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Synthesis and Crystal Structure of a Novel Tri-Nuclear Nickel(II) Complex Derived from N,N'-(2-Hydroxypropane-1,3-diyl)bis(salicylaldimine)[1]

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Abstract—A novel tri-nuclear nickel(II) complex, $[Ni_3L_2(\mu_2\text{-}\eta^1{:}\eta^1\text{-OAc})_2(\mu_1\text{-}\eta^1{:}\eta^0\text{-OAc})_2] \cdot H_2O$ (H_2L is N,N'-(2-hydroxypropane-1,3-diyl)-*bis*(salicylaldimine), was prepared. The complex was characterized by elemental analysis, IR spectra, and single crystal X-ray determination (CIF file CCDC no. 993163). Crystal of the complex crystallizes in the monoclinic space group $P2_1/n$. The unit cell parameters: a = 12.5602(9), b = 13.2104(10), c = 15.0329(10) Å, β = 113.194(2)°, V = 2292.7(3) Å^3, Z = 2, R_1 = 0.0506, wR_2 = 0.1342, S = 1.067. The complex possesses crystallographic inversion center symmetry. The Ni atoms are in octahedral coordination spheres. The Ni···Ni distances are 3.022(1) Å.

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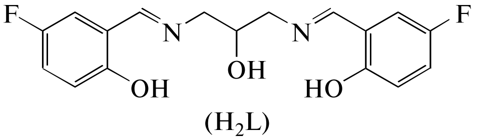
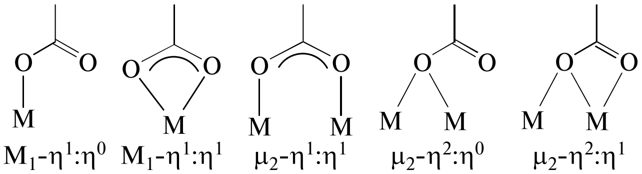
INTRODUCTION

Transition metal complexes with Schiff bases are considered to be among the most important stereochemical models in coordination chemistry due to their preparative accessibility and structural variety [1–3]. Polynuclear complexes with some transition metal atoms usually possess interesting magnetic properties [4–7]. The best way to construct polynuclear complexes is to use bridging ligands, such as multi-carboxylates, multi-pyridines, pseudohalide anions, etc [8–11]. Acetate anion comes from metal salts is also a potential bridging group. It can bind to metal atoms through a variety of coordination modes such as monodentate, chelating, bidentate bridging, monoatomic bridging, and chelating bridging (scheme) [7, 12–16]. In the present paper, a novel tri-nuclear nickel(II) complex, $[Ni_3L_2(\mu_2\text{-}\eta^1{:}\eta^1\text{-OAc})_2(\mu_1\text{-}\eta^1{:}\eta^0\text{-OAc})_2] \cdot H_2O$ (H_2L is N,N’-(2-hydroxypropane-1,3-diyl)bis(salicylaldimine), was prepared and characterized.



(H_2L)

Coordination modes of acetate anion in complex I are looked:



EXPERIMENTAL

Materials and methods. 5-Fluorosalicylaldehyde and 1,3-diaminopropane-2-ol were purchased from Alfa Aesar. All other chemicals and solvents were of analytical grade and used as obtained. Microanalyses of the Schiff base and the nickel complex were performed with a Vario EL III CHNOS elemental analyzer. The infrared spectra were recorded as KBr pellets with an FTS-40 spectrophotometer.

Synthesis of H_2L. A stirred solution of 5-fluorosalicylaldehyde (0.28 g, 2 mmol) and 1,3-diaminopropane-2-ol (0.09 g, 1 mmol) in absolute methanol (20 mL) was mixed and stirred at reflux for 1 h. After cooling to room temperature, yellow crystalline product of the Schiff base was formed. The solid was obtained by filtration and dried in air. The yield was 0.23 g (69%).

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Selected IR data (KBr; ν_{max}, cm^{-1}): 3273 ν(OH), 1637 ν(C=N).

For $C_{17}H_{18}F_2N_2O_3$

anal. calcd., %:	C, 61.07;	H, 4.82;	N, 8.38.
Found, %:	C, 60.89;	H, 4.95;	N, 8.27.

Synthesis of complex I. A stirred solution of H_2L (33.4 mg, 0.1 mmol) in absolute methanol (20 mL) was mixed with nickel acetate tetrahydrate (50.0 mg, 0.2 mmol), and the resulting reaction mixture was refluxed on a water bath for 1 h and then cooled to room temperature, yielding a green solution. The solution was stand still at ambient temperature to slow evaporate of the solvent, yielding green crystals of the complex. The yield was 17 mg (31%, based on H_2L).

Selected IR data (KBr; ν_{max}, cm^{-1}): 3412 ν(OH), 1618 ν(C=N), 1597 ν_{as}(OCO), 1418 ν_{s}(OCO).

For $C_{42}H_{42}F_4N_4O_{14}Ni_3$

anal. calcd., %:	C, 46.76;	H, 3.92;	N, 5.19.
Found, %:	C, 46.54;	H, 4.05;	N, 5.27.

X-ray structure determination. Data were collected on a Bruker SMART 1000 CCD area diffractometer using a graphite monochromator and MoK_α radiation (λ = 0.71073 Å) at 298(2) K. The data were corrected with the SADABS programs and refined on F^2 with the Siemens SHELXL software [17, 18]. The structure of the complex was solved by direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and included in the last cycle of refinement. The C(8)–C(9)–C(10)–O(7) moiety of the Schiff base ligand is disordered over two site, with occupancies of 0.52 and 0.48. A summary of the crystallographic data and structure refinement are shown in Table 1. Selected coordination bond lengths and angles are listed in Table 2.

Supplementary material for the structure has been deposited with the Cambridge Crystallographic Data Centre (no. 993163; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Table 1. Crystallographic data and structure refinement for complex I

Parameters	Value
Formula weight	1079
Crystal system	Monoclinic
Space group	$P2_1/n$
Crystal size, mm	0.20 × 0.17 × 0.17
a, Å	12.5602 (9)
b, Å	13.2104 (10)
c, Å	15.0329 (10)
β, deg	113.194 (2)
V, Å^3	2292.7 (3)
Z	2
ρ_{calcd}, g cm^{-3}	1.563
μ, mm^{-1}	1.305
F(000)	1108
θ Range, deg	3.1–25.7
Index ranges	$-13 \le h \le 15$ $-16 \le k \le 16$ $-18 \le l \le 16$
Measured reflections	20460
Independent reflections (R_{int})	4252 (0.0333)
Observed reflections ($I > 2\sigma(I)$)	3096
Parameters	342
Restraints	35
Absorption correction	multi-scan
GOOF on F^2	1.067
R ($I \ge 2\sigma(I)$)	$R_1 = 0.0506$, $wR2 = 0.1342$
R (all data)	$R_1 = 0.0772$, $wR2 = 0.1558$
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.786/–0.332

RESULTS AND DISCUSSION

The molecular structure of I is shown in Fig. 1. The compound possesses crystallographic inversion center symmetry, with the inversion center located at the Ni(2) atom position. The compound contains a trinuclear nickel complex and one disordered water molecule. The Schiff base ligand coordinate to the Ni atoms through phenolate oxygen and imino nitrogen. The dihedral angle between the two benzene rings of the Schiff base ligand is 57.3(3)°. The acetate ligands adopt two coordination modes in the complex, *viz.* M_1-η^1:η^0 and M_2-η^1:η^1.

The outer Ni(1) atom is coordinated by two N and two O atoms of the Schiff base ligand, and two O atoms respectively from one M_1-η^1:η^0 acetate ligand and one M_2-η^1:η^1 acetate ligand. The displacement of the Ni atom from the least-squares plane defined by the four donor atoms of the Schiff base ligand is 0.061(2) Å, indicating the well planarity of the equatorial plane of the coordination sphere. The bond lengths related to Ni(1) atom in the complex are comparable to those observed in nickel(II) complexes with Schiff bases [19, 20]. The slight distortion of the octahedral coordination sphere can also be observed from the bond angles. The *cis* coordinate bond angles are in the range

Table 2. Selected bond lengths (Å) and angles (deg) for **I***

Bond	*d*, Å	Bond	*d*, Å
Ni(l)–O(1)	1.995(3)	Ni(l)–O(2)	1.998(3)
Ni(l)–N(1)	2.023(4)	Ni(l)–N(2)	2.016(4)
Ni(l)–O(3)	2.177(4)	Ni(l)–O(5)	2.067(4)
Ni(2)–O(6)	2.045(3)	Ni(2)–O(1)	2.059(3)
Ni(2)–O(2)	2.067(3)		
Angle	**ω, deg**	**Angle**	**ω, deg**
O(l)Ni(l)O(2)	82.73(11)	O(l)Ni(l)N(2)	173.12(14)
O(2)Ni(l)N(2)	90.83(13)	O(l)Ni(l)N(l)	90.10(14)
O(2)Ni(l)N(l)	171.70(15)	N(2)Ni(l)N(l)	96.13(16)
O(l)Ni(l)O(5)	91.59(13)	O(2)Ni(1)O(5)	90.28(14)
N(2)Ni(l)O(5)	90.85(15)	N(l)Ni(1)O(5)	94.11(17)
O(l)Ni(l)O(3)	92.57(14)	O(2)Ni(l)O(3)	90.34(15)
N(2)Ni(l)O(3)	85.03(16)	N(l)Ni(l)O(3)	85.79(18)
O(5)Ni(l)O(3)	175.84(14)	O(6)Ni(2)O(6*A*)	180
O(6)Ni(2)O(1*A*)	90.83(13)	O(6)Ni(2)O(l)	89.17(13)
O(1)Ni(2)O(1*A*)	180	O(6)Ni(2)O(2*A*)	90.07(12)
O(1)Ni(2)O(2*A*)	100.48(11)	O(6)Ni(2)O(2)	89.93(12)
O(1)Ni(2)O(2*A*)	79.52(11)	O(2)Ni(2)O(2*A*)	180

*Symmetry operation for the related atoms labeled with the suffix: (*A*) $2 - x$, $1 - y$, $-z$.

82.73(11)°–96.13(16)°, and the *trans* bond angles are in the range 171.70(15)°–175.84(14)°.

The inner Ni(2) atom is coordinated by four O atoms from two Schiff base ligands, and two O atoms from two M_2-η^1:η^1 acetate ligands. The Ni atom is located at the least-squares plane defined by the four donor atoms of the Schiff base ligands, due to the inversion center symmetry. The bond lengths related to Ni(2) atom in the complex are comparable to those observed in nickel(II) complexes with Schiff bases [21, 22]. The slight distortion of the octahedral coordination sphere can also be observed from the bond angles. The *cis* coordinate bond angles are in the range 79.52(11)°–90.83(13)°, and the *trans* bond angles are exactly 180°.

In the crystal structure of the complex (Fig. 2), the nickel complex molecules and water molecules are linked through O(7)–H(7*A*)···O(8) hydrogen bonds (O(7)–H(7*A*) 0.82, H(7*A*)···O(8) 2.02, O(7)···O(8) 2.785(16)°, O(7)–H(7*A*)···O(8) 154°), and stack along the *y*-axis direction *via* weak π···π interactions. The distance and dihedral angle between the centroids C(1)–C(6) and C(12)–C(17) are 4.871 Å and 57°, respectively.

IR spectroscopy is one of the useful techniques used to assign the acetate coordination modes. The IR spectrum of complex I revealed a medium broad band centered at 3412 cm^{-1}, indicating the presence of water molecules in the crystal lattice. The complex revealed an intense band at 1618 cm^{-1}, indicating the presence of C=N groups. The complex also revealed a strong band at 1597 cm^{-1} with two shoulders at 1575 and 1568 cm^{-1} for ν_{as}(OCO) and a strong band at 1418 cm^{-1} with a shoulder at 1390 cm^{-1} for ν_s(OCO). The Δν value of 207 cm^{-1} is higher than that reported for sodium acetate ($\Delta\nu = 164$ cm^{-1}) [16], thus indicates a monodentate acetate coordination mode. The Δν value of 185 cm^{-1} can be assigned to the *syn-syn*

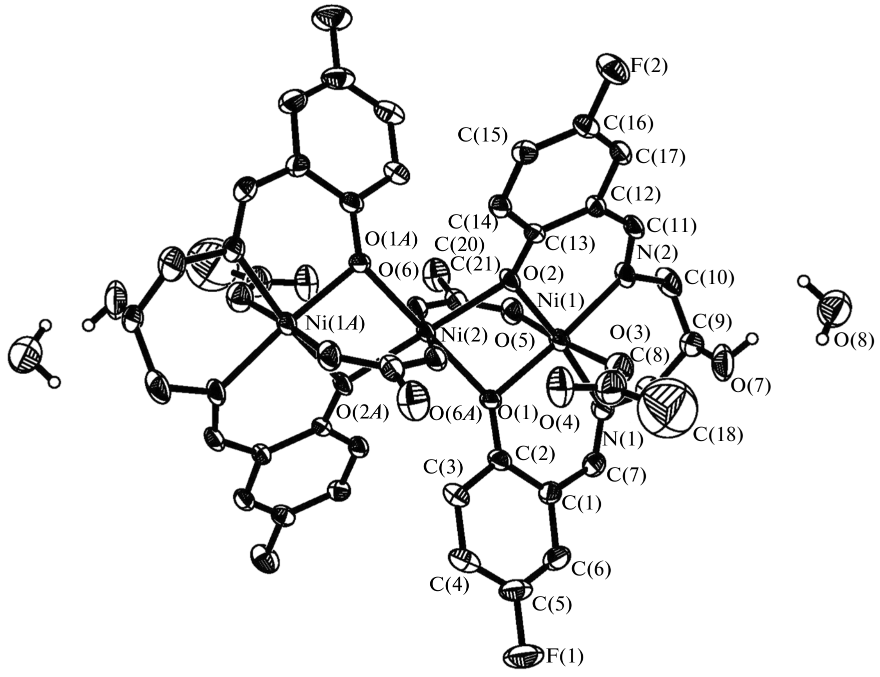

Fig. 1. ORTEP plots (30% probability level) and the numbering scheme for the complex. Only the major component of the disordered C(8)–C(9)–C(10)–O(7) moiety is shown.

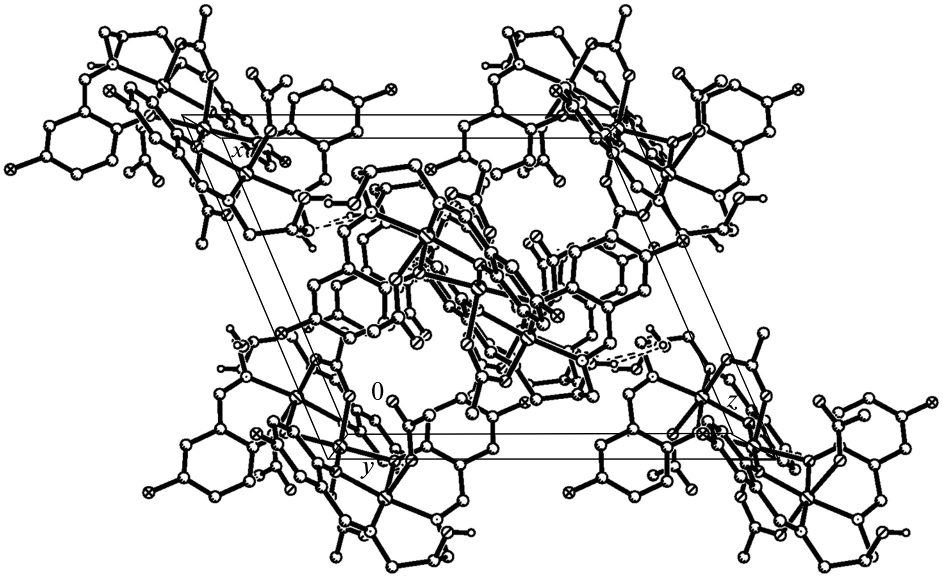

Fig. 2. Molecular packing diagram for the complex viewed along the *y* axis.

bidentate bridging coordination mode, and the other Δν value of 150 cm^{-1} can be assigned to the *syn-anti* bidentate bridging coordination mode.

Thus, a novel centrosymmetric acetate- and phenolate-bridged trinuclear nickel(II) complex with *bis*-Schiff base ligand N,N'-(2-hydroxypropane-1,3-diyl)-*bis*(salicylaldimine) has been prepared and characterized. The complex may be used as an interesting magnetic material or biological agent, which can be studied further.

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