



NOTE

Synthesis and Crystal Structure of Binuclear Ni(II) Complex with Benzoic Acid and Tetramethylethylenediamine

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A new nickel(II) complex $[\text{Ni}_2(\text{ba})_3\text{Cl}(\text{tmen})_2(\text{H}_2\text{O})]$ (**1**), where ba = benzoate, tmen = tetramethylethylenediamine, was synthesized and characterized by single crystal X-ray diffraction. The crystal is monoclinic, space group P121/n with cell dimensions of $a = 16.333(2)$, $b = 12.1117(12)$, $c = 18.784(2)$ Å, $\alpha = 90$, $\beta = 105.744(4)$ and $\gamma = 90^\circ$. The crystal structure analysis shows that each nickel(II) atom is six coordinated in a distorted octahedral environment.

Keywords: Nickel, Tetramethylethylenediamine, Benzoate, Crystal structure.

Transition metal carboxylates have been a subject of interest for their applications as gas storage, ion exchange and catalysts¹. Binuclear nickel complexes bridged by water, hydroxide ion or oxo group represent an important class of compounds due to their relevance to the active site of hydrolytic enzyme urease². Nickel is present in the active sites of several important classes of metalloproteinase such as 2-mercaptoethanol-inhibited urease and Ni/Fe hydrogenases^{3,4}. Some carboxylate compounds (*e.g.*, benzoates) are known to have antibacterial activity. Benzoic acid is used in combination with salicylic acid in dermatology as a fungicidal treatment for fungal skin diseases⁵. In our previous work, we reported the synthesis and crystal structure of a binuclear Ni(II) complex containing 2-nitrobenzoic acid and tetramethylethylenediamine⁶. Herein, we reported the synthesis and crystal structure of complex **1** derived from benzoic acid and tetramethylethylenediamine.

Synthesis: A solution of benzoic acid (0.25 g, 2 mmol) in EtOH (25 mL) was added to a solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.23 g, 1 mmol) in EtOH (25 mL). Tetramethylethylenediamine (0.11 g, 1 mmol) was added to the mixture followed by few drops of Et_3N . The mixture was refluxed for 1 h. After standing at room temperature for 5 days, green single crystals were obtained by slow evaporation.

Structure determination: Single crystal of the complex with appropriate dimension of 0.16 mm × 0.06 mm × 0.01 mm was placed on BerkerSmart APEXII CCD diffractometer. Intensity data were collected with a graphite monochromated MoK_α radiation ($\lambda = 0.71073$ nm) using ω scan technique in

the range of $1.95^\circ \leq \theta \leq 26.33^\circ$ at 150(2) K. The structures were solved by a combination of direct methods with subsequent difference Fourier syntheses and refined by full matrix least squares on F^2 by using the SHELX-97 programme⁷. The crystal data and refinement details are summarized in Table-1.

TABLE-1
CRYSTAL DATA AND STRUCTURE
REFINEMENT FOR COMPLEX 1

Empirical formula	$\text{C}_{33}\text{H}_{49}\text{N}_4\text{OClNi}_2$
Space group	P121/n
a (Å)	16.333(2)
b (Å)	12.1117(12)
c (Å)	18.784(2)
Volume (Å ³)	3576.3(7)
D_c (Mg/m ³)	1.424
h,k,l ranges	-20 13, -15 11, 23 23
Data/restraints/parameters	7130 / 2 / 438
R indices [$I > 2\sigma(I)$]	$R1 = 0.0431$, $wR2 = 0.0983$
Largest diff. peak and hole (Å ⁻³)	0.622 and -0.483
Formula weight	766.63
Crystal system	Monoclinic
α (°)	90
β (°)	105.744(4)
γ (°)	90
Z	4
Absorption coefficient (mm ⁻¹)	1.178
θ Range (°)	1.95 to 26.33
Reflection collected/unique	17358/7130
Goodness-of-fit on F^2	1.022
R indices (all data)	$R1 = 0.0696$, $wR2 = 0.1084$

The coordination geometry of nickel complex **1** with numbering scheme is depicted in Fig. 1. The selected bond lengths and angles are listed in Table-2. Crystal structure of complex **1** shows that the two nickel atoms are bridged by a water molecule, a chloride ion and a bidentate carboxylate ligand. The octahedral environment around each nickel atom is completed by two nitrogen atoms from tmen and one oxygen atom from monodentate carboxylate. The Ni-N bond distances range from 2.143(3) to 2.164(3) Å. The Ni(1)-O(2)-Ni(2) and Ni(1)-Cl(1)-Ni(2) angles are 102.49(10) and 84.68(3)°, respectively. Carboxylate ligands show two coordination modes in the complex, monodentate and bidentate bridging modes. The tetramethylethylenediamine chelate rings are in normal unsymmetrical cauche configuration.

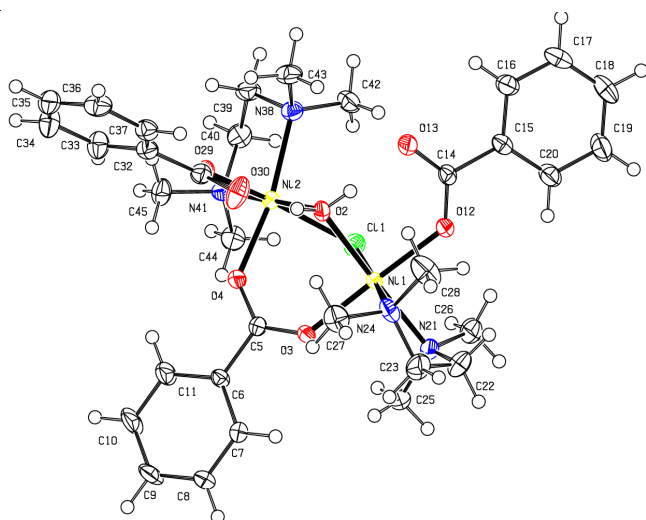


Fig. 1. Coordination geometry of nickel complex **1**

TABLE-2
SELECTED BOND DISTANCES (Å) AND
ANGLES (°) FOR COMPLEX **1**

Ni(1)-N(21)	2.143(3)	Ni(2)-N(38)	2.164(3)
Ni(1)-N(24)	2.146(3)	Ni(2)-N(41)	2.151(3)
Ni(1)-O(2)	2.111(2)	Ni(2)-O(2)	2.109(2)
Ni(1)-O(3)	2.034(2)	Ni(2)-O(4)	2.019(2)
Ni(1)-O(12)	2.075(2)	Ni(2)-O(29)	2.069(2)
Ni(1)-Cl(1)	2.4227(9)	Ni(2)-Cl(1)	2.4630(9)
O(2)-Ni(1)-N(21)	177.80(11)	O(12)-Ni(1)-N(21)	87.83(10)
O(2)-Ni(1)-N(24)	96.15(10)	O(12)-Ni(1)-N(24)	91.45(10)
O(2)-Ni(1)-O(3)	90.96(9)	O(12)-Ni(1)-Cl(1)	89.03(6)
O(2)-Ni(1)-O(12)	90.48(9)	N(21)-Ni(1)-N(24)	85.30(11)
O(2)-Ni(1)-Cl(1)	81.89(7)	N(21)-Ni(1)-Cl(1)	96.67(8)
O(3)-Ni(1)-N(21)	90.72(10)	N(24)-Ni(1)-Cl(1)	177.99(8)
O(3)-Ni(1)-N(24)	88.56(10)	Ni(1)-O(2)-Ni(2)	102.49(10)
O(3)-Ni(1)-O(12)	178.55(9)	Ni(1)-Cl(1)-Ni(2)	84.68(3)
O(3)-Ni(1)-Cl(1)	91.01(6)	—	—

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