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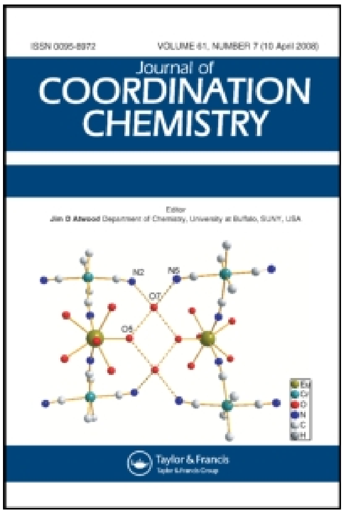

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The Synthesis and Characterization of a Novel (E , E)-Dioxime and its Mono- and Heterotrinuclear Complexes Containing an 18-Membered Dioxadithiadiazamacrocycle

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THE SYNTHESIS AND CHARACTERIZATION OF A NOVEL (*E*,*E*)-DIOXIME AND ITS MONO- AND HETEROTRINUCLEAR COMPLEXES CONTAINING AN 18-MEMBERED DIOXADITHIADIAZAMACROCYCLE

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The novel (*E*,*E*)-dioxime, 5,6:17,18-dibenzo-11,12-(4′-nitrobenzo)-2,3-bis(hydroxyimino)-7,16-dithia-10,13-dioxa-1,4-diazacyclooctadecane) (**H_2L**), has been synthesized from reaction of (*E*,*E*)-dichloroglyoxime (**1**) with 2,3:14,15-dibenzo 8,9-(4′-nitrobenzo)-4,13-dithia-7,10-dioxa-1,16-diazahegzadecane (**2**). The mononuclear Co(III) complex (**4**) of this dioxime was prepared by oxidation of the cobalt (II) complex. The BF_2^+-capped Co(III) complex (**5**) was synthesized by using a precursor Co(III) complex and boron trifluoride dietherate. The heterotrinuclear complexes (**6**) and (**7**) were prepared by reaction of (**5**) with $NiCl_2 \cdot 6H_2O$ and $CdCl_2 \cdot H_2O$, respectively. In addition, the homotrinuclear Cu(II) complex (**8**), has also been prepared by the reaction of this dioxime with $CuCl_2 \cdot H_2O$. The structures of the dioxime and its complexes were identified by using elemental analysis, ^1H- and ^{13}C-NMR, IR, and mass spectral data.

Keywords: Dioxime; Cobalt(III); BF_2^+-capped complex; Heterotrinuclear complex; Homotrinuclear complex; Macrocycle

INTRODUCTION

The design and synthesis of macropolycyclic molecules, containing more than one recognition site for binding several guest species is of considerable current interest in chemical literature [1–5]. The chemistry of mixed donor macrocyclic multidentante ligands with cation complexing ability has been explored extensively in the past 35 years [6]. A rapidly emerging area in recent years concerns the synthesis of heterotrinuclear complexes derived from such ligands [7]. These multisite receptors may exhibit allosteric properties [8,9] by binding sequentially two or more quest metal cations in close proximity to one another. The resulting polynuclear complexes may facilitate electron transfer and serve as models relevant to biological redox processes. The coordination chemistry of chelating *vic*-dioxime ligands has been extensively investigated as

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analytical reagents [10] and models for biological systems [11] such as vitamin B_{12}. They have also been examined as compounds with columnar stacking, which is thought to be the reason for their semiconducting properties [12]. The presence of mildly acidic hydroxyl groups and slightly basic nitrogen atoms make *vic*-dioximes amphoteric ligands which form corrin-type square-planar, square-pyramidal and octahedral complexes with transition metal ions such as Cu(II), Ni(II), Pd(II), Fe(II), Fe(III), Co(II) and Co(III) as central atoms [13].

The hard, ether-oxygen containing macrocycles shows binding preference toward alkali metal or alkaline earth cations, but incorporation of soft sulfide or amine linkages shifts preference towards soft heavy metal ions [14]. One of the best strategies to design and prepare polynuclear compounds is the use of a mononuclear complex as a ligand which contains potential donor groups for metal ions [15]. The interaction between metal centers through extended bridges has been one of the most active research fields in magnetism [16].

In our previous studies we have investigated the synthesis and characterization of (*E*,*E*)-dioxime and its mono- and heterotrinuclear complexes containing a 21-membered trioxadithiadiazamacrocycle [17]. We report herein the synthesis of a novel (*E*,*E*)-dioxime, abbreviated as (**H_2L**), its BF_2^+-capped mononuclear (**5**), heterotrinuclear (**6**,**7**) and homotrinuclear (**8**) complexes.

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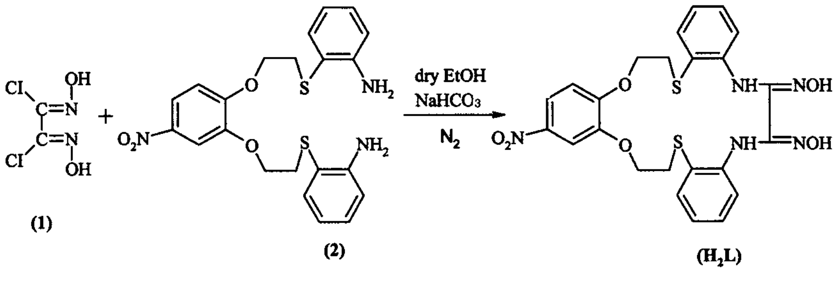
RESULT AND DISCUSSION

The synthesis of (*E*,*E*)-dioxime and its mono- and trinuclear complexes are summarized in (Scheme 1). 2,3:14,15-dibenzo-8,9-(4′-nitrobenzo)-4,13-dithia-7,10-dioxa-1,16-diazahexadecane (**2**) was prepared by a condensation reaction of 1,2-bis(2-chloroethoxy)-4′-nitrobenzene [18] with 2-aminothiophenolate in dry ethanol. The structure was verified by elemental analysis, mass spectrometry, ^{1}H, ^{13}C-NMR, and IR spectroscopy techniques. The electron impact mass spectrum of **2** showed a molecular ion peak at $m/z = 457$ $[M]^+$, which confirmed the proposed structure. In the ^{1}H-NMR spectrum of **2**, there is a singlet at $\delta = 5.40$ ppm for the primary amine protons [19]. The



SCHEME 1

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resonances appear after the condensation reaction. This signal is also easily identified by D_2O exchange. The resonances belonging to OCH_2 and SCH_2 protons are found at 4.20–4.12 and 3.10–3.05 ppm, respectively. In the IR spectrum of **2**, the characteristic vibrations at 3438–3350 cm^{-1} concerning the NH_2 group confirmed the proposed structure. The ^{13}C-NMR spectral data and elemental analysis showed a good agreement with the formation of **2**.

vic-Dioxime (**H_2L**) was prepared by the reaction of 2,3:14,15-dibenzo-8,9-(4′nitrobenzo)-4,13-dithia-7,10-dioxa-1,16-diazahexadecane (**2**) with (*E*,*E*)-dichloroglyoxime (**1**) in dry ethanol and the presence of excess $NaHCO_3$ at reflux temperature for 22 h under nitrogen atmosphere (Scheme 1). The mass spectrum (EI) of this new dioxime **H_2L** exhibited a strong parent ion at $m/z = 541$ $[M]^+$. In the ^{1}H-NMR spectrum of **2**, there was a singlet $\delta = 5.40$ ppm for the aromatic primary amine protons. After the macrocyclization reaction, this singlet belonging to the primary amine protons disappeared and new resonances at $\delta = 8.10$ and 11.25 ppm were observed and this could be assigned to NH and C=N–OH protons. The deuterium-exchangeable protons of NH and =NOH groups showed the formation of the desired compound. The ^{1}H-NMR spectrum of **H_2L**, displayed a singlet at $\delta = 11.25$ ppm, for the =N–OH protons which further confirms the (*E*,*E*) configuration of the dioxime subunit; such a shift is similar to that observed for other (*E*,*E*)-dioximes [20,21]. In the ^{13}C-NMR spectrum of this compound, the carbon resonances of the hydroxyimino, $–OCH_2$ and $–SCH_2$ carbons are found at 141.46, 70.10 and 32.50 ppm, respectively. These equivalent carbon atoms, especially those belonging to hydroxyimino groups, also confirm the (*E*,*E*)-structure of **H_2L** [22]. In the IR spectrum of **H_2L**, the O–H, N–H, C=O and N–O stretching vibrations were observed at 3250, 3326, 1653 and 953 cm^{-1}, respectively [23]. The stretching vibrations (NH_2) for (**2**) disappear after the condensation reaction. These results indicate that the formation of macrocyclization is completed.

The six-coordinate mononuclear Co(III) complex (**4**), was obtained when O_2 was bubbled through a suspension of the cobalt(II) complex in ethanol with pyridine as an axial ligand. This complex has a metal : ligand ratio of 1 : 2 according to elemental analysis data and mass spectra. The six-coordinate mononuclear Co(III) complex **[Co(HL)$_2$pyCl]** was synthesized as previously reported [23]. The fast atom bombardment mass spectrum of this complex exhibits a molecular ion peak at $m/z = 1253$ $[M+1]^+$, which supports the proposed structure [24]. In the ^{1}H-NMR spectrum of the mononuclear Co(III) complex and the resonance of the intramolecular binding O–H···O protons appear as a singlet at $\delta = 16.80$ ppm and this shift could easily be identified by deuterium exchange. The proton decoupled ^{13}C-NMR spectrum of **[Co(HL)$_2$pyCl]** displays a singlet at $\delta = 141.35$ ppm corresponding to the hydroxyimino group. Additional signals at $\delta = 150.15$, 140.27 and 127.55 ppm are due to the coordinated pyridine. In the IR of **[Co(LH)$_2$pyCl]**, the weak deformation vibration band assigned to the intramolecular hydrogen bond O–H···O bending vibration is observed at 1680 cm^{-1}. The C=N stretch decreases from 1653 cm^{-1} in the free ligand to 1625 $^{-1}$ in (**4**). A lowering of the vibration frequency (relative to free ligands) of about 20–28^{-1} for the C=N absorbtion in the H-bonded Co(III) complex indicates coordination through the N atoms [25].

The template synthesis of the macrocyclic Co(III) complex **[Co(LBF$_2$)2pyCl]** (**5**) was performed by adding boron trifluoride ethyl ether complex to a refluxing freshly distilled acetonitrile solution containing the hydrogen-bridged Co(III) complex. The hydrogen bridging protons were replaced by BF_2^+ groups. The fast atom bombardment

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mass spectrum of this complex exhibits a molecular ion peak at $m/z = 1347$ $[M+1]^+$. In the ^{1}H-NMR spectrum of the BF_2^+-capped macrocycle, the deuterium exchangeable $O-H \cdots O$ bridged protons belonging to the precursor Co(III) complex disappeared. Bridging boron groups cause the resonances of the BF_2^+-capped Co(III) complex to shift down-field relative to those of **4**. The IR spectrum of **5** shows significant bands attributable to NH, C=N and N–O stretching vibrations which were observed at 3302, 1638 and 962 cm^{-1}, respectively. A downward shift of the C=N stretching vibration in the hydrogen-bonded complex indicates coordination through the N atoms. In contrast to this downward shift, the BF_2^+ macrocycles exhibit upward shifts of about 13–15 cm^{-1} due to the strong electron withdrawing influence of BF_2^+ groups incorporated in the macrocycles. The bending vibration of O–H···O bond disappeared upon encapsulation of the H-bonded complex with the appearance of peaks due to the BF_2^+ contaminant around 1158 and 1065 cm^{-1} for B–O and B–F groups, respectively [26].

The reaction of **[Co(LBF$_2$)$_2$pyCl]** with **$NiCl_2 \cdot 6H_2O$** gave the corresponding diamagnetic trinuclear complex (**6**) as a brown solid. In this trinuclear complex, the Ni(II) ions are each trapped in a 18-membered macrocycle containing dioxadithiadiaza donors. The fast atom bombardment mass spectrum of this complex exhibits a molecular ion peak at $m/z = 1458$ $[M]^+$ which supports the proposed formation of **6**. In the ^{1}H-NMR spectrum of the trinuclear complex, the singlet at $\delta = 8.05$ ppm in the BF_2^+-capped Co(III) complex belonging to the NH protons disappears. The IR spectrum of this complex was similar to that of the BF_2^+ complex **5** except for the disappearance of N–H resonances.

The trinuclear complex **[Cd$_2$Co(LBF$_2$)$_2$pyCl]** (**7**) was obtained from the reaction of (**5**) with **$CdCl_2 \cdot 2H_2O$**. The trinuclear complex was obtained as a dark brown solid. The fast atom bombardment mass spectra of **7** showed the expected molecular ion peaks at $m/z = 1567$ $[M+1]^+$. The ^{1}H-NMR spectrum of trinuclear complex was similar to that of **6**. The disappearance of resonances for NH protons confirmed the proposed heterotrinuclear complex (**7**). In the IR spectra of this trinuclear complex, the C=N and N–O stretching vibrations were observed at 1635 and 976 cm^{-1}, respectively. The significant shift of some stretching vibrations such as S–C or N–C and disappearance of N–H resonances also support this compound formation.

The homotrinuclear complex **[Cu$_3$(HL)$_2$]**, (**8**) was synthesized by the reaction of (**H$_2$L**) with $CuCl_2 \cdot 2H_2O$ in ethanol [27]. Each copper ion was coordinated with dithia and diaza donor atoms from the 18-member macrocyclic cavity. The third copper ion was coordinated with azomethine groups of each oxime moiety. The fast atom bombardment mass spectra of **8** exhibits a molecular ion peak at $m/z = 1268$ $[M+I]^+$. In the IR spectrum of this compound, the bending vibration, the stretching vibration belonging to O–H···O and C=N groups were found at 1678 and 1632 cm^{-1}. The basicity of N donors in the macrocycles is rather low because of their position near the hydroxyimino groups. Nevertheless, the disappearance of N–H stretching vibtrations belonging to the dioxadiazadithia macrocycle indicates that Cu(II) ions are complexed by the 18-member macrocycles. The appearance of O–H stretching and the shifts of C=N stretching vibrations to lower frequency in the IR spectrum of that complex can be attributed to *N*,*N′*-chelation with a third Cu(II) ion with hydroxyimino groups.

Free **H$_2$L** has an absorption maximum at 273 nm in the UV region. The electronic spectra of all transition metal complexes in DMF are similar to that of free ligand except for the high intensity charge transfer absorptions around 450 nm. A weak *d–d* transition cannot be observed.

EXPERIMENTAL

^{1}H and ^{13}C-NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in DMSO-d_6, and chemical shifts are reported (δ) relative to Me_4Si as an internal standard. Fourier transform infrared spectroscopy using KBr pellets was performed on a Perkin-Elmer 1600 FTIR instrument. Mass spectra were measured on a Varian 711 and VG Zapspec spectrometers. Elemental analyses and metal content of these compounds were determined by a LECO Elemental Analyser (CHNS 0932) and Unicam 929 AA spectrophotometer. Melting points were measured on an electrothermal apparatus and are corrected. 4′-Nitro-1,2-bis(2-chloroethoxy)-benzene was prepared by a reported procedure [18]. Commercially available pure solvents, dried and purified by conventional procedure [28], are used.

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2,3:14,15-Dibenzo-9,10-(4′-nitrobenzo)-7,16-dithia-10,13-dioxa-1,4-diazaoctadecane, (2)

A solution of 2-aminothiophenolate prepared by the reaction of 2-aminothiophenol (6.3 g, 50.7 mmol) with sodium (1.16 g, 50.7 mmol) in dry ethanol (30 mL) was added dropwise to a solution of 4′-nitro-1,2-bis-(2-chloroethoxy)benzene (7.1 g, 25.35 mmol) in dry ethanol (120 mL) under a nitrogen atmosphere at 60°C for 2 h, and then the mixture was stirred 20 h at 60°C. The reaction was monitored by thin layer chromatography [silica gel, petrolum ether; ethyl acetate (3 : 1)]. Then, the reaction mixture was stirred under reflux for 24 h. After cooling to room temperature, the reaction mixture was evaporated to 20 mL. The solution was placed in a refrigerator for 8 h at -5°C and filtered. After filtration, the volume of the filtrate was reduced (10 mL), allowed to stand in a refrigerator overnight at -18°C and then the mixture was filtered. The precipitate was washed with water, cold ethanol and diethyl ether, and the product was recrystallized from ethanol. The product **2** was obtained in 8.2 g (70.8%), m.p. 93–95°C. ^{1}H-NMR (DMSO-d_6): δ 7.83–7.42 (d, H, Ar–H), 7.65 (s, H, Ar–H), 7.25 (d, H, Ar–H), 7.20–7.15 (d, 2H, Ar–H), 7.12 (t, 2H, Ar–H), 6.75 (d, 2H, Ar–H), 6.50 (t, 2H, Ar–H), 5.40 (s, 4H, NH_2), 4.20–4.12 (t, 4H, $-OCH_2$), 3.10–3.05 (t, 414, $-SCH_2$). ^{13}C-NMR (DMSO-d$_6$): δ 154.10, 150.05, 147.95, 140.05, 146.15, 130.00, 118.16, 116.18, 114.05, 112.05, 108.10, 67.90, 31.45. IR (KBr pellets, cm^{-1}): 3438–3350 (NH_2), 3082 (Ar–H), 2972–2926 (C–H), 1612 (NH_2), 1510–1337 (NO_2), 859 (NO). Anal. Calcd. for $C_{22}H_{23}N_3O_4S_2$ (%): C, 57.77; H, 5.03; N, 9.19. Found: C, 57.35; H, 4.97; N, 9.26. Electron impact (El) mass spectrum: $m/z = 457$ $[M]^+$.

5,6:17,18-Dibenzo-11,12-(4′-nitrobenzo)-2,3-bis(hydroxyimino)-7,16-dithia-10,13-dioxa-1,4-diazacyclooctodecane, (H_2L)

A solution of compound (**2**) (2.56 g, 5.60 mmol) was prepared in dry ethanol (225 mL), and $NaHCO_3$ (2.8 g, 33.6 mmol) was added to this solution under nitrogen at 40°C. A solution of (*E*,*E*)-dichloroglyoxime (0.88 g, 5.6 mmol) in dry ethanol (30 mL) was added to this solution under these conditions. The reaction mixture was stirred at under reflux for 22 h and monitored by thin layer chromotography [silica gel, petroleum ether; ethyl

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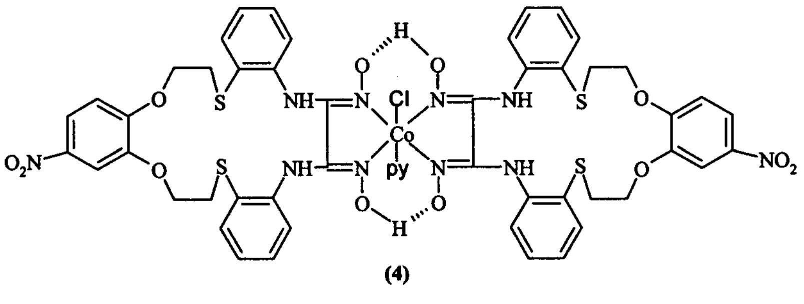
acetate (1 : 1)]. After cooling, the reaction mixture was filtered and the yellow solid washed with water. The filtrate was evaporated to 30 mL under vacuum and cooled in a refrigerator, giving a pale yellow solid. The reaction mixture was filtered, washed with cold ethanol and diethylether and dried *in vacuo*. The product was crystallized from ethanol. Yield: 1.6 g (52.8%), m.p. 230–232°C (dec.). ^{1}H-NMR (DMSO-d$_6$): δ 11.25 (s, 2H, OH), 8.10 (s, 2H, NH), 7.85–7.82 (s, H, Ar–H), 7.80–7.42 (d, 2H, Ar–H), 7.20 (m, 8H, Ar–H), 3.98–3.72 (t, 4H, –OCH$_2$), 3.04–3.01 (t, 4H, –S CH$_2$); ^{13}C-NMR (DMSO-d_6): δ 153.46, 146.77, 141.46, 140.09, 139.17, 139.04, 136.08), 129.64, 120.75, 120.44, 120.31, 114.87, 108.11, 70.10, 32.50. IR (KBr pellets, cm^{-1}): 3326 (N–H), 3250 (O–H), 3060 (Ar–H), 2983–2853 (C–H), 1653 (C=N), 1610 (NH$_2$), 953 (N–O). UV–Vis [λ_{max}/nm (DMF)]: 263 (ε/M^{-1}cm^{-1} 16550), 273 (27330), 310 (24240), 342 (21500). Anal. Calcd. for $C_{24}H_{23}N_5O_6S_2$ (%): C, 53.23; H, 4.25; N, 12.93. Found: C, 53.40; H, 4.28; N, 13.05. Electron impact (El) mass spectrum: $m/z = 541$ [M]$^+$.

[Co(HL)$_2$pyCl], (4)

A solution of $CoCl_2 \cdot 6H_2O$ (0.16 g, 0.67 mmol) in ethanol (15 mL) was added to a solution of (**H$_2$L**) (0.73 g, 1.34 mmol) in ethanol (40 mL) by stirring on a water bath at 60°C. A distinct change in color from pale yellow to brown and a decrease in the pH of the solution to 2.30 were observed. While heating the solution, pyridine (0.053 g, 0.67 mmol) in ethanol (2 mL) was added. The solution was held at 40°C, and a stream of oxygen was bubbled through it for 2 h. Then the solution was concentrated (15 mL) and cooled in a refrigerator at −18°C overnight, whereupon a brown solid precipitated. The solid product was filtered off, washed with cold ethanol, diethyl ether and then dried *in vacuo* to give a brown solid. Yield: 0.6 g (71.43%), m.p. 280–282°C (dec.). ^{1}H-NMR (DMSO-d_6): δ 16.80 (s, 2H, O–H · · O), 8.60 (s, 4H, NH), 7.92–7.85 (s, 2H Ar–H), 7.83–7.66 (d, 4H, Ar–H), 7.62 (d, 2H, pyH), 7.40 (t, 1H, pyH), 7.33 (m, 8H, Ar–H), 7.15 (t, 2H, pyH), 6.95 (m, 8H, Ar–H), 4.23–4.12 (t, 8H, –OCH$_2$), 3.05–2.99 (t, 8H, –SCH$_2$); ^{13}C-NMR (DMSO-d_6): 153.18, 150.15, 146.28, 141.35, 140.27, 136.10, 131.13, 127.55, 122.12, 119.60, 113.63, 109.11, 68.15, 32.02. IR (KBr pellets, cm^{-1}): 3314 (N–H), 3072 (Ar–H), 2927 (C–H), 1680 (H–O· · ·H), 1625 (C=N), 960 (N–O). UV–Vis [λ_{max}/nm (DMF)]: 266 (ε/M^{-1}cm^{-1} 26620), 303 (24350), 348 (19875), 375 (12220). Anal. Calc. for $C_{53}H_{49}N_{11}O_{12}S_4ClCo$ (%): C, 50.74; H, 3.91; N, 12.28; Co, 4.69. Found: C, 50.51; H, 3.98; N, 12.56; Co, 4.58. Fast atom bombardment (FAB positive) mass spectrum: $m/z = 1253$ [M+1]$^+$.



(4)

$[Co(LBF_2)_2pyCl]$, (5)

The suspension of $[Co(HL)_2pyCl]$, (**4**) (0.49 g, 0.39 mmol) in freshly distilled dry acetonitrile (40 mL) was heated to reflux under an oxygen-free nitrogen atmosphere. A solution of borontriflouride diethyl ether complex (0.07 mL, 0.56 mmol) in dry acetonitrile (3 mL) was slowly added with stirring. During this period, all the reaction mixture dissolved and the color of the solution turned to dark red immediately. The reaction continued for 2 h reflux. Then the solvent was removed (5 mL) under reduced pressure and the residue was dissolved in (15 mL) acetonitrile and evaporated to dryness. The last step was repeated and the residue was dissolved in (10 mL) of acetonitrile and allowed to cool in a refrigerator at −5°C overnight whereupon the product crystallized from solution. The product was filtered, washed with cold acetonitrile and diethyl ether and then dried *in vacuo*. Yield: 0.24 g (46%), m.p. 198–200°C (dec.). ^{1}H-NMR (DMSO-d_6): δ 8.05 (s, 4H, NH), 7.95–7.92 (s, 2H Ar–H), 7.90 (d, 4H, Ar–H), 7.55 (d, 2H, pyH), 7.30 (t, 1H, pyH), 7.28 (m, 8H, Ar–H), 7.10 (t, 2H, pyH), 6.93 (m, 8H, Ar–H), 4.10–4.02 (t, 8H, $-OCH_2$), 3.13–3.07 (t, 8H, $-SCH_2$). ^{13}C-NMR ($DMSO_4$-d_6) δ: 153.18, 150.15, 146.28, 141.35, 140.27, 136.10, 131.13, 127.55, 122.12, 119.60, 113.63, 109.11, 68.15, 32.02. IR (KBr pellets, cm^{-1}): 3302 (N–H), 3090 (Ar–H), 2926-2873 (C–H), 1638 (C=N), 1158 (B–O), 1065 (B–F), 962 (N–O). UV–Vis [λ_{max}/nm (DMF)]: 265 (ε/M^{-1}cm^{-1} 26510), 285 (21692), 301 (19355), 341(15860), 434 (12405). Anal. Calcd. for $C_{53}H_{47}N_{11}O_{12}S_4B_2F_4$ CoCl (%): C, 47.12; H, 3.48; N, 11.41; Co, 4.37. Found: C, 47.19; H, 3.56; N, 11.57; Co, 4.51. Fast atom bombardment (FAB positive) mass spectrum: $m/z = 1347$ $[M+1]^+$.

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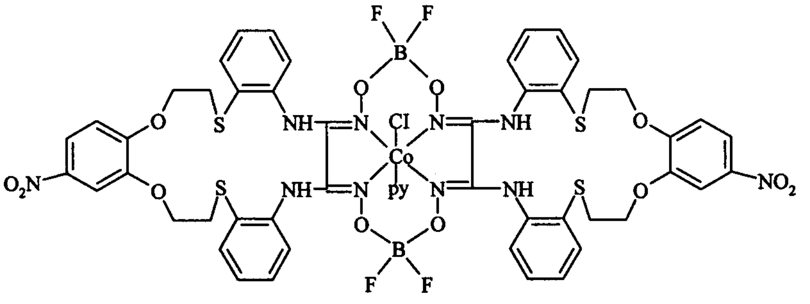
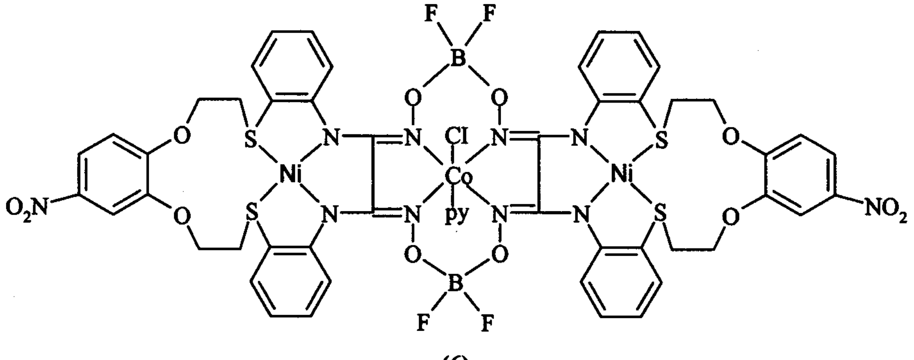


(5)

$[Ni_2Co(LBF_2)_2PyCl]$, (6)

A hot solution of $NiCl_2 \cdot 6H_2O$ (0.026 g, 0.11 mmol) in dry ethanol (20 mL) was added to a hot solution of $[Co(LBF_2)_2pyCl]$ (**5**) (0.075 g, 0.055 mmol) in dry ethanol (30 mL)). After addition, the reaction mixture turned to a brown suspension. The reaction continued for 5 h at reflux and was monitored by thin layer chromatography [silica gel, *n*-butanol : acetic acid : water (4 : 1: 5)]. After cooling, the reaction mixture was evaporated to 20 mL and then cooled in a refrigerator for 10 h. The dark brown product was filtered off, washed with water, cold ethanol and diethyl ether and then dried *in vacuo*. Yield: 0.03 g (37.5%), m.p. > 300°C (dec.). ^{1}H-NMR (DMSO-d_6): δ 7.90–7.63

(s, 2H, Ar–H), 7.58–7.30 (d, 2H, py–H), 7.28 (m, 8H, Ar–H), 7.15 (t, 1H, py–H), 7.05 (t, 2H, py–H), 6.90 (m, 8H, Ar–H), 6.85 (d, 4H, Ar–H), 4.20–4.12 (t, 8H, $-OCH_2$), 3.08–3.01 (t, 8H, $-SCH_2$). IR (KBr pellets, cm^{-1}): 3086 (Ar–H), 2925–2858 (C–H), 1640 (C=N), 1138 (B–O), 1090 (B–F), 968 (N–O). UV-Vis [λ_{max}/nm (DMF)]: 271 ($\varepsilon/M^{-1}cm^{-1}$ 29754), 283 (34120), 305 (23735), 344 (18832), 451 (13280). Anal. Calcd. for $C_{53}H_{43}N_{11}O_{12}S_4B_2F_4Ni_2CoCl$ (%): C, 43.49; H, 2.94; N, 10.53; Co, 4.02; Ni, 8.02. Found: C, 43.70; H, 2.78; N, 10.69; Co, 3.83; Ni, 8.24%. Fast atom bombardment (FAB positive) mass spectrum: $m/z = 1458$ $[M]^+$.



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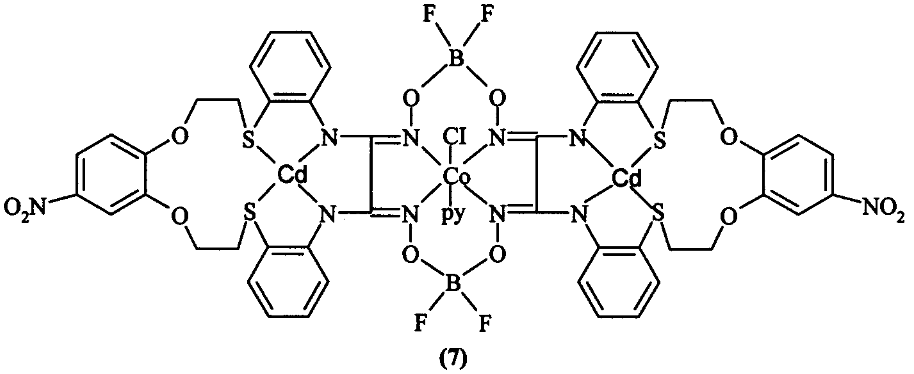
$[Cd_2Co(LBF_2)_2PyCl]$, (7)

A solution of $CdCl_2 \cdot 2H_2O$ (0.022 g, 0.11 mmol) in dry ethanol (20 mL) was added to a hot solution of $[Co(LBF_2)_2PyCl]$ (**5**) (0.075 gr, 0.055 mmol) in dry ethanol 35 mL by heating to reflux and stirring under an oxygen-free nitrogen atmosphere. The reflux was continued for 7 h and the end of the reaction was determined by using a thin layer chromatography [silica gel, chloroform; methanol; water (73 : 25 : 2)]. After cooling to room temperature the reaction mixture was evaporated to 15 mL and then was cooled in a refrigerator for 8 h. The dark brown product was filtered off, washed with water, cold ethanol and diethyl ether and then dried *in vacuo*. Yield: 0.015 g (62.5%), m.p. 293–295°C. ^{1}H-NMR (DMSO-d_6): δ 7.45–7.36 (s, 2H, Ar–H), 7.42



(7)

(d, 2H, py–H), 7.25–7.14 (m, 8H, Ar–H), 7.12 (t, 1H, py–H), 7.01 (t, 2H, py–H), 6.85–6.82 (m, 8H, Ar–H), 6.80 (d, 4H, Ar–H), 4.15–4.08 (t, 8H, $-OCH_2$), 3.10–3.02 (t, 8H, $-SCH_2$). IR (KBr pellets·cm^{-1}): 3090 (Ar–H), 2925–2854 (C–H), 1635 (C=N), 1135 (B–O), 1086 (B–F), 976 (N–O). UV–Vis [λ_{max}/nm (DMF)]: 267 (ε/$M^{-1}cm^{-1}$ 29095), 288 (25469), 302 (19824), 342 (15962), 437 (11689). Anal. Calcd. for $C_{53}H_{43}N_{11}O_{12}S_4B_2F_4$ Cd_2CoCl (%): C, 40.51; H, 2.73; N, 9.81; Co, 3.75; Cd, 14.32. Found: C, 40.68; H, 2.57; N, 9.67; Co, 3.92; Cd, 14.19. Fast atom bombardment (FAB positive) mass spectrum: $m/z = 1567$ $[M+1]^+$.

$[Cu_3(HL)_2]$, (8)

A solution of $CuCl_2 \cdot 2H_2O$ (0.07 g, 0.4 mmol) in 20 mL ethanol was added to the solution of (**H_2L**) (0.15 g, 0.27 mmol) in (25 mL) ethanol. A distinct change in color and a decrease in pH were observed and the mixture was refluxed in a water bath for 2 h. Then, with an equivalent amount of ethanolic solution of KOH (0.1 M). The reaction mixture was monitored by a thin layer chromatography [silica gel, chloroform : methanol : water (73 : 25 : 2)]. After refluxing for 2 h, the reaction mixture was allowed to cool to room temperature and the precipitate was filtered off and washed successively with water, cold ethanol and diethyl ether and dried *in vacuo*. Yield: 0.11 g (62.85%), m.p. 261–263°C (dec.). IR (KBr pellets·cm^{-1}): 3085 (Ar–H), 2975–2856 (C–H), 1678 (O–H···O), 1632 (C=N), 948 (N–O). UV–Vis [λ_{max}/nm (DMF)]: 272 (ε/$M^{-1}cm^{-1}$ 35515), 292 (31230), 305 (27660), 367 (14740), 485 (10720). Anal. Calcd. for $C_{48}H_{40}N_{10}O_{12}S_4Cu_3$ (%): C, 45.46; H, 3.16; N, 11.05; Cu, 15.04. Found: C, 45.24; H, 3.17; N, 11.24; Cu, 15.25. Fast atom bombardment (FAB positive) mass spectrum: $m/z = 1268$ $[MH]^+$.

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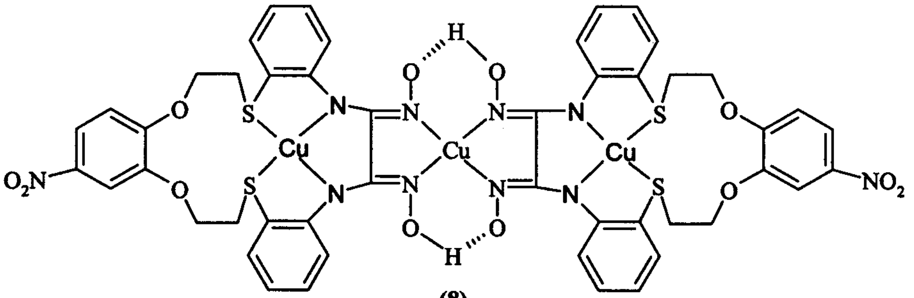

(8)

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