

# Synthesis of N-(4'-Benzo[15-crown-5])thiophenoxyphenylaminoglyoxime and its complexes with some transition metals

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**Abstract** 4-(Chloroacetyl)diphenyl thioether (1) was synthesized from chloroacetyl chloride and diphenyl thioether in the presence of  $\text{AlCl}_3$  as catalyst in a Friedel-Crafts reaction. Subsequently, its keto oxime (2) and glyoxime (3) derivatives were prepared. N-(4'-Benzo[15-crown-5])thiophenoxyphenylaminoglyoxime ( $\text{H}_2\text{L}$ ) and its sodium chloride complex ( $\text{H}_2\text{L} \cdot \text{NaCl}$ ) were prepared from 4-(thiophenoxy)chlorophenylglyoxime (3), 4'-aminobenzo[15-crown-5] and sodium bicarbonate or sodium bicarbonate and sodium chloride. Ni(II), Co(II) and Cu(II) complexes of  $\text{H}_2\text{L}$  and  $\text{H}_2\text{L} \cdot \text{NaCl}$  have a metal–ligand ratio of 1:2 and the ligand coordinates through the two N atoms, as do most of the *vic*-dioximes. The  $\text{BF}_2$ -capped Ni(II) mononuclear complex of the *vic*-dioxime was prepared. The macrocyclic ligands and their transition metal complexes were characterized on the basis of FT-IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR spectroscopy and elemental analyses data.

**Keywords**  $\text{BF}_2^+$ -capped complex · Crown compounds · Glyoximes · Transition metal complexes

## Introduction

The field of coordination chemistry of macrocyclic compounds has undergone spectacular growth during the past 35 years [1–3]. This enormous growth has been due to the

synthesis of a great number and variety of synthetic macrocycles that behave as coordinating agents for metal ions. On the other hand, the development of bioinorganic chemistry has also been another important factor in spurring the growth interest in complexes of macrocyclic compounds [4]. Crown ethers have been found to be powerful extracting agents for alkali metal salts [5]. They are also accepted to be model compounds to mimic antibiotics in cation transport through lipid membranes [6]. There is considerable current interest [7] in complexes of polydentate macrocyclic ligands, because of the variety of geometrical forms available and the possible encapsulation of the metal ion [8].

The coordination chemistry of *vic*-dioximes is interesting and numerous transition metal complexes of this group of ligands have been investigated [9, 10]. Both the presence of mildly acidic hydroxy groups and slightly basic nitrogen atoms make (E,E)-dioximes amphoteric ligands. These ligands form corrin-type square planar, square pyramidal and octahedral complexes with nickel(II), cobalt(II), copper(II), palladium(II) and cobalt(III) as central metal atoms [11–14].

These studies suggest that a suitable combination of a crown ether unit with other donor groups may provide a possibility for preparing new functionalized materials. Addition of crown ether substituents to various coordination compounds causes an increase in their solubility in common organic solvents and water [11]. The derivatives of crown ethers containing different chromophore groups are in the focus of the researchers' attention [15–17] due to their wide application in analytical chemistry as photometric reagents in determination of metals and extractants [18], in supramolecular chemistry (cation receptors, photoswitches, photosensitive molecular antennae) [19, 20].

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The goal of the present study was to obtain and characterize new dioximes containing a macrocycle and prepare their some metal complexes.

## Experimental

Benzo[15-crown-5] [5], 4'-nitrobenzo[15-crown-5] [21], 4'-aminobenzo[15-crown-5] [21, 22] and 4-(chloroacetyl)diphenyl thioether were prepared according to published methods [23]. All reagents were purchased from Merck (Germany) and were used without further purification. Melting points were determined on a Gallenkamp melting point apparatus and were uncorrected. Elemental analyses (C, H, and N) were determined using a Leco, CHNS-932 model analyzer.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DPX-400 400(100) MHz high performance digital FT-NMR, IR spectra on a Perkin Elmer 1605 FT-IR spectrometer in KBr pellets. The UV-visible spectra were recorded on a Shimadzu 160A spectrometer. The metal analyses were determined using a Unicam 929 AAS spectrometer.

### Synthesis of 4-(Chloroacetyl)diphenyl thioether (**1**)

4-(Chloroacetyl)diphenyl thioether was prepared according to the method described in the literature [23]. Yield: (2.07 g; 79%); mp.: 75 °C [Lit: 75–76 °C].

### Synthesis of 4-(Thiophenoxy)phenyloxylohydroxymoyl chloride (**2**), [Keto oxime]

4-(Chloroacetyl)diphenyl thioether (2.62 g, 10 mmol) was dissolved in  $\text{CHCl}_3$  (40 mL) with cooling, and then HCl gas was bubbled through the solution for 30 min. Butyl nitrite (1.5 mL, 11 mmol) was added dropwise to the mixture with stirring and passing HCl gas into the mixture. The mixture was left overnight to form a precipitate at room temperature. The precipitate was filtered and recrystallized from  $\text{Et}_2\text{O}$ –hexane (1:1). The crystallized product was filtered off, washed with hexane and dried. Yield: (2.12 g 73%); m.p.: 135 °C.

Elemental analysis (Found: C, 57.57; H, 3.40; N, 4.74. Calc. for  $\text{C}_{14}\text{H}_{10}\text{ClNO}_2\text{S}$ : C, 57.63; H, 3.45; N, 4.80%); IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3255 (O–H), 3034 ( $\text{C}-\text{H}_{\text{Ar}}$ ), 2380 (OH...O), 1658 (C=O), 1597 (C=N), 1020 (N–O), 699 (C–Cl).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  13.59 (s, 1H, N–OH), 7.94 (d, 2H, Ar–H, J 8.96 Hz), 7.41 (dd, 2H, Ar–H, J 8.6, 7.5 Hz), 7.23 (t, 1H, Ar–H, J 7.5 Hz), 7.08 (d, 2H, Ar–H, J 8.6 Hz), 7.02 (d, 2H, Ar–H, J 8.96 Hz).  $^{13}\text{C}$  NMR

(100 MHz,  $\text{CDCl}_3$ ): 182.86, 161.75, 154.88, 136.39, 133.35, 130.80, 125.45, 120.64, 120.08, 117.38.

### Synthesis of 4-(thiophenoxy)chlorophenylglyoxime (**3**), [Dioxime]

A quantity of (2.91 g, 10 mmol) 4-(thiophenoxy)phenyloxylohydroxymoyl chloride was dissolved in 30 mL of ethanol. Subsequently, solutions of (0.77 g, 11 mmol)  $\text{NH}_2\text{OH} \cdot \text{HCl}$  and (0.82 g, 10 mmol)  $\text{CH}_3\text{COONa}$  (dissolved in the minimum amount of water) were added with stirring. The reaction mixture was heated for 6 h at 40 °C and then the mixture was left to stand for 6 days. The precipitate was filtered off and recrystallized from ethanol. Yield: (1.65 g; 54%); m.p.: 174 °C.

Elemental analysis (Found: C, 54.72; H, 3.54; N, 9.06. Calc. for  $\text{C}_{14}\text{H}_{11}\text{ClN}_2\text{O}_2\text{S}$ : C, 54.81; H, 3.61; N, 9.13%); IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3239 (O–H), 3030 ( $\text{C}-\text{H}_{\text{Ar}}$ ), 2360 (OH...H), 1602 (C = N), 998 (N–O), 689 (C–Cl).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  12.48 (s, 1H, N–OH<sup>a</sup>), 12.04 (s, 1H, N–OH<sup>b</sup>), 7.33 (dd, 2H, Ar–H, J 8.5, 7.2 Hz), 7.23 (d, 2H, Ar–H, J 8.7 Hz), 7.09 (t, 1H, Ar–H, J 7.2 Hz), 6.96 (dd, 2H, Ar–H, J 8.5, 0.91 Hz), 6.89 (d, 2H, Ar–H, J 8.7 Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 157.68, 156.35, 150.34, 136.08, 131.45, 130.68, 126.29, 124.35, 119.94, 117.84.

### Synthesis of N'-(4'-Benzo[15-crown-5]thiophenoxyphenylaminoglyoxime (**4**), ( $\text{H}_2\text{L}$ )

4'-Aminobenzo[15-crown-5] (1.41 g, 5 mmol) dissolved in absolute ethanol (15 mL) was added under an atmosphere of  $\text{N}_2$  at 60 °C to a solution of 4-(thiophenoxy)chlorophenylglyoxime (1.53 g, 5 mmol) in absolute ethanol (10 mL). The mixture was stirred efficiently and heated on a water bath at ca. 60 °C for 3 h. Then mixture was cooled to 0 °C and  $\text{H}_2\text{L}$  was precipitated by addition of cold diethyl ether with continuous stirring. The violet-coloured precipitate was filtered off, washed with cold diethyl ether and dried. Yield: (2.10 g; 76%).

Elemental analysis (Found: C, 60.80; H, 5.46; N, 7.48. Calc. for  $\text{C}_{28}\text{H}_{31}\text{N}_3\text{O}_7\text{S}$ : C, 60.74; H, 5.64; N, 7.59%); IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3390 (N–H), 3198 (O–H), 2945 ( $\text{C}-\text{H}_{\text{Ar}}$ ), 2347 (OH...H), 1591 (C = N), 1268–1235 ( $\text{C}_{\text{Ar}}-\text{O}-\text{C}$ ), 1130–1042 (C–O–C), 948 (N–O).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.80 (s, 1H, N–OH<sup>a</sup>), 10.95 (s, 1H, N–OH<sup>b</sup>), 8.35 (s, 1H, NH), 7.70 (d, 2H, Ar–H, J 8.8 Hz), 7.38 (dd, 2H, Ar–H, J 8.5, 7.4 Hz), 7.25 (d, 2H, Ar–H, J 8.8 Hz), 7.16 (t, 1H, Ar–H, J 7.2 Hz), 7.10 (dd, 2H, Ar–H, J 8.7, 0.96), 6.99 (s, 1H, Ar–H), 6.93 (d, 1H, Ar–H, J 8.4 Hz), 6.89 (d, 1H, Ar–H, J 8.4 Hz), 3.98–3.56 (m, 16H, O–CH<sub>2</sub>–).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 158.38, 157.65, 149.25, 145.36, 138.93, 135.78, 134.51, 131.36, 130.45, 126.12, 124.15, 119.75, 117.66, 115.62, 107.34, 101.43, 73.36, 70.93, 70.48.

Synthesis of sodium chloride complex of  $\text{N}'$ -(4'-benzo[15-crown-5]thiophenoxyphenylaminoglyoxime) (**5**), ( $\text{H}_2\text{L}\cdot\text{NaCl}$ )

A solution of 4-(thiophenoxy)chlorophenylglyoxime (1.53 g, 5 mmol) dissolved in absolute ethanol (10 mL) was added under an atmosphere of  $\text{N}_2$  at 60 °C to a solution of 4'-aminobenzo[15-crown-5] (1.41 g, 5 mmol) in absolute ethanol (15 mL) containing solid  $\text{NaHCO}_3$  (0.82 g, 10 mmol) and  $\text{NaCl}$  (0.29 g, 5 mmol). The mixture was stirred efficiently and heated on a water bath at ca. 60 °C for 3 h. After cooling to room temperature, the mixture was filtered and the solid washed with ethanol (10 mL). The filtrate was cooled to 0 °C and  $\text{H}_2\text{L}\cdot\text{NaCl}$  was precipitated by addition of cold diethyl ether with continuous stirring. The pink-coloured precipitate was filtered off, washed with cold diethyl ether and dried. Yield: (2.51 g; 82%);

Elemental analysis (Found: C, 54.82; H, 4.96; N, 6.78. Calc for:  $\text{C}_{28}\text{H}_{31}\text{N}_3\text{O}_7\text{S}\cdot\text{NaCl}$ : C, 54.93; H, 5.07; N, 6.86%). IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3412 (N–H), 3230 (O–H), 2929 (C– $\text{H}_{\text{Ar}}$ ), 1583 (C = N), 1259–1233 (C $_{\text{Ar}}$ –O–C), 1127–1045 (C–O–C), 950 (N–O).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.71 (s, 1H, N–OH<sup>a</sup>), 10.53 (s, 1H, N–OH<sup>b</sup>), 8.46 (s, 1H, NH), 7.86–6.92 (m, 12H, Ar–H), 4.08–3.52 (m, 16H, O–CH<sub>2</sub>–).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 158.54, 157.83, 149.40, 145.81, 139.09, 135.89, 134.96, 131.43, 130.58, 126.23, 124.21, 119.87, 117.75, 115.71, 107.43, 101.56, 74.25, 71.42, 71.14.

Synthesis of Ni(II), Co(II) and Cu(II) complexes of the ligands (**6–11**)

A solution of 0.25 mmol metal salt [ $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$  (0.06 g),  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$  (0.06 g),  $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  (0.04 g)] dissolved in ethanol (5 mL), was added to a stirred solution of the  $\text{H}_2\text{L}$  (0.27 g, 0.5 mmol) or  $\text{H}_2\text{L}\cdot\text{NaCl}$  (0.30 g, 0.5 mmol) dissolved in ethanol (5 mL). The mixture was heated up to 60 °C and  $\text{NaOH}$  (0.02 g, 0.5 mmol) added dropwise. The reaction was allowed to continue for 3 h at 60 °C. The mixture was allowed to stand a day at room temperature. The precipitated complexes were filtered off, washed with ethanol and dried.

*Data for (6)*. Yield: (0.43 g; 74%); m.p.: 242 °C; Elemental analysis (Found: C, 57.62; H, 5.05; N, 7.08; Ni, 4.97%). Calc. for  $\text{C}_{56}\text{H}_{60}\text{N}_6\text{O}_{14}\text{S}_2\text{Ni}$ : C, 57.79; H, 5.16; N,

7.22; Ni, 5.05%). IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3358 (N–H), 2948 (C– $\text{H}_{\text{Ar}}$ ), 1720 (O–H...O), 1562 (C = N), 1248–1230 (C $_{\text{Ar}}$ –O–C), 1117–1056 (C–O–C), 946 (N–O).

*Data for (7)*: Yield: (0.44 g; 76%); m.p.: 298 °C; Elemental analysis (Found: C, 57.64; H, 5.07; N, 7.12; Co, 4.96%). Calc. for  $\text{C}_{56}\text{H}_{60}\text{N}_6\text{O}_{14}\text{S}_2\text{Co}$ : C, 57.78; H, 5.16; N, 7.22; Co, 5.07. IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3355 (N–H), 2949 (C– $\text{H}_{\text{Ar}}$ ), 1723 (O–H...O), 1560 (C=N), 1245–1227 (C $_{\text{Ar}}$ –O–C), 1117–1056 (C–O–C), 945 (N–O).

*Data for (8)*: Yield: (0.46 g; 79%); m.p.: >300 °C; Elemental analysis (Found: C, 57.43; H, 5.04; N, 7.08; Cu, 5.35%). Calc. for  $\text{C}_{56}\text{H}_{60}\text{N}_6\text{O}_{14}\text{S}_2\text{Cu}$ : C, 57.56; H, 5.14; N, 7.19; Cu, 5.44. IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3356 (N–H), 2950 (C– $\text{H}_{\text{Ar}}$ ), 1725 (O–H...O), 1561 (C = N), 1243–1226 (C $_{\text{Ar}}$ –O–C), 1119–1058 (C–O–C), 944 (N–O).

*Data for (9)*: Yield: (0.43 g; 68%); m.p.: 269 °C; Elemental analysis (Found: C, 52.38; H, 4.45; N, 6.42; Ni, 4.47%). Calc. for  $\text{C}_{56}\text{H}_{60}\text{Cl}_2\text{N}_6\text{Na}_2\text{O}_{14}\text{S}_2\text{Ni}$ : C, 52.51; H, 4.69; N, 6.56; Ni, 4.59. IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3367 (N–H), 2935 (C– $\text{H}_{\text{Ar}}$ ), 1723 (O–H...O), 1568 (C=N), 1258–1233 (C $_{\text{Ar}}$ –O–C), 1115–1061 (C–O–C), 946 (N–O).

*Data for (10)*: Yield: (0.46 g; 72%); m.p.: >300 °C; Elemental analysis (Found: C, 52.36; H, 4.57; N, 6.41; Co, 4.48. Calc. for  $\text{C}_{56}\text{H}_{60}\text{Cl}_2\text{N}_6\text{Na}_2\text{O}_{14}\text{S}_2\text{Co}$ : C, 52.50; H, 4.69; N, 6.56; Co, 4.60%). IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3366 (N–H), 2938 (C– $\text{H}_{\text{Ar}}$ ), 1724 (O–H...O), 1564 (C = N), 1252–1230 (C $_{\text{Ar}}$ –O–C), 1116–1052 (C–O–C), 945 (N–O).

*Data for (11)*: Yield: (0.53 g; 83%); m.p.: 233 °C; Elemental analysis (Found: C, 52.18; H, 4.44; N, 6.36; Cu, 4.79%). Calc. for  $\text{C}_{56}\text{H}_{60}\text{Cl}_2\text{N}_6\text{Na}_2\text{O}_{14}\text{S}_2\text{Cu}$ : C, 52.31; H, 4.67; N, 6.54; Cu, 4.94%). IR (KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3369 (N–H), 2966 (C– $\text{H}_{\text{Ar}}$ ), 1722 (O–H...O), 1560 (C = N), 1249–1223 (C $_{\text{Ar}}$ –O–C), 1117–1055 (C–O–C), 944 (N–O).

Preparation of  $[\text{Ni}(\text{BF}_2)_2\text{L}]$  the nickel(II) complex, (**12**)

A suspension of the precursor nickel complex (0.29 g, 0.25 mmol) in 50 mL of freshly distilled acetonitrile was brought to reflux temperature under an oxygen-free nitrogen atmosphere. Boron trifluoride diethyl etherate (0.06 mL, 0.5 mmol) was slowly added by stirring to the suspension of nickel complex. The resulting reaction mixture immediately turned red. After the colour change, the solution was refluxed for 1.5 h. The solvent was evaporated under reduced pressure up to dryness and the residue was dissolved in dry acetonitrile (15 mL), filtered and evaporated to dryness. The last step was repeated twice and the residue dissolved in 10 mL of dry acetonitrile and allowed to stand at –15 °C overnight. The crystalline red product was filtered off, washed with cold acetonitrile and diethyl ether and dried in vacuum. Yield: (0.18 g; 59%); m.p.: 135 °C.

Elemental analysis (Found: C, 54.82; H, 4.54; N, 6.72. Calc. for  $C_{56}H_{58}B_2F_4N_6O_{14}S_2Ni$ : C, 55.07; H, 4.75; N, 6.88; Ni, 4.81%). IR (KBr)  $\nu_{max}/cm^{-1}$ : 3375 (N–H), 2935 ( $C-H_{Ar}$ ), 1582 ( $C=N$ ), 1239–1226 ( $C_{Ar}-O-C$ ), 1120–1062 ( $C-O-C$ ), 1171 (B–O), 1021 (B–F), 940 (N–O).  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.29 (s, 2H, NH), 7.66–6.78 (m, 24H, Ar–H), 3.94–3.42 (m, 32H,  $O-CH_2-$ ).

## Results and discussion

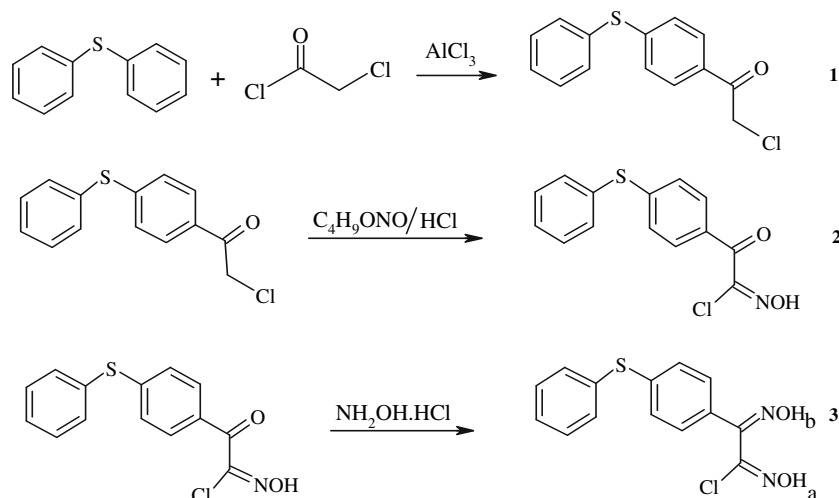
By a method similar to that for  $N,N'$ -bis(4'-benzo[15-crown-5]diaminoglyoxime [24, 25],  $N'$ -(4'-benzo[15-crown-5]thiophenoxyphenylaminoglyoxime (**H<sub>2</sub>L**) and its sodium chloride complex (**H<sub>2</sub>L** · NaCl) have also been originally prepared by the reaction of 4'-aminobenzo[15-crown-5] [21, 22] with 4-(thiophenoxy)chlorophenylglyoxime. To obtain **H<sub>2</sub>L** · NaCl,  $NaHCO_3$  was added to the reaction mixture in order to neutralize HCl formed during the reaction; NaCl was produced as a by-product and the sodium was found to complex with the crown ether groups to yield a product of type; therefore, the ligand was obtained as a sodium chloride salt, **H<sub>2</sub>L** · NaCl. No further attempt was made to isolate the free ligand, since **H<sub>2</sub>L** · NaCl could be used directly to prepare the transition metal complexes.

In the  $^1H$  NMR spectra of the 4-(thiophenoxy)chlorophenylglyoxime, two peaks are present for the –OH protons while the –OH protons of the 4-(thiophenoxy)phenyloxylohydroxy-moyl chloride appear as a singlet. These two deuterium-exchangeable singlets correspond to two non-equivalent –OH protons which indicates an *anti*-configuration of the –OH groups [25, 26–28] (Scheme 1).

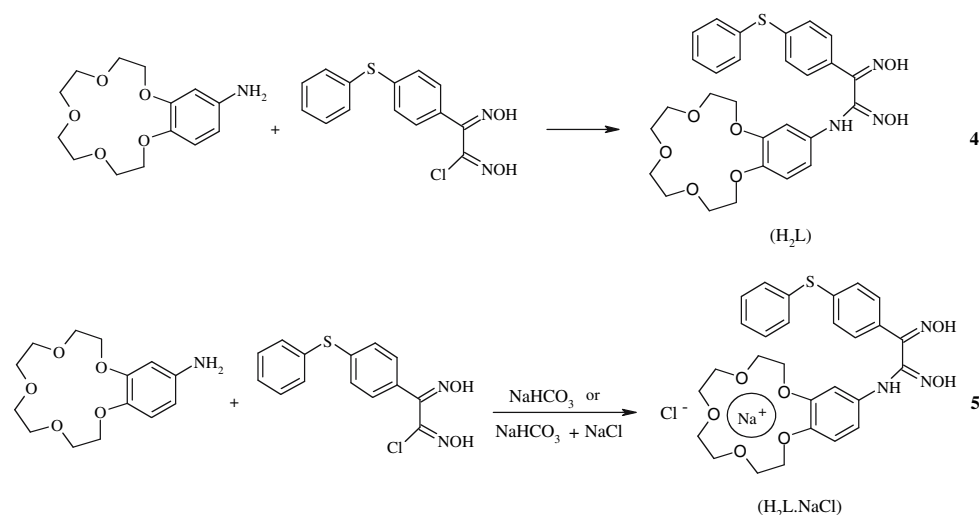
When the chemical shifts of the two –OH groups in the two different ligands are compared, the ones at lower field quite closely resemble each other (11.80–11.71 ppm) whereas a considerable difference is observed for the chemical shifts at higher field (10.95–10.53 ppm). The  $D_2O$  exchangeable –NH– protons of the aminoglyoximes and  $O-CH_2-$  protons are appeared 8.35–8.46 ppm and 4.08–3.52 ppm, respectively. Addition of  $D_2O$  causes the disappearance of the –NH– and –OH peak. The present ligands exhibit the following stretching frequencies –NH (3412–3390  $cm^{-1}$ ), –OH (3230–3198  $cm^{-1}$ ),  $C=N$  (1591–1583  $cm^{-1}$ ) and –NO (950–948  $cm^{-1}$ ) which are similar to substituted aminoglyoximes [14, 24, 26, 27, 29] (Scheme 2).

In the  $^{13}C$  NMR spectrum of (**2**), the signals at 182.86 and 161.75 ppm were assigned to the carbonyl carbon atom and the carbon atom of the oxime group, respectively. In the  $^{13}C$  NMR spectrum of (**3**), carbon resonances of the dioxime groups were observed at 157.68 and 156.35 ppm. In each case, two different frequencies of the dioxime group in  $^{13}C$  NMR indicate that the *vic*-dioxime has an *anti*-structure [30, 31]. While the carbon resonances of the dioxime groups of (**4**) and (**5**) were observed at 158.38, 157.65 ppm, and 158.54, 157.83 ppm, respectively, methylene carbon atoms were observed at the range of 74.25–70.48 ppm. All the signals between 154.88 and 101.43 ppm are assigned to the carbon atoms of the aromatic rings of (**2–5**).

The metal complexes (**6–11**) of the ligands were prepared under similar conditions by adding metal salts and strong base to the ligands. The literature furnishes examples of oximato ions coordinated to a metal center (Ni(II), Co(II), Cu(II), etc.) as a bidentate ligand [22]. The mononuclear complexes (**6–8**) have a metal:ligand ratio of 1:2,



**Scheme 1** The structures of the **1**, **2** and **3**



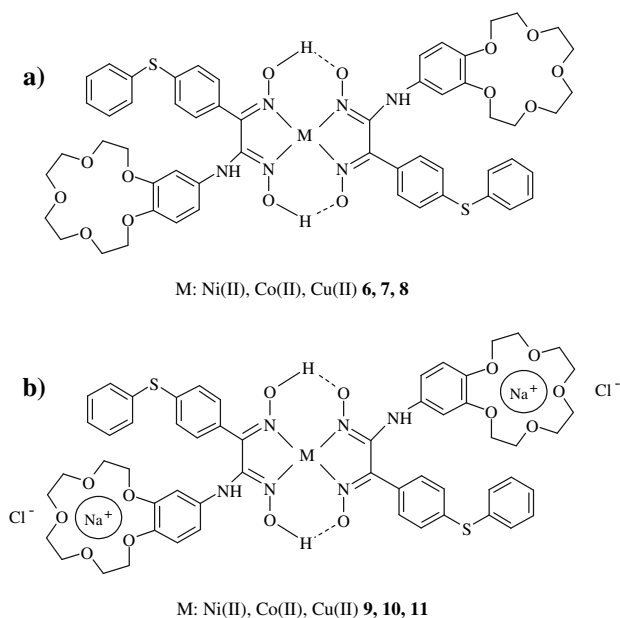
**Scheme 2** General formulas of the ligands

as it is the case for most (*E,E*)-dioxime metal complexes [10, 14, 24–29, 32].

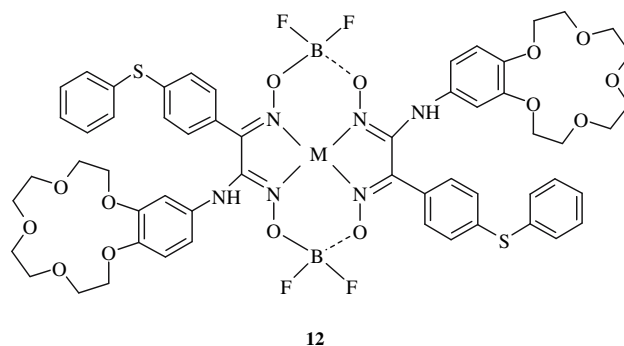
The complexes (**6–11**) of H<sub>2</sub>L and H<sub>2</sub>L · NaCl support the structures shown in Scheme 3 by the weak bending vibration of the O–H...O bridges *et.ca.* 1720–1715 cm<sup>-1</sup> and the shift of the C=N vibration which is due to N,N'-metal coordination to lower frequencies at 1568–1560 cm<sup>-1</sup> [14, 24, 27, 29, 33]. In the IR spectrum, a downward shift, relative to the free ligand, of about 23–31 cm<sup>-1</sup> for C=N absorption, indicates coordination through the N atoms. As a result of the disappearance of the O–H resonances, hydrogen bonds were formed and the

removal of electron density from the N–O bond caused a decrease in the N–O stretching frequency [29]. As with most vic-dioximes [10, 24, 25, 29], the nickel(II) complex of H<sub>2</sub>L is planar N,N' coordination is verified by the elemental analyses of this compound, since it is known that a d<sup>8</sup> metal complex does not have unpaired electrons in a square planar field. The IR spectrum of (**6**) contains a weak band at 1720 cm<sup>-1</sup> which can be attributed to the absorbance of the O–H...O intramolecular hydrogen bridges [34]. IR spectroscopy can be used to distinguish between the hydrogen-bridged (**6**) and the BF<sub>2</sub><sup>+</sup>-bridged (**12**) complexes.

The frequency of the C=N stretching vibration increases by 20 cm<sup>-1</sup> on going from the hydrogen-bridged complex to the BF<sub>2</sub><sup>+</sup>-capped compound. The weak and broad band at 1720 cm<sup>-1</sup> is a characteristic O–H...O in-plane deformation of the hydrogen bond and disappears when substituting the H-bonded Ni(II) complex with BF<sub>2</sub><sup>+</sup>, with the concomitant appearance of peaks around 1171 and 1021 cm<sup>-1</sup> due to the B–O and B–F bonds [35], respectively (Scheme 4).



**Scheme 3** Square-planar metal complexes of the ligands (a) H<sub>2</sub>L and (b) H<sub>2</sub>L · NaCl



**Scheme 4** Structure of [Ni(BF<sub>2</sub>L)<sub>2</sub>] (**12**)

## Conclusions

This work describes the synthesis and characterization of a new keto oxime and dioxime, two new macrocyclic ligands and their nickel(II), copper(II), cobalt(II),  $\text{BF}_2^+$ -capped complexes.

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