Synthesis and Characterization of a Crown-ether Substituted Salicylaldimine Schiff-base Ligand and its Complexes with Cobalt(II), Copper(II), Nickel(II), and Uranyl(VI)

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15-Formyl-16-hydroxy-2,3,5,6,8,9,11,12-octahydrobenzo[1,4,7,10,13]pentaoxacyclopentadecine (HA) has been synthesised from the corresponding 15-hydroxy substituted crown ether and hexamethylenetetramine in trifluoroacetic acid. Condensation of HA with 1,2-diaminoethane gives the corresponding bis(crown ether) substituted ethylenebis(salicylideneimine) ligand (H_2L). Metal–ligand (1 : 1) complexes of this Schiff base with cobalt(II), copper(II), nickel(II), and uranyl(VI) have been prepared from the corresponding metal acetates. Insertion of sodium ions into the crown ether has been accomplished by refluxing H_2L with sodium nitrate in ethanol. The μ-peroxo compound $[\{ML(dmso)\}_2(\mu\text{-}O_2)]$ (dmso = dimethyl sulphoxide) was obtained only for M = Co in dmso solution. The order of the formation constants of the complexes determined by the Calvin–Bjerrum pH-titration technique is as follows: [CuL] > [UO_2L] > [NiL] > [CoL].

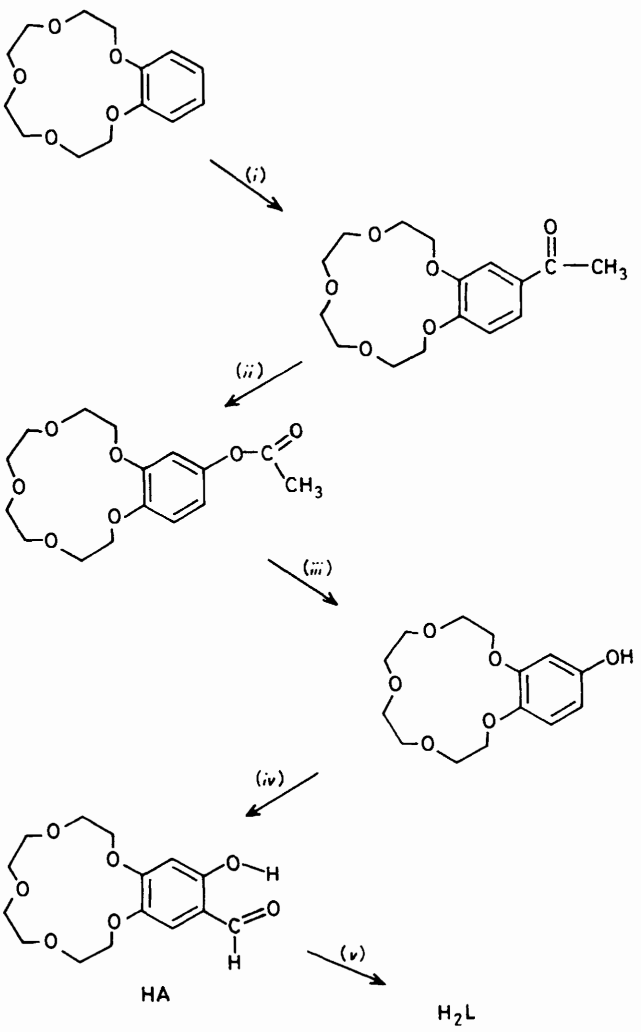
Recently, crown ether groups have been extensively employed to construct new compounds with extraordinary properties; ion channels formed by the superposition of crown ether macrocycles in tetrakis(crown ether) substituted phthalocyanines[1] or the agglomeration of phthalocyanine units induced by alkali metal cations are two outstanding examples.[2–5] Bis(crown ether) Schiff-base ligands containing recognition sites for alkali and transition metal guest cations have been also reported.[6]

In the course of our investigations on the complexes of crown-ether substituted ligands *vic*-dioximes were found to give complexes soluble in common organic solvents.[7–10] The octahedral cobalt(II) complex of 4′,5′-bis(salicylideneimino)benzo-15-crown-5 {15,16-bis(salicylideneamino)-2,3,5,6,8,9,11,12-octahydrobenzo[1,4,7,10,13]pentaoxacyclopentadecine} was found to be capable of binding molecular oxygen.[11] The first crown-ether-containing phthalocyanines were also reported as a part of our research on co-ordination compounds having MN_4 cores.[1–3,12]

Hydroxyformyl substituted benzo-crown ethers are thought to be interesting starting materials because of the utility of the reactive groups on the aromatic ring. In this paper, we describe the synthesis and characterization of 4′-formyl-5′-hydroxybenzo-15-crown-5,† the Schiff-base derived from the related aldehyde and 1,2-diaminoethane, and its complexes with various transition metal ions. Furthermore we examined the formation constants of the complexes by potentiometric methods.

Results and Discussion

The route for the synthesis of 4′-formyl-5′-hydroxybenzo-15-crown-5 (HA) is given in the Scheme. The first step is the synthesis of 4′-hydroxybenzo-15-crown-5. Hydrolysis of the diazonium salt of 4′-aminobenzo-15-crown-5 in aqueous acid or in the presence of copper catalyst afforded mixtures too complex to isolate the desired product. Baeyer–Villiger oxidation of 4′-acetylbenzo-15-crown-5 followed by alkaline hydrolysis was proved to be a convenient route to 4′-hydroxybenzo-15-crown-5.[13]



Scheme. (*i*) Acetic acid in polyphosphoric acid; (*ii*) peracetic acid; (*iii*) aqueous KOH solution (3 mol dm^{-3}); (*iv*) hexamethylenetetramine in trifluoroacetic acid; (*v*) 1,2-diaminoethane in ethanol

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† 4′-Formyl-5′-hydroxybenzo-15-crown-5 (HA) = 15-formyl-16-hydroxy-2,3,5,6,8,9,11,12-octahydrobenzo[1,4,7,10,13]pentaoxacyclopentadecine; systematic numbering for substituents at positions referred to as 4′ and 5′ is 15 and 16 respectively.

Table 1. Analytical* and physical data for the ligands and metal complexes

			Analysis (%)				
Compound	Colour	Yield (%)	C	H	N	M	Na
HA	White	64	57.45 (57.70)	6.60 (6.40)			
$H_2L{\cdot}4H_2O$	Bright yellow	86	53.20 (53.35)	6.95 (7.20)	3.70 (3.90)		
$[CoL]{\cdot}3H_2O$	Claret red	79	50.70 (50.60)	6.05 (6.30)	3.40 (3.70)	7.60 (7.75)	
$[\{CoL(dmso)\}_2(\mu\text{-}O_2)]$	Black-brown	92	51.25 (51.05)	5.70 (6.00)	3.50 (3.50)	7.45 (7.40)	
$[CoL(dmf)_2]$	Black-brown	88	53.65 (53.60)	6.75 (6.60)	6.30 (6.60)	7.00 (6.95)	
$[CuL]{\cdot}H_2O$	Dark brown	75	52.35 (52.80)	6.20 (6.05)	4.00 (3.85)	8.85 (8.75)	
$[NiL]{\cdot}3H_2O$	Brown	70	50.20 (50.60)	6.10 (6.30)	3.50 (3.70)	7.95 (7.75)	
$[UO_2L]{\cdot}2H_2O$	Red	87	40.55 (40.35)	4.50 (4.85)	3.15 (2.95)	24.85 (25.00)	
$[CoL]{\cdot}2NaNO_3{\cdot}4H_2O$	Dark red	65	40.35 (40.55)	5.00 (5.30)	5.75 (5.90)	6.30 (6.25)	4.70 (4.85)
$[CuL]{\cdot}2NaNO_3{\cdot}4H_2O$	Greenish brown	68	40.55 (40.35)	5.45 (5.25)	5.65 (5.90)	6.55 (6.65)	4.75 (4.85)
$[NiL]{\cdot}2NaNO_3{\cdot}2H_2O$	Yellowish brown	61	42.55 (42.15)	5.35 (5.05)	6.05 (6.15)	6.60 (6.45)	4.90 (5.05)
$[UO_2L]{\cdot}2NaNO_3{\cdot}3H_2O$	Orange-red	80	33.15 (33.70)	4.10 (4.20)	4.65 (4.90)	21.00 (20.90)	4.10 (4.05)

* Required values are given in parentheses.

Table 2. Hydrogen-1 n.m.r. spectral data[a] for the ligands and metal complexes

Compound	-OH[b]	H-C=O	H-C=N	$H_{aromatic}$	$H_{aliphatic}$	H-OH
HA	10.78 (1 H, s)	9.95 (1 H, s)		7.16 (1 H, s) 6.51 (1 H, s)	4.11—3.63 (16 H, m)	
$H_2L{\cdot}4H_2O$	13.45 (1 H, s)		8.12 (1 H, s)	6.70 (1 H, s) 6.40 (1 H, s)	4.13—3.66 (18 H, m)	3.38 (4 H, s)
$[NiL]{\cdot}3H_2O$			7.61 (1 H, s)	6.75 (1 H, s) 6.20 (1 H, s)	3.97—3.60 (18 H, m)	3.33 (3 H, s)
$[UO_2L]{\cdot}2H_2O$			9.25 (1 H, s)	7.14 (1 H, s) 6.48 (1 H, s)	4.39—3.64 (18 H, m)	3.36 (2 H, s)
$[NiL]{\cdot}2NaNO_3{\cdot}2H_2O$			7.62 (1 H, s)	6.76 (1 H, s) 6.21 (1 H, s)	3.97—3.60 (18 H, m)	3.33 (2 H, s)
$[UO_2L]{\cdot}2NaNO_3{\cdot}3H_2O$			9.27 (1 H, s)	7.18 (1 H, s) 6.50 (1 H, s)	4.40—3.64 (18 H, m)	3.35 (3 H, s)

[a] Chemical shifts (δ) are reported in p.p.m. relative to $SiMe_4$ at 30 °C in $CDCl_3$; s = singlet, m = multiplet. [b] Disappears on D_2O exchange.

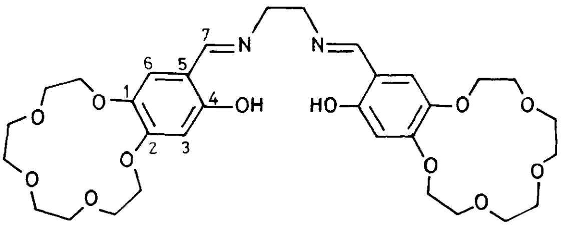

Figure 1. Structure of H_2L, showing the numbering for n.m.r. assignments. In the metal complexes [ML] (M = Co^{II}, Cu^{II}, Ni^{II}, or $U^{VI}O_2$) the metal is bonded through the nitrogen atoms and the deprotonated OH groups

Similar problems were encountered also for the introduction of the formyl group. Even though electrophilic substitution in general seemed to be promising for the synthesis of substituted benzo-15-crown-5, the reactions, especially those carried out under the catalysis of metal salts, resulted in the deactivation of the metal salts or complex reaction products due to the formation of crown ether complexes.[14,15] Formylation by Smith modification of the Duff reaction was found to be most promising because no inorganic reagent was required in the reaction.[16,17] Consequently, formylation of 4′-hydroxybenzo-15-crown-5 was accomplished with hexamethylenetetramine and trifluoroacetic acid.

The condensation of HA with 1,2-diaminoethane gave the ligand H_2L (Figure 1) as an N_2O_2 donor with two crown ether moieties. Colours, yields, and analytical data for the ligands and the metal complexes [ML] (M = Co^{II}, Cu^{II}, Ni^{II}, or $U^{VI}O_2$) are given in Table 1.

In the ^1H n.m.r. spectra of HA and H_2L, the OH protons appear as singlets at 10.78 and 13.45 p.p.m., respectively, which disappear by deuterium exchange; aldehyde and azomethine protons are observed at 9.95 and 8.12 p.p.m. (Table 2). There is almost no chemical shift difference between the ethereal protons of HA and H_2L. Carbon-13 n.m.r. shifts also confirm the structure shown for H_2L. This signal for the benzene carbon C^6 with *ortho*-C-N and -O-CH_2 substituents appears at 116.83 p.p.m. while the other carbon having a proton (C^3), with *ortho*-OH and -O–CH_2 substituents is seen at 101.73 p.p.m.[8] Proton-coupled spectra give a doublet for each of these carbons. The formation of an azomethine bond causes a shift from 193.90 p.p.m. in HA to 165.25 p.p.m. in H_2L for C^7 (Tables 2 and 3).

The O–H stretching absorptions of HA and H_2L did not appear as isolated bands in the i.r. spectra because of the hydrogen bridges formed with the aldehyde O atoms or azomethine N atoms. These bridges were observable as weak broad absorptions between 2 800 and 2 900 cm^{-1}, but they were screened in HA and H_2L by the strong C–H stretches of the crown ether groups[18] (Table 4).

Reaction of H_2L with the acetates of cobalt(II), copper(II), nickel(II), and uranyl(VI) gives products with metal:ligand ratios of 1:1. The insertion of alkali metal ions into the crown ether can be accomplished by refluxing H_2L with the alkali metal salt (*e.g.* $NaNO_3$) before the addition of the transition metal ion (Table 1).

Proton and ^{13}C n.m.r. spectra of the diamagnetic Ni^{II} and $U^{VI}O_2$ complexes are similar to those of H_2L (Tables 2 and 3).

Table 3. Carbon-13 n.m.r. spectral data * for the ligands and metal complexes

Compound	C^7	C^4	C^5	C^1	C^6	C^2	C^3	CH_2–O	CH_2–N
HA	193.90	159.69	157.76	142.36	117.37	113.01	100.75	71.01—68.37	
$H_2L·4H_2O$	165.25	159.39	154.20	141.66	116.83	110.69	101.73	71.03—68.40	59.39
	(166.37)	(159.39)	(154.20)	(141.66)	(118.92)	(110.69)	(103.12)	(73.61—65.15)	(61.35)
	(163.22)				(115.81)		(99.96)		(58.55)
									(55.81)
$[NiL]·3H_2O$	162.60	159.53	157.89	139.88	116.30	111.95	103.96	71.08—67.70	58.27
	(162.60)	(161.05)	(157.89)	(139.88)	(117.72)	(111.92)	(105.38)	(73.62—64.75)	
					(114.66)		(102.23)		(55.39)
$[UO_2L]·2H_2O$	166.99	166.23	156.00	139.75	119.52	115.09	104.08	70.32—67.80	63.88

* Chemical shifts (δ) are reported in p.p.m. relative to $SiMe_4$ at 30 °C in $CDCl_3$. The values in parentheses are ^1H coupled chemical shifts (Hz). Carbon atom numbering is given in Figure 1.

Table 4. Characteristic i.r. bands (cm^{-1}) of the ligands and metal complexes (KBr pellets)

Compound	H_2O	$CH_{aliphatic}$	NO_3	C=N	NO_3	C–O–$C_{aromatic}$	C–O–C	Others
HA	3 420	2 910, 2 860				1 280—1 230	1 130—1 040	1 635 (C=O)
$H_2L·4H_2O$	3 420	2 920, 2 860		1 625		1 300—1 225	1 125—1 040	
$[CoL]·3H_2O$	3 440	2 920, 2 870		1 610		1 280—1 230	1 130—1 060	
$[CuL]·H_2O$	3 420	2 900, 2 860		1 610		1 290—1 220	1 155—1 050	
$[NiL]·3H_2O$	3 440	2 910, 2 860		1 610		1 290—1 230	1 130—1 050	
$[UO_2L]·2H_2O$	3 420	2 910, 2 860		1 610		1 290—1 225	1 125—1 050	890(O=U=O)
$[CoL]·2NaNO_3·4H_2O$	3 420	2 910, 2 860	2 420	1 610	1 380	1 290—1 230	1 130—1 060	
$[CuL]·2NaNO_3·4H_2O$	3 420	2 920, 2 860	2 420	1 610	1 380	1 290—1 225	1 120—1 050	
$[NiL]·2NaNO_3·2H_2O$	3 420	2 910, 2 860	2 420	1 610	1 380	1 290—1 230	1 130—1 050	
$[UO_2L]·2NaNO_3·3H_2O$	3 420	2 910, 2 860	2 420	1 610	1 380	1 290—1 225	1 120—1 050	890(O=U=O)

One obvious difference is the disappearance of OH protons after complex formation. The magnetic anisotropy of the uranyl ion, as discussed in relation to some carboxylate, amine, and oxime complexes does not show any considerable effect in the uranyl complexes of H_2L.[7,19]

The i.r. spectra of the complexes (Table 4) show most ligand absorptions at the same frequencies except for the C=N stretches which are shifted slightly (*ca.* 15 cm^{-1}) to lower energy after complex formation. Similar shifts have been reported for the *NN′*-co-ordinated *vic*-dioxime complexes of various transition metal ions.[7,8,20] Lattice water absorptions are readily observed as broad bands around 3 420 cm^{-1} in the ligand and its complexes.[21] Characteristic O=U=O stretching vibrations are observed at 890 cm^{-1} for the uranyl complexes.[7,8] When sodium ion is inserted into the crown ether group in the transition metal complexes of H_2L, the stretching vibrations of the counter ion (*i.e.* 1 380 cm^{-1} for NO_3^-) show the most significant differences.

NN′-Ethylenebis(salicylideneiminato)cobalt(II), [Co(salen)], complexes have been investigated extensively[22–24] as chelates that can take up and release molecular oxygen reversibly since the synthesis of the complex by Pfeiffer *et al.* in 1933.[22b] Even though [CoL] is a close representative of the parent compound, [Co(salen)], with the addition of two crown ether units, we could not isolate any crystalline form of this compound which bound oxygen reversibly in the solid state.

The cobalt(II) oxygen carriers reported in the literature as oxygen-bridged dimeric species all exhibit little or no paramagnetism.[25] The complex [CoL] is paramagnetic ($\mu_{eff.}$ = 2.43), but the oxygen adduct of [CoL] obtained from its solution in dimethyl sulphoxide (dmso) is diamagnetic. Elemental analysis results indicate a μ-peroxo-complex with two solvent molecules, $[\{CoL(dmso)\}_2(\mu\text{-}O_2)]$. The role of the solvent molecule undoubtedly is to stabilize the Co–O bond by enabling octahedral co-ordination around the metal to be achieved upon oxygenation in solution. The O–O stretching vibration of the μ-peroxo complex cannot be seen due to the centrosymmetric structure of the molecule.[26] When dissolved in chloroform in order to obtain ^1H n.m.r. spectra, the diamagnetic compound quickly decomposes into paramagnetic species, as reported by Floriani and Calderazzo.[27] Even though dimethylformamide (dmf) was also recommended as a suitable solvent for oxygenation in solution, an octahedral complex with two solvent molecules, $[CoL(dmf)_2]$, was the only product isolated under similar conditions.[27]

Contrary to expectation, crown ether substitution on [Co(salen)] does not lead to a new molecule with enhanced molecular oxygen-binding properties, even though crown ether groups will increase the electron density of the nucleus. Steric effects should be taken into account since the addition of crown ether groups diminishes the planar structure of [Co(salen)]. Consequently, no oxygen binding property is observed for $[CoL]·2NaNO_3·4H_2O$.

The electronic spectra of the transition metal complexes in ethanol are very similar to that of H_2L except for the high intensity charge-transfer absorptions around 400 nm. Only in the case of $[CuL]·2NaNO_3·4H_2O$ a weak broad absorption around 550 nm (ε = 160 dm^3 mol^{-1} cm^{-1}), which can be assigned to a *d–d* transition, is observed.

As expected for a d^8 configuration in a square-planar field, the Ni^{II} complexes are diamagnetic, as are the uranyl complexes. The effective magnetic susceptibilities of [CuL] and $[CuL]·2NaNO_3·4H_2O$ closely follow the spin-only formula ($\mu_{eff.}$ = 1.80 and 1.83 respectively) while those of [CoL] ($\mu_{eff.}$ = 2.43) and $[CoL]·2NaNO_3·4H_2O$ ($\mu_{eff.}$ = 2.40) are higher than the calculated values for a d^7 structure but in accordance with the values reported for Co^{II} in square-planar complexes.[28]

An important feature of the complexes of H_2L is their solubility in common organic solvents as well as in water. This property prevented measurement of the alkali picrate extracting capability of crown ethers from water to organic solvents (*e.g.* chloroform).[2,3,10,12,29,30] The solubility of the metal complexes, on the other hand, enabled us to investigate their stability in water. For this purpose, the Calvin–Bjerrum pH-titration technique, as used by Banerjee and Dey,[31] has been applied to

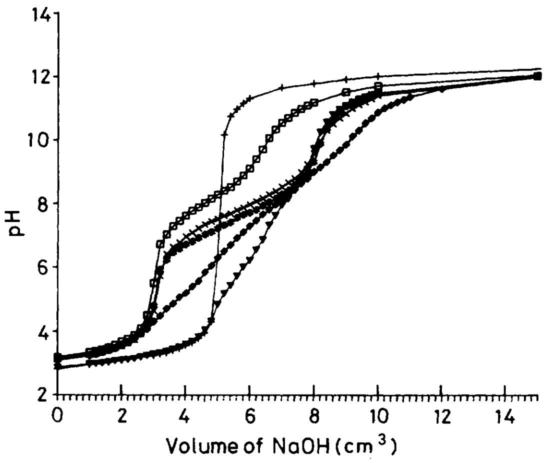

Figure 2. The titration curves of HCl (+), H_2L (□), [CoL] (×), [CuL] (▼), [NiL] (#), and $[UO_2L]$ (◆) with 0.1 mol dm^{-3} NaOH

Table 5. Protonation constants of the ligand H_2L at 25 °C (I = 0.1 mol dm^{-3} KCl)

Method	log K_{A1}	log K_{A2}	log K_{A3}	log K_{A4}	log β_4
Interpolation at half-$\bar{n}$ values	11.6	9.0	7.7	3.2	31.5
Successive approximation	11.45	9.46	7.60	3.20	31.71

Table 6. Formation constants of the complexes at 25 °C (I = 0.1 mol dm^{-3} KCl)

Method		[CoL]	[CuL]	[NiL]	$[UO_2L]$
Interpolation at half-$\bar{n}$ values	log K_1	8.4	18.5	9.9	14.2
	log K_2	4.9	4.5	5.2	6.4
	log β_2	13.3	23.0	15.1	20.6
Successive approximation	log K_1	8.93	17.56	10.39	13.59
	log K_2	5.05	5.19	5.34	6.60
	log β_2	13.98	22.75	15.73	20.19

determine the stepwise protonation constants of H_2L and the stepwise formation constants of the complexes. The protonation constants correspond to the equilibria (1)—(4), and the formation constants, (5) and (6). The values in the titration curves given in Figure 2 were used to calculate the stepwise protonation constants and stepwise formation constants by successive approximation and interpolation at half-$\bar{n}$ values according to Irving and Rossotti.[32] The results obtained by these two methods are given in Tables 5 and 6 and they quite closely follow each other. Evaluation of the stepwise protonation constants shows that the first three protonations are fairly close together, but the fourth one occurs at pH ≈ 3.

$$L^{2-} + H^+ \overset{K_{A1}}{\rightleftharpoons} HL^- \quad (1)$$

$$HL^- + H^+ \overset{K_{A2}}{\rightleftharpoons} H_2L \quad (2)$$

$$H_2L + H^+ \overset{K_{A3}}{\rightleftharpoons} H_3L^+ \quad (3)$$

$$H_3L^+ + H^+ \overset{K_{A4}}{\rightleftharpoons} H_4L^{2+} \quad (4)$$

$$H_2L + M^{2+} \overset{K_1}{\rightleftharpoons} [MHL]^+ + H^+ \quad (5)$$

$$[MHL]^+ \overset{K_2}{\rightleftharpoons} [ML] + H^+ \quad (6)$$

The order of the overall formation constants ($\beta_2 = K_1K_2$) of the complexes is as follows: [CuL] > $[UO_2L]$ > [NiL] > [CoL]. The tendency of complex formation in all four metal ions is high enough to prevent the precipitation of metal hydroxides up to pH ≈ 12. [CoL] and [NiL] are stable only at pH > 6 and dissociate into protonated species at lower pH values.

Experimental

Proton and ^{13}C n.m.r. spectra were measured on a Bruker 200 MHz spectrometer. Infrared spectra were obtained on a Perkin-Elmer 598 spectrophotometer in KBr pellets. U.v.–visible spectra were recorded on a Cary-14 spectrophotometer. The magnetic susceptibilities were measured with a Gouy magnetic balance at room temperature which was calibrated with $CuSO_4 \cdot 5H_2O$ and $Hg[Co(NCS)_4]$. A pH-meter (Orion 701A), with a glass–calomel electrode assembly, was used to determine the change in hydrogen ion concentration of the solution due to complexation.

Benzo-15-crown-5,[33] 4′-acetylbenzo-15-crown-5,[13] 4′-acetoxybenzo-15-crown-5,[13] and 4′-hydroxybenzo-15-crown-5[13] were prepared according to the published methods.

Preparation of the Ligand HA.—The compound 4′-Hydroxybenzo-15-crown-5 trihydrate (17.0 g, 0.05 mol) and hexamethylenetetramine (7.0 g, 0.05 mol) were dissolved by stirring in trifluoroacetic acid (37 cm^3) at 85—90 °C under a nitrogen flow and the mixture refluxed for 20 h. The greenish yellow viscous solution was poured into icy water (350 cm^3) and stirred at room temperature for a further 3 h. The product was extracted with chloroform (10 × 100 cm^3) and the chloroform layer was dried (Na_2SO_4). After evaporation of the solvent, the residual oily product was crystallized from n-heptane as white needles. Yield: 10 g (64%), m.p. 105—106 °C. $\lambda_{max.}$ (EtOH) 209 (ε = 14 180 dm^3 mol^{-1} cm^{-1}), 239 (17 100), 281 (12 500), and 343 nm (6 900). This compound was soluble in ethanol, chloroform, and dmso and slightly soluble in benzene.

Preparation of the Ligand H_2L.—To a solution of 4′-hydroxy-5′-formylbenzo-15-crown-5 (1.65 g, 5 mmol) in ethanol (50 cm^3) at 80 °C was added a solution of 1,2-diaminoethane (0.17 cm^3, 2.5 mmol) in ethanol (10 cm^3) with stirring. The mixture was left overnight at room temperature and bright yellow needles formed. The product was filtered off, washed with ethanol and then with diethyl ether and dried. Yield: 1.65 g (86%), m.p. 165—166 °C. Thermogravimetric and differential thermal analysis curves of the product indicated an endothermic weight loss corresponding to four water molecules at 120 °C, another endothermic peak at 165 °C (m.p.), and exothermic decomposition after 255 °C. $\lambda_{max.}$ (EtOH) 206 (ε = 29 050 dm^3 mol^{-1} cm^{-1}), 230 (26 800), 285 (16 480), 340 (9 660), and 406 nm (8 045). The ligand H_2L was soluble in water, ethanol, chloroform, and dmso.

Preparation of the Transition Metal Complexes of H_2L.—The hydrated ligand $H_2L \cdot 4H_2O$ (0.356 g) was dissolved in ethanol (50 cm^3) by warming on a water-bath. The acetate of the appropriate metal ion [0.5 mmol: $Co(CH_3COO)_2 \cdot 6H_2O$ (0.125 g), $Cu(CH_3COO)_2 \cdot H_2O$ (0.100 g), $Ni(CH_3COO)_2 \cdot 6H_2O$ (0.125 g), $UO_2(CH_3COO)_2 \cdot 2H_2O$ (0.212 g)], dissolved in sufficient amount of ethanol, was added to the ligand solution. The mixture was boiled on a water-bath for 30 min and crystalline complexes were precipitated. The products were filtered off, washed with ethanol, then with diethyl ether, and dried. The m.p.s of all complexes were >250 °C.

$[CoL] \cdot 3H_2O$: $\lambda_{max.}$ (EtOH) 206 (ε = 31 200 dm^3 mol^{-1}

cm^{-1}), 225 (34 100), 260 (61 940), 300 (22 500), and 402 nm (9 970); $\mu_{eff.}$ = 2.43.

[CuL]·H_2O: $\lambda_{max.}$ (EtOH) 205 (ε = 27 000 dm^3 mol^{-1} cm^{-1}), 225 (35 780), 255 (45 000), 285 (28 400), and 361 nm (15 300); $\mu_{eff.}$ = 1.80.

[NiL]·$3H_2O$: $\lambda_{max.}$ (EtOH) 203 (ε = 25 800 dm^3 mol^{-1} cm^{-1}), 243 (34 700), 265 (42 900), 320 (14 970), and 405 nm (8 100); diamagnetic.

[UO_2L]·$2H_2O$: $\lambda_{max.}$ (EtOH) 202 (ε = 21 800 dm^3 mol^{-1} cm^{-1}), 220 (25 120), 251 (32 800), 298 (22 450), and 342 nm (12 430); diamagnetic.

The procedure for the preparation of the complexes of H_2L containing both transition and alkali metals was similar to that above, but before addition of the transition metal solution $NaNO_3$ (0.035 g, 10 mmol) was added to the ligand solution and the mixture refluxed for 30 min.

[CoL]·$2NaNO_3$·$4H_2O$: $\lambda_{max.}$ (EtOH) 205 (ε = 48 600 dm^3 mol^{-1} cm^{-1}), 220 (33 000), 250 (60 300), 301 (21 500), and 394 nm (9 200); $\mu_{eff.}$ = 2.40.

[CuL]·$2NaNO_3$·$4H_2O$: $\lambda_{max.}$ (EtOH) 205 (ε = 35 900 dm^3 mol^{-1} cm^{-1}), 220 (35 100), 258 (40 800), 280 (25 500), 360 (13 500), and 550 nm (160); $\mu_{eff.}$ = 1.83.

[NiL]·$2NaNO_3$·$2H_2O$: $\lambda_{max.}$ (EtOH) 204 (ε = 45 500 dm^3 mol^{-1} cm^{-1}), 244 (43 500), 263 (52 500), 319 (18 500), and 412 nm (9 800); diamagnetic.

[UO_2L]·$2NaNO_3$·$3H_2O$: $\lambda_{max.}$ 202 (ε = 49 000 dm^3 mol^{-1} cm^{-1}), 220 (40 000), 251 (50 000), 280 (22 700), and 340 nm (18 600); diamagnetic.

Preparation of the Octahedral Cobalt Complexes.—The solutions of [CoL] in dry dmf (8×10^{-3} mol dm^{-3}) and dmso (1.3×10^{-3} mol dm^{-3}) were slowly exposed to dry air without stirring. Black-brown crystalline precipitates which formed in 2 d were filtered off, washed with diethyl ether, and dried in a stream of dry air. These products are insoluble in common solvents without decomposition.

Calvin–Bjerrum pH-titration Technique (*ref.* 31).—The following six mixtures were prepared. Mixture A: KCl (10 cm^3, 1 mol dm^{-3}) and HCl (5 cm^3, 0.1 mol dm^{-3}); mixture B: mixture A plus H_2L (25 cm^3, 0.007 mol dm^{-3}); mixtures C—F: mixture B plus metal solution (10 cm^3, 0.01 mol dm^{-3}), separately [C = $CoCl_2$, D = $CuCl_2$, E = $NiCl_2$, F = $UO_2(NO_3)_2$].

Doubly distilled water was added to each mixture up to a total volume of 100 cm^3 in each case. Excess ligand was used to fulfil the maximum co-ordination number of the metal; KCl was added to maintain an ionic strength of 0.1 mol dm^{-3}. The mixtures were then titrated with progressive addition of NaOH solution (0.1 mol dm^{-3}), in increments of 0.2 cm^3. The corresponding change in the pH of the solution was observed and recorded. All the experiments were carried out at a constant room temperature of 25 °C. Six titration curves (Figure 2) were obtained by plotting pH against the volume of NaOH solution added.

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