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Synthesis and characterization of a novel (*E,E*)-Dioxime and its mono and Heterotrinnuclear complexes containing a 15-membered Dioxatrithiamacrocyclic ligand with transition metals

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SYNTHESIS AND CHARACTERIZATION OF A NOVEL (*E,E*)-DIOXIME AND ITS MONO AND HETEROTRINUCLEAR COMPLEXES CONTAINING A 15-MEMBERED DIOXATRITHIAMACROCYCLE LIGAND WITH TRANSITION METALS

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A new macrocyclic *vic*-dioxime, 1,3-bis(benzo-7,9,13-trithia-1,4-dioxacyclopentadecane)-2-thioxo-4,5-bis-(hydroxyimino)imidazoline (H_2L) has been synthesized by reaction of (*E,E*)-dichloroglyoxime (**3**) with *N,N'*-bis(benzo-7,10,13-trithia-1,4-dioxa-cyclopentadecane)thiourea (**2**), which was prepared from 2,3-(4'-aminobenzo)-7,10,13-trithia-1,4-dioxacyclopentadecane and thiocarbonyldichloride. The mononuclear Ni(II) complex of H_2L , $[Ni(HL)_2]$, (**4**) has been prepared by reaction of H_2L with nickel(II) chloride hexahydrate. The mononuclear Co(III) complex of the dioxime $[Co(HL)_2P(Ph)_3Cl]$ (**5**) has been isolated with triphenylphosphine and chloride as axial ligands. In addition, a Co(III) complex containing the BF_4^- bridged macrocycle $[Co(LBF_2)_2P(Ph)_3Cl]$ (**6**) was synthesized using a precursor hydrogen-bridged Co(III) complex via the template effect. The heterotrinnuclear complex of the BF_4^- -capped Co(III) complex $[Ag_2Co(LBF_2)_2P(Ph)_3Cl](CH_3COO)_2$ (**7**) has also been prepared by reaction of this complex with $Ag(CH_3COO)$. The structures of the dioxime and its complexes were identified by elemental analysis together with 1H and ^{13}C NMR, IR and mass spectral data.

Keywords: *vic*-Dioxime; Macrocycle; Heterotrinnuclear complex; BF_4^- -capped complex

INTRODUCTION

Current interest in host–guest chemistry in general, and in metal complexation by macrocyclic ligands in particular, has resulted in the synthesis of several new classes of macrocyclic ligands [1,2]. The chemistry of complexes containing mixed-donor multidentate macrocyclic ligands with cation complexing abilities has been explored extensively [3]. Another rapidly emerging topic of chemical interest concerns synthesis

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of heteronuclear ligands and the coordination chemistry of polynuclear complexes derived from such ligands [4]. Some heteronuclear macrocycles that could serve as “polytopic receptor molecules” for the binding of metal cations, or the co-binding of metal ion and molecular substrates, include molecules containing macrocyclic functionalities appended to porphyrin, phthalocyanine, tetrathia, dithiadiazia or tetraamine centers [5].

Thiacrown ethers, crown ethers in which some or all of the oxygen atoms are replaced by sulfur atoms, are known to show greater affinity for softer metal ions than alkali and alkaline earth metal ions [6,7]. Although thioethers have moderately low δ donor and π acceptor abilities, a bonding comparison of thioether and phosphine ligands suggests that transition metal complexes utilizing SR_2 donor ligands might mimic or complement those carrying PR_3 [8]. The chemistry of transition metal complexes with *vic*-dioxime ligands has been well studied and is the subject of several reviews [9].

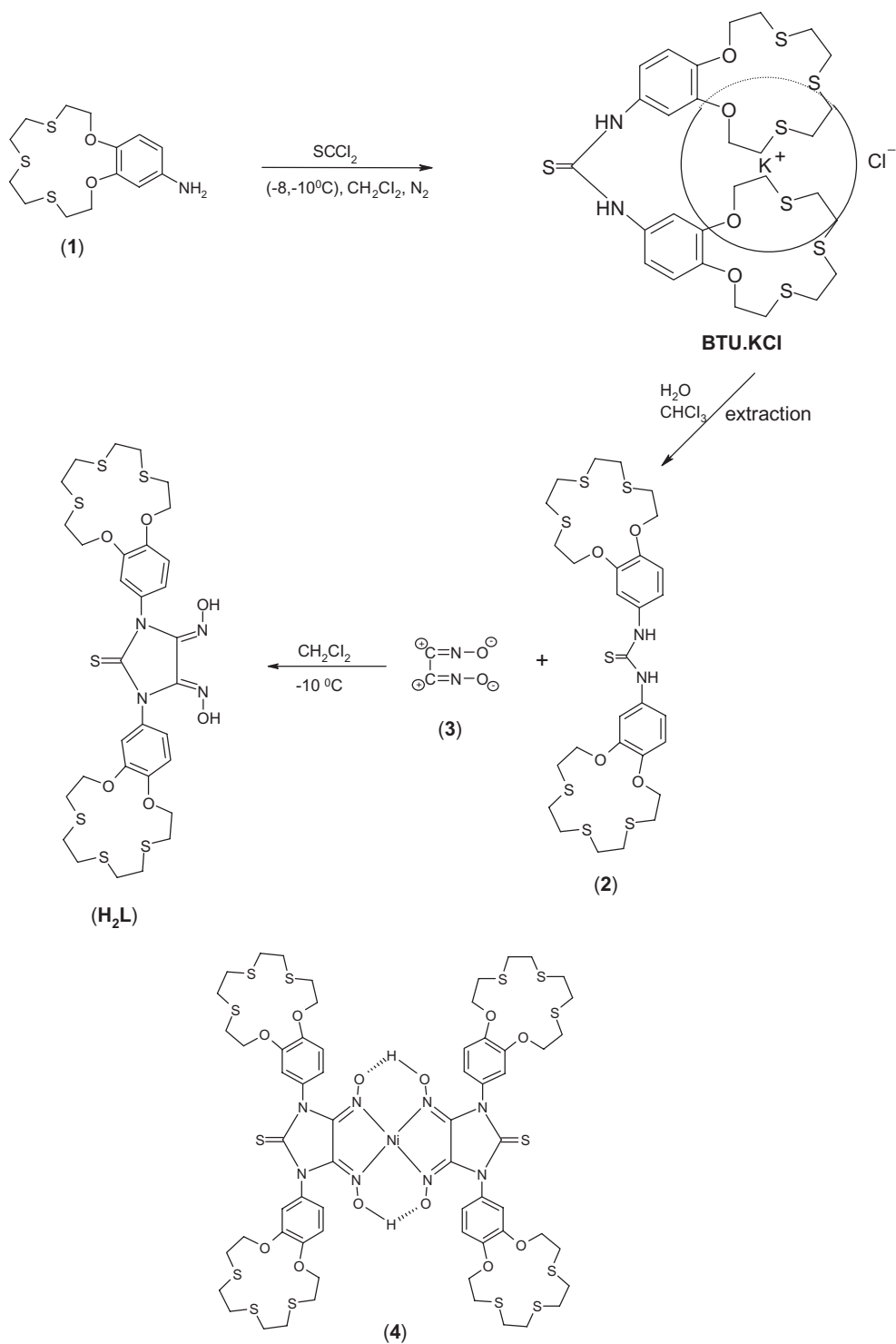
The vicinal dioximes have received considerable attention as model compounds to mimic biofunctions such as reduction of vitamin B_{12} [10]. Their complexes have been the source of a series of interesting reports over the past 20 years. Reactions of amines or thiols with (*E,E*)-dichloroglyoxime or cyanogens di-*N*-oxide yielded various symmetrically substituted diaminoglyoxime or dithioglyoxime derivatives [11]. The bridging protons of the bis (dioxime) ligands have been replaced by BF_2^+ groups, an alteration that strengthens the macrocyclic structure while removing acidic protons from the vicinity of the O_2 binding site [12].

Previous papers have described the synthesis and characterization of various types of (*E,E*)-dioximes and their transition metal complexes [13,14]. We have also initiated studies on transition metal complexes of vicinal dioximes incorporating macrocyclic groups containing diazadithiadioxia and trioxadithia macrocycles which are capable of binding heteropoly metal ions [13,14].

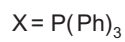
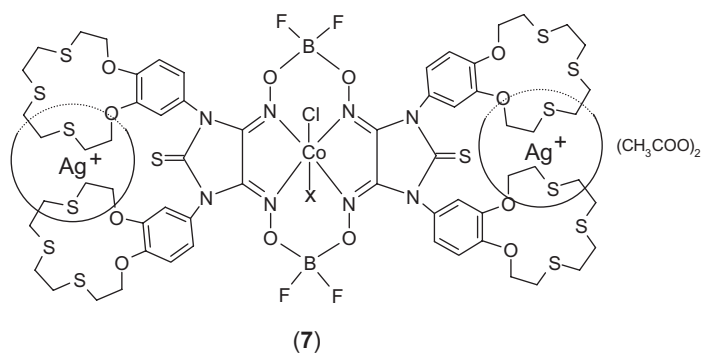
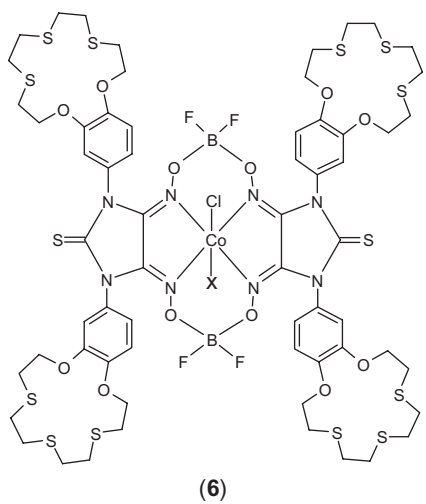
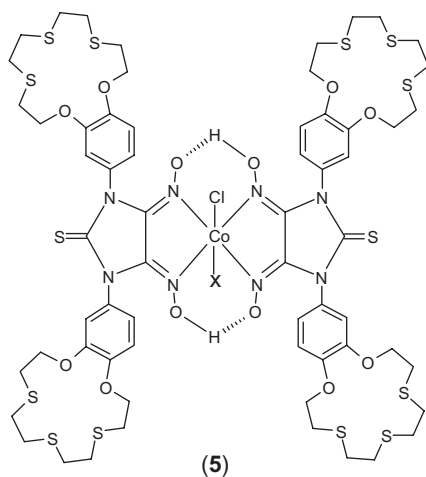
We report here the synthesis of the free macrocyclic ligand 1,3-bis(benzo-7,10,13-trithia-1,4-dioxacyclopentadecane)-2-thiaoxa-4,5-bis(hydroxyimino)imidazoline, abbreviated as H_2L , and the synthesis and investigation of nickel(II) and cobalt(III) complexes.

RESULTS AND DISCUSSION

The aim of the present study was to synthesize and characterize a new (*E,E*)-dioxime containing a 15-membered dioxatrithiamacrocyclic moiety (H_2L), and to prepare its mono and heterotrinary complexes. The syntheses of these new compounds are summarized in Scheme 1. *N,N'*-Bis(benzo-7,10,13-trithia-1,4-dioxacyclopentadecane) thiourea (**2**) was synthesized by the reaction of thiocarbonyldichloride with 2,3-(4'-aminobenzo)-7,10,13-trithia-1,4-dioxacyclopentadecane (**1**) under nitrogen atmosphere at $-10^\circ C$ in 39.2% yield. This compound was identified by elemental analysis together with 1H and ^{13}C NMR, IR and MS spectral data. In the 1H NMR spectrum of **2**, the chemical shifts assigned to NH protons at $\delta = 9.50$ ppm appeared after the addition reaction [15]. These protons were also identified easily by D_2O exchange. The other chemical shifts involving aromatic protons and aliphatic protons such as $-OCH_2$, $-SCH_2$ and $-SCH_2-CH_2S-$ were found at 7.17–6.90, 4.18–4.08, 3.20–3.05 and 3.10–2.75 ppm, respectively. In the proton-decoupled ^{13}C NMR spectrum of this



SCHEME 1.



SCHEME 1 Continued.

compound, a new chemical shift for C=S appeared at $\delta = 179.55$ ppm, in accordance with the proposed structure. In the IR spectrum of **2**, the characteristic vibrations at 3350 cm^{-1} for the NH group confirmed the desired compound. The fast atom bombardment (FAB) mass spectrum of this compound exhibited a molecular ion peak at $m/z = 704.2$ $[\text{M}]^+$, which also confirmed the formulation.

The new (*E,E*)-dioxime H_2L was synthesized by the reaction of cyanogendi-*N*-oxide with **2** under nitrogen atmosphere at -10°C in 44.8% yield. Dichloromethane was chosen as the solvent for the formation reaction of cyanogendi-*N*-oxide. The reaction mixture was stirred at -10°C for 12 h. In the ^1H NMR spectrum of H_2L , the chemical shift assigned to NH protons disappeared and a new chemical shift at $\delta = 10.70$ ppm was observed, which was assigned to C=N-OH protons [16]. This was easily identified by deuterium-exchange between the C=N-OH group and D_2O . At the same time the ^1H NMR spectrum of H_2L displayed a singlet at $\delta = 10.70$ ppm for the =N-OH proton which confirms the (*E,E*)-configuration of dioxime. In the proton-decoupled ^{13}C NMR spectrum of this compound, the carbon resonances of the C=S and C=N-OH groups were found at $\delta = 152.64$ and 142.85 ppm, respectively. These equivalent carbon atoms, especially involving the hydroxyimino groups, also confirmed the (*E,E*)-structure of H_2L [17]. In the IR spectrum of H_2L , the characteristic NH absorptions of Compound **2** disappeared and three new absorptions assigned to OH, C=N and N-O groups were observed at 3247 , 1640 and 1010 cm^{-1} , respectively. These resonances are also in agreement with the proposed structure. The mass spectrum (FAB positive) of H_2L , showing a molecular ion peak at $m/z = 788$ $[\text{M}]^+$, is in accord with the suggested formula. The hydrogen-bridged mononuclear nickel(II) complex was synthesized by reaction of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in ethanol with the new (*E,E*)-dioxime in the presence of ethanolic KOH (0.1 M). In the ^1H NMR spectrum of the mononuclear Ni(II) complex, the resonance of the intramolecular binding O-H...O protons appeared as a singlet at $\delta = 16.25$ ppm and this shift was easily identified by deuterium exchange. The hydrogen-bridged protons and the diamagnetic character of the complex confirmed the formation of the square-planar nickel(II) complex. The chemical shifts, assigned to the protons of O-CH₂, S-CH₂ and -CH₂ groups were found at 4.13–4.05, 3.40–3.15 and 3.05–2.90 ppm, respectively. The proton decoupled ^{13}C NMR spectrum of $[\text{Ni}(\text{HL})_2]$ (**4**) appeared as a singlet at $\delta = 142.10$ ppm, corresponding to the hydroxyimino group. Another carbon resonance assigned to the thiocarbonyl group appeared at $\delta = 155.18$ ppm. The IR spectrum of **4** exhibits a C=N stretching vibration at 1638 cm^{-1} . This vibration is at a lower frequency than that for the free ligand, which can be attributed to *N,N'*-chelation [18]. A weak band at 1690 cm^{-1} can be assigned to the intramolecular hydrogen bond O-H...O bending vibration. The intensity of characteristic stretching and bending vibrations of the free ligand were shifted and lowered on complex formation, and new vibrational bands characteristic of the complex were observed. The FAB mass spectrum of $[\text{Ni}(\text{HL})_2]$ exhibited a molecular ion peak at $m/z = 1632$ $[\text{M}]^+$, which is consistent with the proposed structure.

The six-coordinated mononuclear cobalt(III) complex $[\text{Co}(\text{HL})_2\text{P}(\text{Ph})_3\text{Cl}]$ (**5**) was prepared with a procedure similar to a previously published one [19]. The precursor Co(II) complex was oxidized to a diamagnetic octahedral Co(III) derivative by bubbling air through a solution (ethanol) of the complex in the presence of triphenylphosphine. In the ^1H NMR spectrum of this complex, a singlet at $\delta = 16.80$ ppm from O-H...O protons was observed and this singlet was easily determined by deuterium

exchange [20]. In the proton-decoupled ^{13}C NMR spectrum of this compound, a singlet at $\delta = 142.58$ ppm assigned to the hydroxyimino groups appeared. The carbon resonance for the thiocarbonyl group appeared at $\delta = 165.80$ ppm. In the IR spectrum of the octahedral Co(III) complex, the weak deformation vibration band assigned to intramolecular hydrogen-bond bending vibrations was observed at 1695 cm^{-1} [17]. The mass spectrum (FAB positive) of **5** exhibits an intense peak at $m/z = 1633$ $[\text{M} - \text{PPh}_3 - \text{Cl} + 1]^+$, which is in accord with the proposed structure. The BF_2^+ -capped Co(III) complex $[\text{Co}(\text{LBF}_2)_2\text{P}(\text{Ph}_3)\text{Cl}]$ (**6**) was prepared by adding borontrifluoride etherate to a refluxing suspension of the precursor cobalt(III) complex in acetonitrile. In this mononuclear complex, only the bridging protons were replaced by BF_2 groups; axial ligands were retained at their initial positions. The IR spectrum of BF_2^+ -capped cobalt(III) complex resembles that of the precursor cobalt(III) complex except for the occurrence of new bands characteristic of the BF_2 groups and absence of $\text{O}-\text{H} \cdots \text{O}$ bending vibrations. The sharp absorption at 832 cm^{-1} has been attributed to B-F stretching vibrations of the BF_2 derivative [21]. The mass spectrum (FAB positive) of **6** exhibits intense peaks at $m/z = 1764$ $[\text{M} - \text{PPh}_3 + 1]^+$ and 1728 $[\text{M} - \text{PPh}_3 - \text{Cl}]^+$.

The heterotrimeric complex $[\text{Ag}_2\text{Co}(\text{LBF}_2)_2\text{P}(\text{Ph}_3)\text{Cl}](\text{CH}_3\text{COO})_2$ (**7**) was synthesized by refluxing the BF_2 -bridged cobalt(III) complex with silver(I) acetate in absolute ethanol for 28 h. The desired trinuclear complex **7**, which has a metal:ligand ratio of 2:1 according to its elemental analysis, was obtained in 46.25% yield. The characteristic signals in the ^1H NMR spectrum of this complex were very similar to those of the precursor BF_2^+ -capped Co(III) complex as expected. The chemical shifts assigned to acetate groups which were observed at $\delta = 2.40$ ppm also confirmed the formation of the target trinuclear complex. In the IR spectrum of the heterotrimeric complex, the C=N stretching vibration was observed at 1625 cm^{-1} . The other characteristic stretching vibrations belonging to B-O and N-O groups were observed at 1123 and 1012 cm^{-1} , respectively.

EXPERIMENTAL

All solvents were dried before use. Routine IR spectra obtained using KBr pellets were recorded on a Perkin-Elmer 1600 FTIR spectrophotometer. ^1H and ^{13}C -NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in $\text{DMSO}-d_6$, and chemical shifts are reported relative to Me_4Si as internal standard. Mass spectra were measured on a Varian 711 and VG Zapspec spectrometer. Elemental analysis and metal contents of these compounds were determined by a LECO Elemental Analyser (CHNS O932) and Unicam 929 AA spectrophotometer. Melting points were measured on an electrothermal apparatus. 4'-Nitro-1,2-bis(chloroethoxy)-benzene was prepared by a reported procedure [22]. Commercially available pure solvents were dried and purified by conventional procedures [23].

N,N'-Bis(benzo-7,10,13-trithia-1,4-dioxa cyclopentadecane)thiourea, (**2**) [24]

A solution of thiocarbonyl dichloride (0.52 g, 4.53 mmol) in dry dichloromethane (10 cm^3) was added dropwise to a mixture of 2,3-(4'-aminobenzo)-7,10,13-trithia-1,4-dioxacyclopentadecane [22] (3.0 g, 9.06 mmol) and K_2CO_3 (0.62 g, 4.53 mmol) in dry dichloromethane (35 cm^3) under a nitrogen atmosphere at -10°C for 30 min. The

reaction mixture was stirred continuously at this temperature for 12 h and then evaporated to dryness under reduced pressure. The solid was dissolved in water (100 cm³) and extracted with chloroform (3 × 30 cm³). The solution was dried with anhydrous MgSO₄. The filtrate was concentrated to a volume of about 5 cm³ and kept in a refrigerator for 10 h at -5°C. The resulting pale-yellow precipitate was filtered off. The product was recrystallized from ethanol:acetone (1:1). The pale-yellow product was filtered, washed with cold ethanol and diethyl ether and then dried *in vacuo*. Yield: 1.25 g (39.2%), m.p. 175–176°C; ¹H NMR (DMSO-*d*₆): δ 9.50 (s, 2H, N–H), 7, 17 (s, 2H, Ar–H), 6.90 (d, 4H, Ar–H), 4.18 (m, 8H, Ar–OCH₂), 3.20 (m, 8H, SCH₂), 2.75 (m, 16H, SCH₂CH₂S). ¹³C NMR (DMSO-*d*₆): δ: 179.55, 146.78, 144.50, 132.10, 118.20, 116.52, 112.10, 71.62, 69.20, 32.55, 30.28. IR (KBr pellets, cm⁻¹): 3350 (N–H), 3095 (Ar–H), 2983 (C–H), 1290–1228 (Ar–OCH₂). Anal. Calcd. for C₂₉H₄₀NO₄S₇(%): C, 49.43; H, 5.68; N, 3.97. Found: C, 49.28; H, 5.81; N, 3.76. FAB positive mass spectrum: *m/z* = 704.2 [M]⁺.

1,3-Bis(benzo-7,10,13-trithia-1,4-dioxacyclopentadecane)-2-thioxa-4,5-bis-(hydroxyimino)imidazoline, (H₂L) [24]

A solution of **2** [24] (1.20 g, 1.70 mmol) in dichloromethane (50 cm³) was cooled to -10°C under nitrogen. A solution of cyanogendi-*N*-oxide [25] prepared from (*E,E*)-dichloroglyoxime (**3**) (0.27 g, 1.70 mmol) and 1 N aqueous Na₂CO₃ solution (10 cm³) at -10°C in dichloromethane (10 cm³) was added to the solution of **2**. The reaction was continued for 12 h at -10°C and then allowed to warm to room temperature. Solvent was removed to a volume of about 10 cm³ and the mixture was allowed to stand in a refrigerator overnight at -5°C. The pale-yellow solid was filtered off and washed with cold ethanol. The crude product was recrystallized from ethanol. The pale-yellow solid was filtered, washed with cold ethanol and diethyl ether, and dried *in vacuo*. Yield: 0.69 g (44.8%), m.p. 195–197°C (dec.). ¹H NMR (DMSO-*d*₆): δ 10.70 (s, 2H, O–H), 7.18 (m, 4H, Ar–H), 6.48 (s, 2H, Ar–H), 4.20 (m, 8H, OCH₂), 3.45 (m, 24H, SCH₂). ¹³C NMR (DMSO-*d*₆): δ 152.64, 148.16, 147.81, 142.85, 133.59, 132.10, 113.37, 112.85, 69.80, 32.37, 30.62. IR (KBr pellets, cm⁻¹): 3247 (O–H), 3065 (Ar–H), 2918–2790 (C–H), 1640 (C=N), 1262–1207 (Ar–O–CH₂), 1010 (N–O). Anal. Calcd. for C₃₁H₄₀N₄O₆S₇(%): C, 47.20; H, 5.07; N, 7.10. Found: C, 47.39; H, 5.26; N, 6.92. FAB positive mass spectrum: *m/z* = 788.1 [M]⁺.

[Ni(HL)₂], (**4**)

A solution of NiCl₂ · 6H₂O (0.2011 g, 0.2548 mmol) in ethanol (45 cm³) was added to a solution of H₂L [24] (0.20 g, 0.25 mmol) in ethanol (40 cm³) with stirring at 60°C. After the addition, a distinct change in color from pale yellow to orange and a decrease in the pH of the solution to 0.88 were observed. A solution of KOH (0.056 g, 1 mmol) in ethanol (10 cm³) was added to this solution at 60°C. An increase in the pH of the solution to 5.43 was observed. The reaction mixture was stirred for 2 h at 60°C. After cooling to room temperature, the mixture was filtered and the residue was washed with water, ethanol and diethyl ether then dried *in vacuo* to give an orange solid. Yield: 0.13 g (65%), m.p. 232–235°C (dec.). ¹H NMR (DMSO-*d*₆): δ 16.25 (s, 2H, O–H ··· O), 7.25 (s, 4H, Ar–H), 6.98 (m, 8H, Ar–H), 4.13 (m, 16H, CH₂O), 3.40 (m, 24H, SCH₂). ¹³C-NMR (DMSO-*d*₆): δ 153.18, 148.16, 142.10,

135.25, 134.35, 131.28, 119.70, 114.52, 69.97, 32.10, 30.25. IR (KBr pellets, cm^{-1}): 3090 (Ar–H), 2920–2813 (C–H), 1690 (O–H \cdots O), 1638 (C=N), 1280–1221 (Ar–OCH₂), 1012 (N–O). Anal. Calcd. for C₆₂H₇₈N₈O₁₂S₁₄(%): C, 45.56; H, 4.78; N, 6.86; Ni, 3.59. Found: C, 45.41; H, 4.91; N, 6.99, Ni, 3.40. FAB positive mass spectrum: $m/z = 1632$ [M]⁺

[Co(HL)₂P(Ph)₃Cl], (5)

A solution of CoCl₂ · 6H₂O (0.069 g, 0.29 mmol) in ethanol (10 cm³) was added to a solution of H₂L (0.45 g, 0.57 mmol) in ethanol (100 cm³) with stirring at 60°C. Following the distinct color change and pH drop, air was bubbled through the mixture for 30 min with stirring at 60°C on a water bath and a solution of phosphine, P(Ph)₃, (0.075 g, 0.286 mmol) in ethanol (5 cm³) was added to the reaction mixture which was kept at 60°C for 3 h. The reaction mixture was cooled to room temperature. The brown solid was collected, washed with water, ethanol and diethyl ether then dried *in vacuo*. Yield: 0.225 g (40.9%), m.p. 284–286°C (dec.) ¹H NMR (DMSO-*d*₆): δ 16.80 (s, 2H, O–H \cdots O), 7.91 (m, 15H, PPh₃), 7.15 (s, 4H, Ar–H), 6.78 (d, 8H, Ar–H), 4.18 (t, 4H, OCH₂), 3.40 (t, 8H, SCH₂). ¹³C NMR (DMSO-*d*₆) δ : 165.80, 146.62, 142.58, 136.10, 135.18, 126.83, 124.55, 113.59, 111.62, 70.93, 69.35, 32.65, 31.89. IR (KBr pellets, cm^{-1}): 3085 (Ar–H), 2919–2816 (C–H), 1695 (O–H \cdots O), 1648 (C=N), 1259–1219 (Ar–O–CH₂), 1011 (N–O). Anal. Calcd. for C₈₀H₉₃N₈O₁₂S₁₄PClCo(%): C, 49.73; H, 4.82; N, 5.80; Co, 3.06. Found: C, 49.49; H, 5.07; N, 5.97; Co, 2.82. FAB positive mass spectrum: $m/z = 1633$ [M – PPh₃ – Cl + 1]⁺.

[Co(LBF₂)₂(PPh)₃Cl], (6)

A suspension of [Co(LH)₂P(Ph)₃Cl], (5), (0.19 g, 0.093 mmol) in freshly distilled dry acetonitrile (30 cm³) was heated to reflux under an oxygen-free nitrogen atmosphere. To this suspension boron trifluoride etherate (0.16 cm³, 0.186 mmol) was added with stirring, converting the suspension to a dark-red solution within 10 min. The reaction mixture was allowed to reflux for 2 h then the solvent was removed to dryness under reduced pressure and the residue was dissolved in dry acetonitrile (5 cm³). The solvent was evaporated to dryness again. The residue was dissolved in dry acetonitrile (5 cm³) and allowed to stand in a refrigerator at –18°C overnight. The dark-red solid was filtered off, washed with cold acetonitrile and diethyl ether, and dried *in vacuo*. Yield: 0.09 g (47.6%), m.p. 254–257°C. ¹H NMR (DMSO-*d*₆): δ 7.93 (m, 15H, PPh₃), 7.05 (s, 4H, Ar–H), 6.88 (m, 8H, Ar–H), 4.23 (m, 16H, OCH₂), 3.42 (m, 48H, SCH₂). IR (KBr pellets, cm^{-1}): 3080 (Ar–H), 2919–2850 (C–H), 1655 (C=N), 1250–1199 (Ar–O–CH₂), 1165 (B–O), 945 (N–O). Anal. Calcd. for C₈₀H₉₁N₈O₁₂S₁₄PB₂F₄ClCo(%): C, 47.37; H, 4.49; N, 5.53, Co, 2.91. Found: C, 47.55; H, 4.33; N, 5.79; Co, 2.68. FAB positive mass spectrum: $m/z = 1764$ [M – PPh₃ + 1]⁺, 1728 [M – PPh₃ – Cl]⁺.

[Ag₂Co(LBF₂)₂P(Ph)₃Cl](CH₃COO)₂, (7)

A solution of CH₃COOAg (0.011 g, 0.64 mmol) in absolute ethanol (20 cm³) was added to a solution of precursor BF₂⁺-capped cobalt(III) complex **6** (0.065 g, 0.032 mmol) in absolute ethanol (25 cm³) at reflux with stirring under nitrogen. The reaction mixture was maintained at reflux for 28 h then cooled to room temperature. The solvent

was evaporated to 10 cm³ and mixture was cooled to -18°C and kept at this temperature overnight. The brown solid product was filtered off, washed with water, cold ethanol and diethyl ether and dried *in vacuo*. Yield: 0.04 g (46.25%), m.p. 196–198°C. ¹H NMR (DMSO-*d*₆): δ 7.88 (m, 15H, PPh₃), 6.80 (s, 4H, Ar-H), 6.75 (m, 8H, Ar-H), 4.15–4.18 (m, 16H, OCH₂), 3.32 (m, 48H, SCH₂), 2.40 (s, 12H, CH₃). IR (KBr pellets, cm⁻¹): 3088 (Ar-H), 2917–2852 (C-H), 1625 (C=N), 1257–1218 (Ar-O-CH₂), 1123 (B-O), 1012 (N-O). Anal. Calcd. for C₈₄H₉₇N₈O₁₆S₁₄PB₂F₄ClAg₂Co(%): C, 42.69; H, 4.11; N, 4.74; Co, 2.49; Ag, 9.14. Found: C, 42.88; H, 3.85; N, 4.47; Co, 2.71; Ag, 8.86.

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