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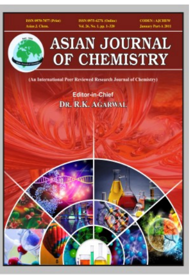

Synthesis and Crystal Structure of New Trinuclear Nickel(II) Complex $\{[(NiL)_2(OAc)_2Ni]\cdot n\text{-}BuOH\cdot CHCl_3\}_2\cdot n\text{-}BuOH$

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A new trinuclear nickel(II) complex with a Salen-type bisoxime chelating ligand (H_2L), $\{[(NiL)_2(OAc)_2Ni]\cdot n\text{-}BuOH\cdot CHCl_3\}_2\cdot n\text{-}BuOH$, has been synthesized and characterized. The X-ray crystal structure of the Ni(II) complex reveals that the unit cell contains two crystallographically independent but chemical identical trinuclear Ni(II) complexes, molecules A and B. Interestingly, the complex possessing different conformational metal centers: penta- and hexa-coordinated geometry. The coordination geometry around the terminal Ni2 and Ni2$^{\#1}$ atom in molecule A (Ni4 and Ni4$^{\#}$ in molecule B) approaches a distorted square pyramid. The coordination sphere of the central Ni1 atom in molecule A (Ni3 in molecule B) constitutes a slightly distorted octahedral geometry.

Keywords: Ni(II) complex, Bisoxime ligand, Synthesis, Crystal structure.

INTRODUCTION

Salen-type bisoxime ligands and their complexes have attracted much attention in recent years for their novel structures and spectral characteristics[1,2], especially for their excellent photoluminescence[3] and interesting magnetic[4] properties. To the best of our knowledge, in many syntheses of nickel complexes[5-7], tri-nickel complexes have been determined and the coordination number of nickel(II) atoms is generally six and the coordination geometry around the nickel(II) atoms is octahedron. Herein, a trinuclear Ni(II) complex, namely $\{[(NiL)_2(OAc)_2Ni]\cdot n\text{-}BuOH\cdot CHCl_3\}_2\cdot n\text{-}BuOH$, was synthesized and characterized. X-Ray crystallographic analysis reveals that the structure of the Ni(II) complex is pseudo-isostructural, in that they are both trinuclear, with two acetate ions coordinated to three Ni(II) atoms through Ni-O-C-O-Ni bridges and four μ-phenoxo oxygen atoms from two [NiL] units also coordinated to Ni(II) atoms.

EXPERIMENTAL

4-Methoxy-2-hydroxybenzaldehyde (≥ 98 %) and 1,2-dibromoethane were purchased from Alfa Aesar and used without further purification. 1,2-*Bis*(aminooxy)ethane was synthesized according to an analogous method reported earlier[3]. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory and were used without further purification. Elemental analysis for Ni was detected by 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.

General procedure: The ligand H_2L was synthesized with a slightly modified method reported literature[8]. Reaction of 1,2-*bis*(aminooxy)ethane (133.7 mg, 1.45 mmol) with 2 equivalents of 4-methoxysalicylaldehyde (456 mg, 3 mmol) in ethanol (10 mL) at 55 ºC for 6 h. After cooling to room temperature, the resulting solid was filtered and washed successively with ethanol and ethanol/hexane (1:4). The product was dried *in vacuo* and obtained the colourless microcrystal. Yield: 78.9 %. m.p. 97-98 ºC. ^1H NMR (400 MHz, $CDCl_3$), δ 3.79 (s, 6H), 4.41 (s, 4H), 6.46 (d, $J = 2.8$ Hz, 2H), 6.47 (s, 2H), 7.04 (d, $J = 2.8$ Hz 2H), 8.17 (s, 2H), 9.94 (s, 2H). Anal. calcd. (%) for $C_{18}H_{20}N_2O_6$ (H_2L): C, 59.99; H, 5.59; N, 7.77. Found (%): C, 59.96; H, 5.85; N, 7.65.

The Ni(II) complex was synthesized as follows: A solution of $Ni(OAc)_2\cdot 4H_2O$ (4.2 mg, 0.015 mmol) in *n*-butanol (3 mL) was added dropwise to a solution of H_2L (6.2 mg, 0.016 mmol) in chloroform (3 mL) at room temperature. Vapour phase diffusion of *n*-hexane into the solution afforded green block-like crystals of the Ni(II) complex. Anal. calcd. (%) for $C_{94}H_{116}N_8O_{35}Cl_6Ni_6$: C, 45.47; H, 4.71; N, 4.51; Ni, 14.18. Found (%): C, 46.18; H, 4.85; N, 4.49; Ni, 14.05.

X-Ray structure determination: The single crystal of the Ni(II) complex with approximate dimensions of 0.47 mm × 0.45 mm × 0.42 mm was placed on a Bruker Smart 1000 diffractmeter equipped with Apex CCD area detector. The diffraction data were collected using a graphite monochromated

MoK$_\alpha$ radition (λ = 0.71073 Å) at 298(2) K. The structure was solved by using the program SHELXS-97[9] and Fourier difference techniques and refined by full-matrix least-squares method on F^2 using SHELXL-97[10]. Details of the data collection and refinements of the Ni(II) complex are given in Table-1. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically. CCDC No.: 909427.

RESULTS AND DISCUSSION

X-Ray crystallographic analysis of the Ni(II) complex reveals a symmetric trinuclear structure. It crystallizes in the triclinic system, space group P-1 and the unit cell contains two crystallographically independent but chemical identical trinuclear complexs, molecules A and B. Both molecules A and B consist of three nickel(II) atoms, two L^{2-} units, two acetate ions, one crystallizing chloroform and one and a half crystallizing *n*-butanol molecules. The molecular structure of the Ni(II) complex is shown in Fig. 1. Selected bond distances and angles are listed in Table-2. In molecule A, the terminal Ni(II) (Ni2) atom is five-coordinated by two nitrogen (N1 and N2) atoms and two oxygen (O3 and O5) atoms in the N$_2$O$_2$ moieties of the ligand and one oxygen (O7) atom from the bridging acetate anion. Consequently, around Ni2 atom is slightly distorted square pyramid geometry. In addition, the central nickel (Ni1) coordination sphere is completed by four μ-phenoxo oxygen (O3, O5, O3$^{\#1}$ and O5$^{\#1}$) atoms from two [NiL] chelates and both of oxygen (O8 and O8$^{\#1}$) atoms from two acetate anions which adopts a familiar μO-C-O fashion[11] and constitute slightly distorted octahedral geometry. Compared with molecule A, molecule B is similar in the structural features but distinct in some bond distances and angles. Furthermore, the trinuclear structure is stabilized by two μ-acetato ligands, which neutralize the whole charge of the Ni(II) complex.

TABLE-1
CRYSTAL DATA AND REFINEMENT PARAMETERS FOR THE Ni(II) COMPLEX

Empirical formula	$C_{94}H_{116}N_8O_{35}Cl_6Ni_6$
Formula weight	2482.91
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Cell dimensions	a = 11.3988(11) Å, b = 13.4488(13) Å, c = 18.5332(18) Å, α = 93.8170(10)°, β = 96.3280(10)°, γ = 100.039(2)°
Volume	2769.9(5) Å^3
Z	1
Density (calculated)	1.488 mg/m^3
Absorption coefficient	1.225 mm^{-1}
$F_{(000)}$	1286
Index ranges	$-12 \le h \le 13, -15 \le k \le 15, -22 \le l \le 20$
Reflections collected	14259
Independent reflections	9533 [R_{int} = 0.0291]
Data/restraints/parameters	9533/0/781
Goodness of fit indicator	1.045
Final R indices [I > 3σ(I)]	R_1 = 0.0587, wR_2 = 0.1016
R indices (all data)	R_1 = 0.0815, wR_2 = 0.1208
Largest diff. peak and hole	0.489 and -0.440 e Å^{-3}

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR THE Ni(II) COMPLEX

Atom	Distance	Atom	Distance	Atom	Distance
Ni1-O8	2.032(7)	Ni2-O7	2.015(8)	Ni3-O12$^{\#2}$	2.076(1)
Ni1-O8$^{\#1}$	2.032(7)	Ni2-N1	2.035(9)	Ni4-O14	1.970(1)
Ni1-O3	2.094(6)	Ni2-N2	2.035(1)	Ni4-O12	1.983(1)
Ni1-O3$^{\#1}$	2.094(6)	Ni3-O16$^{\#2}$	2.015(1)	Ni4-N4	2.017(1)
Ni1-O5$^{\#1}$	2.116(7)	Ni3-O16	2.015(1)	Ni4-O17	2.023(1)
Ni1-O5	2.116(7)	Ni3-O14$^{\#2}$	2.068(1)	Ni4-N3	2.047(1)
Ni2-O5	2.003(7)	Ni3-O14	2.068(1)	Ni3-O12	2.076(1)
Ni2-O3	2.012(7)	–	–	–	–
Atom	Angle	Atom	Angle	Atom	Angle
O8-Ni1-O8$^{\#1}$	180.0(4)	O5-Ni2-O3	83.2(3)	O16$^{\#2}$-Ni3-O16	180.00
O8-Ni1-O3	89.5(3)	O5-Ni2-O7	94.7(3)	O16$^{\#2}$-Ni3-O14$^{\#2}$	89.6(5)
O8$^{\#1}$-Ni1-O3	90.5(3)	O3-Ni2-O7	91.9(3)	O16-Ni3-O14$^{\#2}$	90.4(5)
O8-Ni1-O3$^{\#1}$	90.5(3)	O5-Ni2-N1	163.9(4)	O16$^{\#2}$-Ni3-O14	90.4(5)
O8$^{\#1}$-Ni1-O3$^{\#1}$	89.5(3)	O3-Ni2-N1	89.3(3)	O16-Ni3-O14	89.6(5)
O3-Ni1-O3$^{\#1}$	180.00	O7-Ni2-N1	99.8(4)	O14$^{\#2}$-Ni3-O14	180.0(4)
O8-Ni1-O5$^{\#1}$	91.1(3)	O5-Ni2-N2	88.5(3)	O16$^{\#2}$-Ni3-O12	90.9(4)
O8$^{\#1}$-Ni1-O5$^{\#1}$	88.9(3)	O3-Ni2-N2	169.5(4)	O16-Ni3-O12	89.1(4)
O3-Ni1-O5$^{\#1}$	101.5(3)	O7-Ni2-N2	95.2(4)	O14$^{\#2}$-Ni3-O12	102.5(5)
O3$^{\#1}$-Ni1-O5$^{\#1}$	78.5(3)	N1-Ni2-N2	97.1(4)	O14-Ni3-O12	77.5(5)
O8-Ni1-O5	88.9(3)	O14-Ni4-O12	82.0(5)	O16$^{\#2}$-Ni3-O12$^{\#2}$	89.1(4)
O8$^{\#1}$-Ni1-O5	91.1(3)	O14-Ni4-N4	89.4(6)	O16-Ni3-O12$^{\#2}$	90.9(4)
O3-Ni1-O5	78.5(3)	O12-Ni4-N4	164.3(6)	O14$^{\#2}$-Ni3-O12$^{\#2}$	77.5(5)
O3$^{\#1}$-Ni1-O5	101.5(3)	O14-Ni4-O17	91.6(5)	O14-Ni3-O12$^{\#2}$	102.5(5)
O5$^{\#1}$-Ni1-O5	180.0(2)	O12-Ni4-O17	93.9(5)	O12-Ni3-O12$^{\#2}$	180.00
N4-Ni4-O17	99.4(6)	N4-Ni4-N3	98.4(6)	O12-Ni4-O18	78.4(8)
O14-Ni4-N3	169.2(5)	O17-Ni4-N3	94.6(6)	N4-Ni4-O18	88.2(8)
O12-Ni4-N3	88.7(5)	O14-Ni4-O18	87.6(7)	O17-Ni4-O18	172.3(7)
N3-Ni4-O18	85.1(7)	Ni2-O3-Ni1	95.8(3)	Ni2-O5-Ni1	95.4(3)
Ni4-O12-Ni3	96.6(5)	Ni4-O14-Ni3	97.3(5)	–	–

Symmetry transformations used to generate equivalent atoms: $^{\#1}$-x+1,-y+1,-z+1; $^{\#2}$-x+2,-y+2,-z.

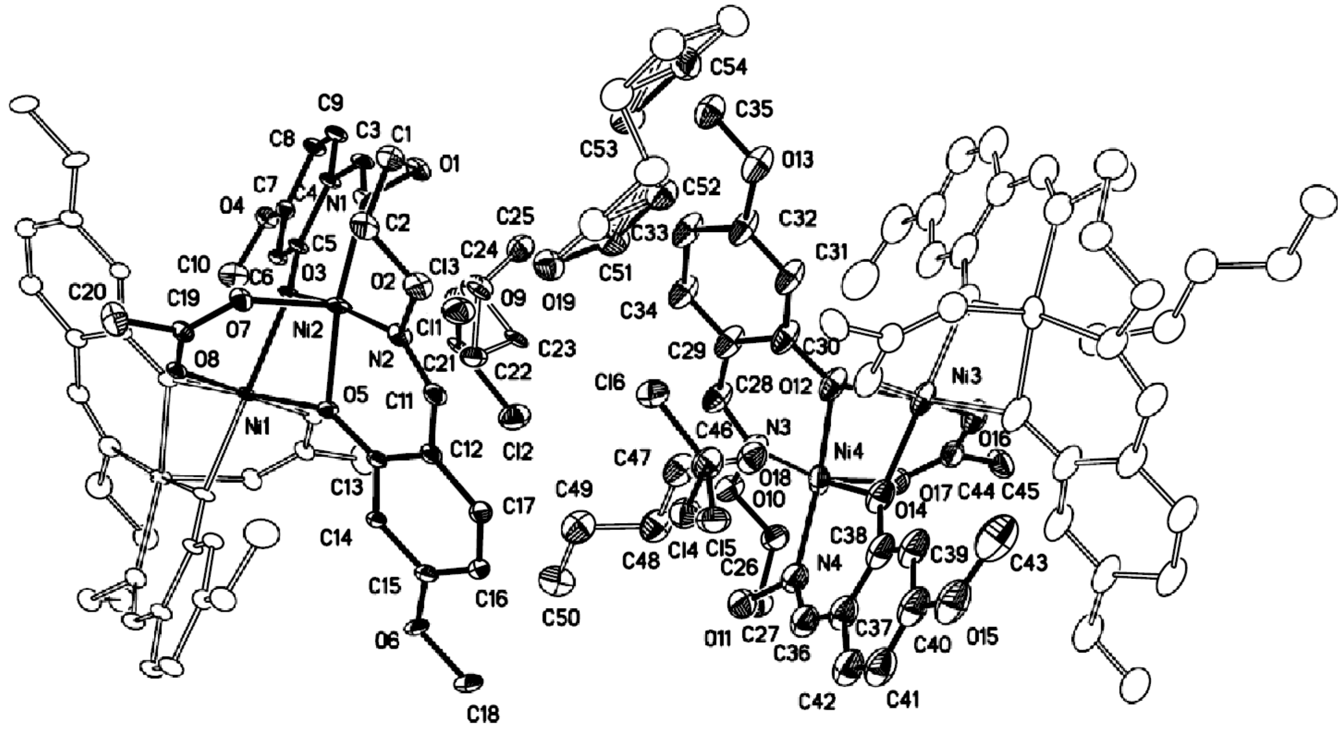

Fig. 1. Molecular structure of the Ni(II) complex

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REFERENCES

1. S. Akine, T. Taniguchi and T. Nabeshima, *Chem. Lett.*, **30**, 682 (2001).
2. L. Xu, Y.P. Zhang and Y.X. Sun, *Chin. J. Inorg. Chem.*, **23**, 1999 (2007).
3. W.K. Dong and Y.J. Ding, *Cryst. Res. Technol.*, **43**, 321 (2008).
4. S. Akine, W.K. Dong and T. Nabeshima, *Inorg. Chem.*, **45**, 4677 (2006).
5. W.K. Dong, J.G. Duan and G.L. Liu, *Transition Met. Chem.*, **32**, 702 (2007).
6. J. Reglinski, S. Morris and D.E. Stevenson, *Polyhedron*, **21**, 2167 (2002).
7. W.K. Dong, Y.X. Sun, C.Y. Zhao, X.Y. Dong and L. Xu, *Polyhedron*, **29**, 2087 (2010).
8. W.K. Dong, L. Li, C.F. Li, L. Xu and J.G. Duan, *Spectrochim. Acta A*, **71**, 650 (2008).
9. G.M. Sheldrick, SHELXS97, Program for Crystal Structure Determination, University of Göttingen, Germany (1996).
10. G.M. Sheldrick, *Acta Crystallogr. A*, **A64**, 112 (2008).
11. W.K. Dong, J.G. Duan, L.Q. Chai, G.L. Liu and H.L. Wu, *J. Coord. Chem.*, **61**, 1306 (2008).