

## Tetranuclear nickel complex of dimethylene bridged diiminedioxime containing different hybridizations of nickel (II)



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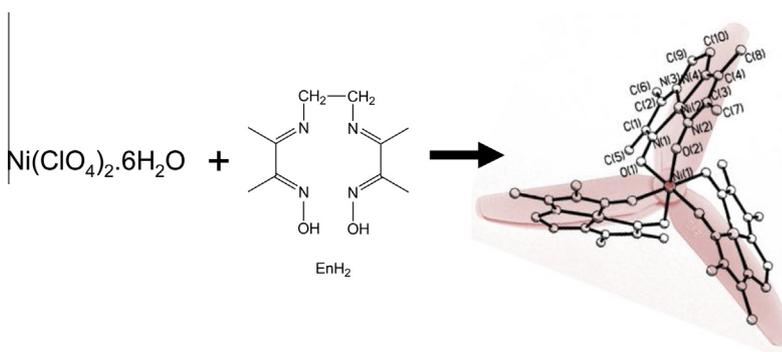
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### HIGHLIGHTS

- Four Ni(II) ions in this complex possess two types of hybridization ( $dsp^2$  and  $sp^3d^2$ ).
- Both hydroxyl hydrogens of two oxime groups in  $EnH_2$  ligand are lost during the reaction.
- Neither inter- nor intra-hydrogen bond is formed.
- The obtained complex has a three-bladed propeller-like structure.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The reaction of ligand 3,3'-(1,4-ethanediyl)dinitrilo)bis(2-butanone)dioxime ( $EnH_2$ ) with  $Ni(ClO_4)_2$  yields  $[Ni(Ni(En))_3](ClO_4)_2$  (**1**). Complex **1** crystallizes in an R-centered trigonal cell with the space group R3. The structure consists of an octahedral  $[Ni(Ni(En))_3]^{2+}$  cation containing four Ni(II) ions with different hybridizations ( $dsp^2$  and  $sp^3d^2$ ) and two perchlorate anions. Three  $dsp^2$  Ni(II) ions coordinate to three  $EnH_2$  ligands via imine nitrogens and oxime nitrogens and the fourth Ni(II) ion octahedrally coordinates to six oxime oxygens of the coordinated  $EnH_2$ . Accordingly, a three-bladed propeller-like structure is observed. Two kinds of  $\nu_{C=N}$  relating to imine and oxime groups are observed at 1623 and 1488  $cm^{-1}$  respectively. The  $\mu_{eff}$  is 3.47 BM. Bands at 413 and 541 nm are assigned to d–d transitions in octahedral field and weak band at 477 nm is assigned to d–d transition in square planar field. The emission spectrum under the excitation wavelength 305 nm shows a broad band with maximum emission wavelength at 350 nm.

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### Introduction

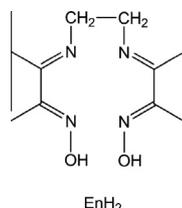
The trimethylene and tetramethylene bridged diiminedioxime ligands can form complexes with Co(II) and Ni(II) ions. These tetradentate ligands can wrap themselves around metal ions in planar

configuration and lose one oxime hydrogen forming a hydrogen bond between two *cis* oxime groups. Moreover, the oxime ligand can act as a bridge between metal ions in order to form polynuclear complexes. The chemistry of oxime complexes of transition metal ions has been attracting continuous attention because of their importance as models for vitamin B<sub>12</sub>, dioxygen carrier, catalysis in chemical transformations, intramolecular hydrogen bonding and metal-metal interaction. The length of alkylene bridge in

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ligands as well as the effect of metal size play a role in the formation of hydrogen bond in the complexes. Comprehensive structural studies of the diiminedioxime complexes of metal ions had been done [1–11]. Ni(II) complexes of trimethylene and tetramethylene bridged diiminedioxime ligands exhibit square planar geometry and existence of hydrogen bond between two oxime groups. For dimethylene bridged ligand, the only structure of complex which has been reported is  $[\text{Co}(\text{EnH})\text{Cl}_2]$  [12]. As part of our diiminedioxime project, the complexation of Ni(II) and  $\text{EnH}_2$  is investigated. The reactions between Ni(II) ion and  $\text{EnH}_2$  ligand were performed several times and resulted in the same complex. This paper thus presents our investigations on the structure, characterization and spectroscopic properties of the complexes.



## Experimental

All chemicals are commercially available (Fluka Co., Scharlau Co., Carlo Erba Co., BHD Co., Fisher Co., Merck Co. and LAB-SCAN Co.) and used without further purification. All X-ray data were collected on a Bruker Smart CCD Diffractometer. The elemental analysis was performed by CHNS/O Analyzer Perkin Elmer Model PE 2400 Series II. Thermogravimetric analyses (TGA) were studied by a Perkin Elmer TGA7 in a  $\text{N}_2$  atmosphere (heating rate =  $10^\circ\text{C min}^{-1}$ ) using platinum pan. Magnetic susceptibility measurements were carried out at room temperature on magnetic susceptibility balance model Magway MSB Mk1. The FTIR spectrum was recorded on a Bruker Model Equinox 55 Spectrophotometer using the KBr pellets. The absorption spectra of complex were recorded in a mixed solvent ( $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH} = 1:5$ ) from Jasco V-530 spectrophotometer.

**Caution!** Perchlorate salts are potentially explosive. Only small quantities of material should be prepared and the samples should be handled with care.

**Synthesis of Ligand:** 3,3'-(1,2-ethanediyldinitrilo)bis(2-butanone)dioxime ( $\text{EnH}_2$ )

Ligand  $\text{EnH}_2$  was prepared using method described in the literature [12] with slight modification. Diacetylmonoxime (20.23 g, 0.20 moles) in  $50\text{ cm}^3$  methanol was added to ethylenediamine ( $6.6\text{ cm}^3$ , 0.10 moles). The resulting solution was stirred at room temperature. After 30 min, white solid precipitated. It was then isolated by a vacuum filtration, washed with cold methanol and diethylether and dried in a desiccator. The yield was 75%. The  $\text{EnH}_2$  ligand has a melting point of 160–161  $^\circ\text{C}$ .

**Synthesis of Tris(3,3'-(1,2-ethanediyldinitrilo)bis(2-butanone)dioximatonicel(II)) nickel(II) perchlorate,  $[\text{Ni}(\text{Ni}(\text{En}))_3](\text{ClO}_4)_2$  (**1**)**

$\text{Ni}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  0.281 g (2.0 mmol) and  $0.5\text{ cm}^3$  1 M NaOH were added to a 0.452 g (2.0 mmol)  $\text{EnH}_2$  dissolved in  $30\text{ cm}^3$  acetone. The resulting orange red solution was allowed to stand for a few days. Red precipitate was collected and dried in a desiccator. The yield was 23%. The red single crystal was crystallized from a mixture of acetone:ethanol (1:1). *Anal. Calc.* for  $\text{C}_{30}\text{N}_{12}\text{O}_{14}\text{H}_{48}\text{Ni}_4\text{Cl}_2$

$\cdot 9\text{H}_2\text{O}(\%)$ : C, 28.40; H, 5.24; N, 13.25. Found: C, 27.97; H, 4.78; N, 13.00

## X-ray crystallographic analysis

The diffraction data were collected at 293(2) K on a 1 K Bruker Smart CCD area detector diffractometer using  $\omega$  rotation scans with a scan width of  $0.3^\circ$  and graphit-monochromated Mo- $\text{K}\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). For the data collection and data integration, the SMART and SAINT programs [13] were used and empirical absorption correction was performed using the program SADABS [14]. The structure was solved by direct methods using the SHELXTL program system [15] and was refined by full-matrix least-squares first with isotropic and then with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atom positions were calculated based on an "ideal" O–H distance of 0.86  $\text{\AA}$ , and C–H distance of 0.96  $\text{\AA}$  for  $-\text{CH}_3$  and 0.97  $\text{\AA}$  for  $-\text{CH}_2$ . The idealized angles agreed with a difference Fourier map. Crystal data and additional details of the data collection and refinement of **1** are presented in Table 1 and the selected bond lengths and angles for  $[\text{Ni}(\text{Ni}(\text{En}))_3](\text{ClO}_4)_2$  **1** are shown in Table 2.

## Result and discussion

### Crystal structure of $[\text{Ni}(\text{Ni}(\text{En}))_3](\text{ClO}_4)_2$ **1**

Complex **1** crystallizes in an R-centered trigonal cell with the space group R $\bar{3}$ . The structure consists of an octahedral  $[\text{Ni}(\text{Ni}(\text{En}))_3]^{2+}$  cation containing four Ni(II) ions with different hybridizations ( $\text{dsp}^2$  and  $\text{sp}^3\text{d}^2$ ) and two perchlorate anions ( $\text{ClO}_4^-$ ). Three  $\text{dsp}^2$  Ni(II) ions coordinate to three  $\text{EnH}_2$  ligands via imine nitrogens and oxime nitrogens forming a square planar geometry around each Ni(II) and the fourth Ni(II) ion octahedrally coordinates to six oxime oxygens of three coordinated  $\text{EnH}_2$  whose all oxime hydrogens are lost. Consequently, a three-bladed propeller-like structure is observed as shown in Fig. 1. Three five-membered chelate rings and one six-membered ring are present in each  $[\text{Ni}(\text{En})]$  moiety. All atoms in the square plane are coplanar. Two perchlorate anions are disordered. The average Cl–O bond length in one perchlorate ion is 1.436(8)  $\text{\AA}$  and the other is 1.443(10)  $\text{\AA}$ . The O–O distance in **1** is 2.962  $\text{\AA}$  which is quite longer than those found in  $[\text{Co}(\text{EnH})\text{Cl}_2]$  (2.708  $\text{\AA}$ ) and  $[\text{Ni}(\text{BnH})]\text{ClO}_4$

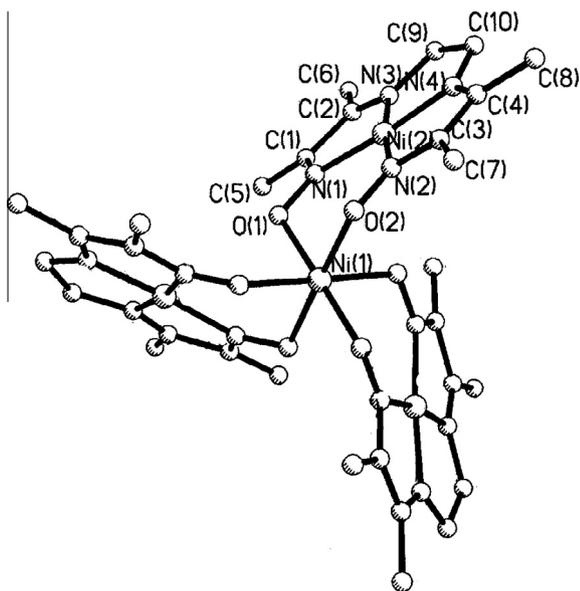
**Table 1**

Crystal data for  $[\text{Ni}(\text{Ni}(\text{En}))_3](\text{ClO}_4)_2$ , **1**.

Chemical formula	$\text{Ni}_8\text{C}_{60}\text{H}_{96}\text{Cl}_{14}\text{N}_{24}\text{O}_{28}$
Formula mass	2212.83
Crystal system	Trigonal
Space group	R- $\bar{3}$
Z	3
Temperature (K)	293
a, b, c ( $\text{\AA}$ )	15.4141(6), 15.4141(6), 33.890 (3)
b ( $\text{\AA}$ )	15.4141(6)
c ( $\text{\AA}$ )	33.890 (3)
$\alpha, \beta, \gamma$ ( $^\circ$ )	90, 90, 120
V ( $\text{\AA}^3$ )	6973.3 (7)
$\lambda$ ( $\text{\AA}$ )	Mo $\text{K}\alpha$ 0.71073
$D_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	1.570
$\mu$ ( $\text{mm}^{-1}$ )	1.78
$2\theta_{\text{max}}$ ( $^\circ$ )	28.3
No. measured reflections	19166
No. independent reflections	3717
Goodness of fit on $F^2$	0.94
$R[F^2 > 2\sigma(F^2)]$	0.088
wR( $F^2$ )	0.251

**Table 2**  
Selected bond lengths (Å) and bond angles (°) for  $[\text{Ni}(\text{Ni}(\text{En}))_3](\text{ClO}_4)_2 \cdot \mathbf{1}$ .

Ni(1)—O(1)	2.043(5)	C(1)—C(2)	1.516(13)
Ni(1)—O(2)	2.027(6)	C(1)—C(5)	1.492(13)
Ni(2)—N(1)	1.879(6)	C(3)—C(4)	1.459(15)
Ni(2)—N(2)	1.873(8)	C(9)—C(10)	1.474(17)
Ni(2)—N(3)	1.816(8)	N(1)—Ni(2)—N(2)	105.3(3)
Ni(2)—N(4)	1.826(8)	N(1)—Ni(2)—N(3)	84.2(4)
N(1)—O(1)	1.306(7)	N(2)—Ni(2)—N(4)	84.6(4)
N(2)—O(2)	1.280(9)	N(3)—Ni(2)—N(4)	85.9(5)
N(3)—C(2)	1.275(11)	O(1)—Ni(1)—O(2)	93.4(2)
N(3)—C(9)	1.476(13)	O(2)—Ni(1)—O(1) <sup>i</sup>	92.1(2)
C(1)—N(1)	1.301(10)	O(1) <sup>i</sup> —Ni(1)—O(2) <sup>i</sup>	93.4(2)
C(2)—N(3)	1.275(11)	O(2) <sup>i</sup> —Ni(1)—O(1) <sup>ii</sup>	92.1(1)
C(3)—N(2)	1.345(11)	O(1) <sup>ii</sup> —Ni(1)—O(2) <sup>ii</sup>	93.4(2)
C(4)—N(4)	1.259(14)	O(2) <sup>ii</sup> —Ni(1)—O(1)	92.1(2)

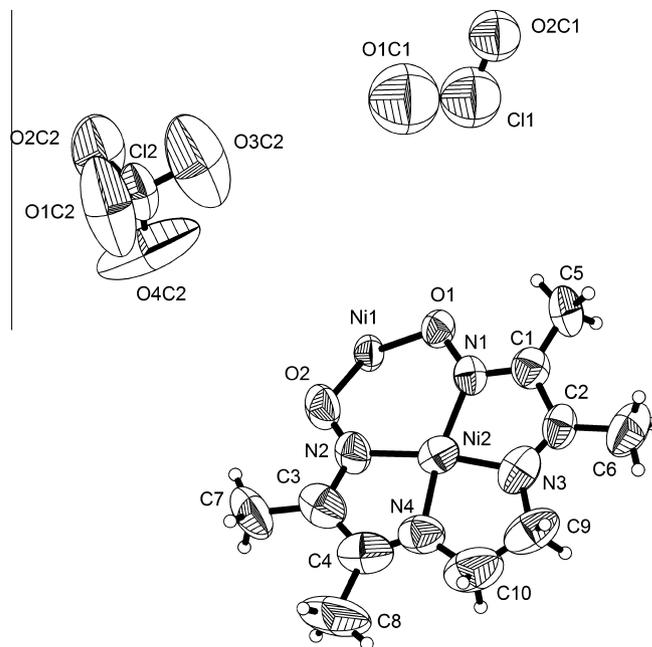
Symmetry codes: (i)  $-x + y, -x + 1, z$ , (ii)  $-y + 1, x - y + 1, z$ .**Fig. 1.** Molecular structure of  $[\text{Ni}(\text{Ni}(\text{En}))_3](\text{ClO}_4)_2 \cdot \mathbf{1}$  showing a three-bladed propeller-like structure.

(2.432 Å) [12]. The elongation of the O—O distance in the diiminedioxime complexes of Ni(II) agrees with the constraint degree of the alkylene bridge between the two imine nitrogens. Such constraint follows the order:  $\text{EnH}_2 > \text{BnH}_2$  [12]. The ethylene bridge between two imine-nitrogens imposes more constraint on the complex geometry. Consequently, the  $\text{N}_{(\text{imine})}\text{—Ni(2)—N}_{(\text{imine})}$  angle ( $85.9(5)^\circ$ ) is smaller than the  $\text{N}_{(\text{oxime})}\text{—Ni(2)—N}_{(\text{oxime})}$  angle ( $105.3(3)^\circ$ ). The  $\text{Ni(2)—N}_{(\text{oxime})}$  bonds (1.879(6) and 1.873(8) Å) are longer than those  $\text{Ni(2)—N}_{(\text{imine})}$  bonds (1.816(8) and 1.826(6) Å) (see Fig. 2).

The C— $\text{N}_{(\text{oxime})}$  bond lengths in free ligand are shorter than those found in complex **1**, but the C— $\text{N}_{(\text{imine})}$  bonds lengths are longer [16]. Such observation is also found in  $[\text{Co}(\text{EnH})\text{Cl}_2]$  [12]. The C1—C2, C3—C4 and C9—C10 bond lengths are 1.516(13), 1.459(15), 1.474(17) Å respectively. No hydrogen bonds between molecules are observed.

#### Thermogravimetric analysis

Thermogravimetric analysis showed that complex **1** was stable up to approximately 200 °C (when signal drops). This leads to an evidence of small explosion due to perchlorate ions. No normal thermogram was obtained.

**Fig. 2.** Perspective view of asymmetric unit of  $[\text{Ni}(\text{Ni}(\text{En}))_3](\text{ClO}_4)_2 \cdot \mathbf{1}$  showing thermal ellipsoids (50% probability) and atom labeling.

#### Infrared spectrum

The ligand contains two kinds of C=N groups relating to the imine and oxime groups. The locations of these bands near 1600 and  $1500 \text{ cm}^{-1}$  clearly manifest that the vibrational energies of these groups are significantly different from each other. On the basis of the available data on structurally related molecules such as dimethylglyoxime and Schiff-bases, the high frequency and the low frequency bands are assigned to the imine and oxime C=N groups respectively. Two  $\nu_{\text{C=N}}$  are observed at higher frequencies than that in free ligand as shown in Table 3. The  $\nu_{\text{C=N}}$  stretching band due to C=N—OH group of  $\text{H}_2\text{dmg}$  appears at  $1450 \text{ cm}^{-1}$  which shifts to a higher frequency regions in its complexes. No peak is observed in the region  $1772\text{--}1783 \text{ cm}^{-1}$ , indicating that no intramolecular hydrogen bond between oxime is formed. This information is consistent with the crystal structure.

#### Magnetic susceptibility

Magnetic susceptibility data was collected at room temperature. The molar magnetic susceptibility ( $\chi_m$ ) values for this complex is  $4.74 \times 10^{-4} \text{ emu mol}^{-1}$ . After doing diamagnetic correction [17], the  $\mu_{\text{eff}}$  is found to be 3.47 BM which is at the upper limit of values observed for octahedral Ni(II) complexes. Many octahedral Ni(II) complexes are found to have magnetic moments in the range 2.81–3.66 BM [18–21]. The higher magnetic moments when compared to the spin-only value 2.8 BM, may be attributed to the slight mixing of a multiplet excited state in which spin-orbit coupling is appreciable [22].

#### Electronic and emission spectrum

The electronic spectrum of complex **1** exhibits several peaks at 206(s), 245(s), 304(m), 413(m), 477(w) and 541(w) nm. The first three peaks are due to intra-ligand transitions. Bands at 413 and 541 nm are assigned to the  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$  and  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$  transitions in octahedral environment respectively. The band at

**Table 3**

The vibrational frequency for the C=N bond in the free ligand and complexes.

Compound	$\nu_{\text{C=N}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{ClO}_x}$ ( $\text{cm}^{-1}$ )	Average C–N bond ( $\text{\AA}$ ) oxime imine	References
EnH <sub>2</sub>	1607(m) 1472(w)	–	1.283(2) 1.286(2)	[16]
[Co(EnH)Cl <sub>2</sub> ]	1628(w) 1471(m)	–	1.305(3) 1.214(3)	[12]
[Ni(Ni(En)) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	1623(w) 1488(m)	1097(s) 717(sh)	1.32(1) 1.27(1)	This work

413 nm is responsible for the reddish color of the compound. Square planar Ni(II) complex exhibits a single band in the range 450–600 nm with second band at very high energies less than 200 nm. Thus weak band at 477 nm is assigned to  $^1A_{1g} \rightarrow ^1B_{1g}$  transition in square planar field.

The emission spectra is investigated in an aqueous solution at room temperature. The emission spectrum under the excitation wavelength 305 nm shows a broad band ranging from 300 to 500 nm with its maximum emission wavelength at 350 nm which results from the effect of the MLCT transition.

### Conclusion

The reaction between Ni(ClO<sub>4</sub>)<sub>2</sub> and EnH<sub>2</sub> ligand results in a new complex containing four Ni(II) ions with different hybridizations ( $dsp^2$  and  $sp^3d^2$ ). Three  $dsp^2$  Ni(II) ions coordinate to three EnH<sub>2</sub> ligands via imine nitrogens and oxime nitrogens resulting in three square planar moieties. The imposed significant constraint in the ligand causes a long O–O distance between two oxime groups. As a result, no intramolecular hydrogen bond is formed. The six oxime oxygens of three coordinated EnH<sub>2</sub> are thus available for coordination to the fourth nickel ion. In addition there is no steric effect on the planar nickel complex, hence the octahedral nickel complex can be formed easily. Three-bladed propeller-like structure is obtained.

### Supplementary data

CCDC 966183 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from the CCDC, 12 Union Road, Cambridge CB2, 1EZ, UK, fax: +44 1223 336 033; or email: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk> on request.

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