

Template Synthesis, Structural Characterization and Antibacterial Activity of an Unsymmetrical Tridentate Schiff Base Nickel(II) Complex

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ABSTRACT: Nickel(II) complex of $[NiL_2](ClO_4)_2$, where *L* is an unsymmetrical tridentate ligand of 2-(2-aminoethyl)imino-3-butanone oxime has been synthesized by a template condensation reaction. The complex was characterized on the basis of microanalytical, spectroscopic, and other physicochemical properties. X-ray diffraction study of the complex reveals nickel(II) center in a distorted octahedral environment through two amine nitrogen donors, two imine donors, and two nitrogen atoms of the oxime moieties of the ligand. The antibacterial activity of the complex has been tested against Gram(+) and Gram(-) bacteria. The results of the antibacterial screening indicated that the complex is effective against bacterial growth retardation activity to some extent and its effectiveness is higher for Gram(+) bacteria.

KEY WORDS: Unsymmetrical tridentate ligand, Nickel(II) complex, Molecular structure, Diacetylmonoxime, Antibacterial Activity.

INTRODUCTION

Oxime chelating ligands have been named to organic compounds including the $-C=N-O$ moiety. Dimethylglyoxime was the first oxime that introduced as a gravimetric reagent for nickel [1] and since then oxime derivatives and their metal complexes have been the subject of a great number of investigations including synthesis of mono nuclear [2-4], homo- [5] hetero polynuclear [6], polymeric metal complexes [7], organic reagents for verity of transformations [8-12], Fluorescence [13], optical [14,15], medicine [16-19], as models in biological processes [20], electrochemical [21-24], thermal properties [25], analytical applications such as determination [26] and extraction of metals [27] and photoelectrical behaviors [28].

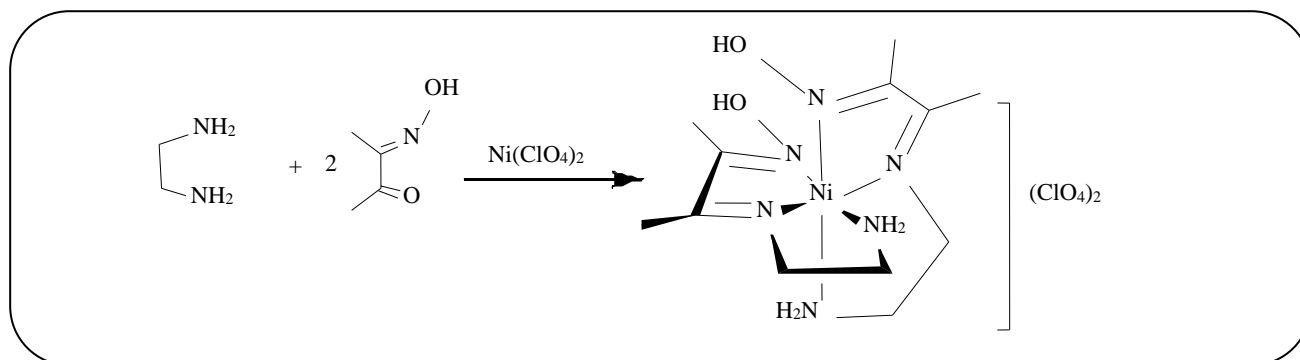
Unsymmetrical ligands involving oxime functionality exhibit an interesting chelating property in the area of complex chemistry [29-32]. The presence of mildly acidic hydroxyl groups and slightly basic nitrogen atoms make oxime moiety in the unsymmetrical ligands amphoteric that form corrin-type, square-planar, square pyramidal and octahedral complexes with transition metal ions such as Ni(II) [33]. Metal ions play a vital function in bioinorganic chemistry and metals such as Ni may exist in trace amounts in biological systems. Therefore, structural study of the complexes of Ni(II) ion with biological compounds is extremely important.

In this paper, we report synthesis, spectral characterization, crystal structure and antimicrobial

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Scheme 1: Synthetic route of the nickel(II) complex.

activity of Ni(II) complex containing unsymmetrical Schiff base ligand of 2-(2-aminoethyl)imino-3-butanone oxime) derived by condensation of acetylmonoxime and ethylenediamine as shown in Scheme 1. The structure of this compound and its oxidized Ni(IV) counterpart were previously investigated [34,35] by single crystal X-ray diffraction. However, the early surveys do not have enough precision for this purpose ($R = 0.101$). Additionally, other refinement parameters were not reported. Thus we report crystal structure of the nickel(II) compound at 150° K.

EXPERIMENTAL SECTION

Chemicals and instruments

Ethylenediamine (Merck), diacetylmonoxime (Aldrich), $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Fluka) were used as received. Infrared spectrum (potassium bromide disk) was recorded using a Bruker FT-IR instrument; only strong peaks are given. The electronic absorption spectra were measured by using a Cecil 5000 model UV/Vis spectrophotometer. Elemental analyses were performed on a LECO 600 CHN elemental analyzer. Absolute metal percentage was determined by an atomic absorption-flame spectrometer. Crystallographic analysis of complex: single crystals suitable for X-ray analysis were obtained by slow evaporation of methanol solution at room temperature. A single crystal was mounted on a Nonius Kappa-CCD area detector diffractometer (Mo $\text{K}\alpha$ $\lambda = 0.71073 \text{ \AA}$). Data reduction, including the absorption correction, was performed with the Denzo software package [36]. The structure was solved using direct methods (SHELXS-97) and refined on F^2 using the SHELXS-97 software [37]. The hydrogen atoms of NH_2 and OH groups were found

in difference Fourier synthesis. The H(C) atom positions were calculated. All hydrogen atoms were refined in isotropic approximation in riding model with the Uiso(H) parameters equal to 1.2 $U_{\text{eq}}(\text{C}_i)$, for methylene groups, where $U(\text{C}_i)$ is the equivalent thermal parameter of the carbon atoms to which corresponding H atoms are bonded. Refinement of F^2 was against all reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) etc., and is not relevant to the choice of reflections for refinement. Crystal, data collection, and refinement parameters are given in Table 1.

Synthesis of complex

To a mixture of diacetylmonoxime (2.2 g, 2.0 mmol) and ethylenediamine (0.06 mL, 1.0 mmol) in ethanol (50%, 10 mL) was added $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (365 mg, 1.0 mmol). The reaction mixture was refluxed for 2 h. During the heating process an orange solid precipitated. After cooling the reaction mixture to the room temperature the solid was separated by filtration and then was crystallized in methanol which yielded 343 mg (63%) desired compound as orange-brown needle crystals. Anal. calc. for $\text{C}_{12}\text{H}_{26}\text{Cl}_2\text{NiN}_6\text{O}_{10}$ ($M_w = 543.97 \text{ g/mol}$) (%): C, 26.50; H, 4.82; N, 15.45; Ni, 10.79%. Found: C, 26.49; H, 4.51; N, 15.33; Ni, 11.42. FT-IR: (KBr, cm^{-1}): 3364 (br) N-OH, 3238, 3203 (m) N-H₂, 2168(b), 1673 C=N_{imin}, 1591(s) C=N_{oxim}, 1419(s) C=C, 1368 (m), 1308 (s), 1111 (s), 630 (m) ClO_4 , 929 (m) N-O, 626 (m) ClO_4 , 547 (m) Ni-N.

Table 1: Crystal data and refinement parameters for the complex.

Empirical formula; (Formula weight)	C ₁₂ H ₂₆ Cl ₂ NiN ₆ O ₁₀ ; (543.97)
Color	Needle, brown
Temperature	150(1) K
Wavelength	0.71073 Å
Crystal system; Space group	Monoclinic; C2/c
Unit cell dimensions	0.30 × 0.30 × 0.10 mm
$a = 21.3380$ (9) Å; $b = 7.1740$ (3) Å; $c = 14.7980$ (5) Å; $\beta = 111.863$ (2)°	
Volume ; Z	2094.42 (16) Å ³ ; 4
Calculated density	1.725 g/cm ³
Absorption coefficient	1.246 mm ⁻¹
$F(0\ 0\ 0)$	1128
θ range for data collection	3.0–27.5°
Index ranges	-27 ≤ h ≤ 27; -9 ≤ k ≤ 8; -19 ≤ l ≤ 15
μ (mm ⁻¹)	1.246
Reflections collected/unique	5519/2376 [$R(\text{int}) = 0.037$]
Completeness to $2\theta = 27.53$	99.9%
Data/restraints/parameters	2376/0/144
Final R indices ^a [$I > 2\sigma(I)$] ^b	$R_1 = 0.038$, $wR_2 = 0.080$
Goodness-of-fit on F^2 ^c	1.07
R indices (all data)	$R_1 = 0.032$, $wR_2 = 0.077$
Extinction coefficient	none
Largest diff. peak and hole	0.37 and -0.60 e Å ⁻³
$(\Delta/\sigma)_{\text{max}}$	< 0.001

$$a) R = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad b) wR = [(\sum [F_o^2 - F_c^2]^2) / \sum [w(F_o^2)^2]]^{1/2}, \quad c) S = \sum [w(F_o^2 - F_c^2)^2 / (N_{\text{obs}} - N_{\text{param}})]^{1/2}.$$

Antimicrobial activity

The *in vitro* biocide screening, antibacterial activities of the synthesized compound was assayed onto LB medium contained (Merck): tryptone, 10.0 g / L; yeast extract, 5.0 g / L; NaCl, 5.0 g / L; and glucose, 1.0 g / L [38]. The medium was dispensed into universal bottles and sterilised at 121 °C for 15 minutes. The complex was dissolved into DMSO and filter sterilised using a 0.22 µm Ministart (Sartorius). The sterile synthesized stock solutions were added into LB medium to give a final concentration of 1-300 µg mL⁻¹ as required. The antibacterial activity of the compound was compared with known antibiotic tetracycline at the same concentration.

Minimum inhibitory concentration (MIC) of the compounds were assayed using a standard method

against some bacteria including *Escherichi coli* PTCC 1330, *Pseudomonas aeruginosa* PTCC 1074, *Staphylococcus aureus* ATCC 35923 and *Bacillus subtilis* PTCC 1023. Late exponential phase of the bacteria were prepared by inoculating 1% (v/v) of the cultures into the fresh LB medium and incubating on an orbital shaker at 37 °C and 100 rpm overnight. Before using the cultures, they were standardised with a final cell density of approximately 10⁸ cfu / mL. An 1% (v/v) inoculum of each culture was inoculated into the LB medium containing different concentration of the synthesised compounds and incubated on the orbital shaker at 37 °C and 100 rpm. The compound sensitivity of the strains was assayed for positive or negative growth after 24-48 hours.

RESULTS AND DISCUSSION

The mononuclear Ni(II) complex was prepared by adding nickel(II) perchlorate to a mixture of diacetylmonoxime and ethylenediamine in solvent of ethanol. The initial studies revealed that the reaction of an equimolar of diacetylmonoxime, ethylenediamine and nickel(II) perchlorate produced a mixture of bis(ethylenediamine)nickel(II) perchlorate (major product) and desired singly condensed monoxime complex. Subsequently, it was found that the use of an equivalent of ethylenediamine and nickel(II) with two equivalents of diacetylmonoxime produces the desired singly condensed product as the major component. However, using more than two equivalents of the diacetylmonoxime over the same reaction conditions and reaction period, resulted bis-diacetylmonoxime and doubly condensed products. In this procedure only one of the amine groups of ethylenediamine is involved in the in situ condensation reaction and another amine group was left intact. The primary amine group of the ligand is engaged in coordination to the nickel(II) ion and can be subsequently condensed with various carbonyl compounds to study the variation and fine tuning of stability, reactivity and electronic properties of such complexes. The complex was characterized by elemental analysis, IR and UV-Vis spectroscopies, electrical conductivity and single crystal X-ray structure analysis. The results are consistent with the mononuclear formula. In acetonitrile solution, the complex behaves as a 1:2 electrolyte as is evident from its Λ_M value (ca. $243 \text{ cm}^2 / \text{mol } \Omega$) [39]. The infrared spectrum of the complex shows a strong band at 1673 cm^{-1} which is assignable to the C=N stretching vibration (ν_{CN}) indicating the formation of the Schiff base product. Appearance of two medium bands at 3238 and 3203 cm^{-1} supports presence of NH_2 moiety in the complex, indicating unsymmetrical nature of the ligand system. The presence of the ClO_4^- group is declared by an intense band at around 1111 cm^{-1} and a medium band at 630 cm^{-1} which are attributed to the anti-symmetric stretching and anti-symmetric bending vibration modes, respectively [40]. At lower frequency the complex also exhibited a band at 547 cm^{-1} which is attributed to the $\nu(\text{Ni-N})$ vibration modes [41]. All other characteristic vibrations including the oxime O-H and C=N stretching vibrations are located in the 3364 and 1591 cm^{-1} , respectively. Thus, the IR spectrum

of the compound is in good agreement with the respective structural feature of Ni(II) Schiff base complex[40].

The X-ray analysis of the complex was determined. An ORTEP view of the complex together with the atom-numbering scheme is illustrated in Fig. 1. Selected bond lengths and bond angles are given in Table 2. In the complex, the ligand is tridentate forming two five-membered rings and the nickel(II) ion lies at the center of a distorted octahedron that is coordinated by two ligands and has a N_6 coordination sphere. The ligand coordinates in a tridentate fashion through oxime, imine and amine nitrogen atoms and the shortest nickel ligand contact in the complex is $2.006(3) \text{ \AA}$ for the N(2) imine nitrogen atom and the longest is $2.128(2) \text{ \AA}$ for N(3), the oxime amine nitrogen atom. The average Ni-N bond distances are in agreement with those found in six coordinate high-spin nickel (II) complexes with chelating ligands [42]. The required bite angle from imine and oxime coordination ($75.63(10)^\circ$) causes the greatest deviation from regular octahedron, with N(1)-Ni(1)-N(3) being $156.44(10)^\circ$. The oxime proton was located crystallographically. The oxime groups same as the primary amine groups are located in cis position around the metal center. In the crystal structure, the perchlorate and oxime oxygen atoms act as hydrogen bond acceptors and the oxime and amine hydrogen atoms serve as hydrogen bond donors, respectively. The number of hydrogen bonds formed by the relevant asymmetric unit is presented in Fig. 2. As shown in Fig. 2, one inter-molecular N-H...O(oxime) and two inter-molecular N-H...O(perchlorate) hydrogen bonding interactions are observed per asymmetric unit.

The UV-Vis spectrum of the complex was studied in aqueous and methanolic solutions. The complex showed an intense transition near 295 nm ($\epsilon = 5720 \text{ M}^{-1} \text{ cm}^{-1}$) in both media attributed to the charge transfer transition. The d-d transition of the nickel (II) complex appeared as two weak broad bands centering at 756 nm ($\epsilon = 104 \text{ M}^{-1} \text{ cm}^{-1}$) and 504 nm ($\epsilon = 174 \text{ M}^{-1} \text{ cm}^{-1}$) in aqueous solution associated to the ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ transitions, respectively [42]. A similar absorptions was also observed at 771 ($\epsilon = 95 \text{ M}^{-1} \text{ cm}^{-1}$) and 508 nm ($\epsilon = 165 \text{ M}^{-1} \text{ cm}^{-1}$) in solvent of methanol. These transitions are characteristic of nickel(II) in an octahedron environment [43].

Table 2: Selected bond lengths (Å) and bond angles (°) for the compound.

Bond	Distances	Bond	Distances
Ni(1)-N(1)	2.1204(17)	Ni(1)-N(1)a	2.1204(17)
Ni(1)-N(2)	2.0101(16)	N(3)-O(1)	1.393(2)
Ni(1)-N(3)	2.1264(16)	N(2)-C(3)	1.275(3)
Ni(1)-N(2)a	2.0101(16)	N(3)-C(4)	1.289(2)
Ni(1)-N(3)a	2.1264(16)	N(3)-O(1)	1.393(2)
Angle	(°)	Angle	(°)
N(1)-Ni(1)-N(2)	81.77 (6)	N(1)-Ni(1)-N(3)	156.50(6)
N(1)-Ni(1)-N(2)a	95.24 (6)	N(1)-Ni(1)-N(1)a	93.87 (10)
N(2)-Ni(1)-N(1)a	95.23 (6)	N(2)-Ni(1)-N(2)a	175.65 (9)
N(3)-Ni(1)-N(1)a	94.70 (6)	N(3)-Ni(1)-N(2)a	107.62 (6)
N(2)-Ni(1)-N(3)a	107.62 (6)	N(2)-Ni(1)-N(3)	75.69(6)
N(3)-Ni(1)-N(3)a	86.96 (9)	N(1)-Ni(1)-N(3)a	94.70 (6)

Symmetry transformation of a: $-x, y, -z+3/2$

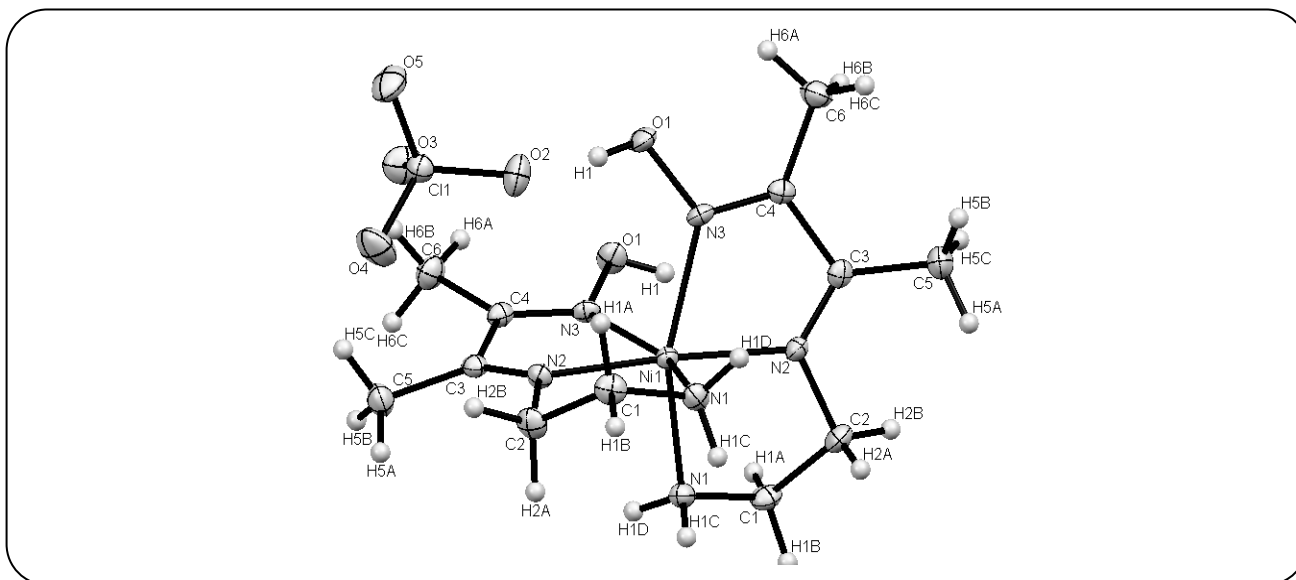
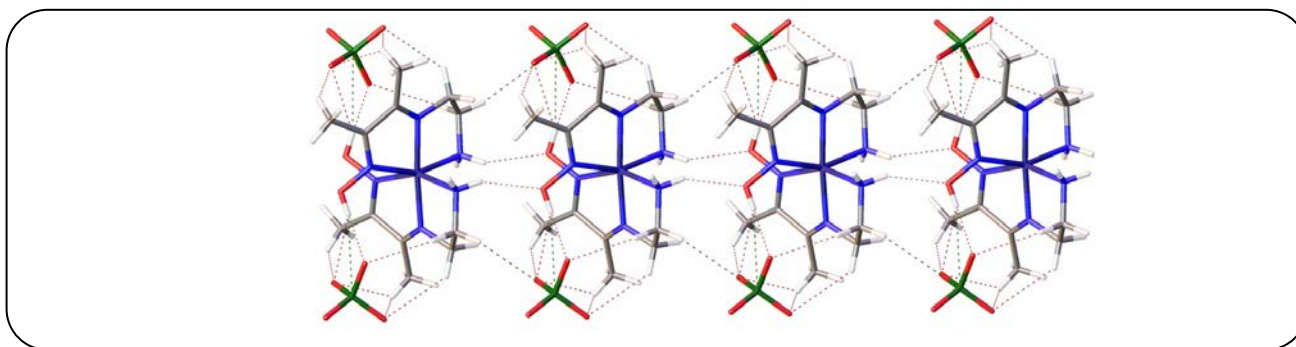
**Fig. 1: ORTEP diagram of Ni complex with atom labels and numbering scheme.****Fig. 2: Packing diagram of the complex containing hydrogen bonding along crystallographic axis.**

Table 3: Minimum inhibitory concentration (MIC) of the compounds ($\mu\text{g}\cdot\text{mL}^{-1}$) against some bacteria.

Strain	Minimum inhibitory concentration ($\mu\text{g}\cdot\text{mL}^{-1}$)		
	blank	complex	Tetracycline
<i>E. coli</i> PTCC 1533	-	200	25
<i>P. aeruginosa</i> PTCC 1707	-	150	50
<i>S. aureus</i> ATCC 25923	-	150	10
<i>B. subtilis</i> PTCC 1156	-	100	25

Antimicrobial activity

To screen for antibacterial activity of synthesized compound, minimum inhibitory concentration was evaluated against gram positive *S. aureus* and *B. subtilis* and gram negative *E. coli* and *P. aeruginosa*. In addition, the finding towards inhibition of microorganisms was correlated with a standard antibiotic tetracycline (Table 3).

The results revealed that the complex has moderate to good inhibitory effect against some microorganisms, and among the bacteria tested the complex exhibited highest antibacterial activity against *B. subtilis*. However the MIC values for the synthesized compound against bacteria was high as compared to the standard antibiotic tetracycline; these results suggest that the compound exhibited good antibacterial activities and can be further developed for application as effective antimicrobial agent.

CONCLUSIONS

It can be concluded that the unsymmetrical tridentate nickel(II) complex formed in situ by condensation of ethylenediamine and diacetylmonoxime in the presence of Ni^{2+} . In this reaction only one of the two NH_2 groups of ethylenediamine participated in the condensation reaction and another NH_2 group is intact. Although the unreacted NH_2 groups involve in the coordination with the nickel ion it can be condensed with various carbonyl compounds. In addition to the synthetic and structural investigations, this study helps to evaluate the potentiality and effectiveness of newer Schiff base complexes of nickel(II) to use as antibacterial agents.

Supplementary data

CCDC 735409 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the

Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

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