

The synthesis and characterization of novel (E,E)-dioxime and its nickel (II) complexes containing compartmental and twofold macrocyclic moieties

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Abstract A new (E,E)-dioxime, S,S'-bis(2-acetophenone)dithioglyoxime, has been synthesized by the reaction of dichloroglyoxime with 2-thioacetophenone. Only mononuclear Ni (II) complex with a metal:ligand ratio (1:2) was prepared and then Ni(II) complex bridged BF_2^+ was obtained with hydrogen-bridged Ni(II) complex and boron trifluoride etherate. The reaction of BF_2^+ -capped Ni(II) complex with 4',5'-diaminobenzo [15-crown-5] gave a twofold complex. The structure of ligand and Ni(II) complexes are proposed according to elemental analyses, ^1H , ^{13}C NMR, IR and mass spectral data and semi-empirical quantum chemical calculations.

Keywords *vic*-Dioxime · BF_2^+ -capped complex · Diloop macrocycle · Twofold compound · Macrocyclization · Nickel(II) complexes

Introduction

The coordination chemistry of *vic*-dioximes has been widely investigated as analytical reagents, as models for biological systems such as B_{12} vitamin, as compounds having columnar stacking thought to be reason for their semiconducting properties [1–3]. Such compounds have been used as chelating agent in coordination chemistry very often since the beginning of the last century [4, 5].

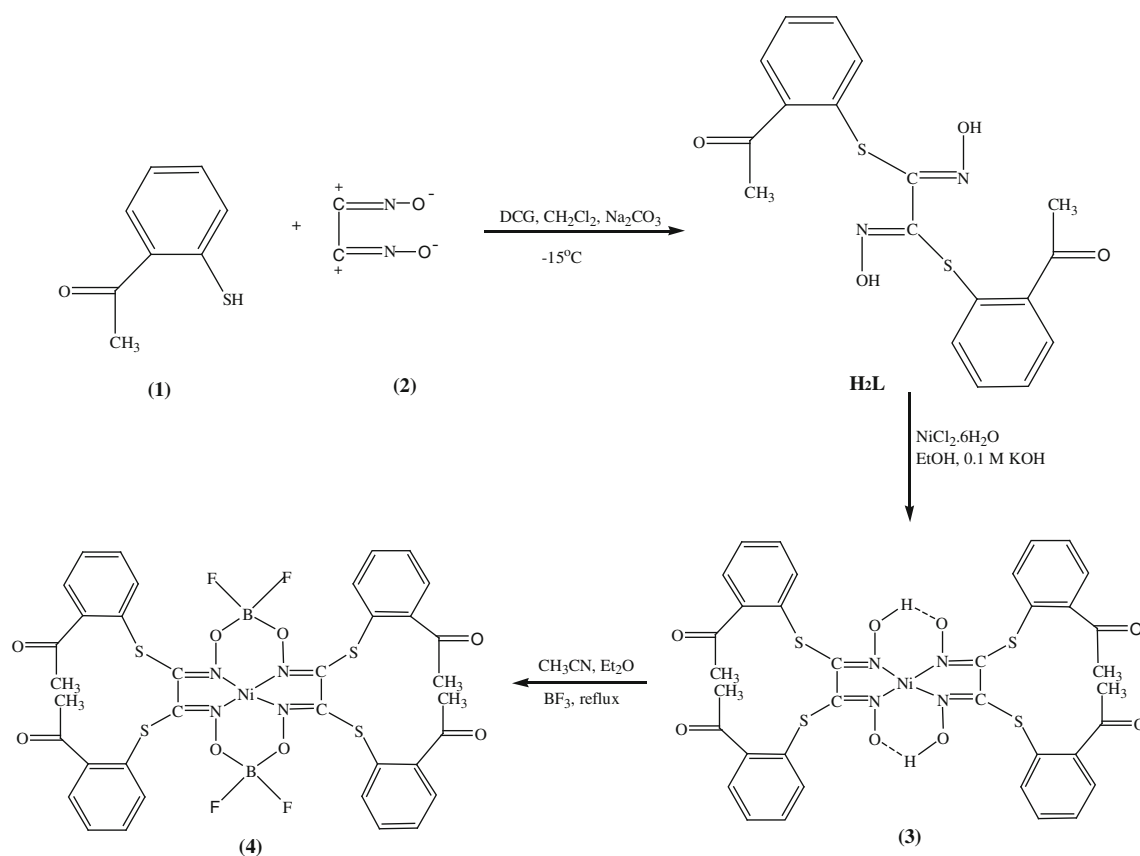
Since that time, several quasi-macrocyclic and BF_2^+ -capped oximes have been synthesized [6, 7]. Schrauzer has synthesized a group of macrocyclic dioxime complexes of cobalt(III) in which the bridging protons of the bis(dioxime) ligand are replaced by BF_2^+ groups, an alteration which firms the macrocyclic structure while removing acidic protons from the vicinity of the O_2 -binding site [8, 9]. Due to the presence of mildly acidic hydroxy groups and slightly basic azomethine groups, *vic*-dioximes are amphoteric chelates that form corrin-type square-planar, square-pyramidal and octahedral complexes with various transition metal ions [10, 11]. The exceptional stability and unique electronic properties of these complexes can be attributed to their structure which is stabilized by intramolecular hydrogen bonding [12, 13]. There are three geometrical isomers, such as anti-(E,E), amphi-(E,Z) and syn-(Z,Z), of the *vic*-dioxime according to the hydroxyimino groups that have to be considered for coordination [14–17].

The very active current research in polymacrocyclic chemistry has led to the development of numerous synthetic routes for affecting macropolycyclization, thus giving access to a great number of novel macropolycyclic molecules [18–21]. Polymacrocyclic ligand system and their polynuclear complexes of transition metals are actively being investigated as models of metalloproteins, metalloenzymes and some biological systems as biomimetics, catalysts and important materials for molecular electronics as molecular magnets [22–25]. Many of macrocyclic ligands involve four nitrogen atoms as donors. In contrast to the enormous amount of information on these systems, less study has been performed on complexes with other combinations of donor atoms such as sulfur [26–28].

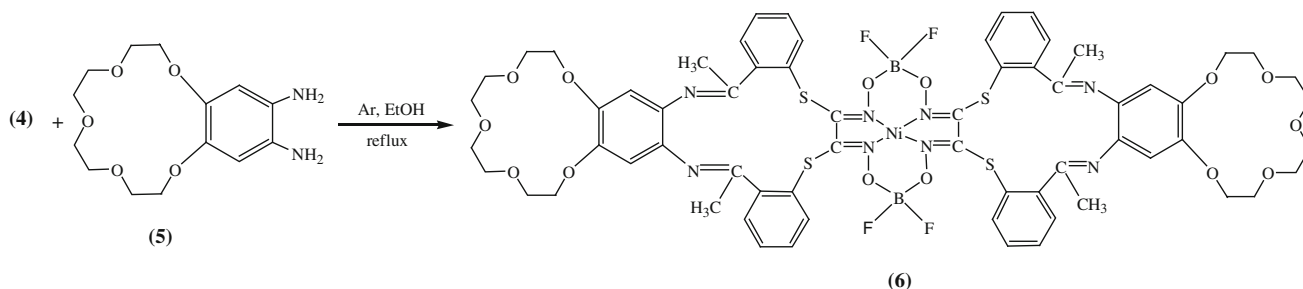
We report here the synthesis and characterization of novel (E, E)-dioxime and its Ni (II) complex as well as the

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Scheme 1 Synthesis of BF_2^+ -capped nickel(II) complex



Scheme 2 Synthesis of compartmental and twofold macrocyclic nickel(II) complex

synthesis and structural properties of the BF_2^+ -capped complex (Scheme 1). Then the nickel (II) complex containing compartmental and twofold macrocyclic moieties has been prepared by the macrocyclization reaction of 4',5'-diaminobenzocrown-5 with the BF_2 bridged nickel(II) complex (Scheme 2).

Experimental

Reagents

2-Mercapto acetophenone [29], 4',5'-diaminobenzocrown-5 [30], dichloroglyoxime [31] and cyanogendi-N-

oxide [12] were prepared according to the described procedure. Analytical grade chemicals were purchased from Aldrich and Alfa Aesar and were used without further purifications. Some synthetic manipulations were performed under argon atmosphere. Some solvents were purified before use by standard procedures [32].

Equipments

Elemental analyses were determined with a CHNS-932 LECO instrument. The metal content of the complexes was determined with a Unicam 929 AA spectrometer. FT-IR spectra were recorded on a Perkin-Elmer SpectrumOne FTIR spectrometer as KBr pellets. ^1H and ^{13}C NMR

spectra were recorded in dimethyl sulfoxide- d_6 (DMSO- d_6) solutions on a Varian Mercury 200 MHz spectrometer using TMS as an internal reference. The mass spectra were recorded on a MicrOTOF equipment with an electrospray source and on a Micromass Quatro LC/ULTIMA LC-MS/MS spectrometer. Melting points were determined with an electrothermal apparatus and are uncorrected. All the quantum chemical calculations were carried out using HYPERCHEM 7.0 software.

Syntheses

Preparation of *S,S'*-bis(2-acetophenone)dithioglyoxime **H₂L**

A solution of cyanogendi-N-oxide in dichloromethane (25 mL), which was prepared from dichloroglyoxime (DCG) (0.785 g, 5 mmol) and an aqueous solution of Na₂CO₃ (0.5 M, 25 mL), was added with stirring to a solution of 2-mercapto acetophenone (1.52 g, 10 mmol) in dichloromethane (200 mL) at $-15\text{ }^{\circ}\text{C}$. The reaction was continued for 12 h at the above temperature and the pale yellow crystallized product was separated from the solvent by filtration and washed with 10 mL of cold dichloromethane and 15 mL of diethyl ether, respectively, then dried in vacuo. Yield: 1.19 g (61.3%) as a pale yellow crystal. Mp. $203\text{ }^{\circ}\text{C}$ (dec.). Elemental analysis calc. For C₁₈H₁₆N₂O₄S₂: C, 55.67; H, 4.12; N, 7.21. Found: C, 55.83; H, 3.90; N, 7.47. ¹H NMR (200 MHz, DMSO- d_6) δ : ppm 12.44 (s, 2H, N-OH), 7.91 (d, 2H, Ar-H), 7.35 (m, 4H, Ar-H), 7.03 (d, 2H, Ar-H), 2.55 (s, 6H, CH₃). ¹³C NMR (50 MHz, DMSO- d_6) δ : ppm 201.29, 146.04, 137.97, 132.62, 132.33, 132.11, 131.65, 127.79, 28.74. IR (ν/cm^{-1} , KBr pellets): 3228, 3051, 2990, 1669 (C=O), 1651 (C=N), 1585, 1559, 1465, 1420, 1360, 1301, 1281, 1248, 1048, 1051, 966, 855, 756. Mass spectrum (ESI): $m/z = 389.06$ [M + 1]⁺.

Preparation of [Ni(HL)₂] **3**

A solution of NiCl₂·6H₂O (0.24 g, 1 mmol) in ethanol (15 mL) was added to a solution of 2 mmol ligand [**H₂L**] (0.776 g) in hot ethanol (100 mL) at $70\text{ }^{\circ}\text{C}$. A distinct change in color and a decrease in the pH value (pH = 1.26) of the solution were observed. While heating and stirring at the same temperature, an equivalent of ethanolic triethylamine (0.1 M) solution was then added to adjust the pH to about 4.5, when orange precipitation of the complex started. The mixture was heated and stirred on a water-bath for another 3 h, until the precipitate was formed. The resulting reaction mixture was filtered off, the precipitate was washed with 25 mL of water, 15 mL of ethanol and 15 mL of diethyl ether, respectively, then dried

in vacuo. Yield: 0.76 g (92%) as a dark orange powder. Mp. $257\text{ }^{\circ}\text{C}$ (dec). Elemental analysis calc. for C₃₆H₃₀N₄O₈S₄Ni: C, 51.87; H, 3.60; N, 6.72; Ni, 7.05. Found: C, 51.99; H, 3.85; N, 6.43; Ni, 7.37. ¹H NMR (200 MHz, DMSO- d_6) δ : 16.91 (s, 2H, O-H O), 7.98 (d, 4H Ar-H), 7.33 (m, 8H, Ar-H), 7.14 (d, 4H, Ar-H), 2.49 (s, 12H, CH₃). ¹³C NMR (50 MHz, DMSO- d_6) δ : 199.28, 146.76, 138.17, 133.08, 132.87, 132.39, 132.01, 127.66, 28.99. IR (ν/cm^{-1} , KBr pellets): 3061, 2994, 1711 (O-H...O), 1673 (C=O), 1641 (C=N), 1560, 1460, 1434, 1359, 1297, 1273, 1256, 1046, 964, 883, 754. Mass spectrum (ESI): $m/z = 833.04$ [M + 1]⁺, 855.02 [M + Na]⁺.

Preparation of [Ni(LBF₂)₂] **4**

A suspension of hydrogen bridged nickel(II) complex [Ni(HL)₂] **3** (0.624 g, 0.75 mmol) in 100 mL of freshly distilled acetonitrile was brought to reflux temperature under argon atmosphere. The equivalent amount of boron trifluoride ethyl ether complex (0.4 mL, 1.5 mmol) was added to the above suspension and the reaction mixture became red immediately. The solution was boiled under reflux with stirring for 2 h and monitored by TLC using BAW [(*n*-butanol:acetic acid:water)(4:1:5)] then allowed to cool room temperature. The solution was concentrated to 10 mL under reduced pressure and then allowed to stand at $-18\text{ }^{\circ}\text{C}$ overnight, whereupon the desired product precipitated. The red solid precipitate was collected by filtration, washed with 10 mL of cold acetonitrile and 15 mL of diethyl ether, respectively, then dried in vacuo. Yield: 0.39 g (62.5%) as a red powder. Mp. $178\text{ }^{\circ}\text{C}$ (dec.). Elemental analysis calc. for: C₃₆H₂₈N₄O₈S₄B₂F₄Ni: C, 46.55; H, 3.01; N, 6.03; Ni, 6.32. Found: C, 46.66; H, 2.86; N, 5.79; Ni, 6.61. ¹H NMR (200 MHz, DMSO- d_6) δ : 7.89 (m, 4H, Ar-H), 7.33 (m, 8H, Ar-H), 7.28 (m, 4H, Ar-H), 2.47 (s, 12H, CH₃). ¹³C NMR (DMSO- d_6) δ : 199.12, 145.40, 140.66, 135.67, 134.55, 133.82, 132.98, 128.01, 28.20. IR (ν/cm^{-1} , KBr pellets): 3058, 2994, 1689 (C=O), 1655 (C=N), 1584, 1467, 1432, 1360, 1307, 1274, 1246, 1120, 1083, 960, 910, 819, 795, 767. Mass spectrum (ESI): $m/z = 928$ [M]⁺.

Preparation of [Ni(LBF₂)₂L'₂] **6**

A solution of 4',5'-diaminobenzo[15-crown-5] (**5**) (0.15 g, 0.5 mmol) and Ni(II) complex (**4**) (0.232 g, 0.25 mmol) in dry ethanol (30 mL) was added with stirring over 8 h to a few drops of formic acid in dry ethanol (750 mL) under argon atmosphere at reflux conditions. The reaction mixture was refluxed with stirring for 48 h and checked by TLC[silica gel (chloroform:methanol)(99:1)], which showed the consumption of stopper. After cooling, ethanol was removed in vacuo and the reaction mixture was

directly purified over silica gel chromatography eluted with an eluent [(chloroform:methanol) (99:1)]. The target compound was obtained as red-brown solid. Yield: 0.215 g (59.3%) as a red-brown powder. Mp > 300 °C (dec.). Elemental analysis calc. for: C₆₄H₆₄N₈O₁₄ S₄B₂F₄Ni: C, 52.88; H, 4.40; N, 7.71; Ni, 4.04. Found: C, 52.61; H, 4.69; N, 7.41; Ni, 4.38. ¹H NMR (200 MHz, DMSO-*d*₆) δ: ppm 7.93 (m, 4H, Ar-H), 7.41 (m, 8H, Ar-H), 7.31 (m, 4H, Ar-H), 6.58 (s, 2H, Ar-H), 4.15–3.42 (m, 32H, -CH₂), 2.58 (s, 12H, CH₃). IR (ν/cm⁻¹, KBr pellets): 3067, 3055, 2924–2874, 1652 (C=N), 1637 (C=N), 1595, 1591, 1489, 1457, 1363, 1346, 1303, 1294, 1280, 1257, 1186, 1125–1063, 942, 853, 762, 7.55. Mass spectrum (ESI): *m/z* = 1475 [M + Na]⁺.

Results and discussion

The substituted dithioglyoxime (**H₂L**) was synthesized in a good yield according to the previously reported procedure [33] involving the reaction of 2 equivalent of **1** with 1 equivalent of cyanogendi-N-oxide [12] in dichloromethane at -15 °C under argon atmosphere. A simple scheme showing synthesis of the ligand **H₂L** is depicted in Scheme 1. Vicinal dioxime is air-stable, non-hygroscopic crystalline solid soluble in some organic solvents such as ethanol, dichloromethane, *N,N*-dimethylformamide. Characterization of this compound was achieved by standard spectroscopic techniques as well as elemental analysis. Complexation of the *vic*-dioxime with Ni(II) was carried out by the addition of a solution NiCl₂·6H₂O, an equivalent amount of triethylamine in ethanol and hot solution of **H₂L** in ethanol to afford the 1:2 (metal:ligand) complex **3** in 92% yield. The template synthesis of **4** was performed in 62.5% yield by adding borontrifluoride ethyl ether complex to a refluxing dry acetonitrile suspension containing the precursor nickel (II) complex (**3**). The hydrogen bridge protons were replaced by BF₂ units and with the exception of this, all characteristics were retained according to spectroscopic data. Nickel(II) complex containing compartmental and twofold macrocyclic moieties was prepared by high-dilution techniques in ethanol (Scheme 1). For this purpose, 4',5'-diaminobenzo(15-crown-5) (**5**) was reacted with BF₂⁺-capped nickel(II) complex (**4**) and the synthesis of nickel(II) complex containing compartmental and twofold macrocyclic moieties (Scheme 2.) has been achieved in considerable yield 59.3%.

The novel (E,E)-dioxime and its nickel(II) complexes are characterized by a combination of elemental analysis and spectroscopic data involving ¹H NMR, ¹³C NMR, FT-IR and MS spectra. The compounds gave satisfactory elemental analyses and spectral data corresponded to

mononuclear complexes in which ligand is bonded to metal centre *N,N'*-donor sites.

In the ¹H NMR spectrum of **H₂L**, the deuterium exchangeable protons of -OH groups appeared a signal at δ = 12.44 ppm as a singlet. This result indicates that the structure of **3** has the *S-trans* form [13, 26, 34, 35]. A significant feature of ¹H NMR spectrum of **3** is absence of resonances associated with S-H protons (δ = 4.45 ppm) in the precursor compound (**1**). In the proton decoupled ¹³C NMR spectrum of **H₂L**, the carbon resonance of the azomethine group was found at δ = 146.04 ppm and this unique signal for the C=N groups also confirmed the (E,E)-form of the *vic*-dioxime [36, 37]. The ¹H NMR spectrum of **H₂L** in dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) indicates a deuteriumoxide (D₂O) exchangeable O-H...O protons appeared at δ = 16.91 ppm with 2H integrated values. In the ¹H and ¹³C NMR spectra, only slight differences between those **H₂L** and **3** were observed after complexation. In the ¹H NMR spectrum of BF₂⁺-capped nickel(II) complex (**4**), the deuterium-exchangeable bridging protons of precursor nickel(II) complex (**3**) disappeared after the formation of BF₂-bridging macrocyclic compound. Bridging boron groups caused the resonances of **4** to shift down field relative to those of hydrogen bridged nickel(II) complex. Similar trends were observed in the ¹³C NMR spectrum as observed in the ¹H NMR spectrum of **4**. The resonance of azomethine carbon observed at δ = 146.89 ppm shifted downfield as much as ppm on going from compound with hydrogen bridge to boron-group bridge [38, 39]. In the ¹H NMR spectrum of **6**, the absence of amine functional groups and the presence of new aromatic and cyclic ether group at δ = 6.75 and 4.15–3.42 ppm indicate the formation of new compound which contains diloop and compartmental macrocyclic moiety.

Comparison of the IR spectral data clearly indicates the formation of **H₂L** with the appearance of stretching vibrations at 3228, 1669, 1651 and 966 cm⁻¹ are assigned to the oxime OH, C=O, C=N and NO groups, respectively. Nickel(II) complex (**3**) had an IR spectrum very similar to that of the *vic*-dioxime, except for a shift of the O-H stretching vibrations due to the formation of O-H...O bonds (1,711 cm⁻¹ bending vibrations). A lowering of the vibration frequency (relative to *vic*-dioxime) of about 10 cm⁻¹ for the C=N absorption in the hydrogen bonded Ni(II) complex indicated coordination through the N-donor atoms [11, 40]. In contrast to this downward shift, the BF₂⁺-capped nickel(II) complex exhibits upward-shift of about 14 cm⁻¹ due to the strong electron-withdrawing influence of BF₂⁺ groups incorporated in the macrocycle [41–43]. The bending vibrations of hydrogen bond disappeared upon encapsulation of the H-bonded complex with appearance of resonances concerning BF₂⁺ group

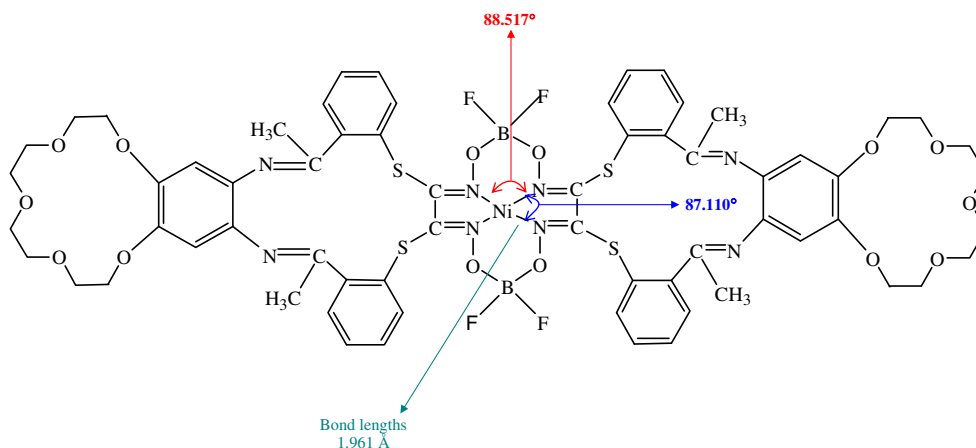


Fig. 1 The calculated of bond length and bond angles of the compartmental and twofold macrocyclic nickel(II) complex

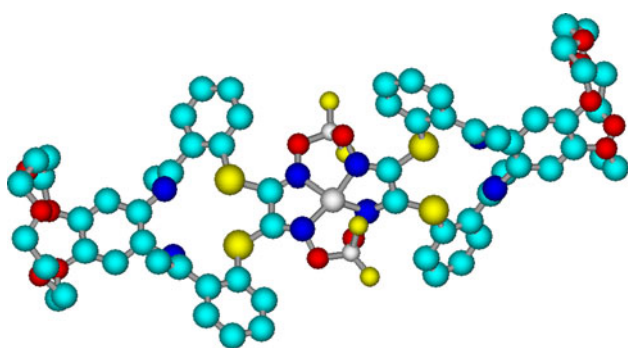


Fig. 2 Optimized geometry of the compartmental and twofold macrocyclic nickel(II) complex

contaminant around 1,180–1,055 and 889–854 cm^{-1} for the B–O and B–F bonds, respectively [40, 44]. In the IR spectrum of **6**, the stretching vibrations belonging to the amino-substituted benzo (15-crown-5) moiety disappear after the macrocyclization reaction and novel resonances, which belong to the azomethine and crown ether groups, appear at 1,637 and 1,130–1,060 cm^{-1} , respectively.

Information about composition of the prepared compounds has also been obtained by MS/MS and micrOTOF spectral studies. Mass spectrum of vicinal dioxime **H₂L** was examined in detail and the peaks appeared at $m/z = 389.06$, 372 and 356 were determined to be molecular ion peak and derived fragment peaks. Accordingly, in the mass spectrum of **3**, the molecular ion peak emerged at $m/z = 833.04$ and 855.02 were calculated as $[M + 1]^+$ and $[M + Na]^+$, respectively. The ESI mass spectra of **4** and **6** exhibited the molecular ion peak at $m/z = 928 [M]^+$ and 1453 $[M + 1]^+$, respectively, which support the proposed formulation.

The totally optimised geometries of the Ni(II) complex containing compartmental and two-fold macrocyclic moieties (Figs. 1, 2) were investigated using ZINDO/1 method [45] in version 7.0 of HYPERCHEM and their stable

Table 1 The calculated total energy, heat of formation, bond length and bond angles of the nickel(II) complex (**6**)

E_{tot} (kJ mol^{-1})	ΔH_f° (kJ mol^{-1})	Ni–N (Å)	$N_1\text{–Ni–}N_2$ (°)	$N_2\text{–Ni–}N_3$ (°)
–211993.54	–142017.50	1.961	87.110	88.517

structure was determined. The calculated total energy, heats of formation and bond lengths between nickel(II) ion and ligand heteroatoms (Table 1) show that square-planar con around the inner Ni(II) ion. The Ni–N distances in the square planar parts of the complex (**6**) are in agreement with the X-ray data for known *vic*-dioxime nickel(II) complex [46].

Conclusions

We have presented a novel pseudomacrocyclic containing BF_2^+ -capped nickel(II) complex as a starting material and its conversion to compartmental and twofold macrocyclic moieties. Starting from novel (E,E)-dioxime and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, the mono-nuclear nickel(II) complex (**3**) was prepared. Then the template synthesis of the BF_2 -bridged nickel(II) complex (**4**) was performed by the reaction of hydrogen-bridged nickel(II) complex with boron-trifluoride ethyl ether complex. The preparation of target nickel (II) complex containing compartmental and twofold macrocyclic moieties (**6**) was accomplished by the reaction of BF_2^+ -capped nickel(II) complex with 4',5'-diaminobenzo[15-crown-5] (**5**). The complete optimization of mononuclear nickel(II) complex containing compartmental and twofold macrocyclic moieties (**6**) was examined using ZINDO/1 method.

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References

- Welcher, F.L.: Organic Analytical Reagents, vol. 3, Chapter VI, pp. 154–234. D. Van Nostrand Company, New York (1947)
- Thomas, T.W., Underhill, A.F.: Metal–metal interactions in transition-metal complexes containing infinite chains of metal atoms. *Chem. Soc. Rev.* **1**, 99–120 (1972)
- Ocak, Ü., Kantekin, H., Gök, Y., Mısırlı, M.N.: Synthesis and characterization of novel (E,E)-dioxime and its polynuclear complex containing macrobicyclic moiety. *New J. Chem.* **27**, 1251–1254 (2003)
- Tschugaeff, L.: Über eine neue Synthese der α -Diketone. *Chem. Ber.* **40**, 186–187 (1907)
- Bekaroğlu, Ö., Sarısan, S., Koray, A.R., Ziegler, M.L.: Die molekül und kristal-struktur von bis(diaminoglyoximato)kobalt(II)diaminoglyoxim, $\text{Co}(\text{C}_2\text{H}_5\text{N}_4\text{O}_2)_2 \cdot \text{C}_2\text{H}_6\text{N}_4\text{O}_2$. *Zeit. Naturforsch* **32b**, 387–392 (1977)
- Uhling, E., Friedrich, M.: Untersuchungen an oximkomplexen. III. nickelchelat des bis (diacetylmonoximimino)propans-1,3 und des bis-(diacetylmonoximimino)-athans 1,2. *Z. Anorg. Allg. Chem.* **343**, 299–307 (1966)
- Addison, A.W., Carpenter, M., Lau, L.K.-M., Wicholas, M.: Coordination sphere flexibility at copper: chemistry of a unipositive copper(II) macrocycle, $[\text{Cu}(\text{cyclops})]^+$. *Inorg. Chem.* **17**, 1545–1552 (1978)
- Schrauzer, G.N., Lee, L.P.: Cobaloximes(II) and vitamin B₁₂ as oxygen carriers. Evidence for monomeric and dimeric peroxides and superoxides. *J. Am. Chem. Soc.* **92**, 1551–1557 (1970)
- Bakac, A., Espenson, J.E.: Unimolecular and bimolecular homolytic reactions of organochromium and organocobalt complexes. Kinetics and equilibria. *IBID* **106**, 5197–5202 (1984)
- Smith, P.A.: The Chemistry of open-chain organic nitrogen compounds, vol. 2. W.A. Benjamin, New York (1965)
- Gök, Y., Kantekin, H.: The synthesis and characterization of new (E,E)-dioximes and their BF_2^{2+} -capped mono and trinuclear complexes with Ni(II), Pd(II) and Co(III). *New J. Chem.* **19**, 461–467 (1995)
- Grundman, C., Mini, V., Dean, S.M., Frommheld, H.D.: Über nitriloyde IV. Dicyan-di-N-oxyd. *Ann. Chem.* **687**, 191 (1965)
- Gök, Y., Ocak, Ü., Sentürk, H.B.: First example of a *vic*-dioxime and its homo- and heteropentanuclear complexes containing a macrobicyclic moiety. *New J. Chem.* **25**, 364–368 (2001)
- Gök, Y., Bekaroğlu, Ö.: The synthesis and complex formation of stereoisomers of some new α -dioximes. *Synth. React. Inorg. Met. Org. Chem.* **11**, 621 (1981)
- Gök, H., Ertepinar, H., Yıldız, S.Z.: The spectroscopic investigation of *amphi-anti* isomerism and interconversion in a novel *vic*-dioxime and its complexes. *Spect. Lett.* **23**, 713–725 (1990)
- Yüksel, F., Gürek, A.G., Durmuş, M., Gürol, I., Ahsen, V., Jeanneau, E., Luneau, D.: New insight in coordination of *vic*-dioximes: bis- and tris(E,E-dioximato) Ni (II) complexes. *Inorg. Chim. Acta* **361**, 2225–2235 (2008)
- Bilgin, A., Ertem, B., Gök, Y.: Synthesis and characterization of a novel quinoxaline-substituted *vic*-dioxime and its complexes containing bis(12-diazacrown-4) derivatives. *Bull. Chem. Soc. Jap.* **80**, 1549–1555 (2007)
- Meade, T.I., Busch, D.H.: Inclusion complexes of molecular transition metal hosts. *Prog. Inorg. Chem.* **33**, 59–126 (1985)
- Christensen, J.J., Hill, J.O., Izatt, R.M.: Ion binding by synthetic macrocyclic compounds. *Science*. **174**, 459–467 (1971)
- An, H., Bradshaw, J.S., Izatt, R.M.: Macropolycyclic polyethers (cages) and related compounds. *Chem. Rev.* **92**, 543 (1992)
- Kantekin, H., Ocak, Ü., Gök, Y., Alp, H.: Synthesis and characterization of new (E,E)-dioxime and its homo and heterotrinnuclear complexes containing dioxo dithiadiazamacrobicyclic moiety. *Polyhedron* **21**, 1865 (2002)
- Feig, A.L., Lippard, S.J.: Reactions of non-heme Iron(II) centers with dioxygen in biology and chemistry. *Chem. Rev.* **94**, 759–805 (1994)
- Cotton, F.A., Adams, R. (eds.): Catalysis by di- and polynuclear metal complexes. VCH, New York (1997)
- Kahn, O.: Molecular magnetism. VCH, Weinheim (1993)
- Voloshin, Y.Z., Varzatskii, O.A., Kron, T.E., Belsky, V.K., Zavadnik, V.E., Strizhakova, N.G., Palchik, A.V.: Tribbed-functionalized clathrochelate iron(II) dioximates as a new and promising tool to obtain polynucleating and polynuclear compounds with improved properties. *Inorg. Chem.* **39**, 1907–1918 (2000)
- Gök, Y., Kantekin, H., Degirmencioglu, I.: The synthesis and characterization of novel dioximes and their heteronuclear complexes containing crown ether moieties. *Polyhedron* **12**, 2097 (1993)
- Gök, Y., Karaböcek, S., Karaböcek, N., Atalay, Y.: The synthesis and characterization of novel (E,E)-dioximes and their mono and trinuclear complexes. *New J. Chem.* **19**, 1275–1283 (1995)
- Atilla, D., Asma, S., Gürek, A.G.: Highly soluble Ni(II) *vic*-dioxime complexes containing branched thioether with alkyl chains of different lengths: synthesis and characterization. *J. Coord. Chem.* **62**, 3050–3059 (2009)
- Coomes, R.C., Fenton, D.E.: On the synthesis of 2-methylchromone-4-thione and 2-methyl-1-thiocromone. *Phosphorus Sulfur* **14**, 139–142 (1983)
- Gök, Y.: An improved synthesis of 4,5-diamino (benzo-15-crown-5). *Org. Prep. Proc. Int.* **22**, 641–643 (1990)
- Ponzio, G., Baldracco, F.: Ricerche sulle diossime. *Gazz. Chim. Italy* **60**(415), 429 (1930)
- Perrin, D.D., Armarego, W.F.L.: Purification of laboratory chemicals. Pergamon, Oxford (1986)
- Kantekin, H., Gök, Y.: A novel *vic*-dioxime with crown ether moieties. *Chem. Ber.* **123**, 1479 (1990)
- Gök, Y.: The synthesis and characterization of novel tetraoxime and its mono- and polynuclear complexes containing 12-membered diaza-dithia macrocycles. *Polyhedron* **15**, 1355–1361 (1996)
- Ahsen, V., Gökçeli, F., Bekaroğlu, Ö.: Synthesis of SS'-bis(4'-benzo[15-crown-5]) dithioglyoxime and its complexes with copper(II) nickel(II), cobalt(II), cobalt(III), palladium(II), platinum(II), and platinum(IV). *J. Chem. Soc. Dalton Trans.* **1987**, 1827–1831 (1987)
- Nakamura, A., Konishi, A., Otsuka, S.: Chiral metal complexes. Part 5. Cobalt(II) and some other transition-metal complexes of chiral *vic*-dioximate ligands derived from D-camphor and L- β -pinene. *J. Chem. Soc. Dalton Trans.* **1979**, 488–495 (1979)
- Lance, K.A., Goldsby, K.A., Busch, D.H.: Effective new cobalt(II) dioxygen carriers derived from dimethylglyoxime by the replacement of the linking protons with difluoroboron(1+). *Inorg. Chem.* **29**, 4537 (1990)
- Bowers, M.J., Hill, C.L.: Synthesis and characterization of several binuclear and mononuclear bis(α -dioximato)nickel(II) complexes. *Inorg. Chim. Acta* **72**, 149–160 (1989)
- Gök, Y., Kantekin, H., Alp, H., Özdemir, M.: Synthesis and characterization of the free ligand 5,6:13,14-dibenzo-9,10-benzo(15-crown-5)-2,3-bis(hydroxyimino)-7,12-dioxo-1,4,8,11-tetraazacyclotetradecane and its mono and tri nuclear complexes. *Z. Anorg. Allg. Chem.* **621**, 1237 (1995)
- Hussain, M.S., Al-Mohdar, H.M., Al-Arfaj, A.R.: Template reactions: axial ligation and macrocyclization of alpha-furylglyoximates and alphaamine-dioximates of cobalt (III) and rhodium(III). *J. Coord. Chem.* **18**, 339–349 (1988)

41. Bigotto, A., Galasso, V., Altì, G.D.: Infrared spectra of transition metal glyoximes. *Spectrochim. Acta Part A*. **27**, 1659–1670 (1971)
42. Kantekin, H., Ocak, Ü., Gök, Y.: Synthesis and characterization of a novel macro-cyclic vic-dioxime and some of its mono and trinuclear complexes. *Z. Anorg. Allg. Chem.* **627**, 1095–1102 (2001)
43. Gök, Y., Kantekin, H.: Synthesis and characterization of novel (E,E)-dioxime and its mono- and heterotrinnuclear complexes. *Acta Chem. Scand.* **51**, 664–671 (1997)
44. Bilgin, A., Ertem, B., Ağın, F.D., Gök, Y., Karshoglu, S.: Synthesis, characterization and extraction studies of a new vic-dioxime and its complexes containing bis (diazacrown ether) moieties. *Polyhedron* **25**, 3165–3172 (2006)
45. Hyperchem Reference Manual, Hypercube Inc, Gainesville, ch. 2, pp 7–8 (1993)
46. Gogycki, L.E., Rundle, R.E.: The structure of nickel dimethylglyoxime. *Acta Cryst.* **6**, 487–495 (1953)