via the reaction of a tridentate ligand HL (2-[O-(1-ethyloxyamide)]oxime-4-bromophenol) and Ni(OAc)_2 \cdot 4H_2O, and characterized using elemental analyses, IR spectra, UV-Vis absorption spectra, X-ray crystallography, and Hirshfeld analysis. Interestingly, single-crystal X-ray analysis showed that the two acetate molecules were bonded simultaneously with the Ni(II) atoms by mono-dentate chelating and bidentate bridging coordination modes, respectively, and the resulting hexa-coordinate geometries were ultimately formed. Furthermore, the Hirshfeld analysis of the complex was studied. Compared with HL, the complex fluorescence intensity was significantly lowered, indicating that the Ni(II) ions have fluorescence quenching characteristics.

Keywords: half-salamo ligand; homo-trinuclear Ni(II) complex; structure; Hirshfeld surface analysis; fluorescence property

1. Introduction

Salen and its derivatives are usually gained via Schiff-base condensation reaction of a diamine with an aldehyde, a ketone or its derivative [1–4]. The coordination environment includes two imine N atoms and two O atoms from the aldehyde or ketone, usually phenolic oxygen atoms. Salamo was developed on the basis of changing the type of amine of the salen-type compound, and after introducing an O atom to the N atom of the salen-type compound possessing a –RC=N– group, the salamo-type compound is more flexible and stable than the salen-type compound [5]. The salamo-type ligands and their metal complexes, due to their unique physical and chemical properties and potential application values, have attracted more and more attention from chemical researchers [6–12]. Therefore, the results of research into these complexes in the fields of catalysts [13–15], biology [16–20], electrochemical processes [21–27], supramolecular structures [28–33], ion recognitions [34–40], magnetic materials [41–47], and luminescence [48–56] are remarkable.

A new trinuclear Ni(II) half-salamo complex was designed and synthesized. The complex is a new symmetric trinuclear Ni(II) structure. Most of the previously reported complexes were coordinated by one acetate molecule to two metal atoms [57–60]. In this paper, not only were two acetate molecules coordinated to two Ni(II) atoms, but also by bidentate bridging and monodentate chelating coordination modes simultaneously connecting two Ni(II) atoms. Most importantly, Hirshfeld surface analysis was also studied while studying fluorescence properties.

2. Experimental

2.1. Materials and Measurements

All solvents and chemicals were obtained from commercial sources and used without further purification. Elemental analyses for nickel(II) were measured by IRIS ER/S-WP-1 ICP atomic emission spectrometer (Elementar, Berlin, Germany), elemental analyses for carbon, hydrogen, and nitrogen were conducted using GmbH VariuoEL V3.00 automatic elemental analysis instrument (Elementar, Berlin, Germany). IR spectra were made via a Bruker VERTEX70 FT-IR spectrophotometer, with samples prepared as CsI (100–500 cm⁻¹) and KBr (500–4000 cm⁻¹) pellets (Bruker AVANCE, Billerica, MA, USA). The UV-Vis spectra were obtained by a Shimadzu UV-3900 spectrometer (Shimadzu, Tokyo, Japan). The ¹H NMR (nuclear magnetic resonance) spectra were measured by German Bruker AVANCE DRX-400/600 spectroscopy (Bruker AVANCE, Billerica, MA, USA). Fluorescence spectra were measured via a F-7000 FL spectrophotometer (Hitachi, Tokyo, Japan). The X-ray single-crystal structure was measured by a SuperNova Dual (Cu at zero) four-circle diffractometer.

2.2. Synthesis of HL

1,2-Bis(aminooxy)ethane was synthesized via a similar method reported earlier in Reference [61]. 5-Bromo-2-hydroxybenzaldehyde (402.04 mg, 0.02 mmol) in ethanol solution (40 mL) was slowly added to 1,2-bis(aminooxy)ethane (368.4 mg, 0.01 mmol) in ethanol (60 mL) over 1 h. The mixture was heated at 50–55 °C for 5 h. The solution was concentrated by reduced pressure and the residue was purified via column chromatography with chloroform:ethyl acetate = 20:1 gaining the ligand HL:2-[*O*-(1-ethyloxyamide)]oxime-4-bromophenol (Scheme 1). Yield: 62.5%. m.p.: 60–61 °C. ¹H NMR (400 MHz, CDCl₃) δ 3.95 (t, *J* = 4.5 Hz, 2H), 4.36 (t, *J* = 4.5 Hz, 2H), 5.50 (brs, 2H), 6.87 (d, *J* = 9.0 Hz, 1H), 7.25 (d, *J* = 2.5 Hz, 1H), 7.37 (dd, *J* = 9.0, 2.5 Hz, 1H), 8.14 (s, 1H), 9.88 (s, 1H). IR (KBr, cm⁻¹): 3234 (m), 2953 (m), 2895 (m), 1608 (s), 1577 (m), 1475 (s), 1428 (s), 1366 (m), 1261 (s), 1170 (w), 1054 (s), 971 (w), 927 (s), 836 (m), 776 (s), 727 (s), 676 (s), 620 (s), 587 (w), 542 (w). UV-Vis (CH₃CH₂OH), λ_{max} (nm) (ε_{max}): 218, 265, and 322 nm (5.0 × 10⁻⁵ M). Anal. Calcd for C₉H₁₁BrN₂O₃ (%): C 39.29; H 4.03; N 10.18. Found: C 39.58; H 4.00; N 10.06.



Scheme 1. Synthetic routes to HL and its Ni(II) complex.

2.3. Synthesis of the Ni(II) Complex

A methanol solution (2.0 mL) of nickel(II) acetate tetrahydrate (5.50 mg, 0.02 mmol) was added to a trichloromethane solution (3.0 mL) of HL (4.98 mg, 0.02 mmol) at room temperature, and the color of the mixed solution turned light brown immediately. After, the mixed solution was stirred for 3–5 min and then the mixture was filtered. The resulting filtrate was left undisturbed for about one week to gain clear light-yellow block-like crystals suitable for X-ray crystallographic analysis (Scheme 1). Yield: 53.1%. IR (KBr, cm⁻¹): 3402 (m), 2945 (w), 1596 (s), 1561 (m), 1457 (s), 1386 (s), 1290 (s), 1248 (s), 1073 (m), 1032 (m), 967(w), 935 (w), 851 (w), 744 (m), 701 (w), 661 (w), 620 (w), 558 (w), 523 (w), 455 (w). UV-Vis (CH₃CH₂OH), λ_{max} (nm) (ε_{max}): 226 and 375 nm (5.0 × 10⁻⁵ M). Anal. Calcd for C₃₀H₄₈Br₂N₄Ni₃O₁₈ (%): C 33.10; H 4.44; N 5.15; Ni 16.17. Found: C 33.32; H 4.21; N 5.11; Ni 16.12.

2.4. Crystal Structure Determination for the Ni(II) Complex

X-ray single crystal diffraction data of the Ni(II) complex was measured at 294.78(16) K with a SuperNova Dual (Cu at zero) using a monochromated Mo-Ka radiation $\lambda = 0.71073$ Å. The LP corrections were used to with SAINT program and semi-empirical correction using the SADABS program. The structures were solved using direct methods (SHELXS-2015) [62,63]. The highest difference Fourier map maximum was about 0.7 with a distance of 1.05 A from Br1. All non-hydrogen atoms were anisotropically refined; all hydrogen atoms were contained at the calculated positions and constrained to ride on their parent atoms. Details of the data collection and refinements of the Ni(II) complex are summarized in Table 1. CCDC (1889237) contain the supplementary crystallographic data for this paper. The date can be obtained free of charge from the Cambridge Crystallographic Data Centre and www.ccdc.cam.ac.uk/conts/retrieving.html.

Compound	Ni(II) Complex
Formula	C ₃₀ H ₄₈ Br ₂ N ₄ Ni ₃ O ₁₈
Formula weight	1088.67
Temperature (K)	294.78(16)
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	P b c n
a (Å)	17.886(2)
<i>b</i> (Å)	9.3664(14)
<i>c</i> (Å)	24.954(4)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
V (Å ³)	4180.5(10)
Z	4
$D_{\text{calc}} (\mathbf{g} \cdot \mathbf{cm}^{-3})$	1.730
μ (mm $^{-1}$)	3.325
F (000)	2216
Crystal size (mm)	0.17 imes 0.15 imes 0.14
θ Range (°)	3.9870-18.3900
	$-21 \le h \le 19$
Index Ranges	$-11 \le k \le 8$
	$-22 \leq l \leq 29$
Reflections collected	13,630
Independent reflections	1967
R _{int}	0.1191
Completeness to θ	99.8% (θ = 24.997)
Data/restraints/parameters	3670/0/263
GOF	1.070

Table 1. Crystal data and refinement parameters for the Ni(II) complex.

	Table 1. Cont.		
hd		Ni(II) Complex	

compound	ititit) complex	
$R [I > 2\sigma(I)]$	$R_1 = 0.0721, wR_2 = 0.1663$	
Largest differences peak and hole (e ${ m \AA^{-3}}$)	0.738/-0.613	
$R_{1} = \Sigma F_{o} - F_{c} / \Sigma F_{o} ; wR_{2} = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{o}^{2})^{2}]^{1/2}$	$w = [\sigma^2(F_0^2) + (0.0475P)^2 + 1.7291P]^{-1}$	¹ , where <i>l</i>
$= (F_0^2 + 2F_c^2)/3; \text{GOF} = [\Sigma w (F_0^2 - F_c^2)^2/n_{\text{obs}} - n_{\text{param}})]^{1/2}.$		

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3. Results and Discussion

3.1. IR Spectra

In the IR spectra (Table 2), HL and its complex show different peaks in the 500–4000 cm⁻¹ region. The $\nu_{(O-H)}$ frequency of HL appeared at 3234 cm⁻¹. This peak disappeared in the Ni(II) complex, while a new peak appeared at 3402 cm⁻¹ which was assigned to the vibration of methanol molecules. The ligand HL showed a $\nu_{(C=N)}$ band at 1608 cm⁻¹, while that of the Ni(II) complex appeared at 1596 cm⁻¹. For the ligand HL, the $\nu_{(Ar-O)}$ band appeared at 1261 cm⁻¹, and that of the Ni(II) complex was observed at 1248 cm⁻¹ [64]. It can be observed from the data that the characteristic $\nu_{(C=N)}$ and $\nu_{(Ar-O)}$ frequencies moved to lower frequencies, showing the formation of Ni–N and Ni–O bonds. The far-infrared spectrum of the Ni(II) complex also gained in the 500–100 cm⁻¹ region in order to distinguish frequencies owing to the Ni–O and Ni–N bonds, and $\nu_{(Ni–O)}$ and $\nu_{(Ni–N)}$ frequencies were found as new peaks at 455 and 532 cm⁻¹ [65], respectively.

Table 2. The major IR spectra of HL and its Ni(II) complex (cm^{-1}) .

Compound	$v_{(O-H)}$	$v_{(C=N)}$	$v_{(Ar-O)}$	$v_{(\rm Ni-O)}$	$\nu_{(Ni-N)}$
HL	3234	1608	1261	-	-
Complex	3402	1596	1248	455	523

3.2. UV-Vis Absorption Spectra

The UV-Vis titration of the Ni(II) complex is depicted in Figure 1. During the UV-Vis titration, we can easily observe that the HL shows three typical absorption peaks at 218, 265, and 322 nm, which can be assigned to the π - π * transition [66]. With the increase of concentration of Ni(II) ions, the three typical peaks of HL changed, the peaks at 265 and 322 nm disappeared. Meanwhile, a new peak appeared at 375 nm, and attributed to HL to metal LMCT [67–69], which is characteristic of the transition metal salen-type complexes. In addition, when the ratio of HL to metal ions is lower than 2:3, the absorption intensity increases linearly with the concentration of Ni(II) ions, and when it reaches 3:2, the absorption spectrum no longer changes with the increase of concentration of Ni(II) ions, indicating that the titration reaches the end point. In the UV-Vis titration, we formulated the ligand HL to a concentration of 5.0×10^{-5} M, and the Ni(OAc)₂·4H₂O was formulated to a concentration of 1.0×10^{-3} M.

3.3. The Crystal Structure Description

The crystal structure of the homo-trinuclear Ni(II) complex is given in Figure 2, and bond lengths and angles are given in Table 3. X-ray crystallographical analysis revealed that the Ni(II) complex crystallizes in the orthorhombic, space group P b c n, Z = 4, all bond lengths are in normal ranges [22,41]. The complex [Ni₃(L)₂(μ_2 -OAc)₂(OAc)₂(CH₃OH)₂]·2CH₃OH is formed by coordination of HL with Ni(OAc)₂·4H₂O, the Ni(II) complex includes three Ni(II) atoms and two completely deprotonated ligand (L)⁻ units. The complex presents a centrally symmetric structure, the central Ni(II) atom (Ni2) is hexacoordinated, consists of six O atoms (O1, O4, O26 and O1[#], O4[#], O26[#]) from the two fully deprotonated ligand (L)⁻ units and four acetate molecules with two kinds of coordination modes, together formed an octahedral coordination geometry. Then, the coordination spheres of the two terminal Ni(II) atoms (Ni1 and Ni1[#]) are both surrounded by two imine N atoms (N9 and N20),

one phenol O atom (O4), one O atom (O3) from the coordinated methanol molecule, and two N atoms (O1 and O2) from two acetate molecules with two kinds of coordination modes to complete together their slightly distorted octahedral geometries.



Figure 1. The UV-Vis titration spectra of the Ni(II) complex (cm^{-1}).



Figure 2. (a) Molecular structure of the Ni(II) complex with 30% probability displacement ellipsoids (hydrogen atoms are omitted for clarity); (b) coordination polyhedrons for Ni(II) atoms.

Bond	Lengths	Bond	Lengths
Ni1-01	2.111(5)	Ni201	2.076(5)
Ni–O2	2.009(5)	Ni2-04	2.082(5)
Ni1–O3	2.091(6)	Ni2-O26	2.078(6)
Ni1-O4	2.018(5)	Ni201 #1	2.076(5)
Ni1–N9	2.036(6)	Ni2-O4 #1	2.082(5)
Ni1-N20	2.065(8)	Ni2-O26 #1	2.078(6)
Bond	Angles	Bond	Angles
O1-Ni1-O2	93.0(2)	O1-Ni2-O4	77.2(2)
O1-Ni1-O3	86.8(2)	O1-Ni2-O26	89.1(2)
O1-Ni1-O4	77.8(2)	O1-Ni2-O1 #1	180.00
O1-Ni1-N9	94.0(3)	O1-Ni2-O4 #1	102.8(2)
O1-Ni1-N20	166.0(3)	O1-Ni2-O26 #1	91.0(2)
O2-Ni1-O3	175.0(3)	O4-Ni2-O26	91.8(2)
O2-Ni1-O4	93.0(2)	O1 #1-Ni2-O4	102.8(2)
O2-Ni1-N9	87.5(3)	O4-Ni2-O4 #1	180.00
O2-Ni1-N20	92.1(3)	O4-Ni2-O26 #1	88.2(2)
O3-Ni1-O4	91.8(2)	O1 #1-Ni2-O26	91.0(2)
O3-Ni1-N9	87.6(3)	O4 #1-Ni2-O26	88.2(2)
O3-Ni1-N20	89.3(3)	O26-Ni2-O26 #1	180.00
O4-Ni1-N9	171.9(3)	O1 #1-Ni2-O4 #1	77.2(2)
O4-Ni1-N20	88.8(3)	O1 #1-Ni2-O26 #1	89.1(2)
N9-Ni1-N20	99.3(3)	O4 #1-Ni2-O26 #1	91.8(2)

Table 3. Bond lengths (Å) and angles (°) of the Ni(II) complex.

Symmetry transformations used to generate equivalent atoms: $^{#1}$ -x, 1 - y, -z.

3.4. Supra-Molecular Interactions

As illustrated in Figure 3a, there are five pairs of different intra-molecular hydrogen bond interactions [70,71], which are N9–H9B···O7, C6–H6···O26, C17–H17A···O2, C24–H24A···O4, and C25–H25A···O22 intra-molecular interactions, and inter-molecular hydrogen bonding interactions (N9–H9A···O7 and C28–H28B···O7) shown in Figure 3b, except for the hydrogen bonding formed, other hydrogen atoms were omitted. Hydrogen bonding interactions of the Ni(II) complex are summed in Table 4. The hydrogen bond interactions play a major role in the building of the Ni(II) complex. Through this inter-molecular hydrogen bonding inter-action, each molecule of the Ni(II) complex is connected to each other to gain a two-dimensional supra-molecular network along the *ab* plane. At the same time, in Figure 3c, through the inter-molecular hydrogen bonding interactions, this network structure is connected to each other to gain an infinite three-dimensional supra-molecular structure.

Table 4. Hydrogen bonding interactions (Å, $^{\circ}$) of the Ni(II) complex.

D-H· · · A	d(D–H)	$d(H \cdot \cdot \cdot A)$	$d(D \cdot \cdot \cdot A)$	∠D–H···A
N9-H9B· · · O7	0.90	2.00	2.808(10)	149
C6-H6···O26	0.93	2.52	3.202(10)	131
C17–H17A···O2	0.97	2.48	3.372(11)	153
C24–H24A···O4	0.96	2.57	3.438(11)	150
C25-H25A···O22	0.96	2.48	3.178(13)	130
N9–H9A···O7	0.90	2.12	2.967(10)	156
C28-H28A···O7	0.97	2.50	3.182(12)	128



Figure 3. (a) View of the intra-molecular hydrogen bonding interactions of the Ni(II) complex (hydrogen atoms are omitted for clarity, except those forming hydrogen bondings); (b) View of the 2D supra-molecular structure of the Ni(II) complex; (c) view of the 3-D supra-molecular structure of the Ni(II) complex.

3.5. Fluorescence Titration Spectra

As shown in the Figure 4, the fluorescence properties of HL and its Ni(II) complex in ethanol solvent were studied. The concentration of the ligand HL was 5.0×10^{-5} M, the concentration of the Ni(II) ions was 1.0×10^{-3} M, and the maximum excitation wavelength was about 315 nm.



Figure 4. Fluorescence spectra of HL and its Ni(II) complex in ethanol upon excitation at 315 nm.

When the excitation wavelength is 315 nm, the ligand HL exhibits a strong absorption peak at 365 nm, which is attributed to the π - π * transition. During the fluorescence titration experiment, the fluorescence intensity decreases as the concentration of the metal(II) ions increases. The decrease in fluorescence intensity was mainly owing to the bonding of the (L)⁻ ligand with the Ni(II) ions. Compared with the emission spectrum of HL, the decrease in the fluorescence intensity of the complex was obtained, showing that the fluorescence was quenched due to the introduction of the Ni(II) atoms.

3.6. Hirshfeld Surface Analysis

Figure 5 shows the Hirshfeld surface distribution of the complex through d_{norm} , d_i , and d_e mapping [72]. It can be clearly seen from the figure that the red region represents the O–H between the O and H atoms in the Ni(II) complex. Inter-action intensity map, the heavier the color of the red region, the stronger the O–H interactions, and the other shallower regions are mainly the distribution of short-range effects such as C–H and H–H. From this figure, the distribution of the approximate hydrogen bondings in the complex can be analyzed, which is helpful to further explore the intrinsic factors of the stable existence of the complex.



Figure 5. Hirshfeld surface analysis of the Ni(II) complex by d_{norm} , d_i , and d_e mapping.

In addition, the proportion of C–H/H–C, O–H/H–O, and H–H/H–H in the complex can also be gained by Hirshfeld surface analysis. Here, we theoretically calculate the short-range action distribution inside the complex. As depicted in Figure 6, in this two-dimensional Hirshfeld surface generation map, the blue region represents the distribution of different interactions. For the entire Ni(II) complex molecule, the ratio of C–H/H–C, O–H/H–O, and H–H/H–H in the surface of Hirshfeld was calculated to be 5.5%, 9.9%, and 55.9%, respectively. In fact, a complex can exist stably, and the short-range effects in these structures are indispensable.



Figure 6. Finger-print plot of the proportion of short-range action on the Hirshfeld surface in the Ni(II) complex.

4. Conclusions

In summary, a new homo-trinuclear Ni(II) complex was designed and synthesized. X-ray crystallography reveals that the Ni(II) atoms in the complex are coordinated to two acetate molecules by two kinds of bidentate bridging and mono-dentate chelating coordination modes, which is a very rare phenomenon. The UV-Vis titration experiment clearly shows the ligand to Ni(II) ions has a stoichiometry of 2:3. Compared with HL, the fluorescence intensity of the complex was significantly lowered, indicating that the Ni(II) ions have fluorescence quenching characteristics. In addition, Hirshfeld surface analysis indicates that the Ni(II) complex can be stable owing to intra-molecular and inter-molecular hydrogen bonding interactions.

Author Contributions: W.-K.D. conceived and designed the experiments; X.-X.A. performed the experiments; Q.Z. and H.-R.M. analyzed the data; W.-K.D. contributed reagents/materials/analysis tools; X.-X.A. and Q.Z. wrote the paper.

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