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Synthesis and Characterization of a Crown Ether Substitued Salicylaldimine[#] and its Complexes with Copper(II), Cobalt(II), Nickel(II), and Uranyl(VI)

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Summary. 4′-(ω-Salicylaldiminoacetyl)benzo(15-crown-5) (*L*H) has been synthesized from 4′-(ω-aminoacetyl)benzo(15-crown-5) and salicylaldehyde. Complexes of this *Schiff* base with copper(II), nickel(II), cobalt(II), and uranyl(VI) have been prepared from the corresponding metal acetates and chlorides. Insertion of sodium ions into the crown ether-moiety has been accomplished by refluxing *L*H with sodium nitrate in ethanol. The complexation of this ligand with Cu(II), Ni(II), Co(II), and $U(VI)O_2$ was investigated by potentiometric titration; the results indicate that all of them afford products with a metal-ligand ratio of 1:2. The order of formation constants of the mononuclear complexes is $Cu(II) > Co(II) > U(VI)O_2 > Ni(II)$.

Keywords. Crown ethers; Salicylaldimines; Benzo(15-crown-5); Stability constants.

Synthese und Charakterisierung eines kronenethersubstituierten Salicylaldimins und seiner Komplexe mit Kupfer(II), Kobalt(II), Nickel(II) und Uranyl(VI)

Zusammenfassung. 4′-(ω-Salicylaldiminoazetyl)benzo(15-crown-5) (*L*H) wurde ausgehend von 4′-(ω-Aminoacetyl)-benzo(15-crown-5) und Salicylaldehyd synthesiert. Komplexe dieser *Schiff*schen Base mit Kupfer(II), Nickel(II), Kobalt(II) und Uranyl(VI) wurden aus den entsprechenden Metallacetaten hergestellt. Einfügung von Natriumionen in den Kronenetherteil der Moleküle wurde durch Kochen mit Natriumnitrat in Ethanol unter Rückfluß erreicht. Die Komplexbildung mit Ni(II), Cu(II), Co(II) und $U(VI)O_2$ wurde durch potentiometrische Titration untersucht; alle Metalle ergeben dieselben Komplexe mit einem Metall-Ligand-Verhältnis von 1:2. Die Reihenfolge der Bildungskonstanten der einkernigen Komplexe lautet $Cu(II) > Co(II) > U(VI)O_2 > Ni(II)$.

[#] 4′-(ω-Salicylaldiminoacetyl)benzo(15-crown-5) = *L*H = 15-salicylaldiminoacetyl-2,3,5,6,8,9,11,12-orthohydrobenzo[1,4,7,10,13]pentaoxacyclopentadecine; systematic numbering for position 4′ is 15.

Introduction

Recently, crown ethers 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) substitued phthalocyanines [1] or the agglomeration of phthalocyanine units induced by alkali metal cations [2–6] are two outstanding examples.

Crown ethers and salicylaldimines are two important groups of ligands extensively studied with respect to their high affinity to interact with alkali and transition metal ions, respectively [7–9]. The reversible oxygen-carrying properties of some of these salicylaldimine complexes have been of considerable interest due to their obvious implications for biological systems [10–14]. *Calvin* and coworkers [15] have discovered that reversible oxygen adducts are formed by crystalline modifications of the solid complexes of various substitued derivatives of salens. The wide spread use of macrocyclic ethers as selective phase transfer agents should also be mentioned [16].

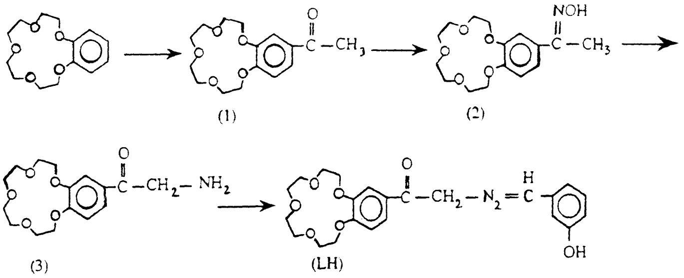
A number of novel compounds composed of multifunctional ligands carrying both hard and soft donor sites, such as crown ethers or macroaza groups together with *vic*-dioximes [17, 18], phthalocyanines [19, 20], or salicylaldimine [21] moieties have been reported. It has been shown that these systems can be used for the formation of supramolecular aggregates or mesophases, enhancing the metal recognition phenomena and even leading to ion channels.

Addition of macrocyclic groups to the transition metal complexes of soft donors also enhance their solubilities in various organic solvents, and their vitality in solution chemistry is evident. Although it is generally possible to isolate a single complex by changing the reaction conditions, there are usually more than one species in equilibrium in solution. With the aid of computer programs it has become possible to obtain reliable results for the stability of each species [22–25]. In this study, we describe the synthesis of 4′-(ω-salicylaldiminoacetyl)benzo(15-crown-5) and investigate its protonation and complexation equilibria in the presence of Cu(II), Co(II), Ni(II), or U(VI)O_2 ions.

Results and Discussion

The synthetic route to 4′-(ω-aminoacetyl)benzo(15-crown-5) (**3**) *via* **1** and **2** steps is shown in the Scheme. The *Neber* reaction was used to convert the oxime derivate into 4′-(ω-aminoacetyl)benzo(15-crown-5). In order to obtain 4′-(ω-salicylaldiminoacetyl)benzo(15-crown-5) (*L*H), 4′-(ω-aminoacetyl)benzo(15-crown-5) was treated with salicylaldehyde in absolute ethanol.

The new compounds were characterized by elemental analysis, IR, and ^{1}H NMR spectra. In the ^{1}H NMR spectrum of *L*H in acetone, the signal of the OH proton appears as a singlet at 10.50 ppm and disappears by deuterium exchange. The resonance of the proton of the azomethine (CH=N) group appears at 9.11 ppm also as a singlet. The aromatic protons appear at 8.13–6.99 ppm as a multiplet. The etheral protons of the crown ether group resonate at 4.53–4.05 ppm. The CO-CH_2-N acetyl amino group appear as a singlet at 2.72 ppm. In the IR spectrum of *L*H, OH and C=N stretching vibrations appear at 3260 and 1620 cm^{-1}. The



Scheme 1

characteristic absorptions of aromatic and aliphatic ether groups of the crown ether moiety appear at 1260 and 1110 cm^{-1} as intense broad peaks.

The interaction of the crown ether moiety in *L*H with Li^+, Na^+, and K^+ salts has been studied; $LH \cdot NaNO_3$ could be isolated. As it is known that the cavity radius of benzo-15-crown-5 perfectly fits with the ionic radius of the sodium ion, we conclude that this metal ion is inserted into the macrocycle. In the case of alkali ions with bigger (K^+) or smaller (Li^+) ionic radius, no crystalline adduct of any stoichiometry could be obtained.

*L*H is capable of complexing with various transition metal ions. In this paper, we report the synthesis and characterization of Cu(II), Co(II), Ni(II), and U(VI)O_2 complexes. All complexes are prepared from stoichiometiric amounts of *L*H and the corresponding metal acetate or chloride in a 1:2 ratio in ethanol.

Protonation equilibria

Initially the cumulative protonation constants of the ligand were calculated by the TITFIT program [27]. The calculated protonation and formation constants ($\log \beta_{pqr}$) of the ligand are given in Table 1. In the normal aqueous titration range, the ligand can liberate two protons: one from the protonated imino group and one from the OH group of salicyl aldehyde.

The values of the macroscopic protonation constants for the ligand are $\log K_1 = 9.33$, and $\log K_2 = 5.63$; they correspond to the following equations:

$$L^- + H^+ \rightleftharpoons LH \quad K_1 = \frac{[LH]}{[L^-][H^+]}$$

$$LH + H^+ \rightleftharpoons LH_2^+ \quad K_2 = \frac{[LH_2^+]}{[LH][H^+]}$$

The stability constants β are defined by the following equations (charges are omitted for simplicity):

$$\mathrm{p}M + \mathrm{q}H + \mathrm{r}L \rightleftharpoons M_\mathrm{p}H_\mathrm{q}L_\mathrm{r}$$

$$\beta_{pqr} = [M_\mathrm{p}\mathrm{H}_\mathrm{q}L_\mathrm{r}]/[M]^\mathrm{p} \cdot [H]^\mathrm{q} \cdot [L]^\mathrm{r}$$

$$(M\colon \mathrm{Cu(II), Ni(II), Cu(II)})$$

Titration data obtained for *L*H in the presence of Cu(II), Ni(II), Co(II), and U(VI)O_2 ions were processed by the TITFIT program to observe the protonated,

Table 1. Protonation and overall formation constants for *L*H and its complexes at 25°C and I = 0.1 *M* KNO_3 ($\log\beta_{pqr}$: mean of two determinations; Δ: standard deviation)

Metal ion	Species	$\log\beta_{pqr}$	Δ
H^+	HL	9.33	$3.4\ 10^{-1}$
	H_2L^+	14.96	$4.6\ 10^{-1}$
Cu^{2+}	ML	9.00	$6.4\ 10^{-4}$
	$ML(OH)$	1.61	$6.4\ 10^{-4}$
	$ML(OH)_2$	−5.66	$6.4\ 10^{-4}$
	$ML(OH)_3$	−16.36	$6.4\ 10^{-4}$
Co^{2+}	ML	8.49	$1.8\ 10^{-1}$
	$ML(OH)$	0.56	$2.9\ 10^{-1}$
	$ML(OH)_2$	−8.82	$2.7\ 10^{-1}$
	$ML(OH)_3$	−17.34	$2.6\ 10^{-1}$
Ni^{2+}	ML	7.10	$2.8\ 10^{-1}$
	MHL	13.76	$2.2\ 10^{-1}$
	$ML(OH)$	−2.62	$4.1\ 10^{-1}$
	$ML(OH)_2$	−11.30	$3.1\ 10^{-1}$
UO_2^{2+}	ML	8.15	$7.1\ 10^{-4}$
	$ML(OH)$	3.36	$7.1\ 10^{-4}$
	$ML(OH)_2$	−2.17	$7.1\ 10^{-4}$
	$ML(OH)_3$	−10.35	$7.1\ 10^{-4}$

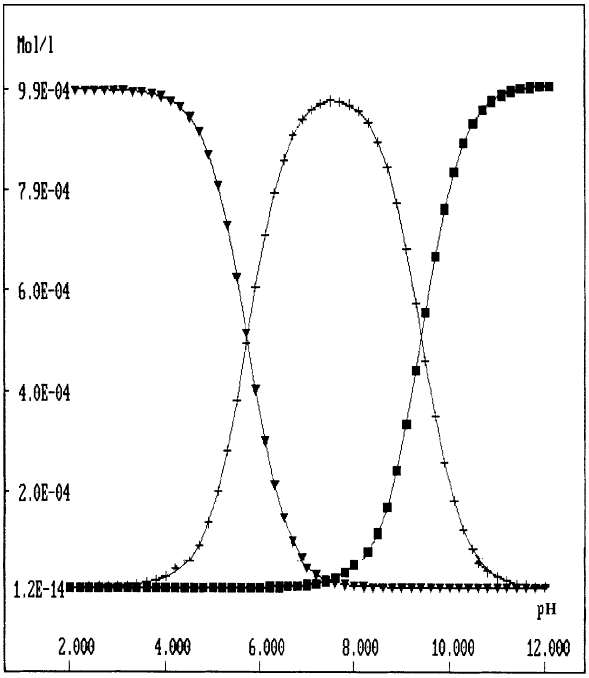


Fig. 1. Typical distribution diagrams for the *L*H system (■■■: L^-, +++: LH, ▼▼▼: LH_2)

neutral, and hydroxo complexes [27]. The cumulative formation constants of the species encountered in the case of four metal ions are summarized in Table 1. The relative predominance of the different species in each *pH* range is shown by the distribution diagrams (Figs. 1–5).

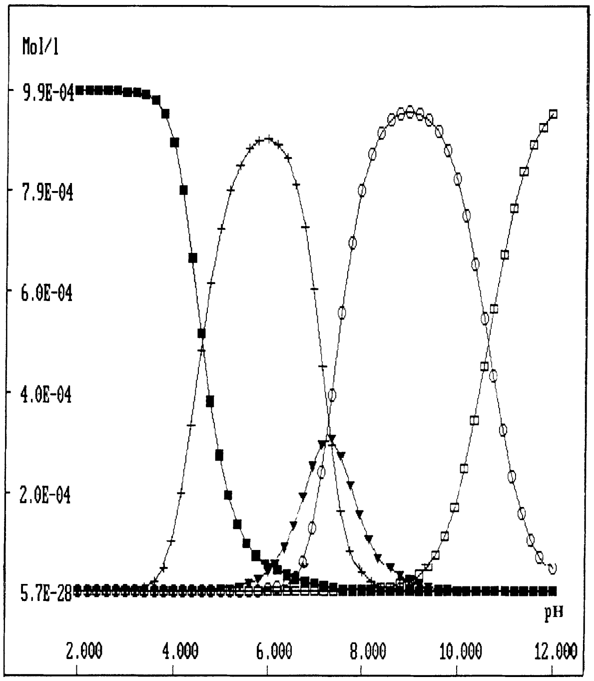


Fig. 2. Typical distribution diagrams for the Cu^{2+}-LH system (■■■: Cu^{2+}, +++: CuL, ▼▼▼: CuLOH, ○○○: $\mathrm{Cu}L(\mathrm{OH})_2$, □□□: $\mathrm{Cu}L(\mathrm{OH})_3$)

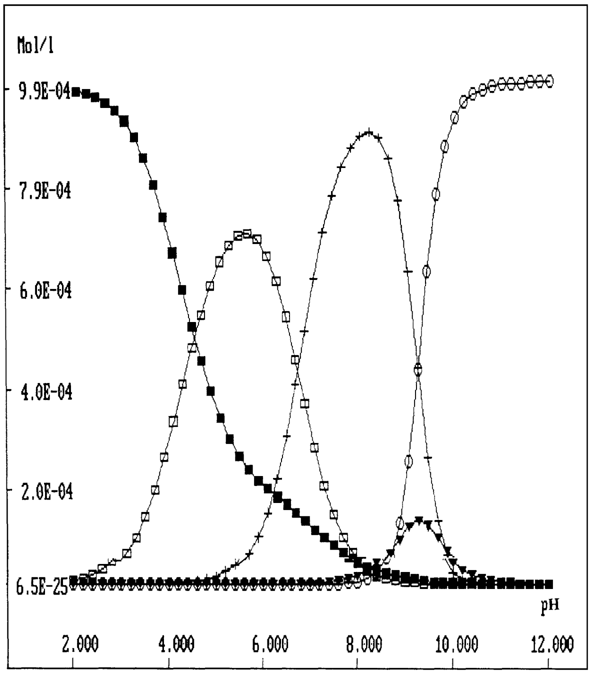


Fig. 3. Typical distribution diagrams for the Ni^{2+}-LH system (■■■: Ni^{2+}, +++: NiL, ▼▼▼: NiLH, ○○○: NiLOH, □□□: $\mathrm{Ni}L(\mathrm{OH})_2$)

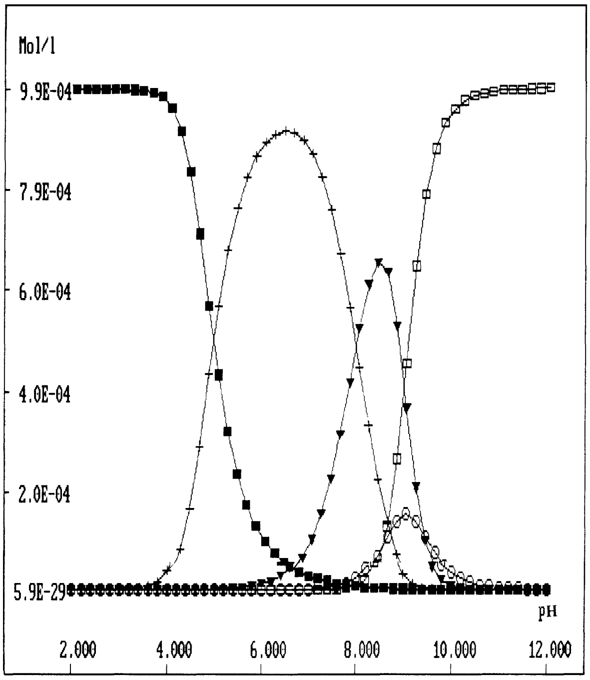


Fig. 4. Typical distribution diagrams for the Co:-*L*H system (■■■: Co^{2+}, +++: Co*L*, ▼▼▼: Co*L*OH, ○○○: $CoL(OH)_2$, □□□: $CoL(OH)_3$)

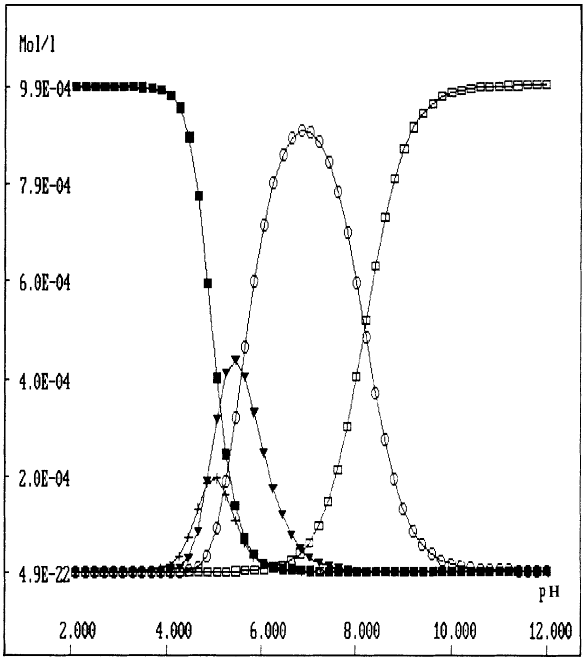


Fig. 5. Typical distribution diagrams for the UO_2^{2+}-*L*H system (■■■: UO_2^{2+}, +++: UO_2L, ▼▼▼: UO_2LOH, ○○○: $UO_2L(OH)_2$, □□□: $UO_2L(OH)_3$)

Some general observations about the behaviour of the various systems are as follows: In the case of the Cu-H*L* system, complexation of Cu(II) with H*L* begins at $pH = 6.0$ with the formation of $[CuL]^+$ and shows a maximum at $pH = 6.0$ (91%) $[CuL(OH)]$ appears at $pH = 6.0$ and shows maximum at $pH = 7.5$ (32%). The dihydroxo complex $[CuL(OH)_2]$ begins to form at $pH = 6.5$ (94%) (Fig. 2).

Figure 3 shows that complexes are formed in the solution containing Ni(II) and *L*H. Complexation begins at $pH = 5.0$ with the formation of NiL^+ and shows a maximum at $pH = 8.0$. The conversion ratio is about 93%. $[NiLH]^{2+}$ begins to form at $pH = 8.0$ (17%). The monohydroxo complex [Ni*L*(OH)] appears at $pH = 2.0$ and show a maximum at $pH = 5.5$ (76%).

The complexation of Co(II) with *L*H begins at $pH = 4.0$ with the formation of $[CoL]^+$; [Co*L*(OH)] appears at $pH = 6.0$ and shows maximum at $pH = 8.5$ (62.6%). The dihydroxo complex $[CoL(OH)_2]^+$ begins to form at $pH = 8.0$ (Fig. 4).

The distribution diagram in Fig. 5 shows that complexation of U(VI)O_2 with *L*H begins at $pH = 4.0$ with the formation of $[UO_2L]$. $[UO_2L(OH)]$ appears at $pH = 4.2$ and shows a maximum at $pH = 5.3$ (42%). The dihydroxo complex $[UO_2L(OH)]$ begins to form at $pH = 4.5$ and shows a maximum at $pH = 7.0$. The conversion ratio is about 95%.

Experimental

Reagents

The reagents used for the equilibrium studies were of analytical grade. Doubly distilled and deionized water was used throughout the potentiometric experiments which were carried out under an atmosphere of purified nitrogen. Concentrations of stock solutions of metal ions were standardized by atomic absorption spectroscopy. All other chemicals employed were of the best grade available. Unless specified otherwise, reagent, grade reactants and solvents were used as received from the suppliers. High purity potassium nitrate (Merck) was used as supporting electrolyte, and an ionic strength of 1.0 M KNO_3 was established at the beginning of each potentiometric titration. The starting solutions for each potentiometric experiment were obtained by adding a known volume of ligand solution and an exact volume of metal chloride successively to the titration vessel. Then the required quantities of potassium nitrate, used as supporting electrolyte in order to minimize variations of the activity coefficients in spite of wide changes in the concentrations of the reagents, and a sufficient amount of ethanol were added to make up the total volume V_0 (20 ± 0.1 ml.) Carbonate free sodium hydroxide solution was prepared and standardized by potentiometric titration.

Potentiometric titrations

Potentiometric titrations were carried out using a Metrohm E-415 dosimate and a Metrohm E-510 *pH* meter. A Metrohm 6.0204.000 combined glass electrode was used for *pH* and e.m.f. measurements. The potentiometric titration apparatus consisted of a water jacketed titration vessel. The ionic strength was kept constant at 1.0 M KNO_3. All titrations solutions were prepared as a total volume of 25.0 cm^3 and thermostatted at 25.0 ± 0.1°C. The solution in the titration vessel was stirred magnetically. A stream of nitrogen was blown over the surface of the solution. All alkalimetric titrations were carried out at 25 ± 0.1°C and $I = 0.1$ mol/dm^3 KNO_3 for solutions of binary systems containing Cu(II), Ni(II), Co(II), U(VI)O_2, and ligand at different molar ratios. Ethanol was added to obtain homogeneous solutions.

The following solutions were prepared to obtain the pH-titration curves:

Solution *A*: $HClO_4$ (2.5 ml, 0.1 *M*), KNO_3 (5 ml, 1.0 *M*), acetone (12.5 ml)

Solution *B*: $HClO_4$ (2.5 ml, 0.1 *M*), KNO_3 (5 ml 1.0 *M*), solution of *L*H in ethanol (5 ml, 0.01 *M*), ethanol (7.5 ml)

Solution C–F: $HClO_4$ (2.5 ml, 0.1 *M*), KNO_3 (5 ml, 1.0 *M*), solution of *L*H in ethanol (5 ml, 0.01 *M*), aqueous solution of metal salt ($CuCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $UO_2(AcO)_2 \cdot 4H_2O$; 2.5 ml, 0.01 *M*), ethanol (7.5 ml)

The above solutions were titrated by addition of 0.1 *M* NaOH in increments of 0.1 ml. The corresponding change in the *pH* of the solution was measured. The values of proton activity and pK_w for these solutions were calculated from solution A as 1.25 and −14.80, respectively.

Synthesis

4′-Acetyl(benzo-15-crown-5)oxime (**2**)

4′-Acetyl(benzo-15-crown-5)oxime was synthesized according to the reported procedure [26].

4′-(ω-Aminoacetyl)benzo(15-crown-5) (**3**)

4′-Acetyl(benzo-15-crown-5) oxime (5.2 g, 16 mmol) was dissolved in dry pyridine (6.2 ml) at −15°C, and a solution of *p*-toluene sulfonyl chloride (3.05 g, 16 mmol) in pyridine (6.2 ml) was added dropwise at the same temperature. After 2 hours, this mixture was poured slowly onto 60 g ice and 60 ml water. The precipitate was filtered off and washed with water until no trace of pyridine was left. Then the precipitate was dried *in vacuo*. The tosylated compound was suspended in dry ethanol (14 ml) at −15°C and reacted with potassium ethylate prepared from 0.7 g potassium in 15 ml of ethanol at −15°C. This mixture was stirred and left to warm up to room temperature. Potassium tosylate was filtered off. The filtrate was poured onto 200 ml dry diethyl ether. This solution was shaken with 2 *N* HCl (3×30 ml). The acidic solution was evaporated to dryness at 30–40°C. When the oily residue was left overnight at room temperature, the product was obtained as brown crystals of **3** HCl.

Yield: 3.2 g (61.5%); IR (KBr): $\nu = 3320$ (NH_2), 1343, 1162 (SO_2) cm^{-1}.

4′-(ω-Salicylaldimineacetyl)benzo(15-crown-5) (*L*H)

To a solution of **3** · HCl (2.78 g, 8.55 mmol) in ethanol (20 ml), first an equivalent amount of NaOH and then salicyl aldehyde (1.04 g, 8.55 mmol) were added. When the reaction mixture was refluxed for 0.5 h precipitation of a yellow solid occurred which was filtered and washed with ethanol to afford 2.8 g (76%) of *L*H.

M.P.: 179°C; IR (KBr): $\nu = 3260$ (OH), 1620 (C=O), 1260, 1110 (C-O-C) cm^{-1}; ^1H NMR (Acetone-d_6): $\delta = 10.5$ (s, 1H, -OH), 9.11 (s, 1H, CH=N), 8.13–6.99 (m, 7H, Ar-H), 4.53–4.05 (m, 16H, CH_2-O), 2.72 (s, 2H, CO-CH_2N) ppm; $C_{23}H_{28}O_7N$ (430); calcd.: C 64.17, H 6.56, N 3.25; found.: C 64.05, H 6.24, N 3.05.

Sodium nitrate salt of 4′-(ω-salicylaldimineacetyl) benzo(15-crown-5) (*L*H · $NaNO_3$)

Stochiometric amounts of *L*H (0.430 g, 1 mmol) and $NaNO_3$ (0.085 g, 1 mmol) were refluxed in 50 ml of ethanol for 10 minutes, and the clear solution was left overnight at room temperature. The orange crystals were filtered, washed with ethanol, and dried in vacuo.

Yield: 0.31 g (72%); the compound is slightly less soluble than *L*H in solvents which dissolve *L*H easily.

CoL_2 complex

In order to prepare the CoL_2 complex, *L*H (0.1 mmol, 43 mg) was dissolved in 15 ml of absolute ethanol, and 0.05 mmol of $CoCl_2 \cdot 6H_2O$ (11.9 mg) were added to this solution. This mixture was

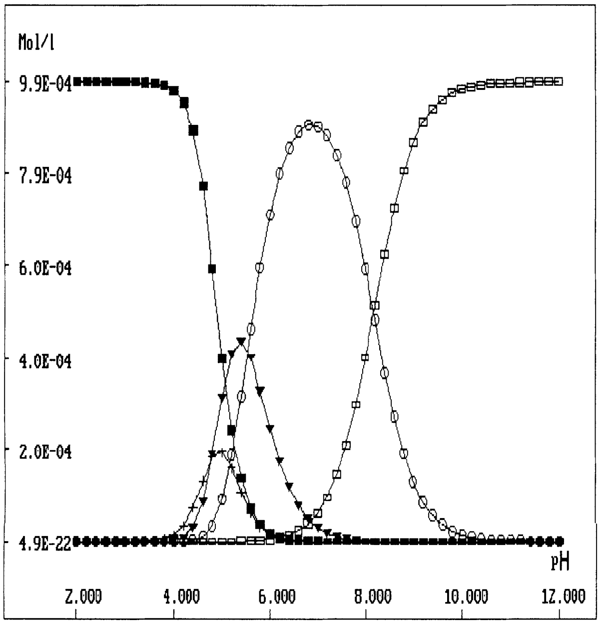


Fig. 6. Structure of ML^2 (M = Cu(II), Ni(II), Co(II))

heated at 60°C for 0.5 h. An orange-red precipitate was obtained upon cooling to room temperature which was filtered, washed first with absolute ethanol and then with diethyl ether, and dried. The product is slightly soluble in *DMSO*.

Yield: 0.030 g (60.7%); m.p.: 276–280°C; IR (KBr): $\nu = 3440$ (OH), 1620 (C=O), 1260–1110 (C-O-C) cm^{-1}; ^{1}H NMR (*DMSO*-d$_6$): $\delta = 8.69$ (s, 1H, CH=N), 7.48 (d, 1H, Ar-H), 7.12 (d, 1H, Ar-H), 6.82 (s, 1H, Ar-H), 4.03 (br s, 4H, Ar-O-CH$_2$), 3.72 (m, 4H, Ar-O-C-CH$_2$), 3.57 (m, 8H, CH$_2$-O-CH$_2$), 2.28 (s, 2H, C(O)-(CH$_2$-N) ppm; $C_{46}H_{54}O_{14}N_2Co$ (917); calcd.: C 60.20, H 5.99, N 3.05, Co 6.43; found: C 60.82, H 5.85, N 3.10, Co 6.44.

Cul$_2$ and NiL$_2$ complexes

In order to prepare the CuL_2 and NiL_2 complexes, *L*H (0.1 mmol, 43 mg) was dissolved in 15 ml of absolute ethanol, and 0.05 mmol of $CuCl_2 \cdot 2H_2O$ (8.55 mg) or $NiCl_2 \cdot 6H_2O$ (11.9 mg) were added to this solution. This mixture was heated at 60°C for 0.5 h. A dark-brown precipitate was obtained when the solution cooled to room temperature. It was filtered, washed with absolute ethanol and dried. The products were soluble in *DMSO*.

$CuCl_2$ yield: 0.025 g (50.2%); m.p.: 280–285°C; IR (KBr): $\nu = 3420$ (OH), 1620 (C=O), 1260, 1110 (C-O-C) cm^{-1}; $C_{46}H_{54}O_{14}N_2Cu$ (922.5); calcd.: C 59.84, H 5.96, N 3.04, Cu 6.88; found: C 60.22, H 5.42, N 2.99, Cu 7.02.

NiL_2: yield: 0.023 g (46.5%); m.p.: 265–270°C; IR (KBr): $\nu = 3430$ (OH), 1620 (C=O), 1260–110 (C-O-C) cm^{-1}; $C_{46}H_{54}O_{14}N_2Ni$ (917.0); calcd.: C 60.20, H 5.99, N 3.05, Ni 6.40; found: C 60.18; H 5.50, N 3.12, Ni 6.43.

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