The synthesis and characterization of a new (*E*,*E*)-dioxime and its homo- and heterotrinuclear complexes containing a hexaoxadiaza macrobicycle moiety

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The novel quinoxaline substituted (*E*,*E*)-dioxime (H_2L) containing a hexaoxadiaza macrobicycle [2.2.2$_B$] has been synthesized from the reaction of 4,7,13,16,21,24-hexaoxa-5,6-(2′,3′-diaminobenzo)-1,10-diazabicyclo[8.8.8]hexacosane (**4**) prepared from 4,7,13,16,21,24-hexaoxa-5,6-(2′,3′-dinitrobenzo)-1,10-diazabicyclo[8.8.8]hexacosane (**3**) and cyanogendi-*N*-oxide (**5**). Only the mononuclear nickel(II) complex with a metal:ligand ratio of 1:2 was prepared. This hydrogen-bridged complex was converted into its BF_2^+ capped analogue by reaction with $BF_3{\cdot}Et_2O$. The reaction of the BF_2^+ bridged complex with KPF_6 gave a heterotrinuclear complex. Structures for the dioxime and its complexes are proposed in accordance with elemental analysis, ^{1}H and ^{13}C NMR, IR and MS spectral data.

Coordination compounds of *vic*-dioximes have been widely investigated as analytical reagents,[1] as models for biological systems such as vitamin B_{12},[2] as compounds having columnar stacking thought to be reason for their semiconducting properties.[3] In recent years, such attention has been given to polynuclear metal complexes because of their role in certain biological systems and their potential to act as multielectron redox catalysts.[4] Some novel studies have been exploring a group of macrocyclic dioxime complexes of Co(III) in which the bridging protons of the bis-dioxime ligands have been replaced by BF_2^+ groups, an alteration that firms up the macrocycle structure while removing acidic protons from the vicinity of the O_2 binding site.[5]

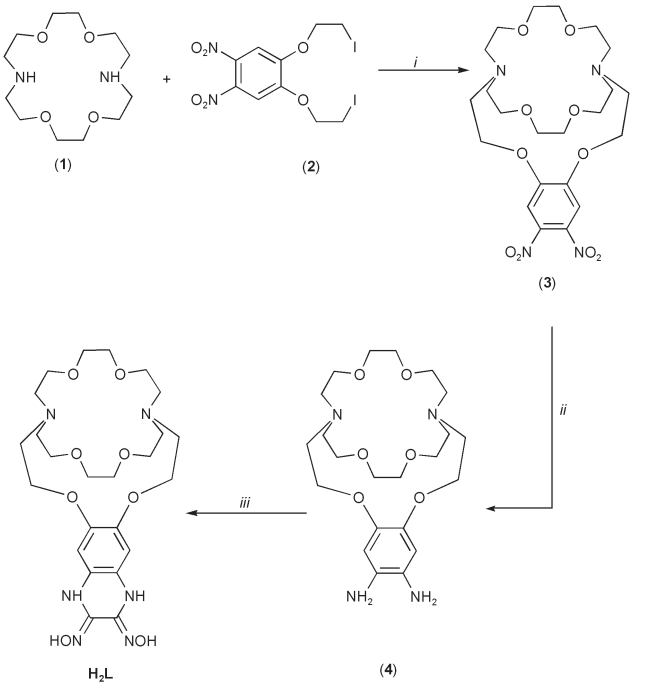
Cryptands are polymacrocyclic ligand system of three-dimentional structure able to encapsulate a metal ion. The remarkable group of these compounds were introduced by Lehn and his coworkers in 1969.[6] Owing to their architectural and functional plasticity, macrobicyclic compounds are especially attractive for designing both biomimetic and abiotic receptor molecules for inorganic and organic substrates.[7] Some macrobicyclic ligands display very high selectivity for alkali or alkaline earth metal ions. For instance, the [$K^+ \subset$ 2.2.2] type cryptate is more stable by a factor of 10^5 than the K^+ complex of its macrocyclic counterpart which is due to cryptate effect.[8]

vic-Dioximes containing macrobicyle moieties and their alkaline earth metal and transition metal complexes have been recently reported.[9] The interesting aspect of these complexes is that they have the features of transition metal, alkaline earth metal and macrobicyclic chemistry all in the same molecule.

We report here the synthesis and characterization of a (E, E)-dioxime containing a hexaoxadiazamacrobicyclic unit and Ni(II) complex as well as the properties of the BF_2 bridged complex. Then heterotrinuclear complex was prepared by the reaction of KPF_6 with BF_2^+-capped complex having the characteristic of mixed-donor cavities.

Results and discussion

The synthesis was initiated (Scheme 1) by condensation of 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane[10] with 1,2-dinitro-4,5-bis(2-iodoethoxy)benzene[11] in the presence of K_2CO_3 and NaI in refluxing acetonitrile; slow macrobicyclization gave the macrobicycle **3** (57% yield) as a crystalline product. The ^{1}H NMR spectrum (DMSO-d_6) shows a singlet at δ = 7.97 ppm, indicating the presence of Ar–H protons with respect to the condensation reaction of compounds **1** and **2**. Three different types of protons are clearly seen. The triplet at δ = 4.29 ppm corresponds to neighbouring Ar–O–CH_2 groups. The multiplets at δ = 3.85 and 3.15 ppm are due to the O–CH_2 and N–CH_2 protons, respectively. The ^{13}C NMR spectrum of **3** exhibits signals at δ = 147.12, 108.51 and



Scheme 1 Reagents and conditions: (i) NaI, K_2CO_3 in dry acetonitrile under nitrogen at 30 °C; (ii) NH_2–$NH{\cdot}H_2O$, 10% Pd/C in *n*-butanol at reflux; (iii) cyanogen di-*N*-oxide under nitrogen at −15 °C.

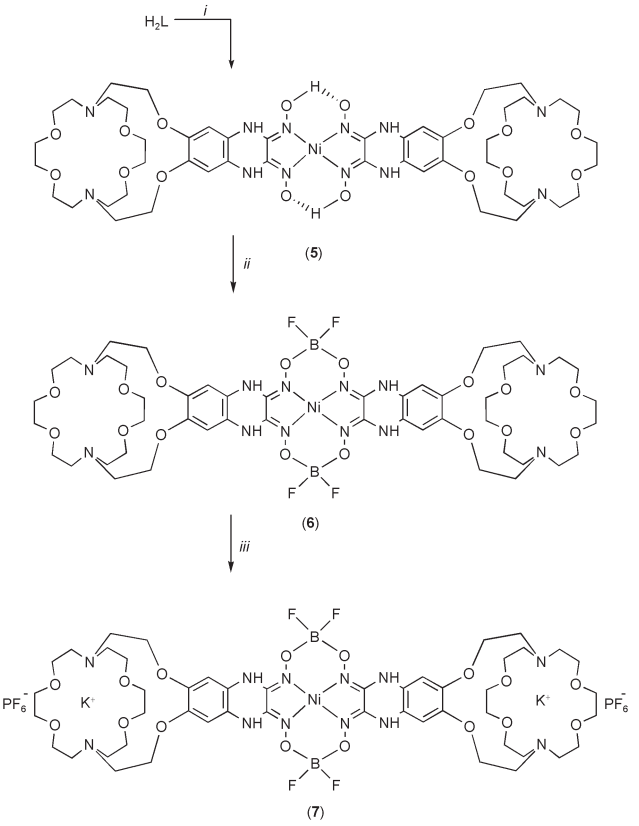
138.50 ppm due to aromatic carbon resonances, which shows that the dinitrosubstituted aromatic linkage is present. The IR spectrum of **3** shows no characteristic absorption assignable to either the N–H or C–I of the precursor compounds (**1** and **2**). In the mass spectrum the M^+ peak was found at 514.1, which is in agreement with the calculated value.

Reduction of the dinitro-substituted macrobicycle **3** using 10% palladium-activated charcoal and hydrazine hydrate (100%) in hot *n*-butanol, as previously utilized,[12] gave the diamine-substituted macrobicycle **4** in 56% yield. The amine (**4**), apparently very sensitive to both light and air and colourless, darkens as expected when it is left to stand at room temperature. In the ^{1}H NMR spectrum of **4**, there is a broad signal at $\delta = 4.25$ ppm due to the aromatic amine protons, which confirms the structure. The proton chemical shift of **4** shows an upfield shift of the aromatic protons at $\delta = 6.48$ ppm with respect to the formation of aromatic primary amine instead of nitro groups. The appearance of stretching and bending vibrations assigned to N–H at 3273 and 1607 cm^{-1} also confirms the formation of **4**. The FAB mass spectrum of **4** shows an expected molecular ion peak at $m/z = 454.2$ $[M]^+$, which supports the proposed formulation.

The aromatic 1,2-diamine compound (**4**) was converted into the corresponding dioxime (H_2L) by the reaction with cyanogendi-*N*-oxide at −15 °C under nitrogen atmosphere; this dioxime derivative was isolated in 48% yield and characterized. In the ^{1}H NMR spectrum of H_2L, the deuterium-exchangeable protons of the OH and NH groups appear as two different signals at $\delta = 9.36$ and 8.92 ppm, respectively. In the proton-decoupled ^{13}C NMR spectrum of H_2L, the carbon resonance of the azomethine group is found at lower field ($\delta = 152.82$ ppm) and this unique signal for the oxime groups confirms the *E*,*E* form of the *vic*-dioxime.[13] In the IR spectrum of H_2L, the stretching vibrations at 3403, 3247 and 1621 cm^{-1} are assigned to the oxime O–H, N–H and C=N groups, respectively.[14] In addition to the spectroscopic data, the elemental analysis and FAB mass spectrum of this ligand at $m/z = 539$ $[M + 1]^+$ were entirely consistent with the proposed structure.

Complexation of the *vic*-dioxime with Ni(II) was carried out by the addition of a solution of $NiCl_2{\cdot}6H_2O$, an equivalent amount of triethylamine in ethanol and a hot solution of H_2L in ethanol (Scheme 2) to afford the 1:2 (metal:ligand) complex **5** in 86.1% yield. Its composition was defined by elemental analysis, ^{1}H NMR, IR and MS spectral data. The FAB mass spectrum of **5** exhibits a molecular ion peak at $m/z = 1133$ $[M + 1]^+$, which supports the structure. This complex had an IR spectrum very similar to that of the ligand, except for a shift of the O–H vibrations due to the formation of O–H···O bonds (1718 cm^{-1} bending vibrations). In the ^{1}H NMR spectrum of **5**, the signal arising from the =N–OH protons disappeared after complexation and a new resonance at lower field ($\delta = 16.52$ ppm) could be assigned to formation of the hydrogen bridge. The IR spectrum of **5** shows a signal at 1611 cm^{-1} for the C=N bonds, which indicates that upon complexation these double bonds have less double-bond character than the oxime moieties in H_2L.

The template synthesis of **6** was performed with considerable yield (58%) by adding borontrifluoride etherate complex to a refluxing dry acetonitrile solution containing the precursor nickel(II) complex (**5**). The hydrogen bridge protons were replaced by BF_2 moieties and with the exception of this, all characteristics were retained according to ^{1}H NMR and IR data. In the IR spectrum of **6**, the C=N vibrations increase by up to 46 cm^{-1} in the process of going from **5** to the BF_2^+ capped complex due to the strong electron-withdrawing effect of the boron linked groups incorporated into the macrocycle.[15] In the ^{1}H NMR spectrum of this compound, the BF_2 bridges cause the signals of the other groups to shift downfield relative to the precursor complex (**5**). The FAB mass spectrum of **6** showed a peak at $m/z = 1226.4$ assigned to $[M]^+$.



Scheme 2 Reagents and conditions: (i) Et_3N, $NiCl_2{\cdot}6H_2O$ in EtOH at 60 °C; (ii) $BF_3{\cdot}Et_2O$ in dry acetonitrile under nitrogen at reflux; (iii) KPF_6 in MeOH–H_2O at room temperature.

The addition of 4 equiv of KPF_6 in methanol–water (1:1) to a solution of **6** in methanol–chloroform leads to precipitation of the 1:2 (ligand:metal) K^+ complex (**7**) exclusively in 89.5% yield. The ^{1}H NMR spectrum of **7** is largely similar to that of the precursor compound (**6**), but the expected shifts due to complexation of K^+ cations by the macrobicyclic moieties (CH_2N and CH_2O) are significant. The resonances appearing at 834 and 532 cm^{-1} and assigned to $[PF_6]^-$ support a structural assingment in which the PF^-_6 ions are not coordinated to the K^+ cations.[16] The FAB mass spectrum of this compound exhibited an intense peak at $m/z = 1595$ $[M + 1]^+$, which is in accord with the proposed structure.

Experimental

^{1}H, ^{13}C NMR and IR spectra were recorded on Varian XL-200 and Perkin–Elmer Spectrum One spectrometers, respectively. Fast atom bombardment mass spectra were recorded on a VG ZapSpec spectrometer using *m*-nitrobenzyl alcohol as matrix. The elemental analyses of the compounds were obtained on a Hewlett–Packard 185 CHN analyser. The metal contents of the complexes were determined with a Unicam 929 AA spectrophotometer in solutions prepared by decomposition of the compounds in concentrated $HClO_4$ and concentrated HNO_3 solutions followed by digestion in concentrated HCl solution. 1,4,10,13-Tetraoxa-7,16-diazacyclooctadecane (**1**)[10] and 1,2-dinitro-4,5-bis(2-iodoethoxy)benzene (**2**)[11] were prepared as described previously. All solvents were reagent grade and purified according to the standard procedures.[17]

Syntheses

4,7,13,16,21,24-Hexaoxa-5,6-(3′,4′-dinitrobenzo)-1,10-diazabicyclo[8.8.8]hexacosane, 3. A round-bottom flask (500 mL) containing dry acetonitrile (150 mL) was evacuated, refilled

several times with oxygen-free nitrogen and connected to a vacuum line. Under nitrogen, the flask was charged with **1** (5.24 g, 20 mmol), finely ground anhydrous K_2CO_3 (16.29 g, 50 mmol) and a 0.25 equivalent amount of NaI (0.745 g); this mixture was stirred at room temperature for 1 h. A solution of **2** (12.69 g, 25 mmol) in dry acetonitrile (75 mL) was then added and the reaction mixture stirred at 30 °C for 96 h. The reaction mixture was monitored by TLC [silica gel, acetone–chloroform–petroleum ether (6:47:1)]. At the end of this period, the mixture was filtered and reduced to 20 mL under reduced pressure whereupon a yellow solid precipitated. The crude product was filtered off, washed with ether and then dried *in vacuo*. The product was crystallized from acetonitrile–ethanol (3 1) to give a pale yellow crystalline solid. Yield: 5.85 g (57%), mp 89–90 °C. Anal. calcd. for $C_{22}H_{34}N_4O_{10}$: C, 51.36; H, 6.61; N, 10.89%; found: C, 51.51; H, 6.45; N, 11.08%. IR (KBr pellets, cm^{-1}): 3047 (Ar–H), 2878 (C–H), 1357 (NO_2), 1222–1102 (CH_2–O–CH_2). ^{1}H NMR ($CDCl_3$): δ 7.97 (s, 2H, Ar–H), 4.29 (t, 4H, Ar–O–CH_2), 3.85 (m, 16H, OCH_2), 3.15 (m, 12H, NCH_2). ^{13}C NMR ($CDCl_3$): δ 147.12 (Ar–CO), 108.51 (ArCH), 138.50 (Ar–C), 72.79 (Ar–OCH_2), 71.39, 70.87, 70.32, 69.86(O–CH_2), 56.33, 55.71 (N–CH_2). MS (FAB): m/z 514.1 $[M]^+$.

4,7,13,16,21,24-Hexaoxa-5,6-(3′,4′-diaminobenzo)-1,10-diazabicyclo[8.8.8] hexacosane, 4. Compound **3** (3.26 g, 6.4 mmol) was dissolved in *n*-butanol (500 mL) by heating at reflux temperature under nitrogen atmosphere. Palladium (10%)-activated charcoal (2.0 g) was added to the solution under the same conditions and 16 mL of hydrazine hydrate (100%) was then added dropwise over 1 h. The reaction mixture was refluxed and stirred for 26 h and then filtered through celite and washed with *n*-butanol. The extent of the reaction was monitored by using TLC [silica gel, tetrahydrofuran–acetone (2:1)]. The pale yellow solution was concentrated to 30 mL and cooled to −18 °C in a refrigerator, giving a white solid. This was filtered off, washed with diethyl ether under nitrogen and dried *in vacuo*. Yield: 1.6 g (56%), mp 67–69 °C. Anal. calcd. for $C_{22}H_{38}N_4O_6$: C, 58.14; H, 8.37; N, 12.33%; found: C, 58.01; H, 8.24; N, 12.50%. IR (KBr pellets, cm^{-1}): 3273 (NH_2), 3057 (Ar–H), 2895 (C–H), 1607 (NH_2), 1234–1116 (CH_2O–CH_2). ^{1}H NMR ($CDCl_3$): δ 6.48 (s, 2H, Ar–H), 4.25 (br, 4H, NH_2), 4.03 (t, 4H, Ar–O–CH_2), 3.60 (m, 16H, OCH_2), 2.96 (m, 12H, NCH_2). MS (FAB): m/z 454.2 $[M]^+$.

2,3-Bis(hydroxyimino)-4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane[2,3-g]quinoxaline, H_2L. A solution of cyanogen di-*N*-oxide in dichloromethane (25 mL), which was prepared from (*E*,*E*)-dichloroglyoxime (0.78 g, 5 mmol) and an aqueous solution of Na_2CO_3 (25 mL, 0.5 M), was added with stirring to a cold solution (−15 °C) of **4** (1.5 g, 3.3 mmol) in cold dichloromethane (100 mL) under nitrogen atmosphere; the reaction was continued for 16 h at this temperature. The solvent was evaporated *in vacuo* and the residue purified by column chromatography [silica gel, ethanol–acetone–ethyl acetate (1:1:1)] to give dioxime. The pale brown solid product was crystallized from ethanol–water (4 1). Yield: 0.86 g (48.6%), mp 213–215 °C (dec.). Anal. calcd. for $C_{24}H_{38}N_6O_8$: C, 53.53; H, 7.06; N, 15.61%; found: C, 53.75; H, 7.19; N, 15.44%. IR (KBr pellets, cm^{-1}): 3403 (N–H), 3247 (O–H), 3059 (Ar–H), 2925 (C–H), 1621 (C=N), 1210–1146 (CH_2OCH_2), 953 (N–O). ^{1}H NMR (DMSO-d_6): δ 9.36 (s, 2H, OH), 8.92 (s, 2H, NH), 6.88 (s, 2H, Ar–H), 4.28 (t, 4H, Ar–O–CH_2), 3.78 (m, 16H, OCH_2), 3.10 (m, 12H, NCH_2). ^{13}C NMR (DMSO-d_6): δ 138.94 (Ar–CO), 152.82 (C=N), 122.94 (Ar–CN), 105.23 (Ar–CH), 70.81 (Ar–OCH_2), 68.61, 68.13, 67.42, 65.00 (OCH_2), 55.42, 54.93 (NCH_2): MS (FAB): m/z 539 $[M+1]^+$.

$[Ni(HL)_2]$, 5. A solution of nickel(II) chloride hexahydrate (0.168 g, 0.7 mmol) in ethanol (10 mL) was added to a solution of H_2L (0.75 g, 1.4 mmol) in hot ethanol (80 mL). A distinct change in colour to red and a decrease in the pH of the solution (pH = 1.9) was immediately observed. An ethanolic solution of triethylamine (0.1 M) was then added to adjust the pH to about 4.35, at which point the precipitation of the complex started. The reaction mixture was heated and stirred in a water bath for 2 h. After precipitation was complete, the reaction mixture was cooled to room temperature and filtered, washed with water, cold ethanol and diethyl ether and then dried *in vacuo*. Yield: 0.68 g (86.1%), mp 290 °C. Anal. calcd. for $C_{48}H_{74}N_{12}O_{16}Ni$: C, 50.85; H, 6.53; N, 14.83; Ni, 5.18%; found: C, 50.98; H, 6.40; N, 15.05; Ni, 4.97. IR (KBr pellets, cm^{-1}): 3416 (N–H), 3055 (Ar–H), 2924 (C–H), 1718 (O–H O), 1611 (C=N), 1605 (N–H), 1205–1108 (CH_2OCH_2), 944 (N–O). ^{1}H NMR (DMSO-d_6): δ 16.52 (s, 2H, O–H O), 8.95 (br, 4H, NH), 6.94 (m, 4H, Ar–H), 4.36 (m, 8H, Ar–O–CH_2), 3.74 (m, 32H, CH_2O CH_2), 3.19 (m, 24H, NCH_2). MS (FAB): m/z 1133 $[M+1]^+$.

$[Ni(LBF_2)_2]$, 6. A suspension of **5** (0.60 g, 0.545 mmol) in freshly distilled dry acetonitrile (20 mL) was brought to reflux temperature under dry nitrogen atmosphere. Borontrifluoride etherate (0.98 mL, 1.19 mmol) in dry acetonitrile (2 mL) was added dropwise while the suspension was refluxed and stirred. The resulting reaction mixture was completely dissolved and immediately turned dark red. After this formation, the solution was refluxed for 2 h, then the solution was evaporated to dryness under reduced pressure. The residue was dissolved in dry acetonitrile (10 mL) and the solvent was removed to dryness. The oily dark red product was dissolved in acetonitrile (8 mL) and allowed to stand in a refrigerator overnight. The deep red crystalline product was filtered off, washed with cold diethyl ether and petroleum ether and then dried *in vacuo*. Yield: 0.49 g (58%), mp 225 °C. Anal. calcd. for $C_{48}H_{72}N_{12}O_{16}B_2F_4Ni$: C, 46.89; H, 5.86; N, 13.67; Ni, 4.77%; found: C, 46.70; H, 5.66; N, 13.81; Ni, 4.90%. IR (KBr pellets, cm^{-1}): 3356 (N–H), 3062 (Ar–H), 2911(C–H), 1657 (C=N), 1610 (N–H), 1217–1105 (CH_2OCH_2), 964 (N–O). ^{1}H NMR ($CDCl_3$): δ 9.08 (br, 4H, NH), 7.22 (m, 4H, Ar–H), 4.34 (m, 32H, OCH_2), 3.82 (m, 32H, CH_2OCH_2), 3.29 (m, 24H, NCH_2). MS(FAB): m/z 1226.4 $[M]^+$.

$[K_2Ni(LBF_2)_2](PF_6)_2$, 7. A solution of potassium hexafluorophosphate (0.23 g, 1.3 mmol) in 10 mL of a methanol–water (4:1) mixture was added while stirring to a solution of **6** (0.4 g, 0.32 mmol) in 10 mL of a methanol–chloroform (1:1) mixture at room temperature over 30 min. Then, the mixture was heated and stirred for 3 h at 50 °C while the reaction was monitored by TLC [silica gel, chloroform–methanol–water (75:23:2)]. Concentrated to 5 ml and allowed to cool at −18 °C in a refrigerator overnight, a cream-coloured solid precipitated. The solid product was filtered off, washed with cold ethanol and diethyl ether then dried *in vacuo*. Yield: 0.44 g (89.5%), mp 157–158 °C. Anal. calcd. for $C_{48}H_{72}N_{12}O_{16}B_2F_{16}P_2K_2Ni$: C, 36.08; H, 4.51; N, 10.52; Ni, 3.67; K, 4.88%; found: C, 35.83; H, 4.69; N, 10.70; Ni, 3.85; K, 4.66%. IR (KBr pellets, cm^{-1}): 3338 (N–H), 3058 (Ar–H), 2923 (C–H), 1649 (C=N), 1604 (N–H), 1205–1090 (CH_2O–CH_2), 834, 532 $(PF_6)^-$, 955 (N–O). ^{1}H NMR (DMSO-d_6): δ 9.14 (br, 4H, NH), 7.24 (m, 4H, Ar–H), 4.46 (m, 8H, Ar–O–CH_2), 3.98 (m, 32H, OCH_2), 3.44 (m, 24H, NCH_2). MS (FAB): m/z 1595 $[M+1]^+$.

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