

# Synthesis and Characterization of Novel (*E,E*)-Dioxime and Its Mono- and Heterotrinnuclear Complexes

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A novel (*E,E*)-dioxime 5,6:13,14-dibenzo-9,10-benzo(15-crown-5)-2,3-bis(hydroxyimino)-1,4,8,11-tetraazacyclotetradecane ( $H_2L$ ) was synthesized by the reaction of (*E,E*)-dichloroglyoxime (**5**) with 2,3:10,11-dibenzo-6,7-benzo(15-crown-5)-1,5,8,12-tetraazadodecane (**4**) obtained from the reduction of 1,2-bis(*o*-nitrobenzylideneimino)benzo(15-crown-5) (**3**). Only mononuclear cobalt(III) and ruthenium(II) complexes with a metal/ligand ratio of 1:2 were isolated then cobalt(III) complexes bridged with  $BF_2^+$  were obtained with hydrogen-bridged cobalt(III) complex and boron trifluoride etherate. The reaction of  $BF_2^+$ -capped mononuclear cobalt(III) complex with  $[Cu(CH_3CN)_4]PF_6$  gave a heterotrinnuclear complex. The alkali metal binding ability of the mononuclear cobalt(III) complex was also studied. The structure of the dioxime and its transition-metal complexes are proposed according to elemental analyses,  $^1H$  and  $^{13}C$  NMR, IR and mass spectra.

The chemistry of transition-metal complexes with vicinal dioxime ligands has been well studied, and is the subject of several reviews.<sup>1</sup> The exceptional stability and unique electronic properties of these complexes can be attributed to their planar structure, which is stabilized by hydrogen bonding.<sup>2</sup> The complexes prepared by *vic*-dioximes have been extensively used for various purposes owing to the high stability of these compounds, including model compounds for vitamin B<sub>12</sub> or trace metal analysis.<sup>3</sup> They have also been examined as compounds with columnar stacking, which is thought to be the reason for semiconducting properties.<sup>4</sup>

A rapidly emerging area of chemical interest in recent years is the synthesis of heterobinucleating ligands.<sup>5</sup> Examples of the heterobinucleating ligands that could serve as 'polytopic receptor molecules'<sup>6</sup> for binding of metal cations include molecules containing macrocyclic functionalities appended with tetrathia<sup>7</sup> or dithia-diaza centers.<sup>8</sup> The relevance of bimetallic compounds to bioinorganic systems has been one of the reasons for the increase in the amount of research on polynuclear compounds.<sup>9</sup>

Although alkali-metal complexes of macrocyclic polyethers which are 'hard' donor sites and the transition-metal complexes of various 'soft' donors are studied separately, only few ligands are reported to contain both 'hard' and 'soft' donor sites.<sup>10</sup> The 'hard' ether containing macrocycles show a binding preference towards 'hard'

alkaline and alkaline earth cations, but the incorporation of 'soft' amine linkages causes a preference towards 'soft' heavy metal ions. The interesting aspect of these compounds is that they have the features of both transition metal chemistry and crown-ether chemistry in the same molecule.

The heteropolymetallic systems are of interest to both biologists and bioinorganic chemists investigating the structure and functions of polynuclear metal centers in proteins and searching for new magnetic materials.<sup>11</sup> In addition, polynuclear complexes may facilitate electron transfer studies and serve as models of relevance to biological processes.<sup>12</sup> On the other hand, it has recently been demonstrated that bis(dioxime)ruthenium complexes act as catalysts in the oxidation of water and in the electrochemical epoxidation of olefins.<sup>13</sup> The investigation of the above mentioned aspects, the synthesis and characterization of heteropolynuclear complexes containing cobalt(III) and copper(I) metal ions have been made. Recently, ruthenium complex has also been synthesized and identified.

In our previous studies we have investigated the synthesis and characterization of various transition metal complexes of *N,N'*-substituted diaminoglyoxime.<sup>14</sup> The (*E,Z*)- and (*E,E*)-stereoisomers and complexes of novel vicinal dioximes have been isolated, and the interconversion of geometric isomers has been studied.<sup>15</sup>

In the present study, our goal was to undertake the synthesis of a novel (*E,E*)-dioxime ligand containing both a 14-membered tetraaza macrocycle and also a

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crown ether moiety linked tetraaza macrocycle. Various mono- and heterotrinnuclear complexes have been synthesized by the reaction of *vic*-dioximes with a variety of transition-metal ions. In addition to that, the alkali-metal binding ability of the  $\text{BF}_2^+$ -capped mononuclear cobalt(III) complex was investigated.

## Results and discussion

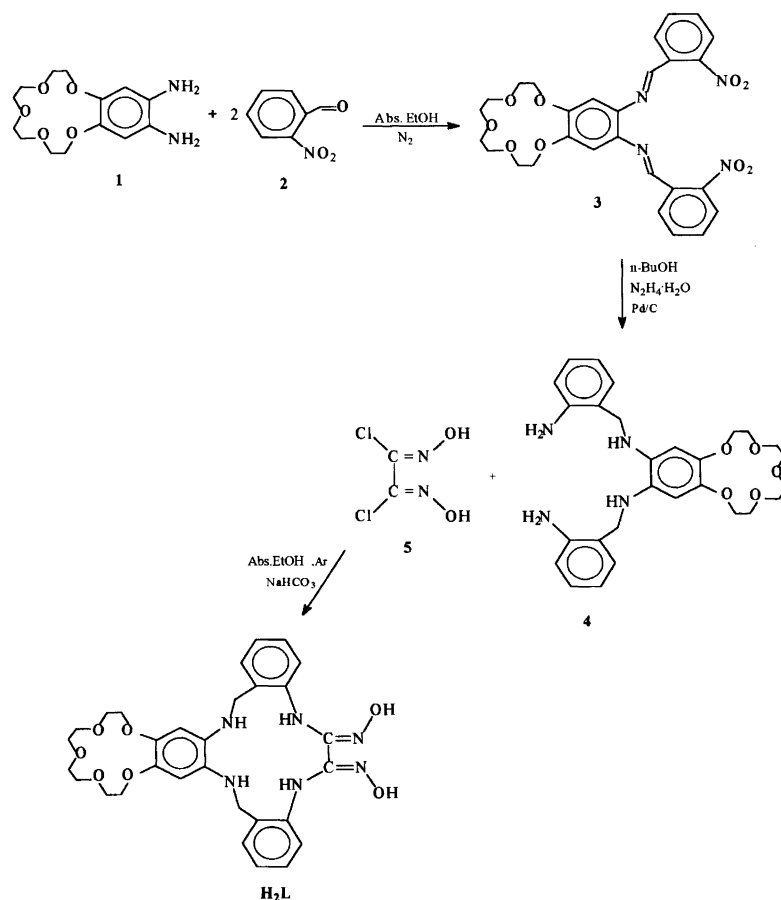
We report herein the synthesis of the free macrocyclic ligand 5,6:13,14-dibenzo-9,10-benzo(15-crown-5)-2,3-bis(hydroxyimino) - 1,4,8,11 - tetraazacyclotetradecane, abbreviated as  $\text{H}_2\text{L}$ , which was prepared from 2,3:10,11-dibenzo-6,7-benzo(15-crown-5)-1,5,8,12-tetraazadodecane (**4**) by reaction of (*E,E*)-dichloroglyoxime (Scheme 1), and the structures and reactivity of the mononuclear cobalt(III) and ruthenium(II) and heterotrinnuclear copper(I) complexes of this ligand. The structures of the ligand and its complexes were demonstrated by a combination of elemental analysis,  $^1\text{H}$  and  $^{13}\text{C}$  NMR, IR and mass spectral data.

1,2-Bis(*o*-nitrobenzylideneimino)benzo(15-crown-5) (**3**) was prepared by the condensation reaction of 4',5'-diaminobenzo(15-crown-5) (**1**) with *o*-nitrobenzaldehyde (**2**) in fairly good yield 30.1%. The infrared data of **3** confirm the presence of imine (ca.  $1630\text{ cm}^{-1}$ ) and the

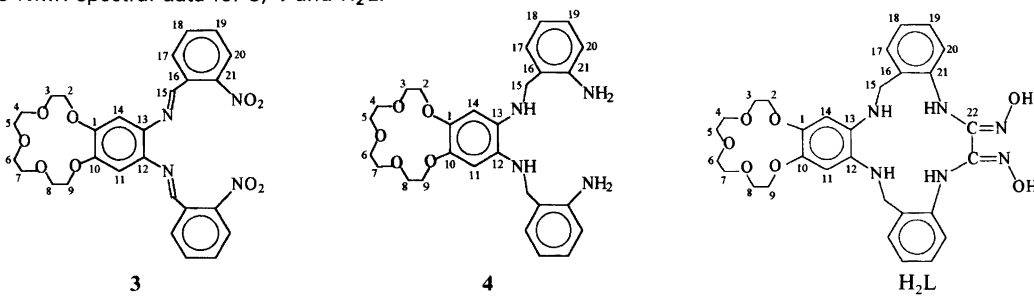
absence of carbonyl and amine functional groups of the starting materials. The asymmetric and symmetric stretching vibrations of  $\text{Ar}-\text{NO}_2$  are at around  $1524$  and  $1340\text{ cm}^{-1}$ , respectively. These values are inconsistent with the previously reported aromatic nitro groups.<sup>16</sup>

In the  $^1\text{H}$  NMR spectra of **3**, the absence of amine functional groups and the presence of azomethine groups at  $\delta=9.00$  ppm indicate the formation of Schiff bases. This singlet disappears upon reduction with palladium/activated carbon and hydrazine hydrate. On the other hand, two chemical shifts belonging to  $\text{NH}_2$  and  $\text{NH}$  protons are in agreement with the expected structure (**4**). These resonances appear as singlets at  $\delta=6.10$  and  $5.21$  ppm, respectively. The proton-decoupled carbon-13 NMR spectra for **3** are consistent with the proposed formulation (Table 1). The chemical shifts for the azomethine carbon (**3**) are found at  $\delta=159.43$  ppm. The disappearance of this resonance in the carbon-13 NMR spectra of **4** can be attributed to the formation of the desired compound (Table 1). The FAB mass spectra of the Schiff base or amine compounds exhibit parent molecular ion peaks at  $m/z=565$  [ $M+1$ ]<sup>+</sup> and  $509$  [ $M+1$ ]<sup>+</sup>, which are accord with the formation of proposed structures.

The desired ligand  $\text{H}_2\text{L}$  was obtained in good yield by a literature method<sup>17</sup> involving the reaction of 1 equiv.



Scheme 1.

Table 1.  $^{13}\text{C}$ -NMR spectral data for **3**, **4** and  $\text{H}_2\text{L}$ .


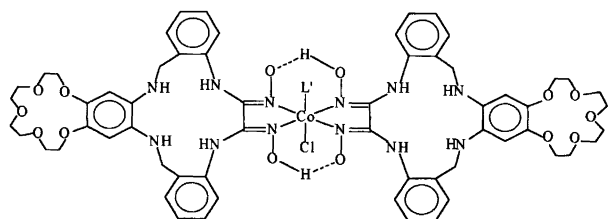
Carbons	<b>3</b> ( $\delta$ ppm)	<b>4</b> ( $\delta$ ppm)	$\text{H}_2\text{L}$ ( $\delta$ ppm)
C <sub>2-9</sub>	68–60–71.45	68–18–70.50	68–60–69.74
C <sub>1-10</sub>	124.19	103.75	104.04
C <sub>11-14</sub>	129.82	127.04	128.04
C <sub>12-13</sub>	145.55	147.91	148.34
C <sub>15</sub>	159.43	41.88	42.76
C <sub>16</sub>	134.05	127.29	128.11
C <sub>17</sub>	132.81	130.05	132.42
C <sub>18</sub>	132.24	125.16	129.36
C <sub>19</sub>	130.32	128.44	131.51
C <sub>20</sub>	125.12	127.17	146.50
C <sub>21</sub>	149.26	151.85	145.89

of **4** with 1 equiv. of (*E,E*)-dichloroglyoxime in absolute ethanol in the presence of 5 equiv. of  $\text{NaHCO}_3$  as a buffer to neutralize  $\text{HCl}$  formed during the reaction (Scheme 1). After being stirred for 10 h at room temperature, the yellow solution containing solid  $\text{NaCl}$  was obtained. Removal of the inorganic salts and concentration *in vacuo* gave a pale yellow product. The IR spectra of this compound suggested that it was the same structure, and the presence of a strong absorption at  $1635\text{ cm}^{-1}$  was strongly indicative of the presence of the hydroxyimino groups. The disappearance of the  $\text{NH}_2$  stretching bands along with the appearance of new absorptions at  $3225\text{ [v(O-H)]}$  and  $946\text{ cm}^{-1}\text{ [v(N-O)]}$  are also in agreement with the structure in the Scheme 1. In the  $^1\text{H}$  NMR spectrum of  $\text{H}_2\text{L}$ , the deuterium-exchangeable protons of  $\text{N-OH}$  and  $\text{NH}$  groups appear as two singlets at  $\delta = 10.80$  and  $9.15$  ppm, respectively. The single chemical shifts for  $\text{N-OH}$  protons indicate that the oxime groups are in the (*E,E*)-structure.<sup>18</sup> More detailed information about the structure of *vic*-dioxime is provided by  $^{13}\text{C}$  NMR spectroscopy. The carbon resonance of the oxime groups is found to be at lower fields ( $\delta = 145.89$  ppm), as given in literature.<sup>19</sup> The equivalent carbon resonances of the proton-decoupled carbon-13 NMR spectra of oxime groups confirm the (*E,E*) form of *vic*-dioxime (Table 1). The FAB mass spectrum of  $\text{H}_2\text{L}$  exhibited intense peaks at  $m/z = 593\text{ [M+1]}^+$ , which is in accord with the macrocycle.

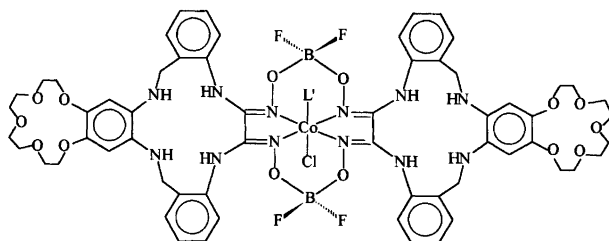
The six-coordinated cobalt(III) complex  $[\text{Co}(\text{HL})_2\text{L}'\text{Cl}]$  (**6**) was obtained when air was bubbled through a suspension of  $[\text{Co}(\text{HL})_2]$  in ethanol in the presence of pyridine as an axial ligand. It was necessary to use the exact stoichiometric amount of pyridine because the presence of excess base in the reaction

mixture has been reported to yield a complex in which one of the linking protons has been removed and which contains two axially bound nitrogen bases.<sup>20</sup> However, attempts to reduce the cobalt(III) complex to cobalt(I), a procedure used extensively to prepare alkylcobaloxime derivatives of (*E,E*)-dioxime was not successful.<sup>21</sup> This complex has a metal:ligand ratio of 1:2 and the ligand is coordinated only by the *N,N'* atoms of the vicinal dioximes. Since a distinct decrease in the pH of the solution was observed during complex formation, deprotonation of the ligands with subsequent *N,N'*-chelation with the (*E,E*)-dioxime groups probably occurs. The disappearance of the  $\text{OH}$  stretching vibrations and the shifts of the  $\text{C=N}$  bands to lower frequencies in IR spectra of cobalt(III) complexes can be attributed to *N,N'*-chelation.<sup>17</sup> The  $\text{C=N}$  bands due to the oxime groups and pyridine are observed as a combined vibrations at around  $1615\text{--}1580\text{ cm}^{-1}$ . In the IR spectrum of this complex, the weak band assigned to the intramolecular hydrogen bonded ( $\text{O-HO}$ ) bending vibrations was observed around  $1700\text{ cm}^{-1}$ . This complex exhibit absorption bands characteristic of the axially bound of pyridine. The out-of-plane and the in-plane deforming vibrations of the pyridine occurring at  $400$  and  $608\text{ cm}^{-1}$ , respectively. In the  $^1\text{H}$  NMR spectra of this diamagnetic cobalt(III) complex, the presence of intramolecular  $\text{O-HO}$  bands at around  $\delta = 16.85$  ppm are identifiable for this complex. This identification can be made easily by deuterium exchange. The mass spectra (FAB-positive) of the  $[\text{Co}(\text{HL})_2\text{L}'\text{Cl}]$  support the structure of **6**, but the peaks at  $m/z = 1276$  do not confirm the presence of pyridine.

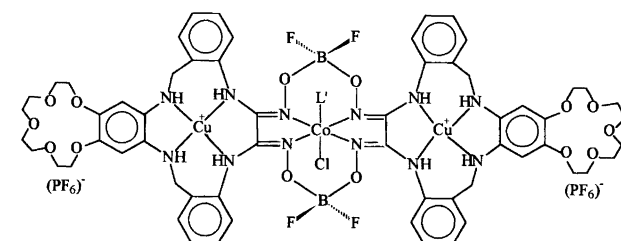
The template synthesis of the macrocyclic cobalt(III) complex  $[\text{Co}(\text{LBF}_2)_2\text{L}'\text{Cl}]$  (**7**) was performed by adding



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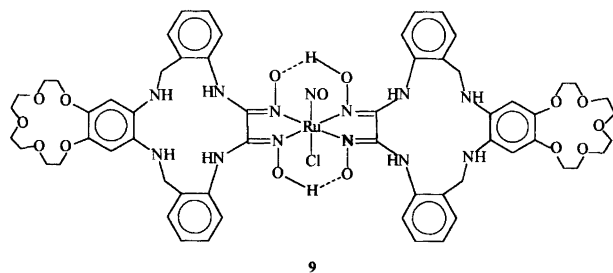


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boron trifluoride ethyl ether complex to the refluxing solution of acetonitrile containing the hydrogen-bonded precursor (**6**). The bridging protons in proton-linked complex were replaced by  $\text{BF}_2^+$  groups and the single mole of axial ligand, pyridine, was retained, according to both proton and carbon-13 NMR, mass spectra and elemental analysis data. In the  $^1\text{H}$  NMR spectra of this diamagnetic cobalt(III) complex, the chemical shifts of O–HO protons belonging to the proton-linked precursor disappear after the formation of  $\text{BF}_2$ -bridging macrocyclic complex (**7**). The downfield shifts observed relative to hydrogen-bridged cobalt(III) complex are due to the bridging boron groups. In contrast to this downward shift, the IR spectra of this complex exhibit upward shifts in the stretching vibrations of the azomethine groups due to the strong electron-withdrawing effects of  $\text{BF}_2^+$  groups incorporated in the macrocycles.<sup>22</sup> In the IR spectrum of  $\text{BF}_2^+$ -capped macrocyclic cobalt(III) complex, some characteristic vibrations of the precursor cobalt(III) complex were observed. The broad band at  $1700\text{ cm}^{-1}$ , belonging to O–HO bending vibrations, disappeared upon encapsulation of the hydrogen-bridged complex with the appearance of peaks due to the  $\text{BF}_2^+$  contaminant around  $1145\text{--}1032$  and  $898\text{--}860\text{ cm}^{-1}$  for the B–O and B–F groups, respectively. The fast atom bombardment mass spectrum of  $[\text{Co}(\text{LBF}_2)_2\text{L}'\text{Cl}]$  exhibits a molecular ion peak at  $m/z=1450$  due to  $[M+1]^+$  and the another intense peak at  $m/z=1202$  attributed to the loss of  $248 [M-4\text{F}-\text{Co}-\text{Py}-\text{Cl}]^+$ .

In order to synthesize heterotrimeric complexes of  $[\text{CoCu}_2(\text{LBF}_2)_2\text{L}'\text{Cl}](\text{PF}_6)_2$ , the heterogeneous reaction of mononuclear  $[\text{Co}(\text{LBF}_2)_2\text{L}'\text{Cl}]$  with a solution of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  was carried out. In this product cobalt(III) is still coordinated to the (*E,E*)-dioxime groups, and the two other metal ions are coordinated two 14-membered macrocyclic tetraaza atoms of the macrocycle. This molecule (**8**) has a metal:ligand ratio of 3:2 according to its elemental analysis. Trinuclear complexation is also confirmed by the mass spectral data. The fast atom bombardment mass spectrum shows a peak for  $[\text{CoCu}_2(\text{LBF}_2)_2\text{L}'\text{Cl}](\text{PF}_6)_2$  at  $m/z=1866$  due to the  $[M+1]^+$  ion and another peak at  $m/z=1802$  attributed to the loss of one copper atom. The basicity of some N donors in this macrocycle is rather low because of their position near the hydroxyimino groups. Their basicity is comparable with that of amides. For this reason, the deprotonation of this NH group in the heterotrimeric complex was not observed owing to the absence of N–H stretching vibrations. Subsequent complexation of the cobalt(III) complex with the corresponding complexation agent gave the respective heteropolynuclear complex **8**, with the copper(I) cation in a square-planar coordinated environment. The planar nature of the phenyl rings and adjacent azomethine groups contribute to the tendency toward planar coordination by these kinds of ligands.<sup>8</sup> In the  $^1\text{H}$  NMR spectrum of this heterotrimeric complex, the singlets representing NH protons appear at  $\delta=9.23$  and  $5.34$  ppm, i.e. the neighbourhood of the oxime and methylene groups, respectively. The other chemical shifts in this complex, which belong to aromatic and aliphatic protons, are very similar to those of the  $\text{BF}_2^+$ -capped cobalt(III) complex. IR spectral data were also especially useful for the identification of the infrared-active anions, such as  $\text{PF}_6^-$ , participating in the complex formation. In the heterotrimeric complex containing  $\text{Cu}^I$ , the bands at  $845$  and  $562\text{ cm}^{-1}$  which belong to  $[\text{PF}_6]^-$  support a structure in which the hexafluorophosphate ions are not coordinated to the central copper(I) atom.<sup>23</sup> Comparing the respective IR spectra of **7** and its heterotrimeric complex reveals that, upon complexation, a shift of the N–H stretching vibration down to  $20\text{ cm}^{-1}$  occurs. As expected, this shift for the aza absorptions to lower wavenumber is observed upon complexation of  $\text{Cu}^I$ . However, a medium-intensity band in the  $460\text{--}415\text{ cm}^{-1}$  region may reasonably be assigned to Co–N stretching vibrations. Little change in the  $^1\text{H}$  NMR spectra of this diamagnetic complex regarding the position of the chemical shifts of the aza groups was evident, supporting the structure of copper(I) cations.

Dark brown crystals of *trans*- $\text{Ru}(\text{HL})_2(\text{NO})\text{Cl}$  (**9**) were prepared by the reaction of 2.0 equiv. of  $\text{H}_2\text{L}$  with  $\text{Ru}(\text{NO})\text{Cl}_3 \cdot 5\text{H}_2\text{O}$  in refluxing ethanol for 24 h. The use of  $\text{Ru}(\text{NO})\text{Cl}_3 \cdot 5\text{H}_2\text{O}$  provided a useful source of ruthenium and yielded a *trans*-bis( $\alpha$ -dioximato) complex that was slightly soluble in common organic solvents, allowing this complex to be fully characterized.<sup>24</sup> IR



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spectroscopy has been the primary characterization method regarding the protonation of the *trans*-bis( $\alpha$ -dioxime)ruthenium complex, where structural assignments were made on the basis of characteristic N–O and O–H stretches. The IR spectrum of  $\text{Ru}(\text{HL})_2(\text{NO})\text{Cl}$  contains a weak absorption at  $1711\text{ cm}^{-1}$ . We assign this absorbance to the O–HO intramolecular hydrogen bridge. The IR absorbances of the N–O stretches of the  $\text{H}_2\text{L}$  ligand are located at  $932\text{ cm}^{-1}$  for complex **9**. The shift of N–O absorbances to lower energy is consistent with the protonation occurring at the hydrogen-bridged oxime oxygen atom, yielding a covalent O–H bond.<sup>25</sup> The formation of an O–HO bond results in the removal of electron density from the N–O bond and a corresponding increase in the N–O bond length and a decreased N–O stretching frequency.<sup>26</sup> N=O stretching vibrations of the nitrosyl ligand coordinated to the ruthenium ion are observed at  $1892\text{ cm}^{-1}$  for this complex. According to this result, the ruthenium complex can be considered to be a  $\text{Ru}^{\text{II}}\text{--NO}^+$ -type complex in which the chlorine ligand is *trans* to the NO group in this octahedral geometry.<sup>27</sup>

The  $^1\text{H}$  NMR spectrum of this complex was obtained in  $(\text{CD}_3)_2\text{SO}$ , where a broad singlet at  $\delta=16.50\text{ ppm}$  with an integrated ratio of 1:1 was observed. This resonance indicates the two equivalent bridging oxime hydrogens of ruthenium complex. The abovementioned O–HO protons can be identified very easily, because of the disappearance of the chemical shifts of protons on  $\text{D}_2\text{O}$  exchange. The FAB mass spectrum of this complex showed the expected molecular ion peak at  $m/z=1368$   $[\text{M}+2\text{H}_2\text{O}+2]^+$  and 1313. The last parent ion indicates the loss of  $m/z=35$ , which can be explained by removal of chloride from the complex.

The complexation of alkali-metal cations has been studied by using only a  $\text{BF}_2^+$ -bridged mononuclear cobalt(III) complex owing to the reasonable solubility of chloroform. The alkali-metal binding ability of **6**, having two benzo(15-crown-5) units, was estimated by solvent extraction of alkali-metal salts from water to a chloroformic solution of the abovementioned complex. Picrate was used as counter-anion for all compounds. The ionic radii of cations which produce a significant change in the electronic spectra of **6** effect the change in absorbance. Thus a considerable change is observed for different metal ions in the  $\text{MN}_4$  core of the octahedral cobalt(III) complex. The addition of lithium perchlorate

in aqueous solution to the chloroformic solution of **6** does not significantly modify its absorption spectrum owing to weak complexation. The extractability (%) of lithium ion into chloroformic solution from aqueous solution was found to be the lowest among the cations (5.2%). On the contrary,  $\text{Na}^+$  has been shown to form the most stable complex (48.7%) with the benzo(15-crown-5) moiety by using picrate.<sup>28</sup> On the other hand, under the same conditions, the selectivity of **6** for potassium (87.8%) is higher than for rubidium (68.5%) and the other alkali-metal cations. For cations bigger than the internal cavity of benzo(15-crown-5), the stoichiometry of complexation can not be estimated with certainty, and the association constant can not be rigorously calculated.<sup>10</sup> Pyridine connected in the axial position in the octahedral complex (**6**) and possible conformational changes due to tetraaza macrocyclic units might be expected to prevent the parallel alignment of the two crown ether units of the two **6** molecules, and therefore, completely to prevent envelope alkali cations such as  $\text{K}^+$  or  $\text{Rb}^+$ . This might be a result of the suitable direction of the crown ether moieties for the formation of a new type of complex which can be denoted a phase-sandwich complex, hypothetically (Fig. 1) due to the steric effect of the octahedral vicinal dioxime complex. This new association between crown ether units and  $\text{K}^+$  or  $\text{Rb}^+$  cations causes dimerization and oligomerization. Phase-sandwich complexes formed with two crown ether units can be expected to aggregate.

## Experimental

**General.** Proton and carbon-13 NMR spectra were recorded on a Varian XL-300 or Varian-Gemini 200 spectrometer. Routine IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrophotometer, as KBr pellets. Fast atom bombardment (FAB) mass spectra were recorded on a VG AutoSpec from VG Analytical. The metal contents of the complexes were determined by a Hitachi 180–80 atomic absorption spectrophotometer in solutions prepared by decomposing the complexes in aqua regia and then subsequently digesting in concentrated HCl. Elemental analyses were performed on a Hewlett-Packard 185 CHN Analyser. (*E,E*)-Dichloroglyoxime,<sup>29</sup> 4',5'-diaminobenzo(15-crown-5)<sup>30</sup> and  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ <sup>26</sup> were prepared by reported procedure. Melting points were determined on an Electrothermal apparatus and are uncorrected. *o*-Nitrobenzaldehyde, palladium/activated carbon and all solvents were reagent grade and used without purification.

### Synthesis of vic-dioxime and its complexes.

*1,2-Bis(o-nitrobenzylideneimino)benzo[15-crown-5]* (**3**). To a stirring solution of *o*-nitrobenzaldehyde (14.22 g, 94.09 mmol) (**1**) in absolute ethanol (400 ml) at  $-10^\circ\text{C}$  and under an atmosphere of nitrogen, was added, dropwise over a period of 30 min a solution of 4',5'-

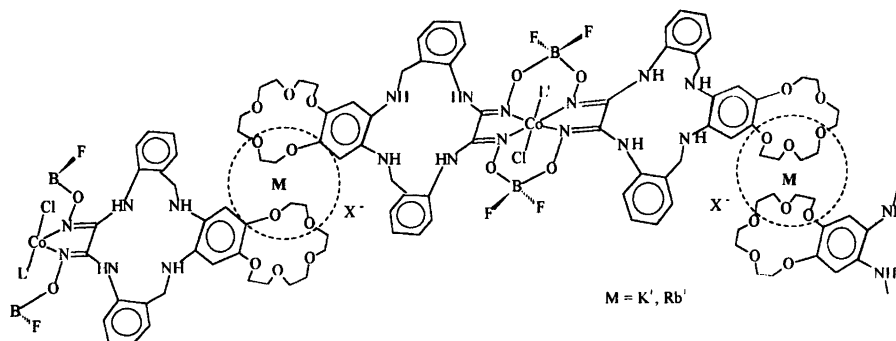


Figure 1.

diaminobenzo(15-crown-5) (**2**) (14.02 g, 47.03 mmol) in absolute ethanol (100 ml). The reaction mixture was kept at that condition for 2 h, allowed to stand at room temperature and stirred for 24 h. The solution was heated to 50 °C for 3 h. Upon standing, the solution was filtered and concentrated to 60 ml *in vacuo* and then cooled to -5 °C; a pale yellow solid product was obtained which was filtered off, washed with cold ethanol and diethyl ether and then dried *in vacuo*. The crude product was crystallized from ethanol (7.99 g, 30.1%), m.p. 213–215 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 9.00 (s, 2H, CH=N), 8.20–7.70 (m, 8H, Ar-H), 6.80 (s, 2H, Ar-H), 4.15–3.35 (m, 16H, CH<sub>2</sub>OCH<sub>2</sub>). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): δ 159.43, 149.26, 145.55, 134.05, 132.81, 132.24, 130.32, 129.82, 125.12, 124.19, 71.45–68.60. IR (KBr): 3125 (Ar-H), 2940 (C-H), 1630 (C=N), 1512, 1280–1250 (Ar-OCH<sub>2</sub>), 1158–1123 (CH<sub>2</sub>OCH<sub>2</sub>), cm<sup>-1</sup>. Mass spectrum (FAB positive): *m/z* = 565 [*M*+1]<sup>+</sup>, 583 [*M*+H<sub>2</sub>O+1]<sup>+</sup>. Found: C, 59.42; H, 4.81; N, 9.78. Calc. for C<sub>28</sub>H<sub>28</sub>N<sub>4</sub>O<sub>9</sub>: C, 59.57; H, 4.96; N, 9.92.

2,3:10,11-Dibenzo-6,7-benzo(15-crown-5)-1,5,8,12-tetraazadecane (**4**). Compound **3** (7.08 g, 12.55 mmol) was dissolved in *n*-butanol (350 ml) and heated to 100 °C. 1.25 g of Pd/C (10%) was then added to this solution at the same temperature and allowed to stand at 120 °C; then 12.0 ml of hydrazine hydrate (100%) was added dropwise. The reaction mixture was stirred and refluxed for 1 h and then filtered and washed with *n*-butanol (20 ml). After having been cooled to room temperature, the solution was concentrated to 50 ml. The crude product was filtered off, washed with cold *n*-butanol and diethyl ether and then dried *in vacuo* over P<sub>4</sub>O<sub>10</sub>. The resulting residue was recrystallized from ethanol to yield white crystals (5.20 g, 81.4%), m.p. 261–263 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 7.81–7.62 (m, 8H, Ar-H), 6.60 (s, 2H, Ar-H), 6.10 (s, 2H, NH), 5.21 (s, 4H, NH<sub>2</sub>), 4.22 (s, 4H, CH<sub>2</sub>-N), 3.30–3.15 (m, 16H, CH<sub>2</sub>OCH<sub>2</sub>). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): δ 151.85, 147.91, 130.05, 129.17, 128.44, 127.29, 127.04, 125.16, 103.75, 41.88, 70.05–68.18. IR (KBr): 3420 (N-H)<sub>asym</sub>, 3385 (N-H)<sub>sym</sub>, 3080 (Ar-H), 2960 (C-H), 1611 (N-H), 1340–1270 (Ar-OCH<sub>2</sub>), 1180–1135 (CH<sub>2</sub>-O-CH<sub>2</sub>) cm<sup>-1</sup>. Mass spectrum (FAB positive): *m/z* = 509 [*M*+1]<sup>+</sup>. Found: C, 65.98; H, 6.90;

N, 10.87. Calc. for C<sub>28</sub>H<sub>36</sub>N<sub>4</sub>O<sub>5</sub>: C, 66.14; H, 7.08; N, 11.02.

5,6:13,14-Dibenzo-9,10-benzo[15-crown-5]-2,3-bis(hydroxyimino)-1,4,8,11-tetraazacyclotetradecane (H<sub>2</sub>L). A solution of (*E,E*)-dichloroglyoxime (**5**) (1.57 g, 10 mmol) in 100 ml of absolute ethanol was added dropwise over 1 h to a cold solution of amine (**4**) (5.1 g, 10 mmol) in 800 ml of degassed absolute ethanol which also contained NaHCO<sub>3</sub> (5.00 g, 59.52 mmol) in excess. After stirring vigorously for about 10 h at room temperature under an argon atmosphere, the white precipitates were formed as in Scheme 1. The reaction mixture was filtered off, and washed with absolute ethanol and diethyl ether. The filtrate was concentrated to 60 ml under vacuum, and 100 ml of water which contained 0.5 g of Na<sub>2</sub>SO<sub>4</sub> was added in order to prevent colloidal dispersion. The precipitate was filtered off, washed with water, ethanol and diethyl ether, and dried *in vacuo*. The product was crystallized from a mixture of water and ethanol (1:5) (2.6 g, 44.1%), m.p. 241 °C (dec.). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 10.80 (s, 2H, OH), 9.15 (s, 2H, NH), 7.75 (d, 2H, Ar-H), 7.42–7.20 (m, 6H, Ar-H), 6.70 (s, 2H, Ar-H), 5.27 (s, 2H, NH), 4.25 (s, 4H, CH<sub>2</sub>-N), 3.60–3.05 (m, 16H, CH<sub>2</sub>OCH<sub>2</sub>). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): δ 148.34, 146.50, 145.89, 132.42, 131.55, 129.36, 128.11, 128.04, 127.47, 104.04, 42.76, 69.74–68.27. IR (KBr): 3460 (N-H), 3255 (O-H), 3090 Ar-H), 2875 (C-H), 1635 (C=N), 1612 (N-H), 1280–1240 (Ar-OCH<sub>2</sub>), 1160–1118 (CH<sub>2</sub>OCH<sub>2</sub>), 946 (N-O) cm<sup>-1</sup>. Mass spectrum (FAB positive): *m/z* = 593 [*M*+1]<sup>+</sup>, 627 [*M*+2H<sub>2</sub>O-1]<sup>+</sup>, 645 [*M*+3H<sub>2</sub>O]<sup>+</sup>, 506 [*M*-2(NOH<sub>2</sub>)]<sup>+</sup>. Found: C, 60.67; H, 5.91; N, 14.04. Calc. for C<sub>30</sub>H<sub>36</sub>N<sub>6</sub>O<sub>7</sub>: C, 60.81; H, 6.08; N, 14.18.

[Co(HL)<sub>2</sub>L'Cl] (**6**). A solution of CoCl<sub>2</sub>·6H<sub>2</sub>O (0.355 g, 1.5 mmol) in absolute ethanol (25 ml) was added to a hot solution of ligand H<sub>2</sub>L (1.78 g, 3 mmol) in absolute ethanol (100 ml) with stirring. A distinct change in colour and a decrease in the pH of the reaction mixture (pH 2.11) was observed. While cooling a solution of Lewis base, pyridine (0.120 g, 1.5 mmol) in absolute ethanol (2.5 ml) was added to above reaction mixture. The reaction mixture was allowed to cool to room

temperature, and a stream of oxygen was bubbled through the solution for 2 h. The solution was concentrated to 30 ml, and the mixture was cooled in a refrigerator at  $-5^{\circ}\text{C}$  overnight, whereupon the product was crystallized from the reaction mixture. The pale brown crystallized product was filtered off, washed with cold ethanol and diethyl ether and then dried *in vacuo* (1.39 g, 68.5%), m.p.  $270\text{--}272^{\circ}\text{C}$  (dec.).  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  16.85 (s, 2H, O-HO), 9.21 (s, 4H, NH), 8.40–7.86 (m, 5H, Ar-H, Py-H), 7.65–6.82 (m, 20H, Ar-H, Py-H), 5.25 (s, 4H, NH), 4.22 (s, 8H,  $\text{CH}_2\text{-N}$ ), 3.80–3.17 (m, 32H,  $\text{CH}_2\text{OCH}_2$ ). IR (KBr): 3439 (N-H), 3078 (Ar-H), 2885 (C-H), 1700 (O-HO), 1615–1580 (C=N), 1305–1254 (Ar-OCH<sub>2</sub>), 1192–1124 ( $\text{CH}_2\text{OCH}_2$ ), 935 (N-O)  $\text{cm}^{-1}$ . Mass spectrum (FAB positive):  $m/z = 1276$  [ $M\text{-py-1}$ ]<sup>+</sup>. Found: C, 57.28; H, 5.42; N, 13.19; Co, 4.17. Calc. for  $\text{C}_{65}\text{H}_{75}\text{N}_{13}\text{O}_{14}\text{CoCl}$ : C, 57.54; H, 5.53; N, 13.42; Co, 4.34.

[ $\text{Co}(\text{LBF}_2)_2\text{L}'\text{Cl}$ ] (7). A suspension of diamagnetic cobalt(III) complex [ $\text{Co}(\text{HL})_2\text{L}'\text{Cl}$ ] (1.10 g, 0.80 mmol) in 60 ml of freshly distilled acetonitrile was brought to reflux temperature in an argon atmosphere. Two equiv. amount of boron trifluoride etherate (0.22 ml) were added with continuous stirring to the abovementioned suspension, which changed its colour to red immediately. The solvent was removed under reduced pressure, and the residue was dissolved in 30 ml of acetonitrile and evaporated to dryness. The crude product was dissolved in 15 ml of acetonitrile and allowed to stand at  $-18^{\circ}\text{C}$  overnight, whereupon the compound crystallized from the solution. The crystallized product was collected by filtration, washed with cold acetonitrile and diethyl ether and then dried *in vacuo* (0.81 g, 69.8%), m.p.  $245\text{--}247^{\circ}\text{C}$ .  $^1\text{H}$  NMR (DMSO- $d_6$ ): 9.05 (s, 4H, NH), 8.35–7.82 (m, 5H, Ar-H, Py-H), 7.68–6.89 (m, 20H, Ar-H, Py-H), 5.12 (s, 4H, NH), 4.18 (s, 8H,  $\text{CH}_2\text{-N}$ ), 3.85–3.12 (m, 32H,  $\text{CH}_2\text{OCH}_2$ ). IR (KBr): 3400 (N-H), 3082 (Ar-H), 2880 (C-H), 1647 (C=N), 1350–1310 (Ar-OCH<sub>2</sub>), 1210–1160 ( $\text{CH}_2\text{OCH}_2$ ), 942 (N-O)  $\text{cm}^{-1}$ . Mass spectrum (FAB positive):  $m/z = 1450$  [ $M+1$ ]<sup>+</sup>, 1202 [ $M-4\text{F-Co-Py-Cl}$ ]<sup>+</sup>. Found: C, 53.58; H, 4.76; N, 12.30; Co, 3.77. Calc. for  $\text{C}_{65}\text{H}_{73}\text{N}_{13}\text{O}_{14}\text{B}_2\text{F}_4\text{CoCl}$ : C, 53.75; H, 5.03; N, 12.54; Co, 4.05.

[ $\text{CoCu}_2(\text{LBF}_2)_2\text{L}'\text{Cl}$ ]( $\text{PF}_6$ )<sub>2</sub> (8). A solution of the [ $\text{Co}(\text{LBF}_2)_2\text{L}'\text{Cl}$ ] complex (0.58 g, 0.40 mmol) in freshly distilled acetonitrile (40 ml) was treated with a solution of an equivalent amount of [ $\text{Cu}(\text{CH}_3\text{CN})_4$ ] $\text{PF}_6$  (0.29 g, 0.80 mmol) in dry acetonitrile (20 ml) under an oxygen-free nitrogen atmosphere, and the mixture was for kept 27 h with stirring. The end of the reaction was determined by thin-layer chromatography [ $R_f = 0.71$ , *n*-butanol:acetic acid:water (4:1:5)]. After cooling to room temperature the reaction mixture was concentrated to 10 ml. The precipitate was filtered off, washed with cold ethanol and diethyl ether and then dried *in vacuo* (0.52 g, 70.0%), m.p.  $380^{\circ}\text{C}$ .  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  9.23 (s, 4H, NH), 8.32–7.76 (m, 5H, Ar-H, Py-H),

7.72–6.85 (m, 20H, Ar-H, Py-H), 5.34 (s, 4H, NH), 4.37 (s, 8H,  $\text{CH}_2\text{-N}$ ), 3.85–3.09 (m, 32H,  $\text{CH}_2\text{OCH}_2$ ). IR (KBr): 3380 (N-H), 3076 (Ar-H), 2877 (C-H), 1644 (C=N), 1350–1300 (Ar-OCH<sub>2</sub>), 1188–1143 ( $\text{CH}_2\text{OCH}_2$ ), 939 (N-O)  $\text{cm}^{-1}$ . Mass spectrum (FAB positive):  $m/z = 1866$  [ $M+1$ ]<sup>+</sup>, 1802 [ $M\text{-Cu}$ ]<sup>+</sup>, 1787 [ $M\text{-Py}$ ]<sup>+</sup>. Found: C, 41.59; H, 3.70; N, 9.52; Co, 2.97; Cu, 6.55. Calc. for  $\text{C}_{65}\text{H}_{73}\text{N}_{13}\text{O}_{14}\text{B}_2\text{P}_2\text{F}_{16}\text{CoCu}_2\text{Cl}$ : C, 41.72; H, 3.90; N, 9.74; Co, 3.15; Cu, 6.79.

[ $\text{Ru}(\text{HL})_2\text{NOCl}$ ] (9). A solution of  $\text{RuCl}_3(\text{NO}) \cdot 5\text{H}_2\text{O}$  (0.083 g, 0.254 mmol) in ethanol (15 ml) was added dropwise to a solution of  $\text{H}_2\text{L}$  (0.30 g, 0.51 mmol) in degassed (with argon) ethanol (30 ml), and the mixture was refluxed and stirred for 24 h under inert conditions. The end of the reaction was determined by thin-layer chromatography [ $R_f = 0.67$ ,  $\text{CHCl}_3$ : $\text{MeOH}$ : $\text{H}_2\text{O}$  (75:23:2)]. The resultant dark-brown solution was cooled in a refrigerator overnight and then filtered. The dark-brown solid product was dissolved in a mixture (1:1) of dichloromethane:ethanol (10 ml), and then the solvent was removed *in vacuo*. The last step was repeated, and the residue was dissolved in 2.5 ml of solvent mixture and then allowed to cool at  $-18^{\circ}\text{C}$  overnight. Dark-brown microcrystals were filtered off, washed with cold ethanol and diethyl ether and then dried *in vacuo* (0.27 g, 40.1%), m.p.  $282^{\circ}\text{C}$  (dec.).  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  16.50 (s, 2H, O-HO), 9.11 (s, 4H, NH), 7.84–7.46 (m, 6H, Ar-H), 7.34–6.83 (m, 14H, Ar-H), 5.28 (s, 4H, NH), 4.25 (s, 8H,  $\text{CH}_2\text{-N}$ ), 3.82–3.10 (m, 32H,  $\text{CH}_2\text{OCH}_2$ ). IR (KBr): 3380 (N-H), 3076 (Ar-H), 2920 (C-H), 1892 (NO), 1711 (O-HO), 1628 (C=N), 1320–1270 (Ar-H), 1180–1135 ( $\text{CH}_2\text{OCH}_2$ ), 932 (N-O)  $\text{cm}^{-1}$ . Mass spectrum (FAB positive):  $m/z = 1368$  [ $M+\text{H}_2\text{O}+2$ ]<sup>+</sup>, 1313 [ $M\text{-Cl}$ ]<sup>+</sup>. Found: C, 53.16; H, 5.00; N, 13.25. Calc. for  $\text{C}_{60}\text{H}_{70}\text{N}_{13}\text{O}_{15}\text{RuCl}$ : C, 53.39; H, 5.19; N, 13.49.

*Extraction measurements.* The chloroform solution (30 ml) carrying 7 ( $4.0 \times 10^{-4}$  M) was shaken with aqueous solution (30 ml) containing alkali-metal picrates ( $2.0 \times 10^{-4}$  M) for 4 h at  $25 \pm 0.1^{\circ}\text{C}$  in a constant-temperature circulator. The concentration of alkali-metal picrates were determined spectrometrically at  $\lambda_{\text{max}} = 353$  nm.

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