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The synthesis and characterization of new (*E*,*E*)-dioxime and its mono and heteronuclear complexes containing 14-membered tetraaza macrocyclic moiety

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Abstract—A new macrocyclic vicinal dioxime, 5,6 : 9,10 : 13,14-tribenzo-2,3-bis(hydroxyimino)-1,4,8,11-tetra-azacyclodecane (H_2L) has been synthesized by the reaction of (*E*,*E*)-dichloroglyoxime with 2,3 : 6,7 : 10,11-tribenzo-1,5,8,11-tetraazadodecane (**4**), which was prepared by the reduction of 1,2-bis(*o*-nitrophenylaldimino) benzene (**3**). The mononuclear cobalt(III) complex (**5**) of the dioxime has been isolated with L′ = pyridine, together with chlorine as axial ligand. In addition, cobalt(III) complex containing the BF_2^+ bridge macrocycle (**6**) was synthesized using a precursor hydrogen-bridged cobalt(III) complex *via* the template effect. The heterotrinuclear complex of the BF_2^+-capped cobalt(III) complex (**7**) has also been prepared by the reaction of this complex with $CdCl_2 \cdot H_20$. The structure of dioxime and its complexes were identified by using elemental analysis, ^1H, ^{13}C NMR, IR and MS spectral data. © 1997 Elsevier Science Ltd

Keywords: (*E*,*E*)-dioxime; tetraaza macrocycle; cobalt(III) complex; template effect; hetero-trinuclear complex; BF_2^+ capped complex.

The field of coordination chemistry of macrocyclic compounds has undergone spectacular growth during the past 40 years. This enormous growth has been due to the synthesis of a great number and variety of synthetic macrocycles which behave as coordinating agents for metal ions. On the other hand, the development of the field of bioinorganic chemistry has also been the other important factor in spurring the growth interest in complexes of macrocyclic compounds [1]. Macrocyclic ligand systems often exhibit unusual properties and sometimes mimic related natural macrocyclic compounds. There is considerable current interest [2] in complexes of polydentate macrocyclic ligands, because of the variety of geometrical forms available and the possible encapsulation of the metal ion [3].

The transition metal complexes of polyaza macrocyclic ligands have been subjects of great interest. Another rapidly emerging field of chemical interest, in recent years, is the synthesis of heteronucleating ligands and the coordination chemistry of the heteronuclear complexes that drive such ligands [4]. Heteropolymetallic assemblies consisting of organometallic redox-active moieties covalently attached to macrocyclic complexes of coordinatively unsaturated transition metals provide exciting future prospects for small-molecule activation at polynuclear metal sites [5]. However, less work has been reported for higher membered polyazmacrocyclic complexes.

The chemistry of transition metal complexes with *vic*-dioxime ligands has been well studied and is the subject of several reviews [6]. Vicinal dioximes have received considerable attention as model compounds to mimic biofunction such as reduction of vitamin B_{12} [7]. Their complexes have been the source, through the past 20 years, of a series of interesting reports. The reaction of amines or thiols with (*E*, *E*)-dichloroglyoxime or cyanogen di-*N*-oxide yielded various symmetrically substituted diaminoglyoxime or dithioglyoxime derivatives [8]. The presence of mildly acidic hydroxy groups and slightly basic nitrogen

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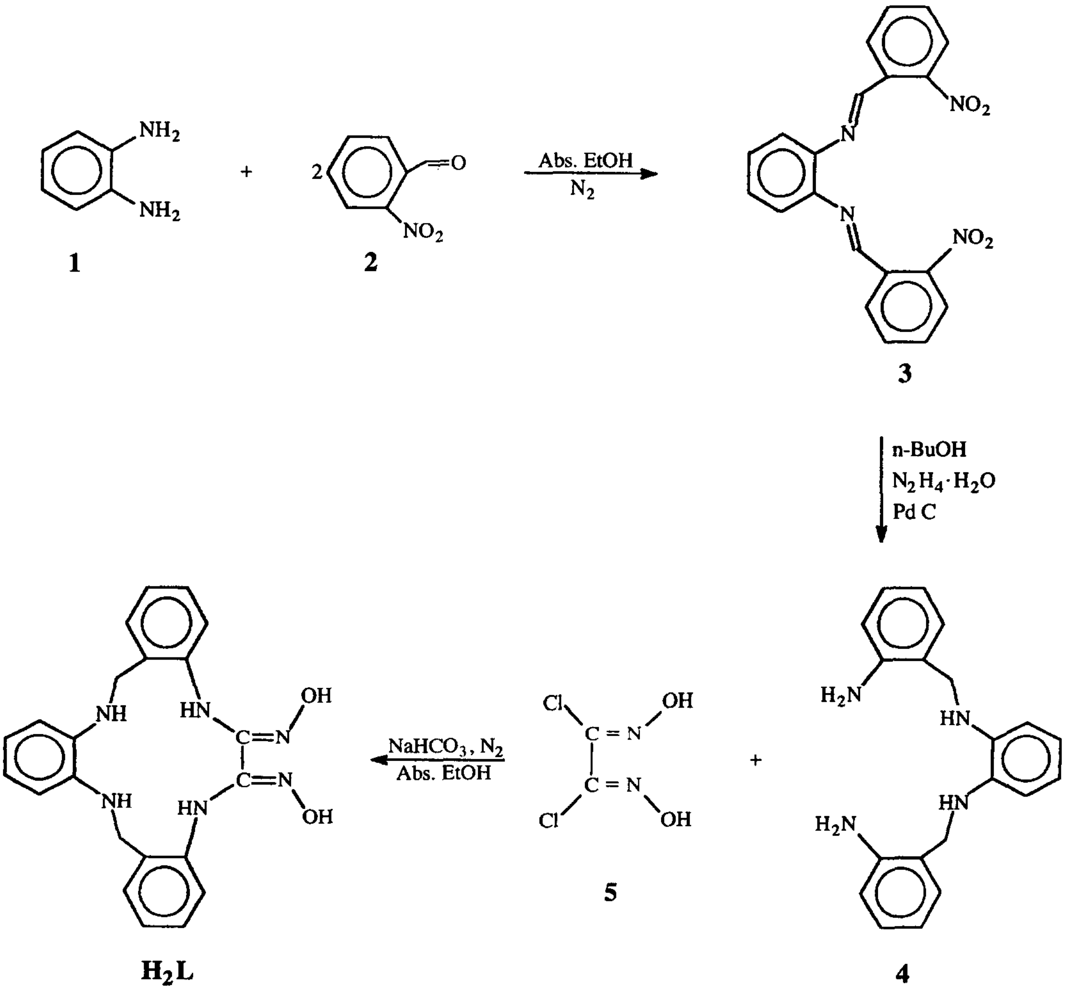
atoms make vicinal dioximes amphoteric ligands which form corrin-type, MN_4, square-planar, square-pyramidal and octahedral complexes with transition metal ions such as copper(II), nickel(II), cobalt(II) and cobalt(III) as central atoms [9].

We have recently described the synthesis and characterization of various types of (*E*, *E*)-dioximes and their transition metal complexes [8,10]. As part of our current programme on the preparation of novel systems that combine features of both transition metal and alkaline or earth alkaline metal chemistry, we have prepared several (*E*, *E*)-dioximes bearing crown ether groups. We have also initiated studies on transition metal complexes of vicinal dioximes incorporating macrocyclic groups containing dithia-diaza or tetraaza macrocycles which are capable of binding heteropoly metal ions simultaneously [11].

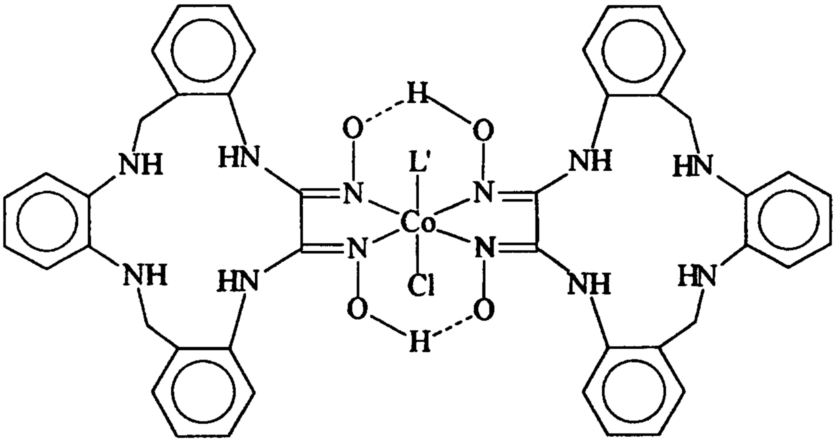
The goal of the present study was to obtain and characterize new (*E*, *E*)-dioximes containing 14-membered tetraaza macrocycle and to prepare its mono- and heteropolynuclear complexes. We report the synthesis of the free macrocyclic ligand 5,6 : 9,10 : 13,14-tribenzo-2,3-bis(hydroxyimino)-1,4,8,11-tetraazacyclotetradecane, abbreviated as H_2L, and the synthesis and reactivity of cobalt(III) complex with cadmium (II) ion.

RESULTS AND DISCUSSION

The route for the synthesis of H_2L is given in Scheme 1. The first step is the synthesis of 1,2-bis(*o*-nitrobenzylidenimino)benzene (**3**), which was prepared from *o*-nitrobenzaldehyde (**1**) and *o*-phenylenediamine (**2**). After reduction of this Schiff base using palladium/activated carbon, the amine compound, 2,3 : 6,7 : 10,11-tribenzo-1,5,8,12-tetraazadodecane (**4**) was prepared. In order to obtain H_2L, the precursor amine compound was reacted with (*E*, *E*)-dichloroglyoxime in absolute ethanol in the presence of $NaHCO_3$ as a buffer to neutralize HCl formed during the reaction (Scheme 1). The structure of the ligand and its complexes were identified by a com-



Scheme. 1.



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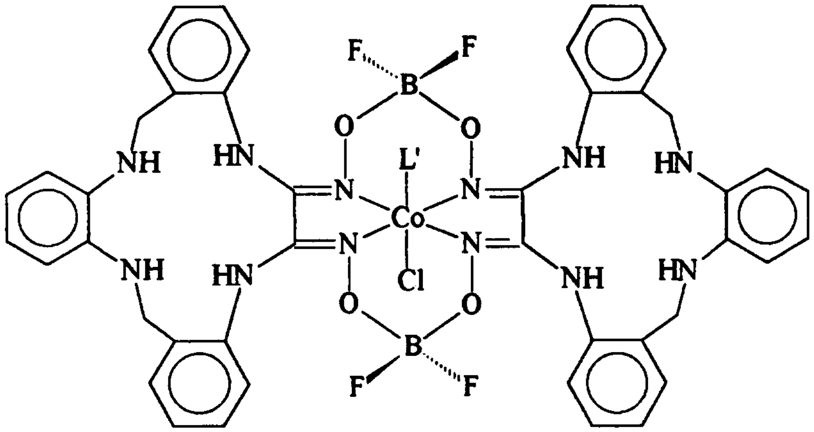

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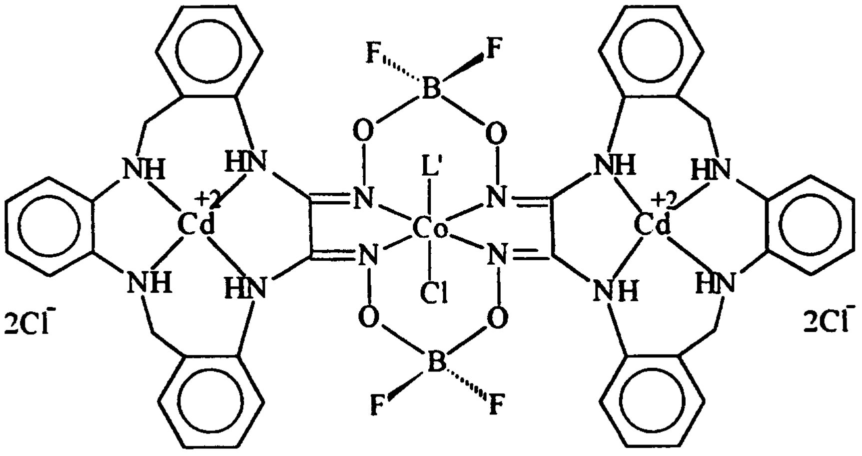

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L' : prydine

Scheme. 1.—*Continued.*

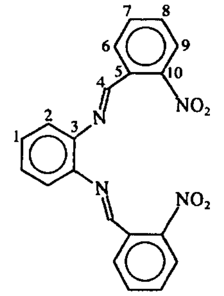

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Fig. 1.

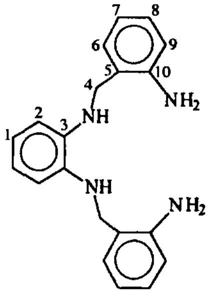

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Fig. 2.

bination of elemental analysis, ^1H and ^{13}C NMR, IR and mass spectral data.

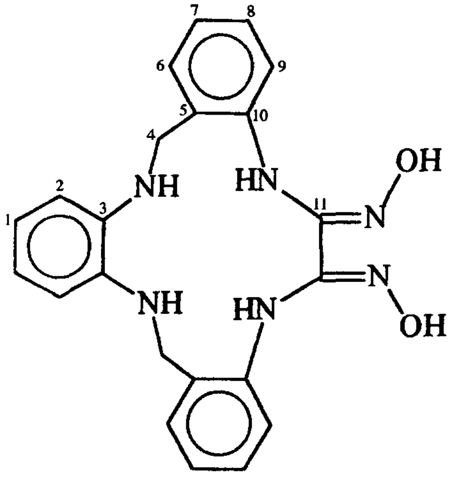
In the ^1H NMR spectrum of **3**, there is a singlet at $\delta = 8.10$ ppm for the protons of azomethine groups, indicating the formation of a Schiff base. The absence of primary aromatic amine groups belonging to **2**, supports the same result. The proton-decoupled ^{13}C NMR spectra for this compound is inconsistent with the proposed formulation (Fig. 1). The chemical shifts at $\delta = 160.4$ ppm correspond to azomethine carbons (Table 1). The IR spectrum of this compound, the stretching vibrations at 1628 cm^{-1}, confirm the presence of imine groups and the absence of carbonyl and aromatic primary amine groups of the starting materials. The mass spectrum (EI) of **3**, which shows a parent peak at $m/z = 392$ $[M+H_2O]^+$, confirms the proposed formula of this compound.

In the ^1H NMR spectrum of **4**, there are singlets at $\delta = 6.28$ and 5.39 ppm belonging to secondary and primary aromatic amine protons, respectively. In addition to this chemical shift, there is a singlet at $\delta = 3.65$ ppm, which is due to the methylene protons. The doublets at $\delta = 7.88$, 6.85, the triplet at $\delta = 6.65$ and the multiplets at $\delta = 7.60$ and 7.25 ppm corresponding to aromatic protons which are slightly shifted compared with the precursor compound **3**. The proton-decoupled ^{13}C NMR spectrum of this compound displayed a resonance at $\delta = 48.6$ ppm, indicating the presence of methylene carbon (C_4). The disappearance of azomethine carbon resonance and the presence of the above-mentioned methylene carbon supports the formation of the desired compound (**4**). Table 1). In the IR spectrum of **4**, N—H stretching and bending vibrations are observed at *ca* 3410 and 1612 cm^{-1}, respectively. The absence of C=N and NO_2 vibrations belonging to the precursor compound also leads to the proposed structure of **4**. The mass spectrum (FAB) of **4** has a parent ion peak at $m/z = 336$ $[M+H_2O]^+$, which is inconsistent with the proposed formulation of this compound (Fig. 2).

Table 1. ^{13}C NMR spectral data for 3 and 4

Carbons	δ (ppm)	Carbons	δ (ppm)
C_1	130.61	C_1	128.10
C_2	134.32	C_2	131.60
C_3	145.79	C_3	148.20
C_4	160.36	C_4	48.60
C_5	135.42	C_5	137.67
C_6	117.29	C_6	115.70
C_7	119.82	C_7	117.20
C_8	125.27	C_8	123.11
C_9	130.98	C_9	126.76
C_{10}	150.12	C_{10}	153.30

The desired compound H_2L was synthesized in good yields according to the previously reported procedure [12]. Elemental analysis, IR, MS and NMR spectral data confirmed the H_2L structure (Fig. 3). The mass spectrum (FAB positive) of H_2L, which shows a molecular ion at $m/z = 403$ $[M+1]^+$, confirms the proposed structure and rules out any polymeric form. In the ^1H NMR spectrum of H_2L, the singlet indicating the primary aromatic amine groups disappears and a new chemical shift at $\delta = 9.21$ ppm, which can be assigned to the NH protons in the neighbourhood of hydroxyimino groups, appears. On the



H_2L

Fig. 3.

Table 2. ^{13}C NMR spectral data for H_2L

Carbons	δ ppm
C_1	129.27
C_2	133.50
C_3	148.76
C_4	51.80
C_5	140.11
C_6	115.83
C_7	117.97
C_8	123.00
C_9	127.17
C_{10}	147.24
C_{11}	142.05

other hand, the other new resonance at $\delta = 11.15$ ppm was observed after the formation of macrocyclization reaction (Scheme 1). It is obvious that this signal indicates hyroxyimino protons. These new NH and OH protons are also easily identified by D_2O exchange. The presence of only one singlet for the =N—OH protons is inconsistent with the assumption that H_2L has an (*E*, *E*) configuration [13]. The equivalent carbon resonances of the proton-decoupled ^{13}C NMR spectra of oxime groups at $\delta = 142.0$ ppm confirm the (*E*, *E*) form of H_2L (Table 2). The other carbon resonances belonging to phenyl and methylene groups are very similar to those of the precursor amine compound. Upon macrocyclization, the chemical shifts of carbons shift slightly, but their numbers are unchanged. In the IR spectrum of H_2L, an OH stretching vibration is observed at 3242 cm^{-1} as a broad absorption. The NH, C=N and NO stretching vibrations are at 3405, 1645 and 963 cm^{-1}, respectively.

The octahedral cobalt(III) complex $[Co(HL)_2L'Cl]$ (**6**) was prepared when air was bubbled through a suspension of $[Co(HL)_2]$ in ethanol in the presence of the Lewis base pyridine as an axial ligand. This mononuclear cobalt(III) complex has a metal : ligand ratio of 1 : 2 according to elemental analysis. The fast atom bombardment mass spectrum of **6** showed an expected molecular ion peak at $m/z = 975$ $[M+1]^+$ and 894. The latter peak indicates the loss of $m/z = 79$, which can be explained by the removal of Lewis base $[M-Py]^+$ from the cobalt(III) complex. The ^1H NMR spectrum of **6** provides the most useful evidence for confirming the six-coordinated cobalt(III) complex. The disappearance of the =N—OH chemical shifts, at $\delta = 11.15$ ppm, and the presence of a new resonance at lower field at $\delta = 17.17$ ppm can be assigned by the formation of a hydrogen bridge. This result can easily be identified by deuterium exchange [14]. The other chemical shifts of the cobalt(III) complex are similar to those of the corresponding free vicinal dioxime. Caused by the coordination to cobalt(III), the ligand resonances are slightly shifted. The upfield shift of the NMR signals of the axial ligand caused by coordination can be explained in terms of a ring-current effect due to the electronic delocalization through the $Co(dioxH)_2^+$ moieties [15]. The low solubility of this complex hindered ^{13}C NMR measurement. In this octahedral complex, the weak deformation band assigned to the intramolecular hydrogen-bonded O—H···O bending vibration was observed at 1689 cm^{-1}. The stretching vibrations of C=N groups were observed as a sharp band at 1625 cm^{-1}. This value is lower than that for H_2L due to the *N*, *N′* coordination to the cobalt(III) ion [16].

The template synthesis of the BF_2^+-bridged macrocyclic cobalt(III) complex (**7**) was performed by adding borontrifluoride etherate to a refluxing acetonitrile containing the precursor cobalt(III) complex. The hydrogen bridging protons were replaced by BF_2^+ groups and the axial ligands were retained, according to both ^1H NMR and MS spectra and elemental analysis data. The mass spectrum (FAB) of this compound did not exhibit a molecular ion; however, peaks at $m/z = 1039$ and 1004 were observed. These peaks indicate $[M—F—B]^+$ and $[M—F—B—Cl]^+$, respectively. In the ^1H NMR spectrum of the BF_2^+-bridged cobalt(III) complex, the deuterium-exchangeable bridging protons of the precursor compound disappeared after the formation of the BF_2^+-capped cobalt(III) complex. BF_2^+ groups cause the resonances of new cobalt(III) complex to shift downfield relative to those of the hydrogen-bridged complex. In the IR spectrum of this complex, the weak band at 1689 cm^{-1}, a characteristic O—H···O in-plane deformation of the hydrogen bond [17], disappears when substituting the hydrogen bond with BF_2^+. On the other hand, an upward shift of 26 cm^{-1} of the C=N stretching vibration was observed due to the strong electron-withdrawing influence of difluoroboron-linked groups incorporated in this macrocycle [18]. A number of new vibrations appear in the region 1180–790 cm^{-1} in the IR spectrum of the BF_2^+-capped cobalt(III) complex. These stretching vibrations at 1184 and 795 cm^{-1} can be interpreted as B—O and B—F bands.

The reaction of $[Co(LBF_2)_2L'Cl]$ with cadmium(II) chloride monohydrate gave the corresponding diamagnetic heterotrinuclear complex $[CoCd_2(LBF_2)_2L'Cl]Cl_4$ (**8**). In this complex, the cadmium(II) ions are trapped in each macrocycle containing 14-membered tetraaza donors and tetradentate coordination is achieved by the use of the four NH groups. The planar nature of the phenyl rings and adjacent azomethine groups contributes to the tendency toward planar coordination by these types of ligands [19]. The FAB mass spectrum of this compound exhibits a parent peak at $m/z = 1433$ due to $[M+1]^+$. On the other hand, this molecule has a metal : ligand ratio of 3 : 2 according to its elemental analysis. The basicity of NH donors in this macrocycle is rather low because of its position just near the hydroxyimino groups. For this reasons, the deprotonation of NH groups in the 14-membered macrocyclic cavity was not observed due to the presence of chemical shifts at $\delta = 9.42$ and 5.66 ppm. The same behaviour was observed in the IR spectrum of this compound due to the presence of N—H stretching vibrations in the 3360 cm^{-1} region. Comparison of the respective IR spectrum of the precursor BF$_2^+$-capped Co^{III} complex and its heterotrinuclear complex reveals that a shift of the N—H stretching vibrations down to 20 cm^{-1} occurs upon complexation. It is obvious that this downshift of the aza stretching vibrations is due to the complexation with Cd^{II} ions.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra of ligand and its complexes were performed on a Varian XL-300 spectrometer. IR spectra were recorded on a Perkin–Elmer 1600 FT-IR spectrophotometer. FAB (positive, matrix = *m*-nitrobenzyl alcohol) and electron impact mass spectra were recorded on a VG AutoSpec from VG Analytical instruments. The elemental analysis was done on a Hewlett–Packard 185 CHN analyser and the metal contents were determined by using a Unicam 929 AA spectrometer. (*E*, *E*)-Dichloroglyoxime (**5**) was prepared by a reported procedure [20]. *o*-Nitrobenzaldehyde, palladium/activated carbon and all solvents were reagent grade and used without purification.

1,2-*Bis*(*o-nitrobenzylidenimino*)*benzene* (3)

A solution of *o*-phenylenediamine (2.16 g, 20 mmol; **2**) in absolute ethanol (100 cm^3) was added dropwise to a solution of *o*-nitrobenzaldehyde (10.82 g, 71.6 mmol; **1**) in absolute ethanol (350 cm^3) for a 30 min period at -10°C under an oxygen-free nitrogen atmosphere. The reaction mixture was kept at that condition for 2 h, then allowed to stand at room temperature and stirred for 18 h. After the end of the period, the reaction mixture was refluxed for 5 h and then cooled to room temperature. The reaction was monitored by thin layer chromatography [$R_f = 0.75$, $CHCl_3:CH_3OH:H_2O$ (75 : 25 : 2)]. The pale yellow reaction mixture was then filtered off and filtrate volume was reduced to 40 cm^3 *in vacuo* to precipitate the rest of the crude product. The combined crude product was filtered off, washed with cold ethanol and diethyl ether and then dried *in vacuo*. After crystallization of the product from ethanol, yield 4.3 g (32.1%) of pale yellow crystals; m.p 256°C (dec.). ^{1}H NMR (DMSO-d_6): δ 8.10 (s, 2H, CH=N), 8.00–7.62 (m, 8H, Ar-H), 7.25 (m, 4H, Ar-H). ^{13}C NMR (DMSO-d_6): δ 160.4, 150.1, 145.8, 135.4, 134.3, 131.0, 130.6, 125.3, 119.8, 117.3. IR (KBr pellets, cm^{-1}): 3090, 1628, 965. Mass spectrum (EI): $m/z = 392$ $[M+H_2O]^+$. Found: C, 64.0, H, 3.6; N, 14.8. Calc. for $C_{20}H_{14}N_4O_4$: C, 64.2; H, 3.7; N, 15.0%.

2,3 : 6,7 : 10,11-*Tribenzo*-1,5,8,12-*tetraazadodecane* (4)

The Schiff base (4.00 g, 10.88 mmol; **3**) was dissolved in *n*-butanol (220 cm^3) by heating at 75°C. The palladium/activated carbon (10%) was added above solution at the same temperature and allowed to stand at 120°C and then 10.4 cm^3 of hydrazine hydrate (100%) was added dropwise to this reaction mixture. The reaction mixture was refluxed and stirred for 1 h and then filtered and washed with *n*-butanol (25 cm^3). The pale yellow solution was concentrated to 35 cm^3 *in vacuo*. The crude product was filtered off, washed with cold *n*-butanol and diethyl ether and then dried *in vacuo*. After crystallization from ethanol, yield 2.5 g (76.5%) of plates white crystals; m.p. 212°C. ^{1}H NMR (DMSO-d_6): δ7.88 (d, 2H, Ar-H), 7.60 (m, 3H, Ar-H), 7.25 (m, 3H, Ar-H), 6.85 (d, 2H, Ar-H), 6.65 (t, 2H, Ar-H), 6.28 (s, 2H, NH), 5.39 (s, 4H, NH$_2$), 3.65 (s, 4H, CH$_2$). ^{13}C NMR (DMSO-d_6): δ 153.3, 148.2, 137.7, 131.6, 128.1, 126.8, 123.1, 117.2, 115.7, 48.6. IR (KBr pellets, cm^{-1}): 3410, 3355, 3060, 2940, 1612. Mass spectrum (EI): $m/z = 336$ $[M+H_2O]^+$. Found: C, 75.3; H, 6.7; N, 17.4. Calc. for $C_{20}H_{22}N_4$: C, 75.5; H, 6.9; N, 17.6%.

5,6 : 9,10 : 13,14-*Tribenzo*-2,3-bis(hydroxyimino)-1,4,8,11-*tetraazacyclodecane* (H_2L)

A solution of (*E*, *E*)-dichloroglyoxime (1.57 g, 10 mmol) in absolute ethanol (50 cm^3) was added dropwise to a solution of **4** (3.36 g, 10 mmol) in absolute ethanol (500 cm^3), which also contained NaHCO$_3$ (4.2 g, 50 mmol) in excess at -5°C an under nitrogen atmosphere. The reaction mixture was kept at the same temperature for 2 h and then allowed to stand at room temperature. After stirring was maintained for 16 h at room temperature, the white precipitates were formed. The end of the reaction was controlled by using thin layer chromatography [$R_f = 0.73$, *n*-butanol : acetic acid : water (4 : 1 : 5)]. The reaction mixture was filtered off, washed with absolute ethanol and diethyl ether. The filtrate was concentrated on an evaporator to 55 cm^3 and the formed solid was filtered off, washed with water, cold ethanol and diethyl ether and then dried *in vacuo*. After crystallization of the solid from ethanol : water mixture (4 : 1), yield 2.1 g (52.3%) of white product; m.p. 281°C (dec.). ^{1}H NMR (DMSO-d_6): δ 11.15 (s, 2H, OH), 9.21 (s, 2H, NH), 7.45 (d, 3H, Ar-H), 7.28 (t, 4H, Ar-H), 6.75 (m, 5H, Ar-H), 5.45 (s, 2H, NH), 3.85 (s, 4H, CH$_2$). ^{13}C NMR (DMSO-d_6): δ 148.8, 147.2, 142.0, 140.1, 133.5, 129.3, 127.2, 123.0, 118.0, 115.8, 51.8. IR (KBr pellets, cm^{-1}): 3405, 2342, 3054, 2936, 1645, 1610, 963. Mass spectrum (FAB positive): $m/z = 403$ $[M+1]^+$, 400 $[M\text{-}2]^+$, 372 $[M\text{-}NOH+1]^+$, 341 $[M\text{-}2(NOH)+1]^+$. Found: C, 65.5; H, 5.3; N, 20.7. Calc. for $C_{22}H_{22}N_6O_2$: C, 65.7; H, 5.5; N, 20.9%.

Synthesis of [Co(HL)$_2$L′Cl](L′ = pyridine) (**6**)

A solution of $CoCl_2 \cdot 6H_2O$ (0.474 g, 2 mmol) in ethanol (25 cm^3) was added to a solution of H_2L (1.61 g, 4 mmol) in hot ethanol (60°C, 120 cm^3) with stirring. A distinct change in colour and a decrease in the "pH" of the reaction mixture were observed (pH = 2.03). Lewis base (0.16 g, 2 mmol) in ethanol (5 cm^3) was added to the above mixture at the same reaction conditions and air bubbled through it, during which the reaction mixture was allowed to cool to room temperature. This reaction was kept at room temperature for 6 h while air was bubbled through. The brown precipitate was filtered off, washed with water, cold ethanol and diethyl ether, and then dried *in vacuo*. Yield: 1.42 g (73.1%); m.p. 312°C (dec.). ^{1}H NMR (DMSO-d_6): δ 17.17 (s, 2H, O—H···O), 9.28 (s, 4H, NH), 8.48–7.51 (m, 11H, Ar-H, Py-H), 7.37–6.68 (m, 18H, Ar-H, Py-H), 5.51 (s, 4H, NH), 3.92 (s, 8H, CH$_2$). IR (KBr pellets, cm^{-1}): 3300, 3090, 2911, 1689, 1625, 952. Mass spectrum (FAB positive): $m/z = 975$ $[M+1]^+$, 895 $[M\text{-}Py]^+$. Found: C, 60.0, H, 4.6; N, 18.4; Co, 5.8. Calc for $C_{49}H_{47}N_{13}O_4CoCl$: C, 60.3; H, 4.8; N, 18.6; Co, 6.0%.

Synthesis of [Co(LBE$_2$)$_2$L′Cl] (**7**)

A suspension of **6** (1.00 g, 1.03 mmol) in 60 cm^3 of freshly distilled acetonitrile was brought to reflux temperature under argon. To this suspension, 0.50 cm^3 (2.05 mmol) of the boron trifluoride diethyl ether complex was added. The resulting mixture turned red within 10 s. The reaction was continued for 1 h at the reflux temperature and the end of the reaction was verified using thin layer chromatography [$R_f = 0.77$, *n*-butanol : acetic acid : water (4 : 1 : 5)]. The solvent was removed under reduced pressure and the residue was dissolved in 20 cm^3 of acetonitrile, then the last step was repeated twice. The red solid was dissolved in 15 cm^3 of acetonitrile and then cooled to −18°C overnight. The red crystallized product was filtered off, washed with cold acetonitrile and diethyl ether and then dried *in vacuo*. Yield: 0.48 g (43.7%); m.p. 299°C. ^{1}H NMR (DMSO-d_6): δ 9.34 (s, 4H, NH), 8.50–7.59 (m, 11H, Ar-H, Py-H), 7.41–6.72 (m, 18H, Ar-H, Py-H), 5.41 (s, 4H, NH), 3.95 (s, 8H, CH$_2$) IR (KBr pellets, cm^{-1}): 3380, 3065, 2940, 1651, 973. Mass spectrum: $m/z = 1039$ $[M\text{-}F\text{-}B]^+$, 1004 $(M\text{-}F\text{-}B\text{-}Cl]^+$. Found: C, 54.0; H, 3.9; N, 16.7; Co, 5.3. Calc for $C_{49}H_{45}N_{13}O_4CoClB_2F_4$: C, 54.9; H, 4.2; N, 17.0; Co, 5.5%.

Synthesis of [Cd$_2$Co(LBF$_2$)$_2$L′Cl](**8**)

A solution of $CdCl_2 \cdot H_2O$ (0.15 g, 0.75 mmol) in absolute ethanol (20 cm^3) was added to a solution of **7** (0.40 g, 0.37 mmol) in absolute ethanol (80 cm^3) and the mixture was refluxed for 35 h with continuous stirring. After the complexation was complete by thin layer chromatography ($R_f = 0.62$, *n*-butanol : acetic acid : water (4 : 1 : 5)], the reaction mixture was cooled and filtered. The dark brown complex was washed with cold ethanol and diethyl ether and then dried *in vacuo*. Yield: 0.20 g (74.6%); m.p. 356°C. ^{1}H NMR (DMSO-d_6): δ 9.42 (s, 4H, NH), 8.52–7.62 (m, 11H, Ar-H, Py-H), 7.45–6.74 (m, 18H, Ar-H, Py-H), 5.66 (s, 4H, NH), 3.98 (s, 8H, CH$_2$). IR (KBr pellets, cm^{-1}): 3360, 3068, 2930, 1642, 938. Mass spectrum (FAB positive): $m/z = 1433$ $[M+1]^+$. Found: C, 40.7; H, 3.0; N, 12.4; Co, 3.8; Cd, 15.3. Calc. for $C_{49}H_{45}N_{13}CoCd_2B_2F_4Cl_5$: C, 40.9; H, 3.1; N, 12.6; Co, 4.1; Cd, 15.6%.

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REFERENCES

1. Melson, G.A., *Coordination Chemistry of Macrocyclic Compounds*. Plenum Press, New York, 1979, p.1.
2. Rasokha, S. V., Lampeka, Y. D. and Moloshtar, L. M., *J. Chem. Soc., Dalton Trans.* 1993, 631.
3. Shakir, M., Varkey, S. P. and Nasmon, O. S. M., *Polyhedron*, 1995, **14**, 1283.
4. Constable, E. C., Sach, C., Palo, G., Tocher, D. A. and Truter, M. R., *J. Chem. Soc., Dalton Trans.* 1993, 1307; Gök, Y. and Karabocek, S. *Z. Anorg. Allgem. Chem.* 1995, **621**, 654; Funkemeier, D. and Mattes, R., *J. Chem. Soc., Dalton Trans.* 1993, 1313.
5. Beer, P. D., Nation, J. E., McWhinnie, S. L. W., Harman, M. E., Hursthouse, M. B., Ogden, M. I. and White, A. H., *J. Chem. Soc., Dalton Trans.* 1991, 2485.
6. Chakravorty, A., *Coord. Chem. Rev.* 1974, **13**, 1; Holm, R. H. and O'Conner, M., *Prog. Inorg. Chem.* 1971, **14**, 277; Schrauzer, G. N., *Angew. Chem., Int. Ed, Engl.* 1976, **15**, 417.
7. Schrauzer, G. N., Windgassen, R. J. and Kohnle, J., *Chem. Ber.* 1965, **98**, 3324; Tan, N. and Bekaroglu, Ö, *Synth. React. Inorg. Met.-Org. Chem.* 1983, **13**, 667.
8. Gök, Y., Kantekin, H. and Degirmencioglu, I., *Polyhedron*, 1993, **12**, 2097; Gök, Y., Senturk, H. B., Ocak, U. and Kantekin, H., *J. Chem. Res. (S)*, 1994, 258; Gök, Y., Karabocek, S. and Kantekin, H., *Trans. Met. Chem.* 1995, **20**, 234.
9. Gök, Y., *Polyhedron*, 1996, **15**, 1355.
10. Gök, Y., *Polyhedron*, 1996, **15**, 3933.
11. Gök, Y., Karabocek, S., Karabocek, N. and Atalay, Y., *New J. Chem.* 1995, **19**, 1275; Gök, Y. and Kantekin, H. 1996, in press.
12. Ertepinar, H., Gök, Y. and Kucükislamoglu, M. *Eur. Poly. J.* 1995, **31**, 603; Gök, Y., *New J. Chem.* 1996, **20**, 971.
13. Gök, Y. and Kantekin, H., *New J. Chem.*, 1995,

19, 461; Gök, Y. and Kantekin, H., *Chem. Ber.* 1990, **123,** 1479.

14. Szczepura, L. F., Muller, J. G., Bessel, C. A., See, R. F., Janik, T. S., Churchill, M. R. and Takeuchi, K. J., *Inorg. Chem.* 1992, **31,** 856; Ahsen, V., Gokceli, F. and Bekaroglu, O., *J. Chem. Soc., Dalton Trans.* 1987, 1827.
15. Gök, Y. and Kantekin, H., *Synth. React. Inorg. Met.-Org. Chem.* 1990, **20,** 1085; Gök, Y. and Karabocek, S., *Z. Anorg. Allg. Chem.*, 1995, **621,** 654.
16. Alexander, V., *Inorg. Chim. Acta.* 1989, **163,** 25; 1993, **204,** 109.
17. Bigotto, A., Galasso, V. and Dealt, G., *Spect. Chim. Acta* 1970, **27,** 1659.
18. Hussain, M. S., Al-Mohdhar, H. M. and Al-Arfaj, A. R., *J. Coord. Chem.* 1988, **18,** 339.
19. Gök, Y., Kantekin, H., Alp, H. and Özdemir, M., *Z. Anorg. Allg. Chem.* 1995, **621,** 1237.
20. Ponzio, G. and Baldrocco, F., *Gazz. Chim. Ital.* 1930, **60,** 415; Brinizinger, H. and Titzman, R., *Chem. Ber.* 1952, **85,** 344.