Syntheses of *NN'*-Bis(4'-benzo[15-crown-5])diaminoglyoxime † and its Complexes with Copper(II), Nickel(II), Cobalt(II), Cobalt(III), Palladium(II), Platinum(II), and Uranyl(VI)

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NN'-Bis(4'-benzo[15-crown-5])diaminoglyoxime (H_2L) has been prepared as a bis(sodium chloride) salt from *anti*-dichloroglyoxime, 4'-aminobenzo[15-crown-5], and sodium bicarbonate in ethanol. Copper(II), nickel(II), and cobalt(II) complexes of $H_2L{\cdot}2NaCl$ have a metal–ligand ratio of 1 : 2 and the ligand co-ordinates through the two N atoms, as do most of the *vic*-dioximes. $[Pt(HL)_2{\cdot}4NaClO_4]$ and $[Pd(HL)_2{\cdot}4NaClO_4]$ complexes form six-membered chelate rings and co-ordinate through N and O atoms. $[Co(HL)_2(L')Cl{\cdot}4NaClO_4]$ has been prepared with L' = triphenylphosphine or pyridine, together with a chloride ion, as axial ligands. $H_2L{\cdot}2NaX$ ($X = Cl^-$ or ClO_4^-) reacts with $UO_2(O_2CMe)_2{\cdot}2H_2O$ to give complexes with a metal–ligand ratio of 1 : 1. All these complexes are soluble in water; n.m.r., i.r., and u.v.–visible data are presented.

Transition metal complexes of crown ethers which have functional groups such as tertiary phosphine,[1] olefin,[2] nitrile, mono-oxime,[3] and azomethine [4] have been reported. The interesting aspect of these complexes is that they have in the same molecule the features of both transition metal chemistry and crown ether chemistry.

In our previous papers, we have studied the structures of various transition metal complexes of diaminoglyoxime.[5,6] The *amphi* and *anti* stereoisomers and complexes of two new α-dioximes, namely 2,3-bis(hydroxyimino)-1,4-diphenylpiperazine [7] and 4,5-bis(hydroxyimino)-1,3-diphenyl-2-thioxoimidazoline [8] have been isolated and the interconversion of *anti* and *amphi* complexes has been studied. Transition metal complexes of 5,6-dihydrocyclopent[*f*,*g*]acenaphthylene-1,2-dione dioxime,[9] acenaphthylene-1,2-dione dioxime,[10] and some new substituted mono- and di-aminoglyoximes [11] have been investigated.

It would be interesting to investigate the effect of the crown ether on the isomerism and complex formation of the *vic*-dioximes. In the present paper, we describe the synthesis of a new *vic*-dioxime with two macrocyclic ether groups in the same molecule and its complexes with various metal salts.

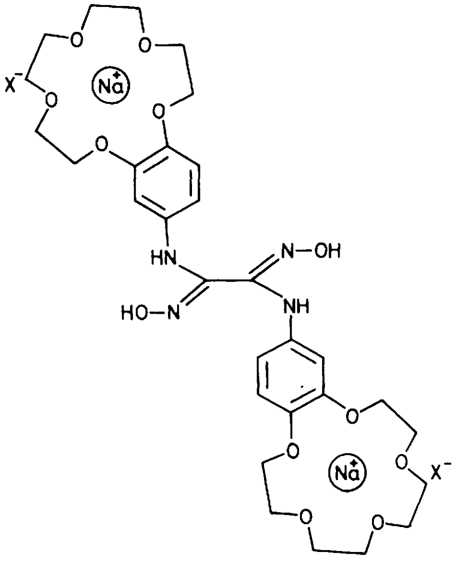

Figure 1. Structure of $H_2L{\cdot}2NaX$ ($X = Cl^-$ or ClO_4^-)

Results and Discussion

By a method similar to that for *NN'*-diphenyldiaminoglyoxime,[12] *NN'*-bis(4'-benzo[15-crown-5])diaminoglyoxime (H_2L) was prepared by the reaction of 4'-aminobenzo[15-crown-5] with *anti*-dichloroglyoxime. Since $NaHCO_3$ was added into the reaction mixture in order to neutralize HCl formed during the reaction, NaCl was produced as a by-product and it complexed with the crown ether groups; therefore the ligand was obtained as a bis(sodium chloride) salt, $H_2L{\cdot}2NaCl$. No further attempt was made to isolate the free ligand, since $H_2L{\cdot}2NaCl$ could be used to prepare the transition metal complexes.

The high stability of the alkali metal complexes of crown ethers [13] has been confirmed during this work, since the alkali metal complex did not change during the synthesis of the transition metal complexes, and by adding a ' proper ' anion (in this case, perchlorate) the new compounds could be precipitated.

In the i.r. spectrum, characteristic absorption bands due to $NaClO_4$ are present at 1 050—1 150 (broad band) and 630—640 cm^{-1} (doublet), both in $H_2L{\cdot}2NaClO_4$ and in the complexes which contain $NaClO_4$.

The structure of diaminoglyoxime has been determined to be the *s-trans* form by ^1H n.m.r. data [14] and *X*-ray structural analysis.[5] For $H_2L{\cdot}2NaX$ (where $X = Cl^-$ or ClO_4^-), a similar structure can be proposed (Figure 1).

In the i.r. spectra of $H_2L{\cdot}2NaX$, OH stretching vibrations are observed at 3 260 cm^{-1} as a broad absorption. Bands due to OH deformation and C=N and N–O stretches are at 1 420, 1 640, and *ca.* 940 cm^{-1} respectively; these absorptions are in agreement with those previously reported for diaminoglyoxime derivatives.[7,8] In the ^1H n.m.r. spectrum of $H_2L{\cdot}2NaClO_4$, the chemical shifts for OH and NH protons are observed at 10.2 and 8.2 p.p.m. respectively. In addition to these two bands, which disappear by deuterium exchange, two multiplets at 3.7—3.4 and 6.9—6.3 p.p.m. correspond to ethereal (CH_2–CH_2–O) and aromatic protons.[15,16]

The reaction of $H_2L{\cdot}2NaX$ with Ni^{II}, Cu^{II}, Co^{II}, Co^{III}, Pt^{II}, Pd^{II}, and $U^{VI}O_2$ salts gives products with metal–ligand ratios of 1 : 2 or 1 : 1.

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† 1,2-Bis(hydroxyimino)-1,2-bis(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-ylamino)ethane.

Table 1. Melting points and analytical data for the *vic*-dioxime and its complexes

Compound	M.p./°C	Analysis (%)[a] C[b]	H[b]	N[b]	Cl[b]	Na[c]	Metal[c]
$H_2L{\cdot}2NaCl$	102	46.75	5.4	7.25	9.2	6.1	—
		(46.95)	(5.45)	(7.3)	(9.25)	(6.0)	
$H_2L{\cdot}2NaClO_4$	140	40.05	4.6	6.2	7.85	5.25	—
		(40.2)	(4.7)	(6.25)	(7.95)	(5.15)	
$[Ni(HL)_2{\cdot}4NaClO_4]$	251[d]	39.1	4.4	6.05	7.65	4.9	3.1
		(39.0)	(4.45)	(6.05)	(7.7)	(5.0)	(3.15)
$[Cu(HL)_2{\cdot}4NaClO_4]$	242[d]	38.7	4.4	6.0	7.6	4.9	3.4
		(38.9)	(4.45)	(6.05)	(7.65)	(4.95)	(3.45)
$[Co(HL)_2{\cdot}4NaClO_4]$	148[d]	39.15	4.4	6.15	7.6	4.85	3.1
		(39.0)	(4.45)	(6.05)	(7.7)	(5.0)	(3.15)
$[Co(HL)_2(PPh_3)Cl{\cdot}4NaClO_4]$	193[d]	43.45	4.5	5.15	8.15	4.2	2.7
		(43.65)	(4.5)	(5.2)	(8.3)	(4.3)	(2.75)
$[Co(HL)_2(C_5H_5N)Cl{\cdot}4NaClO_4]$	188[d]	39.6	4.4	6.4	8.95	4.6	2.95
		(39.75)	(4.45)	(6.4)	(9.05)	(4.7)	(3.0)
$[Pd(HL)_2{\cdot}4NaClO_4]$	183[d]	38.1	4.4	6.2	7.4	4.65	5.5
		(38.0)	(4.35)	(5.9)	(7.5)	(4.85)	(5.6)
$[Pt(HL)_2{\cdot}4NaClO_4]$	185[d]	36.1	4.2	5.75	7.1	4.55	9.75
		(36.3)	(4.15)	(5.65)	(7.15)	(4.65)	(9.85)
$[\{UO_2(HL)(OH)\}_2{\cdot}4NaClO_4]$	257[d]	30.4	3.65	4.8	5.9	3.8	20.05
		(30.5)	(3.55)	(4.75)	(6.0)	(3.9)	(20.15)
$[\{UO_2(HL)(OH)\}_2{\cdot}4NaCl]$	248[d]	33.95	3.9	5.25	6.6	4.25	22.4
		(34.15)	(4.0)	(5.3)	(6.75)	(4.35)	(22.6)

[a] Calculated values are in parentheses. [b] Elemental analyses were performed at the University of Basel (Switzerland) and at the University of Heidelberg (W. Germany). [c] Analyses performed using an atomic absorption spectrophotometer. [d] With decomposition.

Table 2. Hydrogen-1 n.m.r. spectral data for the *vic*-dioxime and its complexes[a]

Compound[b]	$O \cdots H{-}O$	$N{-}OH$[c]	NH[c]	*H* aromatic	$\overset{H^{c}}{/O\backslash}$	$CH_2{-}O$
$H_2L{\cdot}2NaClO_4$	—	10.2s (2 H)	8.2s (2 H)	6.9—6.3m (6 H)	—	3.7—3.4m (32 H)
$[Ni(HL)_2{\cdot}4NaClO_4]$	16.2s (2 H)	—	8.2s (4 H)	6.9—6.3m (12 H)	—	3.65—3.4m (64 H)
$[Pd(HL)_2{\cdot}4NaClO_4]$	—	9.2s (2 H)	8.1s (4 H)	7.0—6.3m (12 H)	—	3.65—3.4m (64 H)
$[Pt(HL)_2{\cdot}4NaClO_4]$	—	9.2s (2 H)	8.1s (4 H)	7.0—6.3m (12 H)	—	3.7—3.5m (64 H)
$[\{UO_2(HL)(OH)\}_2{\cdot}4NaClO_4]$	—	10.7s (1 H)	8.3s (2 H)	7.0—6.3m (12 H)	3.8s (2 H)	3.65—3.4m (64 H)
		10.3s (1 H)	7.9s (2 H)			

[a] In [$^2H_6$]dimethyl sulphoxide at 25 °C. [b] H_2L = *NN′*-bis(4′-benzo[15-crown-5])diaminoglyoxime. [c] Disappears on D_2O exchange; s = singlet, m = multiplet.

$[Cu(HL)_2{\cdot}4NaClO_4]$, $[Ni(HL)_2{\cdot}4NaClO_4]$, *and* $[Co(HL)_2{\cdot}4NaClO_4]$.—As is the case for most *anti*-dioximes, H_2L forms complexes with Cu^{II}, Co^{II}, and Ni^{II} with a metal–ligand ratio of 1 : 2. The i.r. spectra of the complexes exhibit ν(C=N) absorptions at 1 610 cm^{-1} for Cu^{II} and Co^{II} and at 1 570 cm^{-1} for Ni^{II}. These values are lower than the value for the free ligand (1 640 cm^{-1}). This suggests that the HL^- ligand is *NN′*-co-ordinated to Cu^{II}, Co^{II}, and Ni^{II}.[17] The weak bands at 1 720 cm^{-1} in the i.r. spectra of Cu^{II}, Co^{II}, and Ni^{II} complexes can be ascribed to the intramolecular hydrogen bridge OH bending vibrations.[17] Disappearance of the δ(OH) band at 1 420 cm^{-1} which was present in the ligand is further evidence for O–H–O bond formation. As expected for a d^8 configuration in a square-planar field, the Ni^{II} complex is diamagnetic according to the n.m.r. spectrum. In the n.m.r. spectra of similar Ni^{II} complexes, the NH proton has been observed at 7.9 p.p.m. and intramolecular bridging OH protons have been shifted to 16.2 p.p.m.[17,18]

$[Co(HL)_2(L')Cl{\cdot}4NaClO_4]$ (L′ = *triphenylphosphine or pyridine*).—The cobalt(III) complexes were prepared similarly to the complexes of dimethylglyoxime,[19] 5,6-dihydrocyclopent-[*f*,*g*]acenaphthylene-1,2-dione dioxime,[9] and acenaphthylene-1,2-dione dioxime[10] reported previously. The triphenylphosphine and pyridine ligands are co-ordinated axially to the metal in these octahedral complexes (Figure 2). In these complexes, the weak band assigned to the intramolecular hydrogen-bonded OH bending vibration was observed at 1 720 cm^{-1}. The ν(C=N) bands due to the oxime groups and pyridine were observed as a combined band at 1 570 cm^{-1}. When L′ = triphenylphosphine, the ν(Co–P) band appeared at 520 cm^{-1}.[20]

$[Pt(HL)_2{\cdot}4NaClO_4]$ *and* $[Pd(HL)_2{\cdot}4NaClO_4]$.—These two complexes were prepared in a similar way from $PdCl_2$ and $PtCl_2$ in ethanol. Sodium chloride was used to dissolve the two chlorides as $Na_2[PdCl_4]$ and $Na_2[PtCl_4]$. Since $Na_2[PtCl_4]$ is not stable in ethanol, $H_2L{\cdot}2NaCl$ was added simultaneously with the metal salt. Even though they have the same metal–ligand ratio, $H_2L{\cdot}2NaX$ complexes of Pt^{II} and Pd^{II} are co-ordinated differently to Cu^{II} and Ni^{II}. The ^1H n.m.r. spectra of the Pd^{II} and Pt^{II} complexes show that both NH and OH protons are present in the complexes. Even though NH protons are not affected by complex formation, the OH signals are shifted to 9.2 p.p.m. and the integral curve shows a 1 : 2 ratio for OH : NH. Since the formation of O–H ··· O bonds results in a shift to lower field, the ligand should form a six-membered chelate ring by co-ordinating to Pd or Pt through the N and O atoms as shown in Figure 3.

This type of co-ordination is more usual in *amphi*-dioximes

Table 3. Characteristic i.r. bands (cm^{-1}) of the *vic*-dioxime and its complexes (KBr pellets)

Compound	ν(N–H)	ν(O–H)	δ(OH · · · O)	ν(C=N)	δ(N–H)	δ(O–H)
$H_2L\cdot2NaCl$	3 420	3 260	—	1 640	1 610	1 420
$H_2L\cdot2NaClO_4$	3 420	3 260	—	1 640	1 610	1 420
$[Ni(HL)_2\cdot4NaClO_4]$	3 420	—	1 720	1 570	1 610	—
$[Cu(HL)_2\cdot4NaClO_4]$	3 430	—	1 720	1 610	1 600	—
$[Co(HL)_2\cdot4NaClO_4]$	3 420	—	1 720	1 610	1 600	—
$[Co(HL)_2(PPh_3)Cl\cdot4NaClO_4]$	3 430	—	1 720	1 620	1 610	—
$[Co(HL)_2(C_5H_5N)Cl\cdot4NaClO_4]$	3 410	—	1 720	1 570	1 600	—
$[Pd(HL)_2\cdot4NaClO_4]$	3 420	3 260	—	1 630 1 570	1 600	1 420
$[Pt(HL)_2\cdot4NaClO_4]$	3 415	3 260	—	1 640 1 570	1 600	1 420
$[\{UO_2(HL)(OH)\}_2\cdot4NaClO_4]$	3 420	3 260	—	1 640	1 610	1 420
$[\{UO_2(HL)(OH)\}_2\cdot4NaCl]$	3 420	3 260	—	1 640	1 610	1 420

Compound	ν($C_{aromatic}$–O–C)	δ(C–O–C)	ν(N–O)	ClO_4
$H_2L\cdot2NaCl$	1 245—1 225	1 130—1 040	942	—
$H_2L\cdot2NaClO_4$	1 245—1 230	1 150—1 050	940	1 150—1 050, 640—630
$[Ni(HL)_2\cdot4NaClO_4]$	1 245—1 230	*	940	1 150—1 050, 640—630
$[Cu(HL)_2\cdot4NaClO_4]$	1 250—1 220	*	940	1 150—1 050, 640—630
$[Co(HL)_2\cdot4NaClO_4]$	1 260—1 225	*	940	1 150—1 050, 640—630
$[Co(HL)_2(PPh_3)Cl\cdot4NaClO_4]$	1 260—1 225	*	940	1 150—1 050, 640—630
$[Co(HL)_2(C_5H_5N)Cl\cdot4NaClO_4]$	1 260—1 225	*	940	1 150—1 050, 640—630
$[Pd(HL)_2\cdot4NaClO_4]$	1 260—1 225	*	940	1 150—1 050, 640—630
$[Pt(HL)_2\cdot4NaClO_4]$	1 260—1 225	*	940	1 150—1 050, 640—630
$[\{UO_2(HL)(OH)\}_2\cdot4NaClO_4]$	1 245—1 225	*	940	1 150—1 050, 640—630
$[\{UO_2(HL)(OH)\}_2\cdot4NaCl]$	1 250—1 225	1 130—1 040	943	—

* C–O–C vibrations are screened by ClO_4 vibrations.

and in the Ni^{II} complex of δ-camphorquinone dioxime the unco-ordinated –OH protons show a chemical shift of 0.5 p.p.m. to higher field.[18] The weakening of the δ(OH) band at 1 425 cm^{-1} and the appearance of another C=N stretching vibration at 1 570 cm^{-1} also confirm the proposed structure.[17]

The u.v.–visible absorption spectra of $[Pd(HL)_2\cdot4NaClO_4]$ and $[Pt(HL)_2\cdot4NaClO_4]$ in *NN*-dimethylformamide (dmf) show a broad absorption at 372 (ε = 20 644) and 407 nm (ε = 18 838 $dm^3\ mol^{-1}\ cm^{-1}$) respectively; these bands are most likely due to charge transfer.

$[\{UO_2(HL)(OH)\}_2\cdot4NaX]$.—These diamagnetic complexes of $U^{VI}O_2$ were prepared from both $H_2L\cdot2NaCl$ and $H_2L\cdot2NaClO_4$. They are slightly soluble in ethanol even in the case of the NaCl salt. The uranyl complex can be precipitated also in water when excess of sodium perchlorate is added to the solution.

Hydrogen-1 n.m.r. spectra of the complexes show two chemical shifts for N–OH protons (10.7 and 10.3 p.p.m.) and NH protons (8.3 and 7.9 p.p.m.). The ratio of NOH : NH in the integral curve is 1 : 2. This splitting is attributed to the magnetic anisotropy of the uranyl ion as discussed in relation to some carboxylate and amine complexes.[21] It is known that uranyl ion enhances the chemical shift difference between non-equivalent protons. This effect is equivalent to increasing the ^1H n.m.r. observing frequency by a few orders of magnitude.[22] There is also another D_2O exchangeable shift at 4.1 p.p.m. (2 H) which can be assigned to hydroxo-protons co-ordinated to uranyl ions. Consequently, the ^1H n.m.r. data enable us to propose a hydroxo-bridged uranyl(VI) dimer similar to $[(NO_3)_2UO_2(OH)_2UO_2(H_2O)_3]\cdot H_2O$.[23]

The i.r. spectrum is also consistent with the structure in Figure 4. A strong band around 905 cm^{-1} is the characteristic frequency for ν(O=U=O) vibrations.[24] The electronic spectrum shows a strong absorption at 410 nm which is assigned to a charge-transfer transition from the *p*π orbital of the donor atoms to the 5*f* and 6*d* orbitals of uranium. Elemental analysis results also confirm the structure shown in Figure 4.

In concluding this paper, the extraordinary solubility of these complexes in water and in most other common solvents, especially when sodium chloride is the salt complexed in the crown ether moiety, should be mentioned. This property opens new ways to investigate the complexes of *vic*-dioximes, *e.g.* preparation of Co–alkyl derivatives through the reduction of $[Co(HL)_2(L')Cl\cdot4NaCl]$ into Co^I complexes[9,10] and the possibility of transition metal transfer through the membranes by using H_2L as the complexing agent are the topics of continuing research in this laboratory.

The elemental analysis results, and ^1H n.m.r. and i.r. spectral data are given in Tables 1—3 respectively.

Experimental

Infrared spectra were obtained on a Perkin-Elmer 598 spectrophotometer in KBr pellets. The ^1H n.m.r. spectra were recorded on a Varian T60-A spectrometer. The u.v.–visible

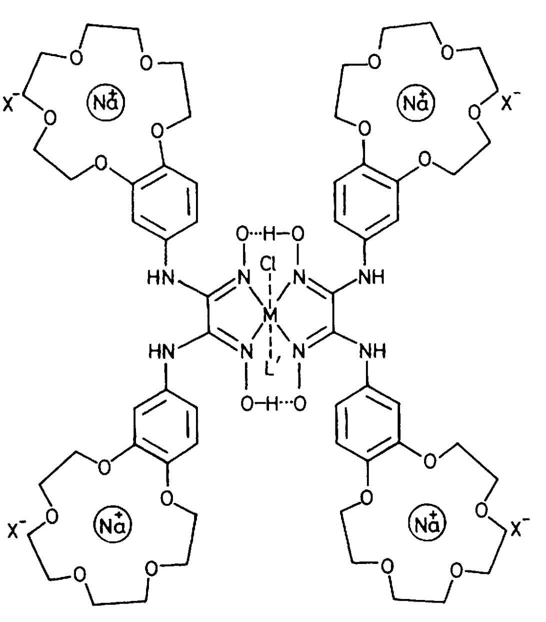

Figure 2. Structure of $[M(HL)_2{\cdot}4NaX]$ (M = Ni^{II}, Cu^{II}, or Co^{II}; X = ClO_4^-) and $[Co(HL)_2(L')Cl{\cdot}4NaX]$ (L′ = C_5H_5N or PPh_3)

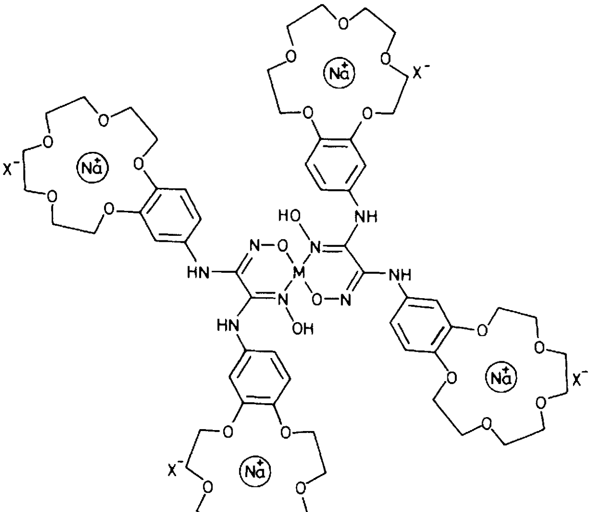

Figure 3. Structure of $[M(HL)_2{\cdot}4NaX]$ (M = Pd^{II} or Pt^{II}; X = ClO_4^-)

spectra were recorded on a Varian Techtron 635 spectrometer. Benzo[15-crown-5],[16] 4′-nitrobenzo[15-crown-5],[15] and 4′-aminobenzo[15-crown-5] [15,25] were prepared according to the published methods.

Bis(sodium chloride) Salt of NN′-*Bis*(4′-*benzo*[15-*crown*-5])-*diaminoglyoxime*, $H_2L{\cdot}2NaCl$.—A solution of *anti*-dichloroglyoxime (1.26 g, 8 mmol) in absolute ethanol (10 cm^3) was added to a solution of 4′-aminobenzo[15-crown-5] (4.53 g, 16 mmol) in absolute ethanol (50 cm^3) which also contained solid $NaHCO_3$ (5 g) and solid NaCl (1 g). The mixture was stirred efficiently and heated on a water-bath at *ca.* 60—65 °C for 1.5 h. After cooling to room temperature, the mixture was filtered and washed with ethanol (20 cm^3). The filtrate was cooled to 0 °C and $H_2L{\cdot}2NaCl$ was precipitated by addition of diethyl ether with continuous stirring. The cream-coloured precipitate was filtered off, washed with diethyl ether, and dried. Yield, 4.19 g (66.8%). U.v.–visible (ethanol): 213 (ε = 17 641), aromatic *E* band; 260 (ε = 14 670), aromatic *K* band; 272 (ε = 11 505), aromatic *B* band; 290 nm (ε = 8 725 dm^3 mol^{-1} cm^{-1}), n $\longrightarrow$ π^* (shoulder).

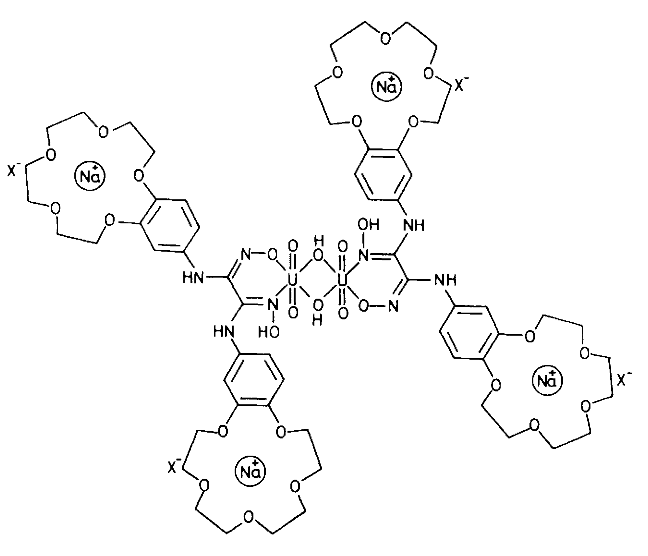

Figure 4. Structure of $[\{UO_2(HL)(OH)\}_2{\cdot}4NaX]$ (X = Cl^- or ClO_4^-)

Bis(sodium perchlorate) Salt of NN′-*Bis*(4′-*benzo*[15-*crown*-5])*diaminoglyoxime*, $H_2L{\cdot}2NaClO_4$.—$H_2L{\cdot}2NaCl$ (0.5 g) was dissolved in ethanol (50 cm^3) and solid $NaClO_4$ (1.0 g, excess) was added to this cooled (−5 °C) and stirred solution. The clear solution was left overnight at −5 °C and the cream-coloured precipitate filtered off, washed first with ethanol saturated with $NaClO_4$ and then with cold ethanol and dried with diethyl ether. Yield, 305 mg (52%). U.v.–visible (ethanol): 214 (ε = 21 256), aromatic *E* band; 260 (ε = 18 348), aromatic *K* band; 272 (ε = 17 228), aromatic *B* band; 290 (ε = 10 740 dm^3 mol^{-1} cm^{-1}), n $\longrightarrow$ π^* (shoulder).

$[Ni(HL)_2{\cdot}4NaClO_4]$, $[Co(HL)_2{\cdot}4NaClO_4]$, *and* $[Cu(HL)_2{\cdot}4NaClO_4]$.—A solution of 0.5 mmol of metal salt [$NiCl_2{\cdot}6H_2O$ (119 mg), $CoCl_2{\cdot}6H_2O$ (119 mg), or $CuCl_2{\cdot}2H_2O$ (86 mg)] in ethanol (10 cm^3) was added to a solution of $H_2L{\cdot}2NaCl$ (767 mg, 1 mmol) in ethanol (30 cm^3). While heating this mixture (60 °C) NaOH (0.1 mol dm^{-3}, 10 cm^3) was added. The clear solution was cooled to room temperature and a saturated solution of $NaClO_4$ was added until complete precipitation took place. The precipitate was filtered off, washed with ethanol, and then dried with diethyl ether. Orange-red $[Ni(HL)_2{\cdot}4NaClO_4]$: yield, 780 mg (85%). U.v.–visible (ethanol): 210 (ε = 39 680), aromatic *E* band; 245 (ε = 32 579), aromatic *K* band; 263 (ε = 31 744), aromatic *B* band; 285 (ε = 28 402), n $\longrightarrow$ π^* (shoulder); 380 nm (ε = 20 257 dm^3 mol^{-1} cm^{-1}), charge transfer. Dark green $[Cu(HL)_2{\cdot}4NaClO_4]$: yield, 590 mg (63%). U.v.–visible (ethanol): 208 (ε = 40 841), aromatic *E* band; 247 (ε = 38 320), aromatic *K* band; 272 (ε = 33 782), aromatic *B* band; 287 (ε = 33 025), n $\longrightarrow$ π^* (shoulder); 460 nm (ε = 7 058 dm^3 mol^{-1} cm^{-1}), charge transfer. Dark brown $[Co(HL)_2{\cdot}4NaClO_4]$: yield, 730 mg (80%). U.v.–visible (ethanol): 210 (ε = 40 530), aromatic *E* band; 248 (ε = 37 810), aromatic *K* band; 270 (ε = 32 110), aromatic *B* band; 290 nm (ε = 32 050 dm^3 mol^{-1} cm^{-1}), n $\longrightarrow$ π^* (shoulder).

$[Co(HL)_2(L')Cl{\cdot}4NaClO_4]$.—A solution of $CoCl_2{\cdot}6H_2O$

(120 mg, 0.5 mmol) in ethanol (10 cm^3) was added into a solution of $H_2L\cdot2NaCl$ (767 mg, 1 mmol) in ethanol (30 cm^3). The ligand L′ [pyridine (240 mg) or triphenylphosphine (810 mg)] in ethanol (10 cm^3) was added. Air was bubbled through the solution for 1 h, and it became reddish brown. This solution was treated with a saturated solution of $NaClO_4$ in ethanol until precipitation was complete. The dark brown precipitate was filtered off, washed with cold ethanol, and dried with diethyl ether. $[Co(HL)_2(C_5H_5N)Cl\cdot4NaClO_4]$: yield, 620 mg (63.2%). U.v.–visible (ethanol): 210 (ε = 42 430), aromatic *E* band; 245 (ε = 32 310), aromatic *K* band; 267 (ε = 26 470), aromatic *B* band; 290 nm (ε = 23 356 $dm^3\ mol^{-1}\ cm^{-1}$), $n \longrightarrow \pi^*$ (shoulder). $[Co(HL)_2(PPh_3)Cl\cdot4NaClO_4]$: yield, 670 mg (62%). U.v.–visible (ethanol): 210 (ε = 45 610), aromatic *E* band; 250 (ε = 27 566), aromatic *K* band; 272 (ε = 25 060), aromatic *B* band; 288 nm (ε = 22 053 $dm^3\ mol^{-1}\ cm^{-1}$), $n \longrightarrow \pi^*$ (shoulder).

$[Pd(HL)_2\cdot4NaClO_4]$.—A mixture of $PdCl_2$ (88 mg, 0.5 mmol) and NaCl (59 mg, 1 mmol) in ethanol (50 cm^3) was stirred at 70 °C until $PdCl_2$ dissolved completely. A solution of H_2L (767 mg, 1 mmol) in ethanol (20 cm^3) was added into this $Na_2[PdCl_4]$ solution. Heating was continued for 1 h and the solution filtered. The filtrate was cooled to room temperature and then precipitated with a saturated solution of $NaClO_4$ in ethanol. The yellow precipitate was filtered off, washed with a saturated solution of $NaClO_4$ in ethanol, ethanol, and diethyl ether, and dried with diethyl ether. Yield, 720 mg (76%). U.v.–visible (ethanol): 210 (ε = 39 685), aromatic *E* band; 245 (ε = 25 927), aromatic *K* band; 272 (ε = 22 224), aromatic *B* band; 290 (ε = 19 049), $n \longrightarrow \pi^*$ (shoulder); 370 nm (ε = 16 932 $dm^3\ mol^{-1}\ cm^{-1}$), charge transfer.

$[Pt(HL)_2\cdot4NaClO_4]$.—This complex was prepared as $[Pd(HL)_2\cdot4NaClO_4]$. The only difference was the addition of $PtCl_2$ (135 mg, 0.5 mmol), NaCl (59 mg, 1 mmol), and $H_2L\cdot2NaCl$ (767 mg, 1 mmol) at the same time. The reaction period was 3 h. Yield, 560 mg (56.4%); the product was orange. U.v.–visible (ethanol): 213 (ε = 38 405), aromatic *E* band; 245 (ε = 33 862), aromatic *K* band; 270 (ε = 25 603), aromatic *B* band; 287 (ε = 22 298), $n \longrightarrow \pi^*$ (shoulder); 403 nm (ε = 24 984 $dm^3\ mol^{-1}\ cm^{-1}$), charge transfer.

$[\{UO_2(HL)(OH)\}_2\cdot4NaClO_4]$.—A solution of $UO_2(O_2CMe)_2\cdot2H_2O$ (212 mg, 0.5 mmol) in ethanol (20 cm^3) was added to a solution of $H_2L\cdot2NaX$ [X = Cl^- (383 mg) or ClO_4^- (450 mg)] in ethanol (30 cm^3). The brick-red complex precipitated immediately. The precipitate was filtered off, washed with ethanol and diethyl ether, and dried with diethyl ether. When this reaction was carried out in water, excess sodium perchlorate was added to the aqueous solution to precipitate the complex. $[\{UO_2(HL)(OH)\}_2\cdot4NaCl]$: yield, 440 mg (85%). U.v.–visible (ethanol): 208 (ε = 31 028), aromatic *E* band; 259 (ε = 35 461), aromatic *K* band; 270 (ε = 28 812), aromatic *B* band; 288 (ε = 20 500), $n \longrightarrow \pi^*$ (shoulder); 410 nm (ε = 6 095 $dm^3\ mol^{-1}\ cm^{-1}$) (in dmf), charge transfer. $[\{UO_2(HL)(OH)\}_2\cdot4NaClO_4]$: yield, 520 mg (90%). U.v.–visible (ethanol): 209 (ε = 30 691), aromatic *E* band: 258 (ε = 34 830), aromatic *K* band; 272 (ε = 29 312), aromatic *B* band; 287 (ε = 21 036), $n \longrightarrow \pi^*$ (shoulder); 410 nm (ε = 6 207 $dm^3\ mol^{-1}\ cm^{-1}$) (in dmf), charge transfer.

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