Synthesis and characterization of a novel (*E*,*E*)-dioxime and its mono- and heterotrinuclear complexes containing a 21-membered trioxadithiadiaza macrocycle

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A new (*E*,*E*)-dioxime (H_4**L**) containing a 21-membered trioxadithiadiaza macrocycle was synthesized from the reaction of 2,3:17,18-dibenzo-4,16-dithia-7,10,13-trioxa-1,19-diazanonadecane (**2**), prepared from 3,6,9-trioxa-1,11-dibromoundecane (**1**) and 2-aminothiophenol, and cyanogendi-*N*-oxide. Only mononuclear Ni(II) and Co(III) complexes with a metal : ligand ratio of 1 : 2 were isolated. These hydrogen-bridged complexes were converted to their BF_2^+-bridged analogues by reaction with boron trifluoride etherate. The reaction of the BF_2^+-bridged complexes with Pd(II) and Ni(II) gave heterotrinuclear complexes. These compounds are significant in that they provide binding sites not only within but also outside the macrocycles. Structures for the dioxime and its complexes are proposed in accordance with the elemental analysis, ^{1}H and ^{13}C NMR, IR and mass spectral data, magnetic susceptibility measurements and semi-empirical quantum chemical calculations.

The chemistry of complexes containing mixed-donor multidentate macrocyclic ligands with cation complexing abilities has been explored extensively over the past 35 years.[1] Another rapidly emerging topic of chemical interest in recent years concerns the synthesis of heterotrinucleating ligands and the coordination chemistry of the polynuclear complexes that derive from such ligands.[2] Some of the heteronucleating macrocycles that could serve as "polytopic receptor molecules" for the binding of metal cations, or the co-binding of metal ions and molecular substrates, include molecules containing macrocyclic functionalities appended to porphyrin, phthalocyanine, tetrathia, dithiadiaza or tetramine centres.[3] Macrocyclic ligands containing both nitrogen and sulfur donor atoms are of interest because of their potential for providing molecules capable of mimicking various aspects of macromolecular biological systems. As might be anticipated, the macrocyclic polyamino polythioether ligands exhibit an interesting range of properties intermediate between those of macrocyclic polythioethers and macrocyclic polyamines.[3f,4]

The chemistry of transition metal complexes with (*E*,*E*)-dioxime ligands is the subject of several reviews.[5] The high stability of the complexes prepared with *vic*-dioxime ligands has been extensively exploited for various purposes, such as use as analytical reagents[6] and as models for some biological systems;[7] they are also useful as catalysts in many chemical processes[8] or as templates in some organic reactions.[9]

The aim of this study was to synthesize and characterize a novel (*E*,*E*)-dioxime containing a 21-membered trioxadithiadiaza macrocycle and to prepare its mono- and heteropolynuclear complexes. We report herein the synthesis of the free ligand 5,6:20,21-dibenzo-2,3-bis(hydroxyimino)-10,13,16-trioxa-7,19-dithia-1,4-diazacyclomonocosane, abbreviated to H_4**L**, and the synthesis, properties and reactivity of the Co(III) and Ni(II) complexes of this ligand. We also report the synthesis of heterotrinuclear BF_2^+-capped complexes of cobalt(III) and nickel(II) which have been prepared with 21-membered mixed-donor macrocyclic cavities.

Results

Synthesis

The preparation of the *vic*-dioxime containing a macrocyclic moiety from a primary amine and cyanogendi-*N*-oxide solution requires direct addition reactions to form the desired macrocyclic compound instead of a polymer. The reaction of 2-aminothiophenol with 3,6,9-trioxa-1,11-dibromoundecane (**1**) in absolute ethanol using potassium as the base resulted in the formation of the aromatic primary amine **2** in 72% yield. To construct the ligand H_4**L**, containing a 21-membered mixed-donor macrocyclic cavity, an equivalent amount of amine **2** was coupled *via* a bis(hydroxyimino) group by reaction with (*E*,*E*)-dichloroglyoxime and aqueous sodium carbonate (0.5 M) in dichloromethane at −10 °C. The ligand was formed in *ca.* 63.1% yield after recrystallization from ethanol (Scheme 1). The Ni(II) complex (**3**) of the *vic*-dioxime was prepared in *ca.* 78% yield by treating nickel(II) chloride hexahydrate in ethanol with the ligand in the presence of a base such as KOH. The template synthesis of the macrocyclic Ni(II) complex [Ni(H_2**L**BF_2)$_2$] (**4**) was performed by adding boron trifluoride etherate to a refluxing acetonitrile solution of the hydrogen-bridged precursor Ni(II) complex, giving the product in *ca.* 52% yield. The preparation of the heterotrinuclear complex [Pd_2Ni(**L**BF_2)$_2$] (**5**) was accomplished by the reaction of **4** with bis(benzonitrile)palladium(II) chloride. Upon refluxing the reaction mixture in an inert atmosphere for 20 h, the formation of the brown target species was observed in a good yield (41%). The six-coordinate Co(III) complex [Co(H_2**L**)$_2$Cl(py)] (**6**) was prepared as previously reported.[3a,10] The Co(II) precursor complex was oxidized to a diamagnetic octahedral Co(III) derivative by bubbling air through an EtOH solution of the complex in the presence of pyridine.[11] When borontrifluoride diethyl ether complex was added to a refluxing MeCN suspension of the H-bridged Co(III) complex **6**, only the bridging protons were replaced by

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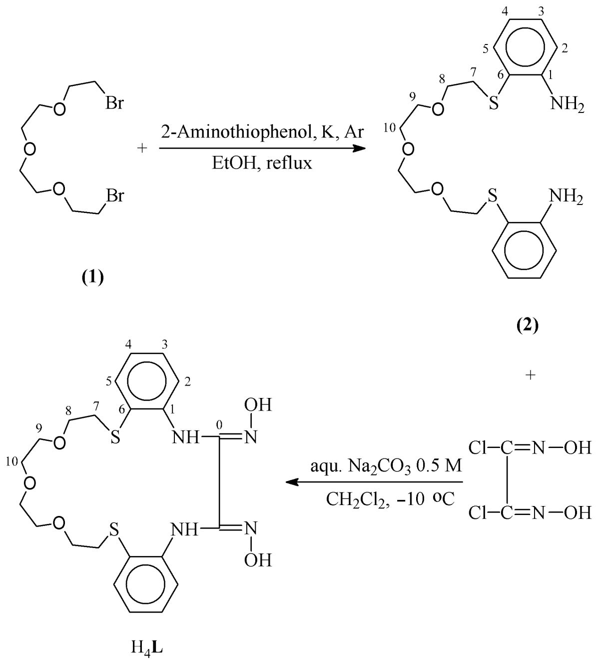
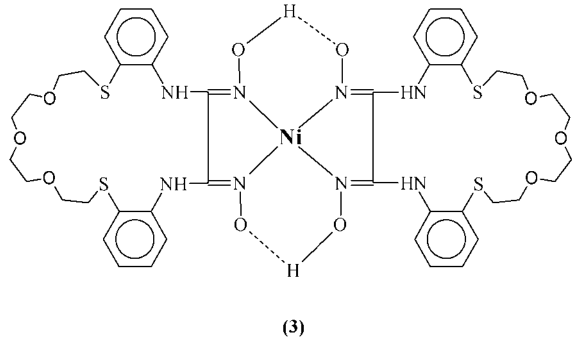


Scheme 1

BF_2^+ groups, but pyridine was retained as an axial base (**7**). In order to synthesize the heteronuclear complex $[Ni_2Co(\mathbf{L}BF_2)_2Cl(py)]$ (**8**), the heterogeneous reaction of the mononuclear BF_2^+-capped Co(III) complex **7** with a solution of Ni(II) perchlorate in EtOH was carried out.

Spectroscopy

All the results are summarized in the Experimental section and they suggest that compound **2** exists as proposed. A singlet at $\delta = 4.24$ in the ^1H NMR spectrum of this compound was assigned to the aromatic primary amine groups, demonstrating that these protons are magnetically equivalent. The low field signals at $\delta = 3.46$ and 2.83 must originate from the polyether fragments. The doublet and triplet resonances of the aromatic rings are indicative of complete replacement of the bromine atoms by the 2-aminothiophenolate groups. The ^{13}C NMR spectrum of **2** exhibits signals characteristic of methylene groups connected to oxygen, sulfur and aromatic carbons. The EI mass spectrum of **2**, which shows a peak at $m/z = 408$ due to $[M]^+$, supports the proposed formula for this compound. In the IR spectrum of $H_4\mathbf{L}$, the presence of a strong absorption at 1636 cm^{-1} is strongly indicative of the presence of hydroxyimino groups. The disappearance of the NH_2 stretching vibrations, together with the appearance of new resonances at 3254 [ν(O–H)], 3319 [ν(N–H)] and 941 cm^{-1} [ν(N–O)], are also in agreement with the proposed structure in Scheme 1. In the ^1H NMR spectrum of $H_4\mathbf{L}$, the deuterium-exchangeable protons of the NOH and NH groups appear as two singlets at $\delta = 11.18$ and 7.82, respectively. The FAB mass spectrum of $H_4\mathbf{L}$ exhibits an intense peak at



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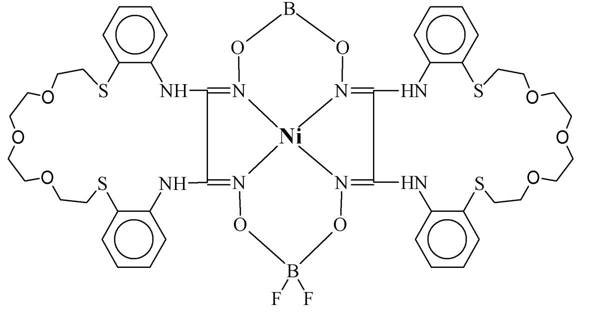

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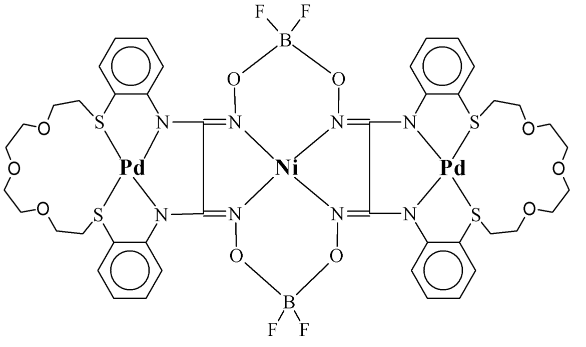

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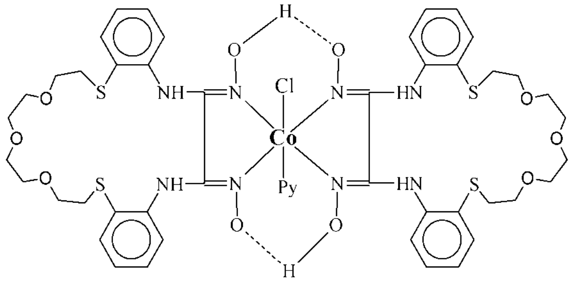

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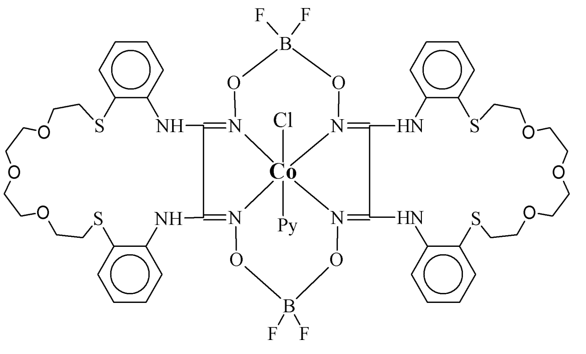

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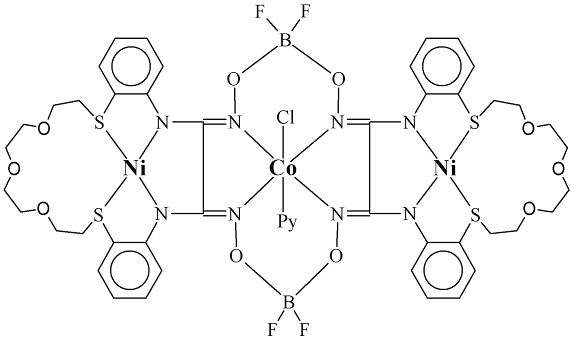

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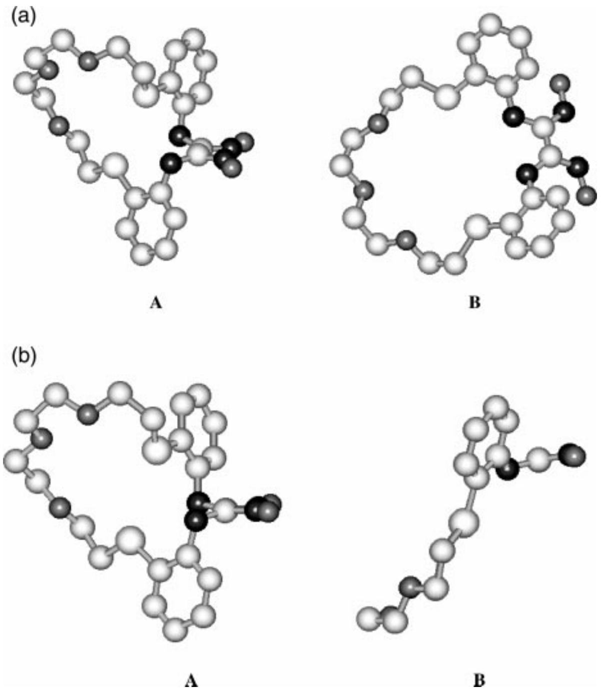

Fig. 1 (a) Top views of the dioxime in conformations (**A**) and (**B**). (b) Side views of the dioxime.

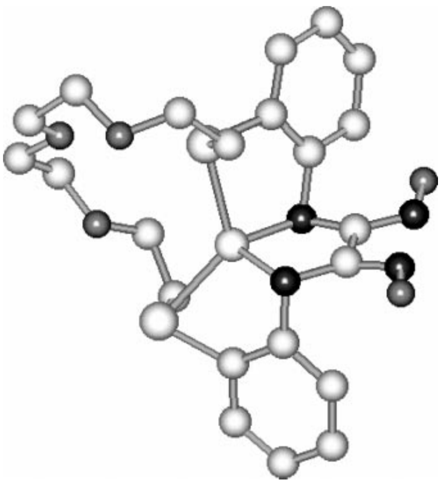

Fig. 2 The configuration of the outer macrocyclic part of the trinuclear complex **5**.

$m/z = 492$ due to $[\mathrm{M}]^+$, which is in accord with the proposed structure and rules out any undesired polymeric form.

The FAB mass spectrum of **3** exhibits a molecular ion peak at $m/z = 1040$. The IR spectrum of **4** contains a weak band at 1720 cm^{-1} which can be attributed to the absorbance of the O–H···O intramolecular hydrogen bridges.[12] The ^{1}H NMR spectrum of this mononuclear complex was collected in DMSO-d_6, where a broad singlet at $\delta = 16.55$ due to two protons was observed. The other proton and carbon chemical shifts are similar to those of the free ligand, except for the azomethine carbons and amide protons.

In the ^{1}H spectrum of the $\mathrm{BF_2}$-bridged Ni(II) complex **4**, the boron-containing moieties cause the resonances of the other groups to shift downfield relative to those in the precursor Ni(II) complex.[13] This effect can be as large as 0.27 ppm in the case of the NH group. Similar trends were observed in the ^{13}C NMR spectrum of this complex. The resonances of the azomethine carbons ($\mathrm{C_1}$), which appear at $\delta = 145.01$, shift downfield by as much as 1.71 ppm on going from the hydrogen-bridged compound to the $\mathrm{BF_2}^+$-capped complex. IR spectroscopy can be used to distinguish between the hydrogen-bridged and the $\mathrm{BF_2}^+$-bridged complexes. The frequency of the C=N stretching vibration increases by 40 cm^{-1} on going from the hydrogen-bridged complex to the $\mathrm{BF_2}^+$-capped compound. The weak and broad band at 1720 cm^{-1}, a characteristic O–H···O in-plane deformation of the hydrogen bond, disappears when substituting the H-bonded Ni(II) complex with $\mathrm{BF_2}^+$, with the concomitant appearance of peaks around 1182 and 848 cm^{-1} due to the B–O and B–F bonds. In the FAB mass spectrum of this complex, the molecular ion peak occurs at $m/z = 1134$ with the base peak at $m/z = 1096$. This mass loss of 38 can be accounted for by the removal of two fluorine atoms from the complex.

The identity of the heterotrinuclear complex **5** was confirmed by the FAB mass spectrum, which shows a peak at $m/z = 1342.2$ corresponding to $[\mathrm{M}]^+$. The magnetic moment of **5** was calculated to be about 2.55 BM per palladium atom, showing that this complex is paramagnetic and comparable with the value reported for slightly distorted tetrahedral Ni(II)

Table 1 The calculated total energy, heat of formation, dipole moment and frontier molecular orbital energies for conformations of $\mathrm{H_4}$**L**

Conformation	E_{tot}/kcal mol^{-1}	$\Delta H_{\mathrm{f}^\circ}$/kcal mol^{-1}	μ/D	E_{HOMO}/eV	E_{LUMO}/eV
A	−127351.77	−14.95	2.78	−8.44	−0.19
B	−127350.71	−13.94	3.27	−8.33	−0.18

Table 2 Stretching energies for conformations of $\mathrm{H_4}$**L** from MM2 calculations (all in kcal mol^{-1})

Conformation	E_{tot}	Bond	Angle bend	Torsion	vdW	Bond str.	Electrostatic
A	44.71	1.90	15.25	13.92	12.11	0.09	1.43
B	50.27	0.91	13.76	13.51	17.80	0.31	3.98

Table 3 The calculated total energy, heat of formation, charge density, bond lengths and bond angles for the outer macrocyclic part [Pd(**L**), Ni(**L**)] of the trinuclear complexes

		E_{tot}/kcal mol^{-1}	$\Delta H_{\mathrm{f}^\circ}$/kcal mol^{-1}	Q_{M}	M–S/Å	M–N/Å	S–M–S/°	S–M–N/°	N–M–N/°
[Pd(**L**)]	Distorted tetrahedral	−213903.925	−12238.534	−0.42	2.375	1.964	105.6	94.5	99.4
	Square planar	−213887.421	−12221.746	−0.25	2.315	1.949	96.0	93.8	88.8
[Ni(**L**)]	Distorted tetrahedral	−220612.413	−11986.915		2.332	1.956	110.0	94.8	96.3
	Square planar	−220590.474	−11965.213		2.305	1.942	98.2	88.6	85.1

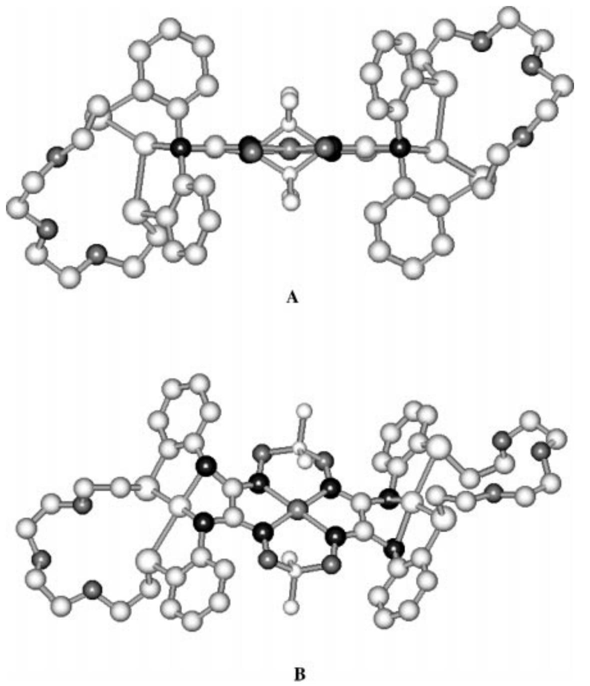

Fig. 3 The totally optimised distorted tetrahedral (**A**) and square-planar (**B**) geometries of the trinuclear complex **5**.

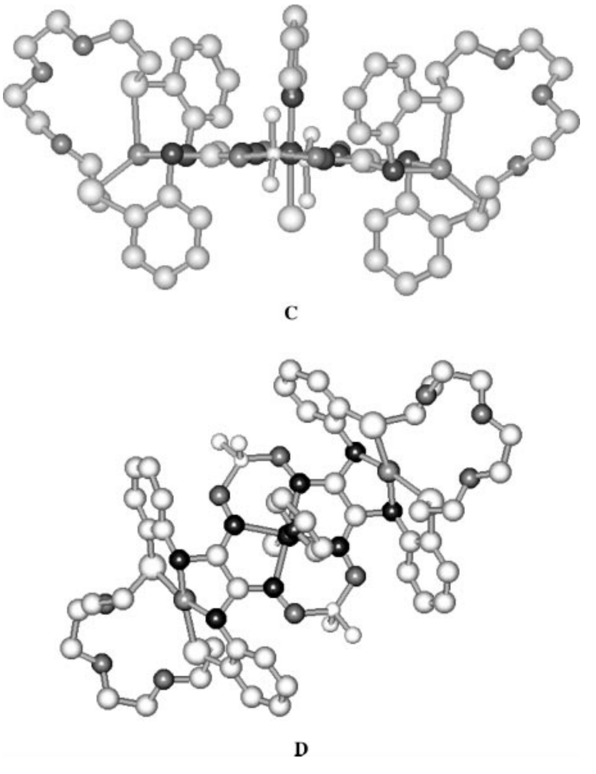

Fig. 4 The totally optimised distorted tetrahedral (**C**) and square-planar (**D**) geometries of the trinuclear complex **8**.

complexes.[14] In the IR spectrum of this complex, the deprotonation of the NH groups is confirmed by the absence of N–H stretching vibrations.[15]

Mononuclear complexation of cobalt in **6** was confirmed by the FAB mass spectrum of [Co(H_2**L**)$_2$Cl(py)Cl], which displays a molecular ion peak at $m/z = 1154.3$. The IR spectrum of **6** exhibits C=N stretching vibrations at 1620 cm^{-1}. This value is lower than that for the free ligand which can be attributed to N,N′-chelation.[16] The weak band at 1700 cm^{-1} can be ascribed to the intramolecular hydrogen bond (O–H···O) bending vibrations.[17] The ^{1}H NMR spectrum of this complex is similar to that of the corresponding free ligand. Upon complexation to Co(III), the ligand resonances shift slightly but the total number remains unchanged. Three additional signals due to the axially coordinated pyridine molecule are also observed. The ^{1}H NMR spectrum confirms the hydrogen bridge structure with a peak at low field ($\delta = 16.92$) for the deuterium-exchangeable O–H···O protons. The resonance due to the NH protons is observed at $\delta = 7.80$, which confirms the mononuclear complexation. In the ^{13}C NMR spectrum of **6**, the ligand resonances shift slightly upon coordination to Co(III), but the total number does not change.

In the mass spectrum of compound **7**, the molecular ion peak was found at $m/z = 1248$ $[M]^+$, with another intense peak at $m/z = 1134$ corresponding to the loss of pyridine and chlorine. The infrared spectrum of [Co(H_2**L**BF_2)$_2$Cl(py)] resembles that of the precursor hydrogen-bridged complex except for the occurrence of new bands characteristic of the BF_2 group and the absence of the O–H···O bending vibrations. The strong sharp absorption at 832 cm^{-1} is attributed to the B–F stretching modes while the weak resonances occurring at 1171 cm^{-1} are ascribed to the B–O stretching vibrations of the BF_2 derivative, as was seen for [Ni(H_2**L**BF_2)$_2$].[2c,18] Deuterium-exchangeable bridging O–H···O proton signals were absent in the NMR spectra of this diamagnetic Co(III) complex, as expected. The resonance of the hydroxyimino carbons observed at $\delta = 144.34$ is shifted downfield by 1.03 ppm with respect to the hydrogen-bridged complex.[13]

The FAB mass spectrum of heterotrinuclear complex **8** shows the molecular ion peak at $m/z = 1360.2$, which supports the proposed formation of **8** and the peak at $m/z = 1246$ confirms the loss of pyridine and chlorine. The IR spectrum of the heterotrinuclear complex is very similar to that of the mononuclear Co(III) complex, except for the disappearance of the N–H stretching frequencies due to the complexation of Ni(II) cations in the macrocycles. This heterotrinuclear complex is paramagnetic with a calculated magnetic moment of about 3.11 BM per Ni(II) atom, which supports the proposed structure.[19]

Quantum chemical calculations

In this study, the conformation analysis of the newly synthesized ligand H_4**L** was carried out using the PM3 method.[20] Two stable conformations were determined (Fig. 1, Table 1). The stretching energies were calculated with the MM2 method.[20] Free ligand in the **B** conformation had a higher stretching energy, at *ca.* 5.57 kcal mol^{-1}, than configuration

Table 4 The calculated total energy, heat of formation, bond lengths and bond angles for the **A**, **B**, **C** and **D** configurations of the trinuclear complexes **5** and **8**

Configuration	E_{tot}/kcal mol^{-1}	$\Delta H_{f°}$/kcal mol^{-1}	M–N/Å	M–S/Å	M–N/Å	N_1–M–N_2/°	N_2–M–N_3/°	S–M–S/°	S–M–N/°	N–M–N/°
5 A	−520706.836	−25691.234	1.954	2.339	1.934	96.405	84.515	108.185	92.281	97.771
B	−520659.483	−25643.126	1.947	2.301	1.947	95.612	85.385	93.455	92.104	83.451
8 C	−566271.365	−27460.732	1.949	2.320	1.950	94.285	85.537	115.654	92.792	90.959
D	−566237.916	−27427.635	1.944	2.301	1.972	94.567	85.412	101.806	87.721	82.543

A. The stretching energies of the **A** and **B** conformations are composed of bond stretching, angle bending, bond rotation (torsion), electrostatic and van der Waals interaction energies (Table 2). The geometries of the outer macrocyclic part of the heteronuclear complexes (Fig. 2, Table 3) and of the entire complexes (Fig. 3 and 4, Table 4) were also investigated using the ZINDO/1 method[22] in version 6 of HYPERCHEM and their stable structures were determined. The metal parameters used in this study for the quantum chemical calculations were those used in ref. 23. However, the values for M–N (metal–nitrogen) binding in the trinuclear metal complex structures obtained by the ZINDO/1 method contradict the values in the literature.[24]

Discussion

The synthesis of a new *vic*-dioxime containing macrocyclic unit was one of the aims of this study. Many different macrocyclization procedures have been developed, such as high-dilution techniques[14] and template processes.[25] The high-dilution technique is, however, inconvenient as it requires the simultaneous addition of the reactants to a large volume of solvent over an extended period of time. Template processes are those in which the metal ions or another centre have a definite stereochemistry and electronic state plays a paramount role. After the macrocyclization reaction, removing the metal cations from the macrocyclic cavity can cause some problems. Despite this, we decided to take a similar approach to the synthesis of a dioxime-containing macrocyclic moiety.[3a,26] Elemental analysis, MS, IR, NMR spectral data and quantum chemical calculation confirm the structure of $\mathbf{H_4L}$, which is mainly determined by the conformation of the macrocycle. Whether or not the benzene rings are on the same side affects the properties of the macrocycle. According to the results of the quantum chemical calculations, in the macrocycle the heteroatoms move in different directions. In the stable conformation of the free ligand (Fig. 1, **A**), the heteroatoms take on a transoid–transoid configuration but the benzene rings are *trans* relative to the oxime plane. This conformation is more stable than **B** (Fig. 1, **B**), in which the heteroatoms of the macrocycle are still transoid–transoid but the benzene rings are now on the same side of the macrocycle and *cis* relative to the oxime plane. Having the benzene rings on different sides of the macrocycle (*anti*-conformation) is more stable than the *syn*-conformation, in which the benzene rings are on the same side of the macrocycle, according to the PM3 calculations.

The reason why the **B** conformation has a higher stretching energy than the **A** conformation can be explained by the following. Since the distance between the hydrogen atoms bound to amide nitrogen atoms in **B** conformation is 1.961 Å, while it is 4.90 Å in **A**, the van der Waals interaction energy in **B** is 5.69 kcal mol^{-1}, which is higher than in the **A** conformation. The single peak ($\delta = 11.18$) for the hydroxyimino protons indicates that the oxime groups are in an *E*,*E*-structure.[27] In the proton-decoupled ^{13}C NMR spectrum of this compound, the equivalent carbon resonance of the oxime groups (C_1) at $\delta = 142.21$ also confirms the structure of the dioxime.[28] In the IR spectrum, bands due to O–H, N–H, C=N and N–O stretches are found at 3254, 3319, 1636 and 941 cm^{-1}, respectively, in agreement with previously reported values for diaminoglyoxime derivatives.[10a,15b,29]

The literature furnishes examples of oximato ions coordinated to a metal centre (Ni^{II}, Co^{II}, Cu^{II}, *etc.*) as a bidentate ligand.[30] The mononuclear complex **3** has a metal : ligand ratio of 1 : 2, as is the case for most (*E*,*E*)-dioxime Ni(II) complexes.[31] The FAB mass spectral data also confirms this result. In the IR spectrum, a downward shift, relative to the free ligand, of about 22 cm^{-1} for the C=N absorption, indicates coordination through the N atoms. The disappearance of the O–H resonances and the formation of hydrogen bonds also results in the removal of electron density from the N–O bond and a decrease in the N–O stretching frequency.[32] In the ^{1}H NMR spectrum of **3**, the downfield signals at $\delta = 16.55$ are probably due to the formation of hydrogen bonds. The identification of these hydrogen bridges can be easily confirmed by deuterium exchange. Similar trends were observed in the proton-decoupled ^{13}C NMR spectrum.

In the BF_2^+-capped Ni(II) complex **4**, the bridging protons observed in the precursor Ni(II) complex are replaced with BF_2^+ groups and, as expected, all their characteristics are retained according to the spectral and analytical data. The ^{1}H and ^{13}C NMR resonances of the BF_2-bridged macrocycle exhibit downfield shifts due to the incorporation of these strongly electron-withdrawing groups in the macrocycle. The formation of **4** is supported by the following evidence: (i) the disappearance of the O–H···O IR absorbances with the simultaneous appearance of new vibrations assigned to *v*(B–O) and *v*(B–F);[16] (ii) the shift of *v*(C=N) to higher frequencies;[33] (iii) the disappearance of signals arising from the hydrogen bridges and the downfield shifts of peaks in the ^{1}H and ^{13}C NMR spectra, relative to the starting compound **3**; (iv) the elemental analysis and mass spectral data.

The six-coordinate Co(III) complex **6** was obtained when air was bubbled through a suspension of the Co(II) complex in ethanol in the presence of pyridine[11] to serve as an axial ligand. The Lewis base and chlorine ligands are coordinated axially to the Co(III) in this complex. It is necessary to use a single equivalent of pyridine because the presence of excess base in the reaction media was reported to yield a complex in which one of the linking protons had been removed and which contained two axially bound nitrogen bases.[34] Since a distinct decrease in the pH of the solution (pH = 2.43) was observed during complexation, deprotonation of the ligands and subsequent N,N′-chelation with the (*E*,*E*)-dioxime groups probably occurs. The disappearance of the OH stretching vibrations and the shifts of the C=N bands to lower frequencies in the IR spectrum of this complex are probably related to the N,N′-chelation.[15c] The ^{1}H NMR spectrum of **6** supports this assumption through the disappearance of the OH and the appearance of O–H···O signals, the identity of which can be easily confirmed by deuterium exchange. The new resonances in the ^{1}H and ^{13}C NMR spectra of this compound can be attributed to the presence of the axially coordinated pyridine.

The bridging protons in the proton-linked complex **6** were replaced by BF_2^+ groups and the single axial pyridine ligand was retained, according to both the spectral and analytical data for **7**, which was obtained by the treatment of **6** with $BF_3 \cdot Et_2O$. The BF_2 bridges in compound **7** caused the remaining ^{1}H NMR peaks to shift downfield relative to the starting complex **6**. This effect can be explained in terms of a ring current due to electron delocalization through the $Co(dioxBF_2)_2^+$ moiety.[35] Similar trends were observed in the ^{13}C NMR spectrum of this BF_2-bridged Co(III) complex. The IR spectrum of this complex exhibits increases in the frequencies of the stretching vibrations of the azomethine groups due to the strong electron-withdrawing effects of the BF_2^+ groups incorporated in the macrocycle.[36]

After reaction of the BF_2-bridged Ni(II) complex and bis(benzonitrile)palladium(II) chloride, the corresponding heterotrinuclear complex **5** was obtained. In this complex, a Pd(II) ion is coordinated through two aza nitrogens and two sulfur atoms of each of the 21-membered macrocyclic moieties, while the third metal ion [Ni(II)] is coordinated by the N atoms of each *vic*-dioxime group in the two $\mathbf{H_4L}$ molecules. Mass spectroscopy, elemental analysis, IR, magnetic measurements and semi-empirical quantum chemical calculations confirmed the structure of this compound (Fig. 3). The basicity of the N donors in the macrocycles is rather low because of their position near the hydroxyimino groups. Nevertheless, the absence of N–H stretching vibrations belonging to the trioxadiazadithia macrocycle indicates that the Pd(II) ions are trapped in the 21-membered macrocycles. The S–C vibrations of the BF_2^+-capped precursor compound **4** appear as split bands at 692 and 598 cm^{-1}, which are shifted in the IR spectrum of **5** to 675 and 579 cm^{-1}, suggesting the bonding of the palladium ion to the macrocyclic sulfur atoms.[26] The magnetic susceptibility results (*ca.* 2.55 BM) closely follow the spin-only formula calculated for a square-planar Ni(II) ion as a central metal and the two tetrahedrally coordinated Pd(II) ions.

The other heterotrinuclear complex (**8**), in which Co(III) is still coordinated to the *vic*-dioxime moiety, contains two other Ni(II) ions coordinated to aza nitrogen and sulfur atoms of the two mixed donor macrocyles. This complexation is confirmed by the mass spectral and elemental analysis data. The significant absorption at 3317 cm^{-1}, due to N–H stretching vibrations, disappears after formation of **8** with absorptions due to the Ni–S bonds appearing around 680–580 cm^{-1}. The magnetic susceptibility measurement, which gave a result of about 3.11 BM per Ni(II) ion, also provided sufficient data to characterize the structure. While $Co^{III}N_4$ has a diamagnetic structure with a *vic*-dioxime moiety, the trioxadithiadiaza macrocycle is distorted to form a tetrahedral complex,[14] a similar distortion was seen for $[Pd_2Ni(\mathbf{L}BF_2)_2]$ above.

The totally optimised geometries of trinuclear complexes **5** and **8** were determined using the ZINDO/1 method. The calculated total energies, heats of formation and bond lengths between the metal ions and ligating heteroatoms (Table 4) show that the distorted tetrahedral configuration around the outer Pd(II) or Ni(II) macrocycle ions is more stable than the square-planar structure, while surrounding the central metal ion [Ni(II) or Co(III)] coordination is square-planar or octahedral, respectively.[37] The polyether groups in the macrocycle exhibit a transoid–transoid configuration in the heterotrinuclear complexes. Binding distances for Ni–N and Pd–N in the macrocyclic cavity range between 1.90–2.00 Å, according to the quantum chemical calculations. $r_{Pd–Ni}$ in the $[Pd_2Ni(\mathbf{L}BF_2)_2]$ complex is 5.15 Å in the **A** configuration, longer than in the **B** configuration ($r_{Pd–Ni} = 4.40$ Å). For the $[Ni_2Co(\mathbf{L}BF_2)_2Cl(py)]$ complex, the **C** configuration is more stable than the **D** configuration, according to the calculated total energy. In the **C** configuration, $r_{Ni–Co}$ is longer (5.26 Å) than in the **D** configuration (4.60 Å).

The equatorial Ni–N or Co–N distances in the square-planar (**5**) or octahedral (**8**) parts of the trinuclear complexes are in agreement with the X-ray data for known *vic*-dioxime complexes.[17,31,38] The interatomic angles N–Ni–N (**5**: 96.405–84.515°) and N–Co–N (**8**: 94.285–85.537°) in the heterotrinuclear complexes are also comparable to the average values found in other vicinal dioxime complexes [(N–Ni–N: 100.0–80.0°) and (N–Co–N: 90.6–81.4°)].[39] The Ni–S, Ni–N and Pd–S, Pd–N bond distances (Pd–S: 2.339, Pd–N: 1.954, Ni–S: 2.320, Ni–N: 1.949 Å) found for the trinuclear complexes **5** and **8** are longer than the values given for similar compounds in the literature.[40] This can presumably be attributed to the tetrahedral distortion, which increases steric hinderance between the aromatic groups and the macrocyclic backbone, and the poorer donor abilities of nitrogen and sulfur atoms bound to aromatic groups compared to their aliphatic analogues.[41]

Experimental

General methods

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 on a Varian-Mercury 200 spectrometer (200 MHz). Routine IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer calibrated with polystyrene, with the samples in KBr pellets. Fast atom bombardment (FAB) mass spectra were measured on a Varian MAT 711 spectrometer (*m*-nitrobenzyl alcohol as matrix). Elemental analyses and metal contents of the compounds were determined with a Hewlett-Packard 185 CHN analyzer and a Unicam 929 AA spectrophotometer, respectively. Magnetic moments of the complexes were measured on a Newport Instruments type D-104. Melting points were determined on an Electrothermal apparatus and are uncorrected. All the quantum chemical calculations were carried out using the HYPERCHEM 6 software on an HP Pentium-III 550 computer.

3,6,9-Trioxa-1,11-dibromoundecane was prepared by a reported procedure.[42] Cobalt(II) chloride hexahydrate (Merck), nickel(II) chloride hexahydrate (Fluka) and bis(benzonitrile)palladium(II) chloride (Fluka) were used as received for the synthesis of the ligand and complexes. Boron trifluoride diethyl etherate (Aldrich) was distilled just before use. Commercially available pure grade solvents and other chemicals, dried and purified by conventional procedures,[43] were used.

Syntheses

2,3-Dibenzo-7,10,13-trioxa-4,16-dithia-1,19-diazanonadecane, 2. A solution of 2-aminothiophenolate, prepared by the reaction of 2-aminothiophenol (5.45 g, 43.6 mmol) with potassium (1.7 g, 43.6 mmol) in absolute ethanol (100 mL), was added dropwise to a solution of **1** (7.0 g, 21.8 mmol) in absolute ethanol (100 mL) under an argon atmosphere at room temperature over a period of 2.5 h. After stirring the reaction mixture at room temperature for 41 h, it was heated at reflux for an additional 7 h, before being cooled to room temperature. During this process, the reaction was monitored by TLC (petroleum ether–ethyl acetate 2 : 1). At the end of this period, the reaction mixture was filtered, washed with absolute ethanol and then concentrated under reduced pressure to 15 mL. The reaction mixture was solidified by the addition of 75 mL of water and then extracted with chloroform (3 × 40 mL). After drying over Na_2SO_4, the solution was passed through a silica gel column and the solvent evaporated under reduced pressure to 15 mL. After crystallization at −18 °C, the product was filtered off, washed with cold chloroform and dried under vacuum. A white crystalline product was obtained with a yield of 6.4 g (72%), mp 65–66 °C. Anal. calc. for $C_{20}H_{28}N_2O_3S_2$: C, 58.82; H, 6.86; N, 6.86%. Found: C, 58.60; H, 6.71; N, 7.06%. IR (KBr pellet, cm^{-1}): 3462–3355 (NH_2), 3090 (ArC–H), 2899–2878 (C–H), 1606 (NH_2). ^1H NMR ($CDCl_3$) δ: 7.25 (d, 2H, Ar-H), 7.06 (t, 2H, Ar-H), 6.71 (d, 2H, Ar-H), 6.52 (t, 2H, Ar-H), 4.24 (s, 4H, NH_2), 3.46 (m, 12H, $-OCH_2-$), 2.83 (t, 4H, $-SCH_2-$). ^{13}C NMR ($CDCl_3$) δ: 148.04 (C_1), 134.51 (C_2), 129.47 (C_4), 116.66 (C_3), 115.07 (C_5), 113.89 (C_6), 69.32–68.13 (C_{8-10}), 32.45 (C_7). MS (FAB) *m*/*z*: 408 (100) $[M]^+$ 284 (47), 160 (29).

5,6:20,21-Dibenzo-2,3-bis(hydroxyimino)-10,13,16-trioxa-7,19-dithia-1,4-diazacyclomonocosane, H_4L. A solution of cyanogendi-*N*-oxide, prepared by the reaction of (*E*,*E*)-dichloroglyoxime (1.57 g, 10 mmol) in dichloromethane (50 mL) with an aqueous solution of Na_2CO_3 (0.5 M, 50 mL) at −10 °C, was added to a solution of **2** (4.08 g, 10 mmol) in dichloromethane (150 mL) at −10 °C under an argon atmosphere over a period of 10 h. After addition was complete, the mixture was stirred at room temperature for an additional 16 h. The volume of the reaction mixture was reduced to 20 mL and it was cooled to −18 °C. The crystalline solid which precipitated was isolated by filtration, dried *in vacuo* and then recrystallized from ethanol to yield yellow crystals of the product. Yield: 3.1 g (63.1%), mp 227–228 °C (dec.). Anal. calc. for $C_{22}H_{28}N_4O_5S_2$: C, 53.65; H, 5.69; N, 11.38%. Found: C, 53.41; H, 5.87; N, 11.66%. IR (KBr pellets, cm^{-1}): 3319

(N–H), 3254 (O–H), 3083 (ArC–H), 2929–2875 (C–H), 1636 (C=N), 1604 (N–H), 941 (N–O). ^{1}H NMR (DMSO-d_6) δ: 11.18 (s, 2H, OH), 7.82 (s, 2H, NH), 7.34 (d, 2H, Ar-H), 7.22 (t, 2H, Ar-H), 7.36 (d, 2H, Ar-H), 6.88 (t, 2H, Ar-H), 3.62 (m, 12H, –OCH$_2$–), 3.08 (s, 4H, –SCH$_2$–). ^{13}C NMR (DMSO-d_6) δ: 143.76 (C$_1$), 142.21 (C$_0$), 135.72 (C$_2$), 129.63 (C$_4$), 120.16 (C$_5$), 117.46 (C$_3$), 116.61 (C$_6$), 69.15–68.48 (C$_{8-10}$), 33.79 (C$_7$). MS (FAB) *m*/*z*: 492 (89) [M]$^+$ 430.1 (18), 295.3 (28), 242.1 (11), 211 (17), 179.5 (14).

[Ni(H$_2$L)$_2$], 3. A solution of nickel(II) chloride hexahydrate (0.24 g, 1 mmol) in ethanol (15 mL) was added to a solution of **H$_4$L** (0.98 g, 2 mmol) in hot ethanol (100 mL). A distinct change in colour to dark red and a decrease in the pH of the solution (pH = 1.92) was immediately observed. An ethanolic solution of KOH (10^{-2} M) was then added to adjust the pH to about 4.25, at which point precipitation of the complex started. The reaction mixture was heated on a water bath for an additional 3 h at 60 °C. After precipitation was complete, the mixture was cooled to room temperature and filtered, the resulting solid washed with water, ethanol and diethyl ether and then dried *in vacuo*. Yield: 0.81 g (77.8%), mp 278–280 °C. Anal. calc. for $C_{44}H_{54}N_8O_{10}S_4Ni$: C, 50.73; H, 5.18; N, 10.76; Ni, 5.64%. Found: C, 50.86; H, 5.41; N, 10.53; Ni, 5.38%. IR (KBr pellets, cm^{-1}): 3375 (N–H), 3073 (ArC–H), 2911–2876 (C–H), 1720 (O–H···O), 1614 (C=N), 1602 (N–H), 936 (N–O). ^{1}H NMR (DMSO-d_6) δ: 16.55 (s, 2H, O–H···O), 7.87 (s, 4H, NH), 7.28 (m, 8H, Ar-H), 6.95 (m, 8H, Ar-H), 3.76 (m, 24H, –OCH$_2$–), 3.17 (m, 8H, –SCH$_2$–). ^{13}C NMR (DMSO-d_6) δ: 143.92, 143.29, 135.37, 129.91, 121.86, 117.93, 116.79, 70.21–68.90, 34.28. MS (FAB) *m*/*z*: 1040 (66) [M]$^+$ 893.2 (10), 807.1 (7), 633 (21), 580.3 (24), 552 (63), 497.2 (72).

[Ni(H$_2$LBF$_2$)$_2$], 4. A suspension of the precursor nickel complex **3** (0.70 g, 0.67 mmol) in 50 mL of freshly distilled acetonitrile was brought to reflux temperature under an argon atmosphere. Boron trifluoride diethyl etherate (0.33 mL, 1.35 mmol) was slowly added with stirring to the suspension of **3**. The resulting reaction mixture immediately turned red. After the colour change, the solution was refluxed for 1.5 h and completion of the reaction confirmed by TLC (*n*-butanol–acetic acid–water 4 : 1 : 5). The solvent was evaporated to dryness under reduced pressure and the residue dissolved in dry aceronitrile (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 −18 °C overnight. The crystalline red product was filtered off, washed with cold acetonitrile and diethyl ether and dried *in vacuo*. Yield: 0.40 g (52.3%), mp 140–142 °C. Anal. calc. for $C_{44}H_{52}N_8O_{10}S_4B_2F_4Ni$: C, 46.46; H, 4.57; N, 9.85; Ni, 5.16%. Found: C, 46.20; H, 4.73; N, 9.68; Ni, 5.34%. IR (KBr pellets, cm^{-1}): 3365 (N–H), 3065 (ArC–H), 2919–2890 (C–H), 1654 (C=N), 1601 (N–H), 947 (N–O). ^{1}H NMR (CDCl$_3$) δ: 8.14 (s, 4H, NH), 7.55 (d, 4H, Ar-H), 7.17 (t, 4H, Ar-H), 6.92 (d, 4H, Ar-H), 6.80 (t, 4H, Ar-H), 3.68 (m, 24H, –OCH$_2$–), 3.16 (m, 8H, –SCH$_2$–). ^{13}C NMR (CDCl$_3$) δ: 145.01, 144.49, 135.64, 130.48, 122.27, 118.27, 117.33, 70.58–68.51, 34.61. MS (FAB) *m*/*z*: 1134 (44) [M]$^+$, 1096 (13) [M − 2F]$^+$ 893.3 (19), 582.1 (6), 474.4 (19).

[Pd$_2$Ni(LBF$_2$)$_2$], 5. A solution of bis(benzonitrile)palladium(II) chloride (0.1 g, 0.26 mmol) in absolute ethanol (10 mL) was added to a solution of **4** (0.15 g, 0.13 mmol) in absolute ethanol (50 mL) under an argon atmosphere on a vacuum line. The reaction mixture was refluxed and stirred under an argon atmosphere for 20 h and the completion of the reaction was determined by thin-layer chromatography (*n*-butanol–acetic acid–water 4 : 1 : 5). After being cooled to room temperature, the reaction mixture was evaporated to 20 mL under reduced pressure and allowed to stand at −18 °C overnight. A brown solid product was obtained which was filtered off, washed with cold ethanol and diethyl ether and then dried *in vacuo*. Yield: 0.10 g (40.8%), mp > 300 °C. Anal. calc. for $C_{44}H_{48}N_8O_{10}S_4B_2F_4NiPd_2$: C, 39.25; H, 3.56; N, 8.32; Ni, 4.36; Pd, 15.82%. Found: C, 39.47; H, 3.84; N, 8.10; Ni, 4.11; Pd, 16.08%. IR (KBr pellets, cm^{-1}): 3084 (ArC–H), 2932–2874 (C–H), 1646 (C=N), 938 (N–O). MS (FAB) *m*/*z*: 1342.2 (58) [M]$^+$ 1284 (18), 1177.3 (11), 1050 (13), 895.2 (16), 824.1 (14), 559.1 (71).

[Co(H$_2$L)$_2$Cl(py)], 6. A solution of cobalt chloride hexahydrate (0.24 g, 1 mmol) in absolute ethanol (15 mL) was added to a solution of **H$_4$L** (0.98 g, 2 mmol) in absolute ethanol (100 mL) with stirring in a water bath at 60 °C. After addition of the Co(II) solution, the acidity of the solution dropped to pH = 2.43 and a distinct change in colour from pale yellow to brown was observed. While being heated at 60 °C, a solution of Lewis base [pyridine (0.079 g, 1 mmol) in ethanol (2 mL)] was added to the reaction mixture. This was allowed to cool to room temperature and a stream of air was bubbled through overnight. Then the solution was concentrated to 20 mL and cooled in a refrigerator at −18 °C overnight, whereupon a brown solid precipitated from the reaction mixture. The pale brown crystalline product was filtered off, washed with cold ethanol and diethyl ether and dried *in vacuo*. Yield: 0.75 g (64.9%), mp 250–251 °C. Anal. calc. for $C_{49}H_{59}N_9O_{10}S_4ClCo$: C, 50.89; H, 5.10; N, 10.90; Co, 5.09%. Found: C, 51.10; H, 5.35; N, 11.14; Co, 4.88%. IR (KBr pellets, cm^{-1}): 3350 (N–H), 3087 (ArC–H), 2978–2876 (C–H), 1700 (O–H···O), 1620 (C=N), 936 (N–O). ^{1}H NMR (DMSO-d_6) δ: 16.92 (s, 2H, O–H···O), 8.21 (d, 2H, py-H), 7.80 (s, 4H, NH), 7.54 (t, 1H, py-H), 7.34 (m, 8H, Ar-H), 7.11 (t, 2H, py-H), 6.90 (m, 8H, Ar-H), 3.71 (m, 24 H, –OCH$_2$–), 3.18 (m, 8H, –SCH$_2$–). ^{13}C NMR (DMSO-d_6) δ: 151.31, 143.88, 143.31, 140.19, 135.53, 129.30, 126.43, 122.02, 117.68, 116.89, 70.22–68.90, 34.41. MS (FAB) *m*/*z*: 1154.3 (25) [M]$^+$, 1075 (14) [M − py]$^+$ 1099 (10), 983 (19), 897.2 (8), 797 (5), 703.2 (25), 621 (33).

[Co(H$_2$LBF$_2$)$_2$Cl(py)], 7. A suspension of precursor cobalt(III) complex **6** (0.58 g, 0.5 mmol) in freshly distilled dry acetonitrile (50 mL) was heated to reflux temperature under an argon atmosphere. A solution of boron trifluoride diethyl etherate (0.25 mL, 2 mmol) in dry acetonitrile (2 mL) was slowly added with stirring. During this period, all the reactants dissolved and the solution immediately turned dark red. The reaction was continued for 2 h at reflux temperature and monitored by thin-layer chromatography (*n*-butanol–acetic acid–water 4 : 1 : 5). At the end of this period, the solvent was evaporated to dryness under reduced pressure, filtered, the residue dissolved in 10 mL of dry acetonitrile and then evaporated to dryness again. The residue was dissolved in dry acetonitrile (10 mL) and allowed to stand in a refrigerator at −18 °C overnight. The dark red crystalline product was filtered off, washed with cold acetonitrile and diethyl ether and dried *in vacuo*. Yield: 0.61 g (48.8%), mp 163–164 °C. Anal. calc. for $C_{49}H_{57}N_9O_{10}S_4B_2F_4ClCo$: C, 47.00; H, 4.55; N, 10.07; Co, 4.70%. Found: C, 47.23; H, 4.31; N, 9.88; Co, 4.96%. IR (KBr pellets, cm^{-1}): 3317 (N–H), 3088 (ArC–H), 2918–2882 (C–H), 1652 (C=N), 1604 (N–H), 940 (N–O). ^{1}H NMR (DMSO-d_6) δ: 8.27 (d, 2H, py-H), 7.85 (s, 4H, NH), 7.58 (t, 1H, py-H), 7.38 (m, 8H, Ar-H), 7.06 (t, 2H, py-H), 6.84 (m, 8H, Ar-H), 3.84 (m, 24H, –OCH$_2$–), 3.26 (m, 8H, –SCH$_2$–). ^{13}C NMR (DMSO-d_6) δ: 151.72, 144.86, 144.34, 140.57, 135.76, 129.73, 126.69, 122.24, 117.93, 117.19, 70.62–68.96, 34.34. MS (FAB) *m*/*z*: 1248 (41) [M]$^+$, 1134 (27) [M − py − Cl]$^+$ 1059.1 (19), 999.3 (15), 894.2 (32), 809 (22), 741.5 (34), 634.1 (36), 554.3 (57).

[Ni$_2$Co(LBF$_2$)$_2$Cl(py)], 8. A solution of anhydrous nickel(II) perchlorate (0.18 g, 0.66 mmol) in absolute ethanol (25 mL) was added to a solution of the precursor BF$_2$$^+$-

capped cobalt(III) complex **7** (0.58 g, 0.33 mmol) in absolute ethanol (100 mL) at reflux temperature with stirring under an argon atmosphere. The reflux was maintained for 35 h and the completion of the reaction was determined by thin-layer chromatography (chloroform–methanol–water 7:2:1). After being cooled to room temperature, the mixture was evaporated to 30 mL and then was cooled to $-18\,^{\circ}\mathrm{C}$ overnight. The dark brown product was filtered off, washed with water, cold ethanol and diethyl ether and dried *in vacuo*. Yield: 0.30 g (66.6%), mp $> 300\,^{\circ}\mathrm{C}$. Anal. calc. for $C_{49}H_{53}N_9O_{10}S_4B_2F_4ClCoNi_2$: C, 43.09; H, 3.88; N, 9.23; Co, 4.31; Pd, 8.60%. Found: C, 42.79; H, 3.51; N, 9.40; Co, 4.52; Pd, 8.37%. IR (KBr pellets, $\mathrm{cm^{-1}}$): 3090 (ArC–H), 2915–2860 (C–H), 1637 (C=N), 938 (N–O). MS (FAB) *m/z*: 1360.2 (38) $[M]^+$, 1246 (26) $[M - py - Cl]^+$ 1131 (17), 1071.2 (14), 1048.4 (57), 1035 (14), 899.5 (29), 703.2 (12).

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