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NOTE

Synthesis, Structure and Characterization of the Oxo-Bridged Binuclear Nickel(II) Complex $\{[Ni_2(C_6H_4NO_2)_4]O\cdot 1.5H_2O\}_n$

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The novel coordination polymer with the molecular formula $\{[Ni_2(C_6H_4NO_2)_4]O\cdot 1.5H_2O\}_n$ was obtained by self-assembly and the structure was determined by X-ray crystallography. Two Ni atoms bridged with oxygen atoms form a non-linear complex. The analytical conclusions reveal that nicotinic acid adopts two coordination modes: μ_2-nic-N, O and μ_3-nic-N, O, O and two octahedral coordinated nickel(II) atoms bridged with oxygen.

Key Words: Ni(II) complexes, Nicotinate, Crystal structure.

Recently, great effort has been devoted to the self-assembly of organic and inorganic molecules in the solid state because it extends the range of new solids with desirable physical and chemical properties[1,2]. The range and variety of self-assembled inorganic structures can be constructed relies on suitable metal-ligand interactions and hydrogen bondings and the various types of polymeric structures include 1-D, 2-D and 3-D network stuctures[3,4]. Carboxylate ligands are advantageous due to their ability to engage in diverse bonding modes, allowing wide structural diversity[5,6].

Elemental analysis was carried out on a Carlo Erba 1106 full-automatic trace organic elemental analyzer.

Synthesis of $\{[Ni_2(C_6H_4NO_2)_4]O\cdot 1.5H_2O\}_n$: A mixture of $NiCl_2\cdot 6H_2O$ (0.236 g, 1 mmol), nicotinic acid (0.332 g, 2 mmol), NaOH (0.8 g, 2 mmol) and distilled water (18 mL) was heated in a 25 mL stainless-steel reactor with a Teflon liner at 160 ºC for 96 h, followed by slow cooling to room temperature. Blue crystals of the complex formed. Anal. calcd. (%) for $[Ni_2(C_6H_4NO_2)_4]O\cdot 1.5H_2O$: C, 44.43; H, 2.95; N, 8.63 %. Found (%): C, 44.16; H, 2.91; N, 8.37 %.

Structural determination: A suitable white block crystal was mounted on a glass fiber and the data were collected on a Bruker Smart 1000 CCD diffractometer with a MoK_α radiation (λ = 0.71073 Å) at 293(2) K by using an ω scan mode. The hydrogen atoms bound to carbon were located by geometrically calculations and their positions and thermal parameters were fixed during the structure refinement. All non-hydrogen atoms were refined by full-matrix least-squares techniques. All calculations were performed by the SHELXTL 97 program[7]. Crystallographic data and experimental details for structural analyses are summarized in Table-1. CCDC: 684094. Crystal and refinement data of the present complex are listed in Table-1.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR THE TITLE COMPOUND

Empirical	$C_{48}H_{38}N_8Ni_4O_{21}$
Formula weight	1297.70
Crystal system, space group	Monoclinic, P2(1)/c
a (Å)	10.728(2)
b (Å)	19.576(4)
c (Å)	13.790(3)
β(°)	104.49(3)
Volume (Å^3), F(000)	2803.9(10) ,1324
θ range for data collection (°)	1.85-27.52
Goodness-of-fit on F^2	1.112
Final R indices [I > 2σ(I)]s	R_1 = 0.0433, wR_2 = 0.1072
R indices (all data)	R_1 = 0.0584, wR_2 = 0.1133
Largest diff. Peak and hole (e Å^{-3})	0.599 and -0.366

The molecular structure of the nickel(II) compound is illustrated in Fig. 1. The nickel(II) atom is coordinated by 6 atoms. The central Ni1(II) atom adopts a distorted octahedron geometry with O6, O9, O1 and N2, lying on the equatorial plane. The binuclear Ni(II) atoms (Ni1, Ni2) are bridged by the O9 and four oxygen atoms (O3, O4, O5, O6) from the different nic$^-$ and the distance of two nickel atoms is 3.558 Å. The Ni-O-Ni linkages is nonlinear, exhibiting an angle of 114.10(9) for Ni(1)-O(3)-Ni(2). The N4 and O3 are located at two axial sites. In the complex, the nic$^-$ ligands adopts two coordination modes: μ_2-nic-N, O and μ_3-nic-N, O, O. The selected bond lengths and angles of this complex are given in Table-2.

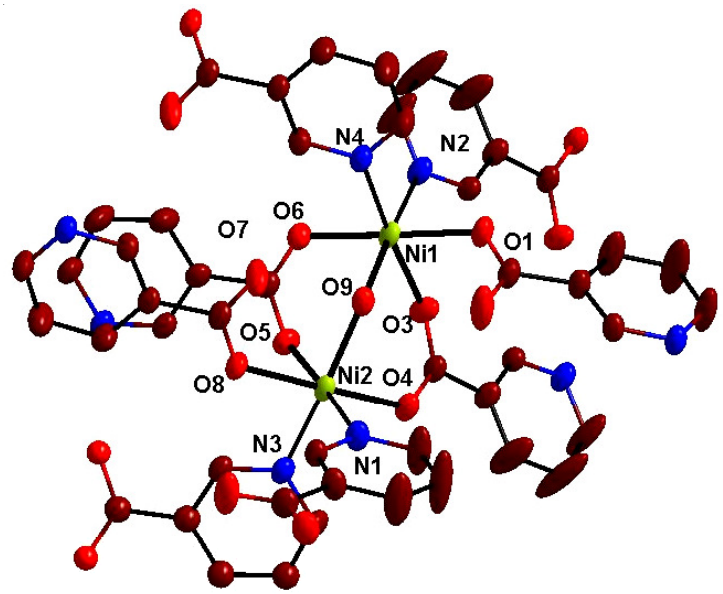

Fig. 1. Local coordination environments of Ni metal

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

Ni(1)-O(6)#1	2.033(2)	Ni(1)-O(1)	2.063(2)
Ni(1)-O(3)#1	2.094(2)	Ni(1)-N(2)#2	2.096(3)
Ni(2)-N(3)	2.081(3)	Ni(2)-O(5)	2.095(2)
Ni(2)-N(1)	2.101(3)	Ni(2)-O(9)	2.128(2)
O(6)#1-Ni(1)-O(1)	177.13(9)	O(6)#1-Ni(1)-O(3)#1	95.56(9)
O(6)#1-Ni(1)-N(4)#3	88.70(9)	O(1)-Ni(1)-N(4)#3	92.20(10)
O(3)#1-Ni(1)-N(4)#3	175.73(10)	N(2)#2-Ni(1)-N(4)#3	90.91(10)
O(9)#1-Ni(1)-N(4)#3	91.04(9)	Ni(1)#4-O(9)-Ni(2)	114.10(9)

Symmetry codes: #1: x,-y+1/2, z-1/2 ; #2: -x+1, y-1/2, -z+1/2; #3: -x, y-1/2, -z-1/2.

REFERENCES

1. D.T. Vodak, M.B. Braun, J. Kim, M. Eddaoudi and O.M. Yaghi, *Chem. Commun.*, **24**, 2534 (2001).
2. M.L. Tong, Y.M. Wu, J. Ru, X.M. Chen, H.C. Chang and S. Kitagawa, *Inorg. Chem*., **41**, 4846 (2002).
3. A.J. Blake, N.R. Champness, P. Hubberstey, W.-S. Li, M.A. Withersby and M. Schroder, *Coord. Chem. Rev*., **183**, 117 (1999).
4. C.W. Yeh, M.C. Suen, H.L. Hu, J.D. Chen and J.C. Wang, *Polyhedron*, **23**, 1947 (2004).
5. Z. He, Z.M. Wang, S. Gao and C.H. Yan, *Inorg. Chem.*, **45**, 6694 (2006).
6. H.S. Huh and S.W. Lee, *J. Mol. Struct*., **829**, 44 (2007).
7. G.M. Sheldrick, SHELXTL97, Program for the Refinement of Crystal Structure, University of Göttingen, Germany (1997).

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