Letter

First example of a *vic*-dioxime and its homo- and heteropentanuclear complexes containing a macrobicyclic moiety

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The novel *N*,*N*′-substituted diaminoglyoxime (H_2L) containing a diazadioxadithiacyclo macrobicycle has been synthesized from an aromatic primary amine containing a cryptand unit and (*E*,*E*)-dichloroglyoxime. The homopentanuclear nickel(II) and heteropentanuclear complexes of dioxime were obtained.

Due to the presence of mildly acidic hydroxy groups and slightly basic azomethine groups, *vic*-dioximes are amphoteric ligands that form corrin-type square-planar, square-pyramidal and octahedral complexes with transition metal ions such as nickel(II), copper(II), palladium(II), cobalt(II) and cobalt(III) as the central atoms.[1] The exceptional stability and unique electronic properties of these complexes can be attributed to their structure which is stabilized by intramolecular hydrogen bonding.[2] The complexes prepared from (*E*,*E*)-dioximes have been extensively used for various purposes, including model compounds to mimic biofunctions such as reduction of vitamin B_{12} and as analytical reagents for trace element analysis.[3] They have also been examined as compounds with columnar stacking, which is thought to be the reason for their semiconducting properties.[4] Recently, the two hydrogen bridges have been substituted with metal complexes to obtain polynuclear compounds in order to investigate the magnetic interactions.[5]

Cryptand, which contain two macrocycles, show an extraordinary selectivity for metal ion complexation in aqueous and organic solutions, more so than do macrocyclic polyethers. The formation of cryptates with alkali metal or alkaline earth metals involves the inclusion of a cation into the molecular cavity of a cryptand. This cryptate effect, which leads to a high complexation stability, is greater than the macrocyclic effect.[6] The optimal cryptates for alkali or alkaline earth cations have stabilities several orders of magnitude higher than those of either the natural ionophores or synthetic macrocyclic ligands. Suitable structural modifications allow control over the M^{2+}/M^{+} selectivity, from a preference for alkaline earth metal cations to a preference for alkali metal cations.[6,7] On the other hand, owing to their architectural structure and functional plasticity, macropolycyclic systems are attractive for designing both biomimetic and abiotic receptor molecules for inorganic and organic substrates.[8]

We report here the synthesis and structural properties of an unusual vicinal dioxime containing a macrobicyclic unit, afforded in high yield by the 1 : 2 reaction of cyanogen-di-*N*-oxide[9] and an aromatic primary amine containing a diazadithiadioxa mixed-donor macrobicyclic moiety (Scheme 1). Then, the mono Ni(II), penta-nuclear Ni(II) and heteropentanuclear complexes of the dioxime have been isolated (Scheme 2).

The synthesis of the macrobicyclic compound **3** was performed by starting from the 14-membered diazadithia macrocycle[10] **1** and **2** using Cs^+ cations as promotors.[11] After crystallization, the desired product was isolated from a mixture of chloroform–acetone (1 : 1) and characterized. The ^{1}H NMR spectrum of **3** showed new signals due to methylene and aromatic protons at δ 4.22 and 7.90, respectively, which confirms the formation of **3**. The disappearance of the N–H stretching vibrations seen in the IR spectrum of the starting material **1** also suggests the formation of **3**. Compound **3** displays the expected molecular ion peak in its FAB mass spectrum (*m*/*z* 537). Proton-decoupled ^{13}C NMR of this compound clearly suggests that macrobicyclic formation has occurred.

Reduction of the nitro-substituted macrobicycle **3** using hot 10% palladium–activated charcoal and hydrazine hydrate (100%) in dioxane, as previously utilized,[12] gave the amine-substituted macrobicycle **4**. In the ^{1}H NMR spectrum of **4**, there is a broad peak at δ 4.60 due to the primary aromatic amine protons, which confirms the structure. The ^{13}C NMR spectrum for **4** is also consistent with the proposed formulation. In the IR spectrum of **4**, N–H stretching and bending vibrations are observed at *ca.* 3448 and 1617 cm^{-1}, respectively. The mass spectrum of **4**, which shows a molecular ion peak at *m*/*z* 507, confirms the formula of this compound.

The first example of a *vic*-dioxime containing a macrobicyclic moiety was synthesized in good yield according to the previously reported procedure[13] involving the reaction of 2 equiv. of **4** with 1 equiv. of cyanogen-di-*N*-oxide[9] in dichloromethane (Scheme 1). In the ^{1}H NMR spectrum of H_2L, the deuterium exchangeable protons of the N–OH and NH groups appear as two singlets at δ 10.38 and 7.93, respectively. This result indicates that the structure of H_2L has the *S-trans* form.[14] The resonances due to the azomethine carbon atoms in the ^{13}C NMR spectrum of this compound are found at lower fields (δ 148.24) compared to other *vic*-dioximes reported in the literature.[15] The equivalent carbon resonances of the hydroxyimino groups also confirm the *S-trans* form of the *vic*-dioxime.[16] The disappearance of the NH_2 stretching vibrations, along with the appearance of new absorptions at 3242 [ν(O–H)] and 1044 [ν(N–O)] cm^{-1}, are in agreement with the proposed structure. Analysis by mass spectrometry (FAB), shows a molecular ion peak at 1098.4, confirming that a vicinal dioxime has been formed, consistent only with the formation of H_2L.

The reaction of H_2L with nickel(II) chloride hexahydrate (Scheme 1) gave the 1 : 2 (metal : ligand) complex **5** in 81.9% yield, and its composition was defined by elemental analysis, ^{1}H NMR, IR and MS spectral data. In the ^{1}H NMR spectra however, only slight differences between those of H_2L and **5** were observed. For **5**, the presence of intramolecular O–H$\cdots$O bands at around δ 16.92 identify the complexation product. In the IR spectrum, the C=N stretching vibration (1637 cm^{-1}) in H_2L is shifted to a lower wavenumber compared with that of **5** (1611 cm^{-1}), and ν(O–H$\cdots$O) of **5**

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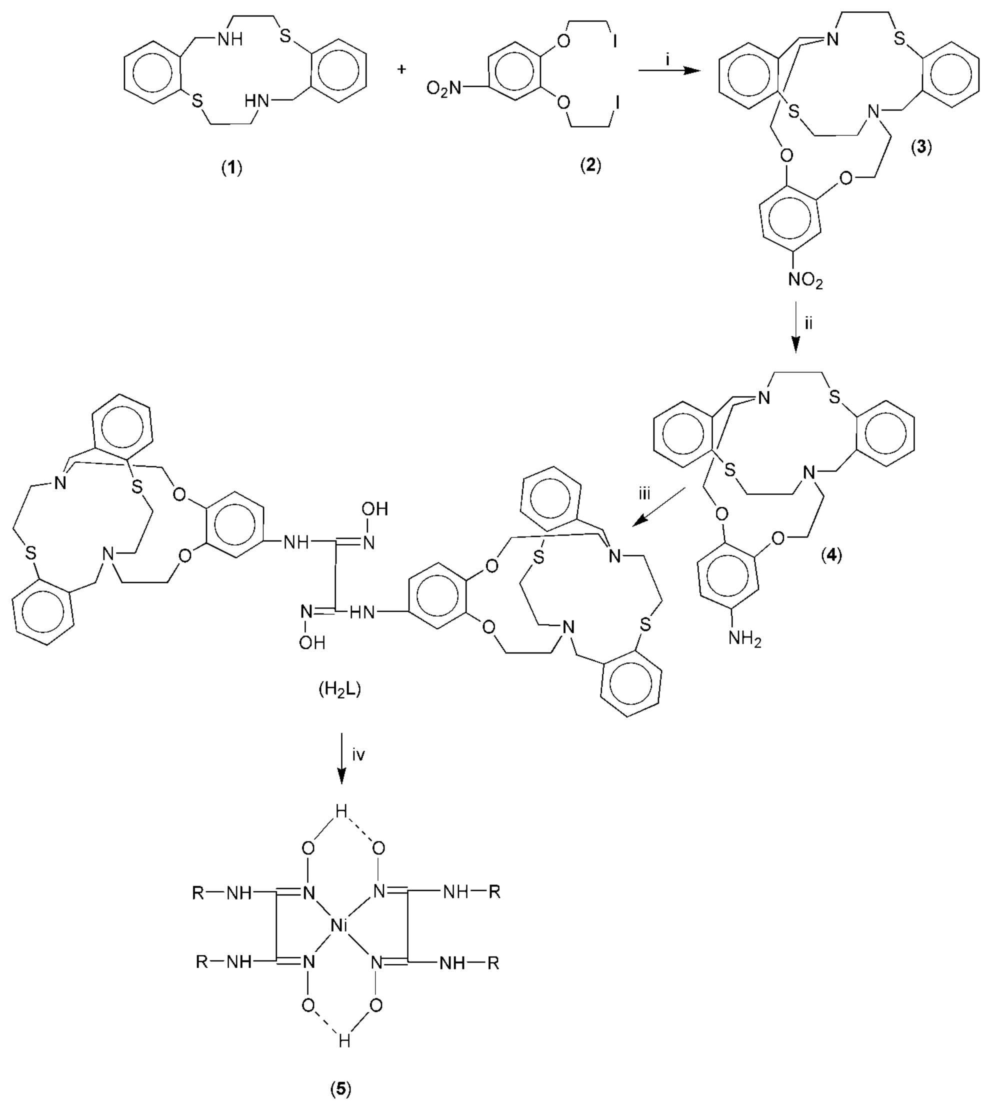


Scheme 1 *Reagents and conditions*: (i) Cs_2O_3 in dry acetonitrile under argon at 60 °C; (ii) NH_2–$NH_2 \cdot H_2O$, 10% Pd/C in dry dioxane at 60 °C; (iii) cyanogen di-*N*-oxide in CH_2Cl_2 at −15 °C; (iv) $NiCl_2 \cdot 6H_2O$ in EtOH at 65 °C.

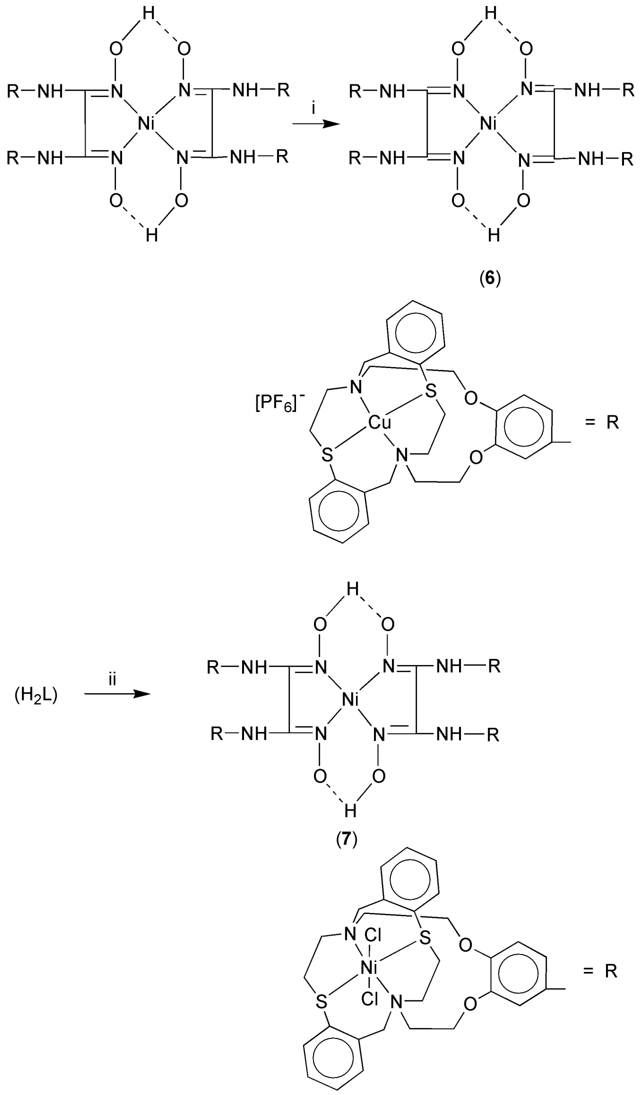
appears at 1723 cm^{-1}, whereas H_2L shows an absorption band at 3242 cm^{-1} for the O–H groups. These results suggest coordination of the nitrogen atoms of the azomethine groups. The fast atom bombardment mass spectrum of **5** exhibits a molecular ion peak at *m*/*z* 2252.2, which supports the structure.

Yellow–orange crystals of **6** were prepared in 53.3% yield by the reaction of the mononuclear Ni(II) complex **5** with $[Cu(CH_3CN)_4]PF_6$ in refluxing ethanol–DMF. In contrast to the literature,[10] the copper(I) complex of the dithiadiaza macrocycle was successfully derived using rigorously anhydrous and inert reaction conditions. ^1H NMR and IR spectral and elemental analysis data confirm the formulation of the heteropentanuclear complex. In the IR spectrum of this compound many of the bands arising from characteristic groups such as N–H, O–H···O, C=N are very similar to those of the precursor Ni(II) complex **5**, as expected. This complex contains Cu(I) cations in the macrobicyclic cavities; the resonances at 849 and 557 cm^{-1}, assigned to $[PF_6]^-$, support a structure in which the hexafluorophosphate ions are not coordinated to the copper(I) atoms.[17] The ^1H NMR spectra of **5** and **6** are largely similar, but the expected shifts due to complexation with Cu(I) ions belonging to macrobicyclic moieties such as CH_2–S and CH_2–N are significant.

The synthesis of the homopentanuclear complex of *vic*-dioxime was accomplished in one step (Scheme 2). The desired complex **7** which has a metal : ligand ratio of 5 : 2 according to its elemental analysis, can be obtained in good yield (58.5%). The FAB mass spectrum of this complex exhibited an intense peak at *m*/*z* 2764.3 $[M]^+$, which is in accord with the proposed structure. Compound **7** shows significant IR absorptions at 1715 and 841 cm^{-1}, which may be assigned to the stretching and out-of-plane deformation modes of the hydrogen-bonded O–H···O groups, respectively.[18] The disappearance of the O–H stretching vibrations and the shifts of the C=N bands to lower frequencies in the IR spectrum of **7** can be attributed to *N*,*N*′-chelation.[19] This homopentanuclear Ni(II) complex is paramagnetic. The magnetic susceptibility (μ_{tot} = 12.46 BM) is very similar to the value obtained from the spin-only formula calculated for four Ni(II) ions located in octahedral coordination environments, consisting of the N_2S_2 donor atoms of the macrobicylic cavities in an approximately square-planar array and two chloride ions in axial sites, while one of the Ni(II) forms a diamagnetic structure with the dioxime moieties. When the magnetic moment of this complex is calculated per Ni the result is about 3.12 BM, comparable with values given for high-spin octahedral Ni(II) complexes.[20] This complex is a non-electrolyte, consistent with the proposed formulation. This observation can be attributed to the fact that the chloro groups are in the coordination sphere.

Experimental

Reagent grade chemicals were used as received. THF was distilled from sodium benzophenone ketyl under oxygen-free nitrogen, prior to use. Other solvents were purified according



Scheme 2 *Reagents and conditions*: (i) $[Cu(CH_3CN)_4]PF_6$ in dry DMF–EtOH under argon, reflux; (ii) $NiCl_2 \cdot 6H_2O$ in EtOH at 60 °C; NEt_3 in EtOH at reflux.

to standard methods[21] before use. Silica gel (70–230 mesh) was used for chromatographic separations. The structures of novel compounds were identified by using elemental analysis, magnetic susceptibility and conductance measurements, ^1H, ^{13}C NMR, IR and MS spectral data.

Syntheses

2. 4-Nitro-1,2-bis(2-chloroethoxy)benzene (12.3 g, 43 mmol) was dissolved in dry acetone (250 mL) containing anhydrous NaI (39.5 g, 260 mmol) under an argon atmosphere and refluxed for 27 h. After a while, the solution turned cloudy and then the solid product precipitated. At the end of this period, the reaction mixture was evaporated to dryness and treated with ethyl acetate (100 mL). The reaction mixture was filtered and washed with ethyl acetate and then dried over Na_2SO_4 overnight. After removal of the drying agent, the filtrate was evaporated to 15 mL, then the residue was placed in a refrigerator. The pale yellow crystals were separated by filtration and dried *in vacuo* at room temperature. Yield: 14.3 g, 70.2%, mp 81–82 °C. Anal. calc. for $C_{10}H_{11}NI_2O_4$: C, 25.92; H, 2.37; N, 3.02%. Found: C, 25.80; H, 2.21; N, 3.23%. IR (KBr pellets, cm^{-1}): 3085 (Ar–H), 2993 (C–H), 1346 (NO_2), 1261–1227 (Ar–O–C), 660 (C–I). ^1H NMR ($CDCl_3$) δ: 7.84 (d, 1H, ArH), 7.71 (s, 1H, ArH), 6.83 (d, 1H, ArH), 4.32 (t, 4H, CH_2O), 3.41 (t, 4H, CH_2I). MS (FAB) *m*/*z*: 461 $[M]^+$.

3. A 300 mL round-bottom flask containing dry acetonitrile (100 mL) and fitted with a condenser was evacuated, refilled three times with argon and connected to a vacuum line. Under argon, the flask was charged with 6,7,8,9,15,16,17,18-octahydrodibenzo[*f*,*m*][1,4,8,11]dithiadiazacyclotetradecine[10] (**1**; 1.65 g, 5 mmol) and finely ground anhydrous Cs_2CO_3 (3.26 g, 10 mmol) and the mixture was stirred at room temperature. A solution of **2** (2.3 g, 5 mmol) in dry acetonitrile (50 mL) was added to this mixture and the reaction mixture was heated and stirred at 60 °C for 92 h. The reaction was monitored by thin layer chromatography [chloroform–acetone–petroleum ether (4 : 6 : 1)]. At the end of this period, the mixture was cooled to room temperature and the product filtered off, washed with water and then dried *in vacuo*. The solid product was re-crystallized from chloroform–acetone. Yield: 1.67 g, 62.3%, mp 220 °C. Anal. calc. for $C_{28}H_{31}N_3O_4S_2$: C, 62.56; H, 5.77; N, 7.82%. Found: C, 62.41; H, 5.96; N, 7.60%. IR (KBr pellets, cm^{-1}): 3087 (Ar–H), 3056 (Ar–H), 2948–2787 (C–H), 1337 (NO_2), 1278–1218 (Ar–O–C). ^1H NMR ($CDCl_3$) δ: 7.90 (d, 1H, ArH), 7.67 (s, 1H, ArH), 7.24–6.93 (m, 8H, ArH), 6.82 (d, 1H, ArH), 4.22 (t, 4H, CH_2O), 3.68 (s, 4H, $ArCH_2$), 3.37 (m, 8H, NCH_2), 2.74 (t, 4H, SCH_2). ^{13}C NMR ($CDCl_3$) δ: 148.04, 140.385, 134.72, 134.36, 132.03, 131.85, 127.74, 126.97, 126.78, 117.53, 110.66, 107.31, 66.22, 59.77, 52.88, 46.45, 33.32. MS (FAB) *m*/*z*: 537 $[M]^+$.

4. Compound **3** (1.5 g, 2.8 mmol) was dissolved in dry dioxane (120 mL) by heating at 60 °C. Palladium (10%)/activated carbon (1.2 g) was added to the solution at the same temperature and allowed to stand at the same temperature for

10 min; 5 ml of hydrazine hydrate (100%) was then added dropwise. The reaction mixture was heated and stirred for 8 h at 60 °C and then filtered and washed with dioxane (25 mL). The extent of the reaction was monitored by using TLC [petroleum ether–acetone (1 : 2)]. The pale yellow solution was concentrated on an evaporator to 20 mL and the solid formed was filtered off, washed with diethyl ether and then dried *in vacuo*. Yield: 1.18 g, 83.6%, mp 195–196 °C. Anal. calc. for $C_{28}H_{33}N_3O_2S_2$: C, 66.27; H, 6.50; N, 8.28%. Found: C, 66.40; H, 6.44; N, 8.42%. IR (KBr pellets, cm^{-1}): 3448–3365 (NH_2), 3050 (Ar–H), 3024 (Ar–H), 2920–2787 (C–H), 1617 (NH_2), 1289–1219 (Ar–O–C). ^1H NMR (DMSO-d_6) δ: 7.22–6.96 (m, 8H, ArH), 6.67 (d, 1H, ArH), 6.27 (s, 1H, ArH), 6.10 (d, 1H, ArH), 4.60 (s, 2H, NH_2), 4.18 (t, 4H, $ArOCH_2$), 3.62 (s, 4H, $ArCH_2$), 3.46 (m, 8H, NCH_2), 2.96 (t, 4H, SCH_2). ^{13}C NMR (DMSO-d_6) δ: 145.31, 142.42, 138.25, 134.04, 132.10, 128.13, 127.41, 126.15, 125.52, 114.90, 106.97, 100.10, 65.78, 58.20, 52.26, 45.21, 33.76. MS (FAB) *m*/*z*: 507 $[M]^+$.

H_2L. A solution of cyanogen di-*N*-oxide in dichloromethane (20 mL), which was prepared from (*E*,*E*)-dichloroglyoxime (0.157 g, 1 mmol) and an aqueous solution of Na_2CO_3 (10 mL, 0.5 M), was added to a cold solution (−15 °C) of **4** (1.01 g, 2 mmol) in dichloromethane (50 mL). The reaction was continued for 10 h at this temperature and the yellow product formed separated by filtration, washed with cold dichloromethane and diethyl ether and then dried *in vacuo*. The filtrate was removed *in vacuo* and the oily product was purified by column chromatography [silica gel (70–230), dioxane]. Yield: 0.83 g, 75.6%, mp 212 °C (dec.). Anal. calc. for $C_{58}H_{66}N_8O_6S_4$: C, 63.38; H, 6.01; N, 10.20%. Found: C, 63.53; H, 5.88; N, 9.97%. IR (KBr pellets, cm^{-1}): 3378 (N–H), 3242 (O–H), 3053 (Ar–H), 2917–2792 (C–H), 1637 (C=N), 1607 (N–H), 1277–1220 (Ar–O–C), 1044 (N–O). ^1H NMR (DMSO-d_6) δ: 10.38 (s, 2H, OH), 7.93 (s, 2H, NH), 7.31–6.98 (m, 16H, ArH), 6.76 (d, 2H, ArH), 6.62 (s, 2H, ArH), 6.33 (d, 2H, ArH), 4.27 (m, 8H, $ArOCH_2$), 3.77 (m, 8H, $ArCH_2$), 3.55 (m, 16H, NCH_2), 3.09 (t, 8H, SCH_2). ^{13}C NMR (DMSO-d_6) δ: 146.41, 143.65, 142.53, 138.49, 135.16, 132.31, 128.34, 127.66, 126.27, 125.71, 115.20, 107.35, 100.32, 67.58, 58.38, 52.60, 56.16, 33.87. MS (FAB) *m*/*z*: 1098.4 $[M]^+$.

5. A solution of nickel(II) chloride hexahydrate (0.077 g, 0.32 mmol) in ethanol (10 mL) was added to a solution of H_2L (0.71 g, 0.65 mmol) in ethanol (100 mL) at 60 °C, a distinct change in colour from colourless to red and a decrease in the pH of the solution was observed. While heating the mixture to 65 °C an ethanolic solution of KOH (0.1 M) was added and an orange precipitate of **5** formed. After heating the mixture for 4 h in a water bath, the precipitate was filtered off, washed with water, ethanol and diethyl ether and then dried *in vacuo*. Yield: 0.59 g, 81.9%, mp 276 °C (dec.). Anal. calc. for $C_{116}H_{130}N_{16}O_{12}S_8Ni$: C, 61.79; H, 5.77; N, 9.94; Ni, 2.60%. Found: C, 61.96; H, 5.61; N, 10.13; Ni, 2.44%. IR (KBr pellets, cm^{-1}): 3420 (N–H), 3048 (Ar–H), 2925–2805 (C–H), 1723 (O–H···O), 1611 (C=N), 1601 (N–H), 1284–1229 (Ar–O–CH_2), 1022 (N–O). ^1H NMR (DMSO-d_6) δ: 16.92 (s, 2H, O–H···O), 8.11 (s, 4H, NH), 7.43–7.05 (m, 32H, ArH), 6.83 (d, 4H, ArH), 6.70 (s, 4H, ArH), 6.48 (d, 4H, ArH), 4.24 (m, 16H, $ArOCH_2$), 3.86 (m, 16H, $ArCH_2$), 3.58 (m, 32H, NCH_2), 2.92 (m, 16H, SCH_2). MS (FAB) *m*/*z*: 2252.2 $[M]^+$.

6. This compound was synthesized under an argon atmosphere in dry and degassed solvents in a vacuum line. A solution of compound **5** (0.225 g, 0.1 mmol) in a mixture of dry ethanol and dry DMF [80 mL (10 : 1)] was refluxed and stirred for 2 h, then the hot solution was filtered under inert conditions. An excess of freshly prepared $[Cu(CH_3CN)_4]PF_6$[22] (0.125 g, 0.05 mmol) in dry acetonitrile (25 mL) was added slowly to the stirred hot solution of **5** and the mixture was refluxed and stirred for 4 h. The end of the reaction was determined by thin layer chromatography [*n*-butanol–acetic acid–water (4 : 1 : 5)]. After cooling to room temperature the reaction mixture was concentrated under reduced pressure to 8 mL. The crude product was allowed to stand at −18 °C overnight whereupon the compound crystallized from the solution. The yellow–orange crystallized product was collected by filtration, washed with cold ethanol and acetonitrile and then dried *in vacuo*. Yield: 0.16 g, 53.3%, mp > 300 °C. Anal. calc. for $C_{116}H_{130}N_{16}O_{12}S_8F_{24}P_4NiCu_4$: C, 45.10; H, 4.21; N, 7.25; Ni, 1.90; Cu, 8.22%. Found: C, 44.83; H, 4.02; N, 7.42; Ni, 2.15, Cu, 8.02%. IR (KBr pellets, cm^{-1}): 3411 (N–H), 3044 (Ar–H), 2933–2811 (C–H), 1710 (O–H···O), 1622 (C=N), 1598 (A–H), 1276–1220 (Ar–O–CH_2), 1009 (N–O), 849, 557 $(PF_6)^-$. ^1H NMR (DMSO-d_6) δ: 17.00 (s, 2H, O–H···O), 8.17 (br, 4H, NH), 7.51–7.10 (m, 32H, ArH), 6.88–6.67 (m, 8H, ArH), 6.42 (m, 4H, ArH), 4.36 (m, 16H, $ArOCH_2$), 3.80 (m, 16H, $ArCH_2$), 3.66 (m, 32H, NCH_2), 2.88 (m, 16H, SCH_2).

7. An excess solution of nickel(II) chloride hexahydrate (0.20 g, 0.85 mmol) in dry ethanol (30 mL) was added in small portions to a stirred solution of H_2L (0.33 g, 0.3 mmol) in dry ethanol (80 mL) at 60 °C over a period of 10 min; a distinct change in colour from colourless to blue and a decrease in the pH of the solution was observed. While heating the mixture to reflux temperature, a stoichiometric amount of triethylamine (0.03 g, 0.3 mmol) in ethanol (1 mL) was added and the resulting mixture was refluxed with stirring for 6 h. After cooling to room temperature, the solution was concentrated to 20 mL and diethyl ether (4 mL) was added. A dark-blue crystalline product of the homopentanuclear complex deposited from the solution overnight which was filtered off, washed with cold ethanol and diethyl ether and then dried *in vacuo*. Yield: 0.24 g, 58.5%, mp > 300 °C. Anal. calc. for $C_{116}H_{130}N_{16}O_{12}S_8Cl_8Ni_5$: C, 50.23; H, 4.69; N, 8.08; Ni, 10.59%. Found: 50.39; H, 4.41; N, 8.43; Ni, 10.38%. IR (KBr pellets, cm^{-1}): 3403 (N–H), 3045 (Ar–H), 2912–2800 (C–H), 1715 (O–H···O), 1618 (C=N), 1603 (N–H), 1292–1221 (Ar–O–CH_2), 996 (N–O), 841 (O–H···O. MS (FAB) *m*/*z*: 2764.3 $[M]^+$.

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