Synthesis of *SS'*-Bis(4'-benzo[15-crown-5])dithioglyoxime‡ and its Complexes with Copper(II), Nickel(II), Cobalt(II), Cobalt(III), Palladium(II), Platinum(II), and Platinum(IV)

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SS'-Bis(4'-benzo[15-crown-5])dithioglyoxime (H_2L) has been prepared from 4'-mercaptobenzo[15-crown-5], *anti*-dichloroglyoxime, and sodium bicarbonate in ethanol. Nickel(II), palladium(II), platinum(II), copper(II), cobalt(II), and cobalt(III) complexes of H_2L 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. The complex $[Pt(HL)_2Cl_2{\cdot}4NaClO_4]$ forms six-membered chelate rings and co-ordinates through N and O atoms. $[Co(HL)_2(PPh_3)Cl{\cdot}4NaClO_4]$ and $[Co(HL)_2(C_5H_5N)Cl{\cdot}2NaClO_4]$ have been prepared with triphenylphosphine or pyridine and chloride as axial ligands. The ion-extraction properties of the Ni^{II}, Pd^{II}, and Pt^{II} complexes towards lithium, sodium, and potassium picrate from aqueous solution to dichloromethane have been measured. Extraction values, n.m.r., i.r., and u.v.–visible data are presented.

The synthesis of various *vic*-dioximes and their transition-metal complexes have been the essential topics of research carried out in our laboratory.[1] Since observations on the ion-binding ability and selectivity of crown ethers, considerable interest has been shown in incorporating these functional groups into different new compounds.[2] We have started to study the effect of crown ether groups on the isomerism and complex formation of *vic*-dioximes.[3] Our main interest in compounds which contain both macrocyclic ether groups and a *vic*-dioxime moiety in their molecules lies in investigating the influence of transition-metal ions on the alkali-metal ion extraction capability of crown ether groups.

In the present paper we report the synthesis of a novel *vic*-dioxime substituted with two crown ether functions and its complexes with various metal ions.

Results and Discussion

SS'-Bis(4'-benzo[15-crown-5])dithioglyoxime (H_2L) (Figure 1) was prepared by the reaction of 4'-mercaptobenzo[15-crown-5][4] with *anti*-dichloroglyoxime in ethanol with excess of $NaHCO_3$ as a buffer to neutralize HCl formed during the reaction (Scheme). Similar reaction routes were followed for the synthesis of bis(2-pyridylthio)glyoxime and $[HON{=}CHC({=}NOH)SCH_2{-}]_2$ from the corresponding mercapto-compounds.[5,6]

In the ^1H n.m.r. spectrum of H_2L, the OH proton resonance appears as a singlet at 9.1 p.p.m., which disappears by deuterium exchange; two multiplets at 3.6—4.1 and 6.8—7.0 p.p.m. correspond to etheral ($CH_2{-}CH_2{-}O$) and aromatic protons.[3] The presence of a singlet for OH is consistent with the assumption of an *s-trans* configuration for H_2L. The i.r. spectrum of H_2L exhibits ν(O–H) as a broad absorption at 3 207 cm^{-1}. Bands due to C=N and N–O stretches are at 1 639 and 981 cm^{-1} respectively.

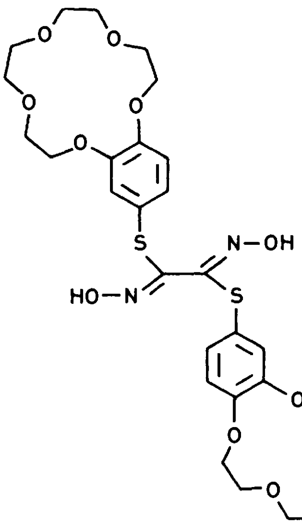

Figure 1. Structure of H_2L

The crystalline lithium chloride, sodium thiocyanate, potassium thiocyanate, and ammonium thiocyanate complexes of H_2L were isolated by treating H_2L with the corresponding salts in ethanol. According to elemental analyses (Table 1) it was found that two Li^+ or Na^+ ions are incorporated into the two cavities of H_2L. In the case of K^+ and $NH_4{}^+$ ions, however, alkali metal:ligand ratios are definitely 1:1, which reflects unequivocally the effect of the higher diameters of these two cations. In the i.r. spectra of the thiocyanate complexes ν(SCN) bands appear at 2 070 cm^{-1}.

Reaction of H_2L with Ni^{II}, Pd^{II}, and Pt^{II} salts gives products with metal:ligand ratios of 1:2. The products obtained from the reaction of Cu^{II}, Co^{II}, and Co^{III} ions with H_2L were highly soluble in EtOH; thus they could only be precipitated as sodium perchlorate complexes.

$[Ni(HL)_2]$, $[Pd(HL)_2]$, *and* $[Pt(HL)_2]$ (*Figure 2*).—The i.r. spectra of these three complexes exhibit ν(C=N) at 1 630 cm^{-1}. This value is lower than that of the free ligand (1 639 cm^{-1}). In

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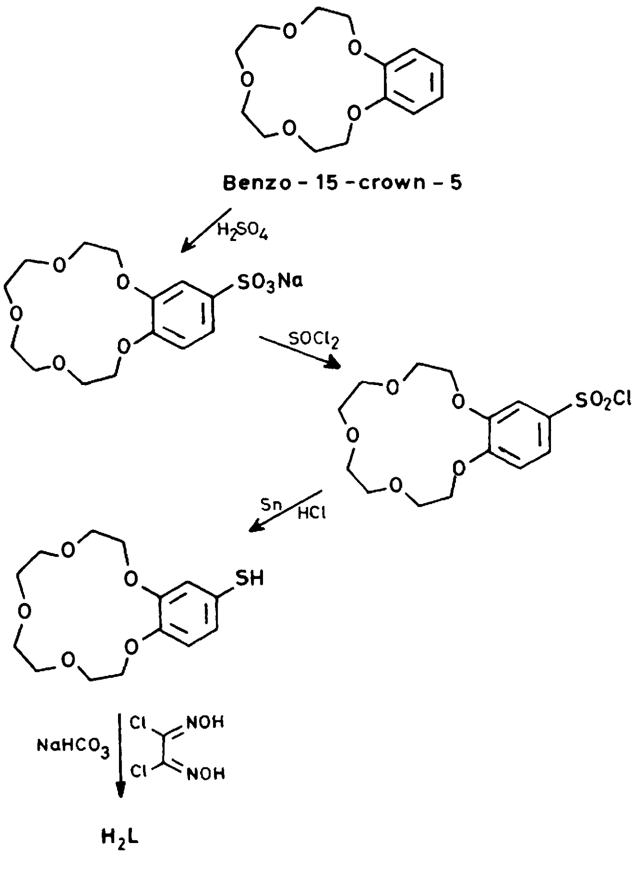
‡ 1,2-Bis(hydroxyimino)-1,2-bis(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-ylthio)ethane.

Table 1. Analytical[a] and physical data for the *vic*-dioxime and its complexes

Compound	M.p.[b] (°C)	Colour	Yield (%)	Analysis (%) C	H	N
H_2L	126	White	83	51.2	5.9	4.2
				(52.6)	(5.8)	(4.1)
$H_2L{\cdot}2LiCl$	125	White	62	47.6	5.5	3.9
				(46.8)	(5.2)	(3.6)
$H_2L{\cdot}2NaSCN$	201–203	White	32	44.8	4.8	6.5
				(45.4)	(4.8)	(6.6)
$H_2L{\cdot}KSCN$	233	White	95	46.7	5.2	5.4
				(47.6)	(5.2)	(5.4)
$H_2L{\cdot}NH_4SCN$	212–214	White	83	48.2	5.7	7.2
				(48.9)	(5.8)	(7.4)
$[Ni(HL)_2]$	220	Red	76	50.7	5.5	4.2
				(50.5)	(5.5)	(3.9)
$[Pd(HL)_2]$	210	Orange	88	48.7	5.5	3.9
				(48.9)	(5.3)	(3.8)
$[Pt(HL)_2]$	216	Red	23	46.3	5.0	3.6
				(46.1)	(5.0)	(3.6)
$[Cu(HL)_2{\cdot}4NaClO_4]$	170	Brown	26	38.1	4.3	3.1
				(37.5)	(4.1)	(2.9)
$[Co(HL)_2{\cdot}2NaClO_4]$	197	Dark brown	54	42.9	4.9	3.3
				(43.1)	(4.7)	(3.4)
$[Co(HL)_2(C_5H_5N)Cl{\cdot}2NaClO_4]$	145	Brown	40	43.6	4.7	4.1
				(43.7)	(4.7)	(3.9)
$[Co(HL)_2(PPh_3)Cl{\cdot}4NaClO_4]$	181	Brown	38	41.9	4.2	2.9
				(42.3)	(4.2)	(2.5)
$[Pt(HL)_2Cl_2{\cdot}4NaClO_4]$	239	Yellow	47	32.1	3.8	2.8
				(33.9)	(3.7)	(2.6)

[a] Required values are given in parentheses. [b] With decomposition.



Scheme.

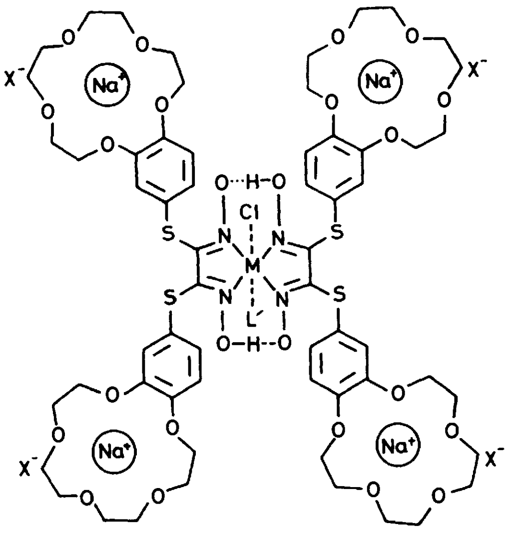


Figure 2. Structures of $[M(HL)_2]$ [M = Ni^{II}, Pd^{II}, or Pt^{II}), $[Cu(HL)_2{\cdot}4NaX]$, $[Co(HL)_2{\cdot}2NaX]$, $[Co(HL)_2(L')Cl{\cdot}2NaX]$ (L′ = C_5H_5N), and $[Co(HL)_2(L')Cl{\cdot}4NaX]$ (L′ = PPh_3) (X = ClO_4^-)

addition the ν(OH) band at 3 207 cm^{-1} disappears. These facts suggest that the HL^- ligand is *NN′*-co-ordinated to Ni^{II}, Pd^{II}, and Pt^{II}.

In the n.m.r. spectrum of $[Ni(HL)_2]$ the intramolecular bridging, deuterium exchangeable, OH protons are observed at 17.4 p.p.m.[3,7] (Table 2).

$[Cu(HL)_2{\cdot}4NaClO_4]$ *and* $[Co(HL)_2{\cdot}2NaClO_4]$ (*Figure 2*).—These two complexes were prepared by treating equivalent

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

Compound	O ··· H-O[b]	N-OH[b]	H aromatic	CH_2-O
4′-Mercaptobenzo[15-crown-5][c,d]			6.9—6.7 (m) (3 H)	4.1—3.6 (m) (16 H)
H_2L[d]		9.1 (s) (2 H)	7.0—6.8 (m) (6 H)	4.1—3.6 (m) (32 H)
$[Ni(HL)_2]$[d]	17.4 (br s) (2 H)		6.9—6.7 (m) (12 H)	4.1—3.7 (m) (64 H)
$[Pd(HL)_2]$[d]	*e*		6.9—6.7 (m) (12 H)	4.1—3.6 (m) (64 H)
$[Pt(HL)_2]$[d]	*e*		6.9—6.7 (m) (12 H)	4.1—3.7 (m) (64 H)
$[Co(HL)_2(C_5H_5N)Cl{\cdot}2NaClO_4]$[d]	18.1 (br s) (2 H)		6.8—6.5 (m) (12 H)	4.1—3.7 (m) (64 H)
			C_5H_5N: 7.9—7.1 (br m) (5 H)	
$[Co(HL)_2(PPh_3)Cl{\cdot}4NaClO_4]$[d]	17.7 (s)—18.5 (s) (2 H)		6.8—6.4 (m) (12 H)	4.1—3.6 (m) (64 H)
			PPh_3: 7.9—7.1 (m) (15 H)	
$[Pt(HL)_2Cl_2{\cdot}4NaClO_4]$[f]		11.9 (s) (2 H)	6.8—6.7 (m) (12 H)	4.1—3.6 (m) (64 H)

[a] Chemical shifts (δ) are reported in p.p.m. relative to $SiMe_4$ at 30 °C; s = singlet, m = multiplet. [b] Disappears on D_2O exchange. [c] δ(S–H) 3.5 p.p.m. [d] In CD_2Cl_2. [e] Not observed. [f] In $(CD_3)_2SO$.

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

Compound	ν(O–H)	ν(C=N)	ν($C_{aromatic}$–O–C)	ν(C–O–C)	ν(N–O)	ν(ClO_4)
H_2L	3 207	1 639	1 255—1 219	1 131—1 046	981	
$H_2L{\cdot}2LiCl$	3 200	1 635	1 255—1 220	1 130—1 045	980	
$H_2L{\cdot}2NaSCN$	3 210	1 628	1 255—1 215	1 135—1 045	978	
$H_2L{\cdot}KSCN$	3 210	1 630	1 255—1 220	1 131—1 046	985	
$H_2L{\cdot}NH_4SCN$	3 200	1 630	1 255—1 220	1 130—1 045	980	
$[Ni(HL)_2]$		1 630	1 259—1 220	1 133—1 048	981	
$[Pd(HL)_2]$		1 630	1 259—1 221	1 132—1 054	982	
$[Pt(HL)_2]$		1 630	1 257—1 220	1 130—1 055	980	
$[Cu(HL)_2{\cdot}4NaClO_4]$		1 630	1 257—1 216	1 122—1 055	980	640—626
$[Co(HL)_2{\cdot}2NaClO_4]$		1 630	1 257—1 216	1 130—1 055	980	635—625
$[Co(HL)_2(C_5H_5N)Cl{\cdot}2NaClO_4]$		1 630	1 257—1 216	1 130—1 055	980	635—625
$[Co(HL)_2(PPh_3)Cl{\cdot}4NaClO_4]$		1 630	1 257—1 216	1 140—1 055	980	635—630
$[Pt(HL)_2Cl_2{\cdot}4NaClO_4]$	3 210	1 630	1 255—1 215	1 122—1 050	980	635

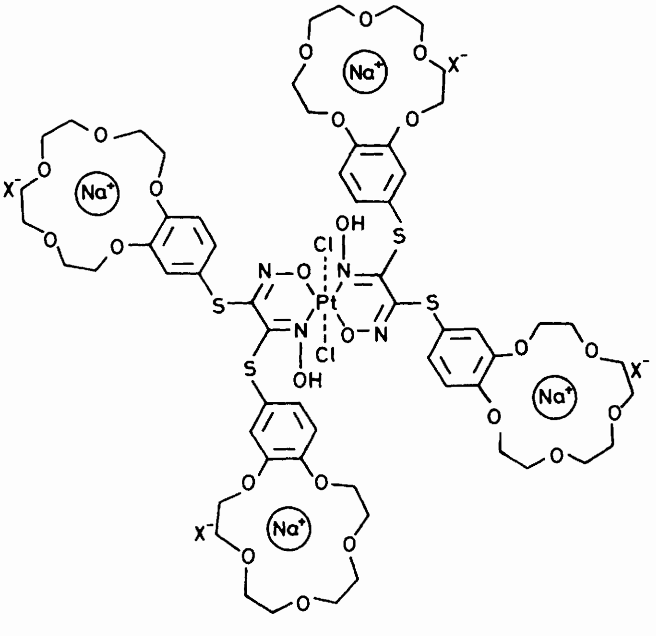


Figure 3. Structure of $[Pt(HL)_2Cl_2{\cdot}4NaX]$ ($X^- = ClO_4^-$)

amounts of H_2L and the corresponding metal salt in ethanol with NaOH solution and subsequently adding a saturated solution of $NaClO_4$ in ethanol to ensure complete precipitation. The difference in solubility of both complexes causes various numbers of sodium perchlorate ion pairs to incorporate into the crown ether groups of H_2L. The ν(C=N) bands are observed at 1 630 cm^{-1} for both complexes (Table 3).

$[Co(HL)_2(C_5H_5N)Cl{\cdot}2NaClO_4]$ *and* $[Co(HL)_2(PPh_3)Cl{\cdot}4NaClO_4]$.—These cobalt(III) complexes were prepared similarly to a previously reported complex of *NN′*-bis(4′-benzo[15-crown-5])diaminoglyoxime.[3] The triphenylphosphine and pyridine ligands are co-ordinated axially to the metal in these octahedral complexes[3,8,9] (Figure 2). The deuterium exchangeable, intramolecular bridging, OH protons appear as a singlet at 18.1 p.p.m. for the pyridine derivative. Both complexes exhibit ν(C=N) absorptions at 1 630 cm^{-1}. The ν(Co–P) band for the triphenylphosphine derivative appeared at 520 cm^{-1}.[3,10]

Schrauzer and Kohnle[9] showed that a dimethylglyoxime complex of Co^{III} could be reduced to a Co^{I} compound which was used to prepare many alkylcobaloximes. When $[Co(HL)_2(PPh_3)Cl{\cdot}4NaClO_4]$ was treated with $NaBH_4$ in a N_2 atmosphere, a blue solution of a Co^{I} complex was obtained. This property might be taken to indicate the superiority of thioglyoximes over aminoglyoximes which decompose under these reducing conditions.[3] The S atoms of H_2L probably stabilize the six-co-ordinate metal core of the complex.

$[Pt(HL)_2Cl_2{\cdot}4NaClO_4]$ (*Figure 3*).—This compound was prepared by treating H_2L with a saturated solution of $NaClO_4$ in ethanol and subsequently adding $Na_2PtCl_6{\cdot}6H_2O$. The ^1H n.m.r. spectrum shows one singlet at 11.9 p.p.m. 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 Pt through the N and O atoms as shown in Figure 3. The presence of a broad and strong OH vibration at 3 210 cm^{-1} also confirms the proposed structure.

In all the perchlorate containing complexes bands due to ClO_4^- are present as doublets at 625—640 cm^{-1}.

Extraction.—The extraction of metal salts into organic

Table 4. % Extraction of alkali-metal picrates from aqueous solution to dichloromethane*

	Li^+	Na^+	K^+
Benzo[15-crown-5]	0.9	18.2	33.7
$[Ni(HL)_2]$	7.1	8.5	79.3
$[Pd(HL)_2]$	23.6	26.5	99.2
$[Pt(HL)_2]$	10.2	8.5	15.6

* Organic phase: [crown ether unit] = 7.0×10^{-4} mol dm^{-3}; aqueous phase: 0.1 mol dm^{-3} MOH–7.0×10^{-5} mol dm^{-3} picric acid.

solvents by neutral, ion-binding molecules has been described in detail by Haines *et al.*[11] According to their procedure we have measured the ability of dichloromethane solutions of Ni^{II}, Pd^{II}, and Pt^{II} complexes of H_2L to extract alkali-metal picrates from aqueous solution. Due to the good solubility of H_2L in alkaline, aqueous media (formation of metal salt of *vic*-dioxime) we were not able to include this compound in our extraction experiments. For comparison, however, we measured the extraction capability of benzo[15-crown-5]. The results are given in Table 4.

Two points are worthy of mention. First, the percentage extractions for K^+ are the highest and secondly the Ni^{II} and Pd^{II} complexes exhibit a higher selectivity for K^+ than the Pt^{II} complex. It is well known that poly- and bis-(crown ether)s containing pendant crown ether moieties exhibit a type of co-operative effect in complexing metal cations, especially in forming sandwich type 2:1 complexes.[4] The greater ionic radius of Pt^{II} than the other d^8 metal ions might be expected to prevent parallel alignment of the two crown ether units of the same molecule completely to envelope alkali-metal cations. Thus we can attribute the high extractability of K^+ ions by the crowned *vic*-dioxime complexes of Ni^{II} and Pd^{II} to the fact that these two compounds exhibit a remarkable capability for forming 1:2 potassium ion–crown sandwich-type complexes. This might be a result of the suitable direction of the crown ether groups for sandwich-type complex formation due to the *NN*-chelated metal core of the molecule.

In conclusion, we were able to show the effect of different transition metals on the alkali-metal ion extraction ability of the new crown ether containing *vic*-dioxime complexes.

Investigations into the preparation of new Co-alkyl derivatives through the reduction of $[Co(HL)_2(PPh_3)Cl{\cdot}4NaClO_4]$ into Co^I complexes is the topic of continuing research in this laboratory.

Experimental

The ^1H n.m.r. spectra were recorded on a Bruker spectrometer at 360 MHz. Infrared spectra were recorded on a Perkin-Elmer 330 spectrophotometer in KBr pellets. The u.v.–visible spectra were recorded on a Varian DMS 90 spectrophotometer (1-cm quartz cells). Elemental analyses were performed on a Perkin-Elmer 240 C elemental analyzer. 4′-Mercaptobenzo[15-crown-5] was prepared according to a literature procedure.[4]

SS′-Bis(4′-benzo[15-crown-5])dithioglyoxime (H_2L).—4′-Mercaptobenzo[15-crown-5] (1 600 mg, 5.33 mmol) was dissolved in ethanol (70 cm^3) and $NaHCO_3$ (895 mg, 10.65 mmol) added under an atmosphere of N_2. A solution of dichloroglyoxime (418 mg, 2.66 mmol) in ethanol (60 cm^3) was added dropwise. The reaction was allowed to continue for 1 h at room temperature and then 1 h at 50—60 °C. After cooling to room temperature, water (*ca.* 1 l) was added. The resulting white precipitate was filtered off, washed with water, and then recrystallized from ethanol. $\lambda_{max.}$(MeOH): 210 (ε = 56 495 dm^3 mol^{-1} cm^{-1}), 254 (19 203), and 282 nm (11 042).

$H_2L{\cdot}KSCN$.—To a stirred solution of H_2L (50 mg, 0.073 mmol) in ethanol (5 cm^3) was added potassium thiocyanate (709 mg, 7.3 mmol) in ethanol (7 cm^3). The resulting white precipitate was filtered off and washed with ethanol. $\lambda_{max.}$(MeOH): 209 (ε = 56 747 dm^3 mol^{-1} cm^{-1}), 252 (17 784), and 284 nm (90 961) (sh).

Lithium, sodium, and ammonium complexes of H_2L were prepared similarly. $H_2L{\cdot}2LiCl$: $\lambda_{max.}$(MeOH), 210 (ε = 63 937 dm^3 mol^{-1} cm^{-1}), 255 (22 478) (sh), and 284 (12 961) (sh); $H_2L{\cdot}2NaSCN$: $\lambda_{max.}$(MeOH), 209 (57 759), 256 (16 257), and 282 (10 000) (sh); $H_2L{\cdot}NH_4SCN$: $\lambda_{max.}$(MeOH), 210 (57 472), 252 (18 333) (sh), and 283 nm (10 305) (sh).

$[Ni(HL)_2]$.—To an ethanol (20 cm^3) solution of H_2L (200 mg, 0.292 mmol) was added a solution of $NiCl_2{\cdot}6H_2O$ (34.7 mg, 0.146 mmol) in ethanol (7 cm^3) at room temperature. A solution of triethylamine (2.92 cm^3, 0.1 N in ethanol) was added dropwise, while heating this mixture (60 °C). The resulting red precipitate was filtered off and washed with ethanol. $\lambda_{max.}$(CH_2Cl_2): 227 (ε = 57 143 dm^3 mol^{-1} cm^{-1}) (sh), 249 (55 143), 283 (41 086), 390 (11 657), and 435 nm (11 943).

$[Pd(HL)_2]$.—A mixture of $PdCl_2$ (26 mg, 0.1466 mmol) and LiCl(12.6 mg, 0.296 mmol) was dissolved in ethanol (25 cm^3) and added dropwise into a solution of H_2L (200 mg, 0.292 mmol) in ethanol (20 cm^3). An orange precipitate was observed during the stirring at 60 °C. A triethylamine solution (2.92 cm^3, 0.1 N in ethanol) was added to the mixture to complete the complex formation. The resulting orange precipitate was filtered off and washed with ethanol. $\lambda_{max.}$(CH_2Cl_2): 229 (ε = 61 886 dm^3 mol^{-1} cm^{-1}), 247 (63 486), 283 (35 886), 325 (8 968) (sh), and 384 nm (5 716).

$[Pt(HL)_2]$.—H_2L (100 mg, 0.146 mmol) was dissolved in ethanol (20 cm^3) and K_2PtCl_4 (30.3 mg, 0.073 mmol) added. The mixture was stirred and heated to 60 °C. Water was added to the mixture, maintained at this temperature, until the K_2PtCl_4 had dissolved (the mixture must be clear at this point). The colour of the mixture turned red and the pH was adjusted to 6 with KOH (0.1 N in ethanol). The precipitate was filtered off and washed with a small amount of ethanol. $\lambda_{max.}$(CH_2Cl_2): 228 (ε = 59 257 dm^3 mol^{-1} cm^{-1}), 246 (49 631), 284 (29 004) (sh), 331 (9 876), and 406 nm (10 001).

$[Cu(HL)_2{\cdot}4NaClO_4]$ *and* $[Co(HL)_2{\cdot}2NaClO_4]$.—To a stirred solution of H_2L (100 mg, 0.146 mmol) in ethanol (20 cm^3) was added a solution of the metal salt ($CuCl_2{\cdot}2H_2O$ or $CoCl_2{\cdot}6H_2O$) (3.65 cm^3, 0.02 N in ethanol). The mixture was heated to 60 °C and NaOH (1.46 cm^3, 0.1 N in ethanol) added dropwise. The reaction was allowed to continue for 15 min at 60 °C. In order to precipitate the complex a saturated solution of $NaClO_4$ (5 cm^3) in ethanol was added. The precipitate was filtered off and washed with ethanol and then diethyl ether. $[Cu(HL)_2{\cdot}4NaClO_4]$: $\lambda_{max.}$(CH_2Cl_2), 229 (ε = 63 137 dm^3 mol^{-1} cm^{-1}), 245 (62 549), 285 (39 706) (sh), and 340 (23 529) (sh); $[Co(HL)_2{\cdot}2NaClO_4]$: $\lambda_{max.}$(CH_2Cl_2), 228 (ε = 54 952), 249 (58 019), 285 (37 125) (sh), and 347 nm (18 722) (sh).

$[Co(HL)_2(C_5H_5N)Cl{\cdot}2NaClO_4]$ *and* $[Co(HL)_2(PPh_3)Cl{\cdot}4NaClO_4]$.—$H_2L$ (100 mg, 0.146 mmol) was dissolved in ethanol (20 cm^3) and a solution of $CoCl_2{\cdot}6H_2O$ (17.4 mg, 0.073 mmol) in ethanol (5 cm^3) added. The mixture was heated with stirring to 70 °C. A solution of pyridine (48 mg, 0.6 mmol) or triphenylphosphine (157 mg, 0.6 mmol) in ethanol was added and air bubbled through the mixture for 30 min. A saturated solution of $NaClO_4$ in ethanol (5 cm^3) was added. The brown precipitate was filtered off and washed with ethanol. $[Co(HL)_2(C_5H_5N)Cl\cdot 2NaClO_4]$: $\lambda_{max.}(CH_2Cl_2)$, 230 (ε = 64 551 dm^3 mol^{-1} cm^{-1}), 244 (64 370), 279 (37 897) (sh), and 338 (15 866) (sh); $[Co(HL)_2(PPh_3)Cl\cdot 4NaClO_4]$: $\lambda_{max.}(CH_2Cl_2)$, 230 (ε = 67 838), 242 (64 122), 282 (36 068) (sh), and 350 nm (18 514).

$[Pt(HL)_2Cl_2\cdot 4NaClO_4]$.—To a solution of H_2L (100 mg, 0.146 mmol) in ethanol (20 cm^3) was added a saturated solution of $NaClO_4$ in ethanol (5 cm^3) followed by a solution of $Na_2PtCl_6\cdot 6H_2O$ (41 mg, 0.073 mmol) in ethanol (15 cm^3). The mixture was stirred at 60 °C for 30 min. The yellow precipitate was filtered off and washed with ethanol.

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