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**STRUCTURE OF A NEW TRINUCLEAR NICKEL(II) COMPLEX
WITH A SALEN-TYPE BISOXIME LIGAND****W.-K. Dong¹, Y.-X. Sun¹, J. Yao¹, L. Wang¹, X.-Y. Dong¹, X.-H. Gao²**¹*School of Chemical and Biological Engineering, Lanzhou Jiaotong University, P. R. China*

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A new trinuclear Ni(II) complex $\{[\text{NiL}(\text{DMF})]_2(\text{OAc})_2\text{Ni}\} \cdot 2\text{DMF}$ ($\text{H}_2\text{L} = 4,4'$ -dichloro-2,2'-[(1,3-propylene)dioxybis(nitrilomethylidene)]diphenol) is synthesized and characterized by elemental analyses, IR spectra, UV—Vis spectra and X-ray crystallography. The results show that the Ni(II) complex consists of three Ni(II) ions, two tetradentate $(\mu\text{-L})^{2-}$ units, two coordinated μ -acetate ions, two coordinated DMF molecules, and two crystallization DMF molecules. All hexacoordinated Ni(II) ions of the complex have a slightly distorted octahedral geometry. The crystal packing of the Ni(II) complex reveals a notable feature of this structure: the formation of an infinite supramolecular 2D layered structure by virtue of intermolecular C—H \cdots O hydrogen bonding.

Key words: salen-type bisoxime ligand, Ni(II) complex, synthesis, crystal structure.

Salen (*N,N'*-bis(salicylaldehyde)ethylenediamine) and its metal complexes have been known since the 19th century. Their unique functionalities such as host-guest chemistry, magnetism, asymmetric catalysis, electronic conductivity have been in focus of the metal complex chemistry [1–4]. Since the highly electronegative oxygen atom strongly affects azomethine nitrogen of N_2O_2 salen-type bisoxime ligands, thus influencing the N_2O_2 coordination core and possibly leading to diverse novel structures of the resulted complexes, we began to study monomers where the nitrogen and oxygen environment of the metal center is provided by tetradentate ligands [5]. Some of these studies show that such compounds can evolve oxygen in aqueous solutions [6]. The studies of salen-type bisoxime ligands and their complexes have made enormous progress in recent years [7–10]. In addition, these complexes display novel magnetic [11–14], structural, and redox properties [15–18], thus providing continuous interest.

It is common knowledge that acetate ions often play an important role in coordination chemistry, and they can adopt various binding modes such as terminal monodentate, chelating to one metal center, bridging bidentate in a *syn-syn*, *syn-anti* and *anti-anti*, and bridging tridentate to two metal centers [19–21]. This contribution reports a new trinuclear Ni(II) cluster $\{[\text{NiL}(\text{DMF})]_2(\text{OAc})_2\text{Ni}\} \cdot 2\text{DMF}$ ($\text{H}_2\text{L} = 4,4'$ -dichloro-2,2'-[(1,3-propylene)dioxybis(nitrilomethylidene)]diphenol) and its structural characterization.

EXPERIMENTAL

Reagents and physical measurements. 5-Chloro-2-hydroxybenzaldehyde ($\geq 98\%$) from Alfa Aesar was used without further purification. Other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory, and were used without further purification. Elemental

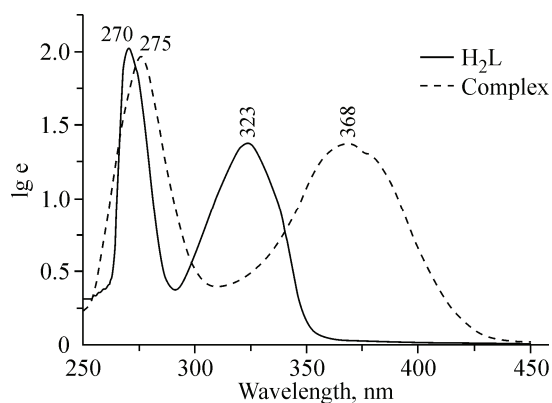
analysis for Ni(II) was carried out on an IRIS ER/S-WP-1 ICP atomic emission spectrometer. C, H and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. FT-IR spectra were recorded on a VERTEX70 FT-IR spectrophotometer with samples prepared as KBr ($400 \sim 4000 \text{ cm}^{-1}$) and CsI ($100 \sim 500 \text{ cm}^{-1}$) pellets. UV—Vis absorption spectra were recorded on a Shimadzu UV-2550 spectrometer. X-ray single crystal data were collected on a Bruker Smart 1000 CCD area detector. Uncorrected melting points were measured on a hot-plate microscope (Beijing Taike Instrument Limited Company). Molar conductance measurement was carried out on a model DDS-11D type conductivity bridge using a $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ solution in DMF at $25 \text{ }^\circ\text{C}$.

Synthesis of H₂L. H₂L was synthesized according to the method reported previously [22].

Synthesis of the Ni(II) complex. A solution of nickel(II) acetate tetrahydrate (4.0 mg, 0.015 mmol) in DMF (5 ml) was added dropwise to a solution of H₂L (5.8 mg, 0.015 mmol) in acetone (10 ml). The color of the solution immediately turned to pale-green. The mixture was allowed to stand at room temperature for about one month. When the solvent was partially evaporated, several green block-shaped single crystals suitable for X-ray crystallographic analysis were obtained, yield 28.6 %. Anal. Calc. for $\text{C}_{50}\text{H}_{62}\text{Cl}_4\text{Ni}_3\text{N}_8\text{O}_{16}$ (%): C, 44.52; H, 4.63; N, 8.31; Ni, 13.05. Found: C, 44.61; H, 4.77; N, 8.19; Ni, 13.01.

Crystal structure determination. A single crystal of the Ni(II) complex with approximate dimensions of $0.19 \times 0.15 \times 0.12 \text{ mm}$ was mounted on a Bruker Smart 1000 diffractometer equipped with an Apex CCD area detector. The diffraction data were collected using graphite monochromated MoK_α radiation ($\lambda = 0.071073 \text{ nm}$) at $298(2) \text{ K}$. The LP factor and semi-empirical absorption corrections were applied to the intensity data. The structure was solved using the SHELXS-97 program and difference Fourier techniques, and refined by full-matrix least-squares on F^2 using SHELXL-97. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added in geometrical positions. The details of data collection and refinement of the Ni(II) complex are given in Table 1. The complete crystallographic data were deposited as a CIF file in the Cambridge Structural Database (CCDC No. 757708) and are available freely upon request citing the deposition number from the web site: www.ccdc.cam.ac.uk/data_request/cif.

Analysis of FT-IR spectra. IR spectra of H₂L and the corresponding Ni(II) complex exhibit several distinguishable bands in the $400\text{--}4000 \text{ cm}^{-1}$ region. The O—H stretching frequency of the salen-type ligand is expected in the $3300\text{--}3800 \text{ cm}^{-1}$ region, but this frequency is displaced to 3424 cm^{-1} for H₂L because of the internal hydrogen bond $\text{OH} \cdots \text{N}=\text{C}$ [23]. For the Ni(II) complex, the disappearance of this band is expected due to the metal substitution for hydrogen on complexation [24]. The characteristic C=N stretching band of the free H₂L ligand appears at 1610 cm^{-1} , whereas the C=N band of the Ni(II) complex is observed at 1607 cm^{-1} [25]. The Ar—O stretching frequencies appear within $1263\text{--}1213 \text{ cm}^{-1}$ as reported for similar salen-type ligands [26]. These bands occur at 1265 cm^{-1} for H₂L and 1262 cm^{-1} for the Ni(II) complex. The weaker bands at 534 cm^{-1} and 471 cm^{-1} of the Ni(II) complex are assigned to $\nu(\text{Ni—N})$ and $\nu(\text{Ni—O})$ respectively [27, 28]. These bands are observed in the Ni(II) complex as new bands and are not present in the spectrum of the free H₂L ligand. The metal—oxygen and metal—nitrogen frequency assignments pointed out by Percy and



Thornton [29] sometimes can be ambiguous.

Analysis of UV—Vis spectra. The UV—Vis absorption spectra of H₂L and its corresponding Ni(II) complex in a diluted DMF solution are shown in Fig. 1. The UV—Vis spectrum of the free H₂L ligand exhibits two intense peaks at 270 nm and 323 nm. The former absorption peak at 270 nm can be assigned to the $\pi\text{--}\pi^*$ transition of the benzene rings, whereas the latter can be attributed to the intraligand $\pi\text{--}\pi^*$ transi-

Fig. 1. UV—Vis absorption spectra of H₂L and the Ni(II) complex in DMF ($5 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$)

Table 1

Crystal data and structure refinement for the Ni(II) complex

Empirical formula	C ₅₀ H ₆₂ Cl ₄ Ni ₃ N ₈ O ₁₆
Formula weight	1349.01
<i>T</i> , K	298(2)
Wavelength, nm	0.071073
Crystal system, space group	Triclinic, <i>P</i> -1
<i>a</i> , <i>b</i> , <i>c</i> , Å	11.297(1), 11.319(1), 12.107(2)
α , β , γ , deg.	100.255(2), 102.970(2), 94.455(1)
Volume, Å ³	1473(3)
<i>Z</i> , calculated density, g/cm ³	1, 1.521
Absorption correction, mm ⁻¹	1.202
<i>F</i> (000)	698
Crystal size, mm	0.19×0.15×0.12
θ range for data collection, deg.	1.76—25.02
Limiting indices	-13 ≤ <i>h</i> ≤ 12, -13 ≤ <i>k</i> ≤ 10, -14 ≤ <i>l</i> ≤ 14
Reflections collected / unique	7769 / 5136 [<i>R</i> _{int} = 0.0241]
Completeness to θ , deg.	98.4 % (θ = 25.02)
Absorption correction	Semi-empirical from equivalents
Max. / min. transmission	0.8691 / 0.8037
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	5136 / 0 / 372
GOOF on <i>F</i> ²	1.018
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0394, <i>wR</i> ₂ = 0.0920
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0631, <i>wR</i> ₂ = 0.1030
Largest diff. peak / hole, e/Å ⁻³)	0.633 / -0.454

tion of the C=N bonds [30]. The absorption peak of the free ligand at 270 nm shifts to the low energy region by *ca.* 5 nm in the Ni(II) complex, indicating the coordination of Ni(II) ions with L²⁻ units. The absorption peak of the free ligand at 323 nm is absent in the Ni(II) complex. Meanwhile, a new moderate absorption peak is observed at 368 nm in the Ni(II) complex, which is assigned to the *n*— π^* charge transfer transition.

Determination of molar conductance. The Ni(II) complex is soluble in DMF, DMSO, but not soluble in ethanol, methanol, acetonitrile, acetone, THF, ethyl acetate, and hexane. The molar conductance value of the Ni(II) complex at 25 °C in 10⁻³ mol·l⁻¹ DMF solution is 17.1 $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$, indicating that the Ni(II) complex is non-electrolyte. This implies that in solution all acetate groups in the Ni(II) complex are always held in the coordination sphere, as in the solid state.

RESULTS AND DISCUSSION

Crystal structure description. X-ray crystallographic analysis reveals the crystal structure of the Ni(II) complex. Selected bond lengths and angles are summarized in Table 2. The ORTEP representation of the Ni(II) complex is shown in Fig. 2. The Ni(II) complex crystallizes in the triclinic system, space group *P*-1, and consists of three Ni(II) ions, two tetradentate (μ -L)²⁻ units, two coordinated μ -acetate ions, and two crystallization DMF molecules. The Ni(1) atom of the molecule of the Ni(II) complex lies on the inversion center giving 1/2 of the molecule per asymmetric unit. The Ni(II) complex involves three six-coordinated Ni(II) ions; the two Ni(II) centers (Ni(1) and Ni(2)) are linked by two oxygen (O(6) and O(5)) atoms from one acetate ion and two phenoxo oxygen atoms (O(4) and O(3)) of one tetradentate L²⁻ dianion, forming a μ -acetato(O,O')-bis(μ -phenoxo) bridged Ni(1)—Ni(2) motif.

Selected bond lengths (Å) and bond angles (deg.) for the Ni(II) complex

Bond lengths					
Ni(2)—O(3)	2.009(2)	Ni(2)—O(5)	2.024(2)	Ni(2)—O(4)	2.027(2)
Ni(2)—N(1)	2.043(3)	Ni(2)—N(2)	2.066(3)	Ni(2)—O(7)	2.164(2)
Ni(1)—O(6) [#]	2.033(2)	Ni(1)—O(6)	2.033(2)	Ni(1)—O(3)	2.105(2)
Ni(1)—O(3) [#]	2.105(2)	Ni(1)—O(4) [#]	2.088(2)	Ni(1)—O(4)	2.088(2)

Bond angles					
O(3)—Ni(2)—O(5)	90.89(9)	O(3)—Ni(2)—O(4)	82.89(9)	O(5)—Ni(2)—O(4)	91.71(9)
O(3)—Ni(2)—N(1)	88.3(1)	O(5)—Ni(2)—N(1)	94.1(1)	O(4)—Ni(2)—N(1)	169.5(1)
O(3)—Ni(2)—N(2)	169.2(1)	O(5)—Ni(2)—N(2)	92.4(1)	N(1)—Ni(2)—N(2)	101.7(1)
N(1)—Ni(2)—N(2)	101.7(1)	O(3)—Ni(2)—O(7)	91.99(9)	O(5)—Ni(2)—O(7)	176.84(9)
O(4)—Ni(2)—O(7)	89.93(9)	N(1)—Ni(2)—O(7)	84.7(1)	N(2)—Ni(2)—O(7)	85.0(1)
O(6) [#] —Ni(1)—O(6)	180.000	O(6) [#] —Ni(1)—O(3)	89.89(9)	O(6)—Ni(1)—O(3)	90.11(9)
O(6) [#] —Ni(1)—O(3) [#]	90.11(9)	O(6)—Ni(1)—O(3) [#]	89.89(9)	O(3)—Ni(1)—O(3) [#]	180.000
O(6) [#] —Ni(1)—O(4)	92.36(9)	O(6)—Ni(1)—O(4)	87.64(9)	O(4)—Ni(1)—O(3) [#]	100.85(8)
O(3)—Ni(1)—O(4)	79.15(8)	O(6) [#] —Ni(1)—O(4) [#]	87.64(9)	O(6)—Ni(1)—O(4) [#]	92.36(9)
O(4) [#] —Ni(1)—O(3) [#]	79.15(8)	O(4) [#] —Ni(1)—O(3)	100.85(8)	O(4)—Ni(1)—O(4) [#]	180.000

Symmetry transformations used to generate equivalent atoms: [#] $-x+3, -y+3, -z+1$.

All hexacoordinated Ni(II) ions of the Ni(II) complex have a slightly distorted octahedral coordination polyhedron. The terminal Ni(2) ion is located between the N₂O₂ donor atoms of the L²⁻ unit. The O(5) atom from the μ -acetato bridge and the O(7) atom from the DMF molecule are also coordinated to the Ni(2) ion. The dihedral angle between the coordination plane of O(3)—Ni(2)—N(1) and that of O(4)—Ni(2)—N(2) is about 6.76(2)°, indicating a slight distortion of the coordination square. The Ni(2)—N(2) bond (2.067(4) Å) is slightly longer than the Ni(2)—N(1) bond (2.043(4) Å), which may be attributed to steric hindrance caused by the DMF molecule coordinated to the terminal Ni(2) ion. The equatorial plane of Ni(2) is defined by N(1), N(2), O(3), and O(4) atoms with a 0.084(2) Å

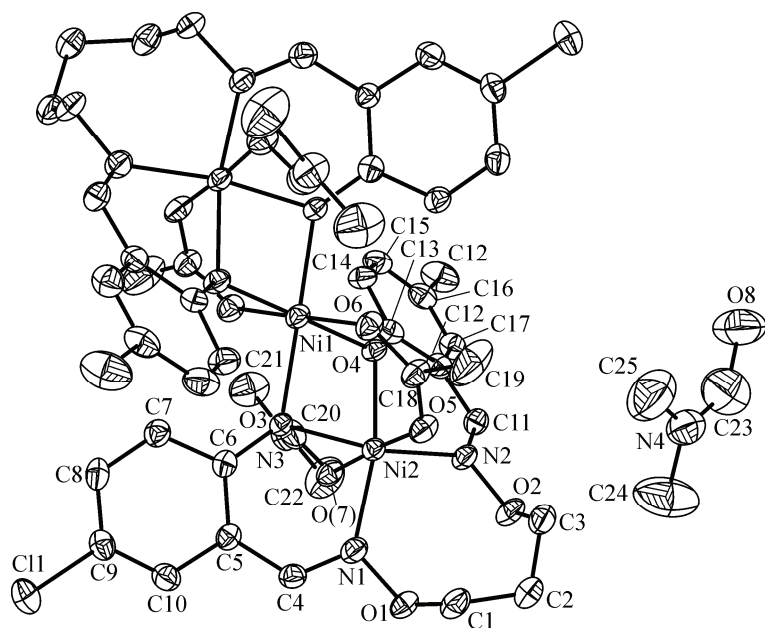


Fig. 2. Molecular structure of the Ni(II) complex with atom numbering

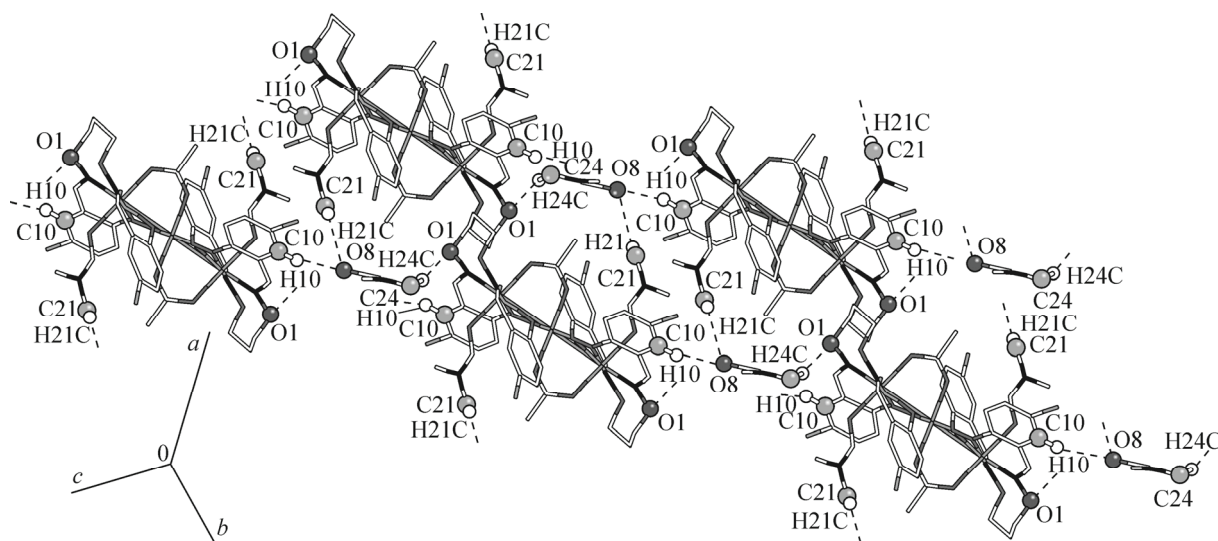


Fig. 3. Diagram illustrating the self-assembled network structure resulting from C—H···O interactions

Table 3

Hydrogen bonding distances (Å) and bond angles (deg.) for the Ni(II) complex

D—H···A	$d(\text{D—H})$	$d(\text{H···A})$	$d(\text{D···A})$	$\angle\text{DHA}$
C(21)—H(21C)···O(8)	0.960	2.715	3.301(1)	119.98
C(10)—H(10)···O(8)	0.929	2.467	3.291(9)	145.81
C(24)—H(24C)···O(1)	0.961	2.453	3.381(3)	162.48

deviation of Ni(2); the apical positions are occupied by O(5) of the acetate and O(7) of DMF. So, the three Ni(II) ions are six-coordinated and the trinuclear structure is probably stabilized by two μ -acetato ligands that neutralize the whole charge of the Ni(II) complex. The intramolecular Ni(1)···Ni(2) separation is 3.062(3) Å, which is not sufficiently short to imply weak metal—metal bonding interactions.

The special feature of the Ni(II) complex is its self-assembling by intermolecular hydrogen bonds (Fig. 3). The hydrogen bond data are summarized in Table 3. In the crystal structure, intermolecular C(21)—H(21C)···O(8), C(10)—H(10)···O(8), and C(24)—H(24C)···O(1) hydrogen bonds are formed. C(21)—H(21C)···O(8), C(10)—H(10)···O(8) are formed between the O(8) atom of the solvate DMF molecule and the methyl group (—C(21)H(21C)) of coordinated DMF of the Ni(II) complex, and methylene (—C(10)H(10)) of the benzene ring of the L^{2-} unit of another neighboring Ni(II) complex molecule respectively. Simultaneously, the —C(24)H(24C) methyl group of the solvate DMF molecule is hydrogen-bonded to the oxime O(1) atom of the L^{2-} unit of the third Ni(II) complex molecule. The crystal packing of the Ni(II) complex shows that a notable feature of this structure is the formation of an infinite 2D layered supramolecular structure in the crystallographic bc plane through intermolecular C—H···O hydrogen bond interactions.

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