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NOTE

Synthesis and Crystal Structure of Nickel(II) Complex of Hydrazone Derived from Benzohydrazide and 4-Acetylpyridine and Tetramethylethylenediamine as Secondary Ligand

ADNAN M. QADIR* and BAYAN A. FAIQ

Department of Chemistry, Collage of Science, Salahaddin University, Erbil 44001, Kurdistan Region, Iraq

*Corresponding author: E-mail: adnanmqadir2000@gmail.com

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A new nickel(II) complex of formula $[Ni(L)_2(tmed)]$ (**1**) (LH = 4-acetylpyridine benzoyl hydrazone, tmed = tetramethylethylenediamine) has been synthesized and characterized by single crystal X-ray diffraction method. The compound crystallizes in monoclinic space group $P2_1/c$ with a = 10.4479 (6), b = 18.8907 (10), c = 16.5022 (9) Å, α = 90, β = 94.527(3), γ = 90° V = 3246.8 (3) Å^3, Z = 4, F(000) = 1376.0, D_c = 1.333 Mg/m^3, μ = 0.642 mm^{-1}. Nickel(II) ion exhibited distorted octahedral geometry. The hydrazone acted as anionic ligand.

Keywords: Hydrazone, Nickel, Synthesis, Crystal.

Hydrazones have gained much attention due to their extensive biological properties, such as anti-inflammatory [1], anticonvulsant [2,3], antimicrobial [4], anticancer [5] and cardioprotective activities [6]. One important aspect of hydrazones is their ability to exist in tautomeric forms (Fig. 1). The existence of tautomeric equilibrium in these compounds makes it possible to obtain coordination compounds containing either neutral ketonic form or deprotonated enolic form [7]:

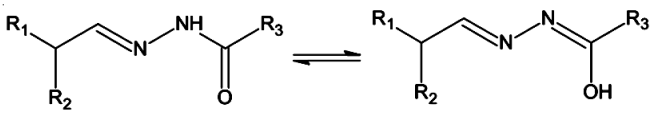

Fig. 1. Tautomerism of acylhydrazone

Nickel(II) is known to form complexes with a variety of molecular geometry (*e.g.*, tetrahedron, octahedron and square planar). Furthermore, nickel atom is present in the active sites of several hydrogenases [8]. Metal complexes with hydrazones have potential applications as catalysts, luminescent probes and molecular sensors [9]. Here we report the synthesis and crystal structure of a new Ni(II) complex containing 4-acetylpyridine benzoyl hydrazone and tetramethylethylenediamine.

Crystal structure determination: X-ray single-crystal diffraction data were recorded on Bruker APEX-II CCD diffractometer equipped with a graphite-monochromated MoK_α radiation (λ = 0.71073) at 100.0(2) K. The structure was solved by Patterson method using XS solution program and refined by least-squares techniques using XL [10] refinement package. All hydrogen atoms were placed in geometrically calculated positions and allowed to ride on the parent carbon atoms.

Synthesis: 4-Acetylpyridine benzoyl hydrazone (1 mmol, 0.24 g) and tetramethylethylenediamine (0.5 mmol, 0.06 g) were added to a solution of $NiCl_2{\cdot}6H_2O$ (0.5 mmol, 0.12 g) in EtOH (20 mL) with stirring. The green solution was allowed to stand at room temperature. Single crystals suitable for X-ray diffraction were obtained after 1 weak. Molecular formula: $C_{34}H_{40}N_8O_2Ni$; elemental analysis (%): Found: C, 62.56; H, 6.17; N, 17.2. Calcd.: C, 62.69; H, 6.19; N, 17.2.

IR spectrum and magnetic moment: The IR spectrum of hydrazone ligand exhibits two bands at 1654 and 3216 cm^{-1} attributed to C=O and NH groups, respectively. Both of these bands disappear on complexation and a new C–O absor-ption band appears at 1066 cm^{-1} in the complexes, indicating that the hydrazone ligand has undergone deprotonation on complexation. Magnetic moment of Ni(II) complex is 3.1 BM corresponding to two unpaired electrons in octahedral environment.

Crystal structure: The molecular structure of the Ni(II) complex is shown in Fig. 2. Crystallographic data and refinement details are given in Table-1. Selected bond lengths and angles are listed in Table-2. The crystal belongs to monoclinic space group $P2_1/c$ with a = 10.4479 (6), b = 18.8907 (10), c = 16.5022 (9) Å, α =90, β = 94.527 (3), γ = 90°, V = 3246.8 (3) Å^3, Z = 4, F(000) = 1376.0, D_c = 1.333 Mg/m^3.

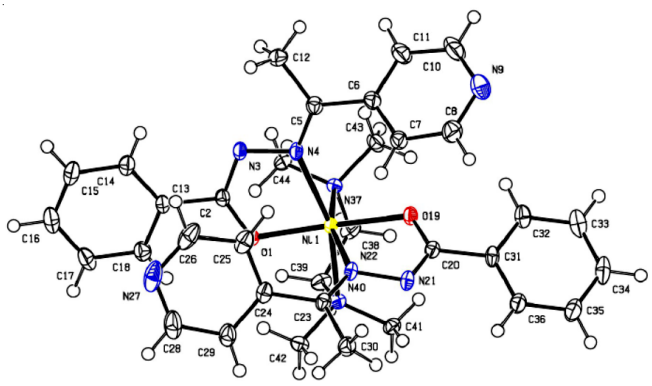

Fig. 2. Molecular structure of nickel complex with 50 % probability displacement ellipsoids

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTUREREFINEMENT FOR Ni(II) COMPLEX

Chemical formula	$C_{34}H_{40}N_8O_2Ni$
Formula weight	651.45
Cell system, space group	Monoclinic, $P2_1/c$
a (Å)	10.4479(6)
b (Å)	18.8907(10)
c (Å)	16.5022(9)
α (°)	90
β (°)	94.527(3)
γ (°)	90
Volume (Å^3)	3246.8(3)
Z	4
Dc (Mg m^{-3})	1.333
μ (mm^{-1})	0.642
Crystal size (mm)	0.72 × 0.42 × 0.36
2θ range for data collection	3.282 to 58.458°
Index ranges	$-14 \le h \le 14$, $-25 \le k \le 25$, $-22 \le l \le 22$
Reflection collected	58916
Independent reflections	8757[R_{int} = 0.0625, R_{sigma} = 0.0483]
Data/restraints/parameters	8757/0/412
F(000)	1376.0
Goodness-of-fit on F^2	1.046
R1 [I > 2σ(I)]	R1 = 0.0394,
wR2 [I > 2σ(I)]	wR2 = 0.0872
R1 (all data)	R1 = 0.0594,
wR2 (all data)	wR2 = 0.0960
Min. and max. resd. dens. [e/Å^3]	0.43/-0.56

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

Bond length (Å)			
Ni1-O1	1.9806(12)	C2-O1	1.273(2)
Ni1-O19	1.9907(12)	N3-C2	1.325(2)
Ni1-N4	2.1981(15)	N4-N3	1.4035(19)
Ni1N22	2.1579(14)	C20-O19	1.277(2)
Ni1-N37	2.1987(14)	N21-C20	1.324(2)
Ni-N40	2.2367(14)	N22-N21	1.4095(19)
Bond angle (°)			
N40Ni1N37	83.11(5)	O1C2N3	126.57(15)
N22Ni1N4	101.14(5)	C2N3N4	111.05(14)
N37Ni1N4	90.82(5)	N3N4Ni1	110.03(10)
N40Ni1N22	89.16(5)	C5N4N3	112.54(14)
O1Ni1O19	177.80(5)	N3C2C13	116.19(15)

The X-ray crystallography shows that Ni(II) has an octahedral geometry with two oxygen and two nitrogen atoms from two hydrazone ligands and two nitrogen atoms from tetramethylethylenediamine. The Ni1-O bond lengths are (1.9806(12)-1.9907(12) Å). The Ni-$N_{hydrazone}$ bond distances range from 2.1981(15) to 2.1579(14) Å while the Ni-N_{tmed} vary from 2.1987(14) to 2.2367(14) Å.

Supplementary material

CCDC 1040718 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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