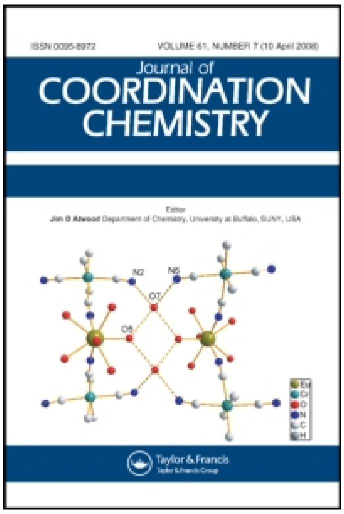

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INVESTIGATIONS OF THE INTERACTION OF 4',5'-*BIS*(SALICYLIDENEIMINO) BENZO-15-CROWN-5 WITH TRANSITION AND ALKALI METAL IONS AND THE URANYL CATION

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Formation constants for complexes of Co(II), Cu(II), Ni(II) and U(VI)O_2 and 4,'5-*bis*(salicylideneimino)benzo-15-crown-5 (H_2L) have been measured at 25 ± 0.1°C and $I = 1$ M (KCl) by potentiometric techniques. Protonation constants of the ligand and overall formation constants have been calculated from potentiometric data using the program TITFIT. Both imino nitrogen and phenol groups provide donor atoms together with hydroxyl ions at higher pH values. The alkali ion binding capability of the crown ether groups of CuL and NiL measured by alkali extraction experiments gives the order $K^+ > Na^+ > Li^+$.

KEYWORDS: crown ethers, 4',5'-*bis* (salicylideneimino)benzo-15-crown-5, protonation constants, formation constants, alkali extraction

INTRODUCTION

Crown ethers and salicylaldimines are two important groups of ligands extensively studied for their high affinity to interact with alkali and transition metal ions, respectively.[1,2] The reversible oxygen binding capability of Co(II)-salicylaldimines provides a synthetic analogue of oxygen carriers.[3] The wide use of macrocyclic ethers as selective phase transfer agents should also be mentioned.[4]

During a continuing period on the synthesis of multifunctional ligands carrying both "hard" and "soft" donor sites, we have reported a number of novel compounds simultaneously carrying crown ether or macroaza-groups together with either *vic*-dioximes,[5,6] phthalocyanines[7,8] or salicylaldimine[9,10] moieties. It has been shown that these systems can be used for the formation of supramolecular aggregates or mesophases, enhancing metal recognition phenomena and even leading to ion channels.[11]

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Addition of macrocyclic groups to the transition metal complexes of soft donors also enhances their solubilities in various organic solvents and its application to solution chemistry is unambiguous. 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.[12,13]

We are confident that potentiometric titration alone can be effectively applied to estimate the complex species in different pH ranges by carefully applying appropriate mathematical procedures. In the present work, we report the stabilities of the Co(II), Cu(II), Ni(II) and $U(VI)O_2$ complexes of a salicylaldimine ligand (LH_2) obtained by condensation of 4'-5'-diamino-benzo-15-crown-5 and salicylaldehyde.[10] Interaction of the crown ether groups with alkali metals has been also estimated by extraction experiments from aqueous to organic phases.

EXPERIMENTAL

H_2L and its transition metal complexes with Co(II), Ni(II), Cu(II) and $U(VI)O_2$ were prepared according to reported procedures.[10] The concentrations of stock solutions of metal ions were standardized by atomic absorption spectroscopy.

Potentiometric Measurements

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 ionic strength was kept constant at 1M KCl. All titration solutions were prepared in a total volume of 40.0 cm^3 and thermosttated at 25.0 ± 0.1°C.

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

Solution A : HCl (2 ml, 0.1 M), KCl (4 ml, 1 M), acetone (10 ml), water (24 ml).

Solution B : HCl (2 ml, 0.1 M), KCl (4 ml, 1M), solution of H_2L in acetone (10 ml, 0.01 M), water (24 ml).

Solution C-F: HCl (2 ml, 0.1 M), KCl (4 ml, 1M), solution of H_2L in acetone (10 ml, 0.01 M), aqueous solution of metal salt (*i.e.* $CuCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $UO_2(AcO)_2 \cdot 4H_2O$)(5 ml, 0.01 M), water (19 ml).

These solutions were titrated with 0.1 M NaOH in increments of 0.2 ml. The corresponding change in the pH of the solution was measured.

RESULTS AND DISCUSSION

A maximum of four protons can be liberated from the ligand, 4',5'-*bis*(salicylideneimino)-benzo-15-crown-5 (H_2L), in the protonated form (H_4L^{2+}) on titration with a strong base in the pH range 2.0–12.0. The titration indicates the presence solely of simple H_2L, HL^- and L^{2-} entitities. Although this result appears to contradict the four protonation constants in the same pH range obtained for an analogous ligand prepared by the condensation of 4'-hydroxy-5'-formyl-benzo-15-crown-5 with 1,2-diaminoethane[9] it is a consequence of the lower basicity of the azomethine groups derived from aromatic amines in the case of H_2L. The values for the macroscopic protonation constants for H_2L are $\log K_1 = 6.50$ and $\log K_2 = 6.06$.

The assignment of the two protons to the phenolic groups in H_2L can be made on the basis of comparable values obtained for each of them and by analogy with known values for related compounds.[13] Titration data obtained for H_2L in the presence of Cu(II), Ni(II), Co(II) and $U(VI)O_2$ ions was processed by the program TITFIT to observe protonated, neutral and hydroxo complexes.[14] Cumulative formation constants of the species encountered with all four metal ions are summarized in Table 1.

In the case of the Cu-H_2L system, complexation begins at pH *ca* 3.0 with the formation of $[CuHL]^+$ and then CuL appears at pH values above 5.0. While most of the metal ion is converted into the monoprotonated complex at pH 5.2, the completely deprotonated product only reaches 22% of the total metal concentration around pH 6.2. The reason for this lower conversion to CuL is the rapid increase in the concentration of CuL(OH), starting from pH 5.8, and which reaches a maximum of about 100% near pH 7.6.

Similar complexes form in solutions containing Co(II) and H_2L. Here the monoprotonated $[CoLH]^+$ and deprotonated [CoL] complexes show maxima at pH 5.9 and 7.8, respectively. Conversion ratios are about the same (~80%). The monohydroxo complex [CoL(OH)] appears above pH 7.2 and reaches a maximum near pH 10.

The complexation behaviour of Ni(II) with H_2L follows a different pattern. No monoprotonated complex is observed. Instead mono- and dihydroxo compounds appear after the deprotonated NiL complex which has a maximum concentration at pH 6.5 (75% conversion). The monohydroxo complex [NiL(OH)] can be considered as an intermediate for $[NiL(OH)_2]$, which is the only stable species in solution above pH 8.5.

The $U(VI)O_2$-H_2L system shows a completely different range of complexes. The high coordination number of this f-block element enables the coordination of one or two tetradentate ligands together with one or two hydroxo ions.[15] A uranyl-deprotonated H_2L complex has a maximum around pH 5.0. The monohydroxo

Table 1 Protonation and overall formation constants for H_2L and its complexes.

Metal ion	Species	logβ
H^+	HL^-	6.50(1)
	H_2L	12.55(1)
	ML	5.03(1)
Cu^{2+}	MLH	11.20(1)
	ML(OH)	-0.95(1)
	ML	4.40(1)
Co^{2+}	MLH	11.00(1)
	ML(OH)	-4.00(1)
	ML	4.11(1)
Ni^{2+}	ML(OH)	-3.12(1)
	$ML(OH)_2$	-11.00(1)
	ML	6.20(1)
$UO_2{}^{2+}$	ML_2	11.60(1)
	ML(OH)	0.80(1)
	$ML_2(OH)_2$	-1.35(1)

Table 2 Alkali metal extraction data

	Li^+		Na^+		K^+	
	%	$10^{-2}K_e$ l^2mol^{-2}	%	$10^{-2}K_e$ l^2mol^{-2}	%	$10^{-2}K_e$ l^2mol^{-2}
H_2L	0.3	0.4	5.6	8.6	20.6	37.7
CuL	2.8	4.1	7.2	11.2	22.1	41.4
NiL	1.7	0.2	2.2	3.2	6.5	10.0

derivative of this 1:1 (UO_2/L) complex and the 1:2 (UO_2/L) complex also are stable in the pH range from 4.4 to 7.8, the latter species maintaining the higher percentage. Almost all the metal ions are converted to $[UO_2L_2(OH)_2]$ above pH 8.

Alkali metal ion extraction from aqueous to organic phases is accepted as a conventional method to determine the binding tendency of ligands with alkali metal cations.[16,17] In this technique, a picrate salt is dissolved in water and the ligand (*i.e.* the transition metal complexes of H_2L) is in an immiscible solvent such as chloroform or dichloromethane. At equilibrium, the amount of picrate salt extracted to the organic phase is related to the stability constant of the cation/ligand adduct[18,19] Although it is possible theoretically to calculate the asociation constant for each ligand, the absolute values of these constants will differ from the calculated ones due to the amount of water extracted together with the cation.[19] Also, the larger diameter of K^+ ion relative to the internal cavity of 15-crown-5 macrocycle leads to uncertainty in the stoichiometry of complexation so the association constant cannot be rigorously calculated. Therefore, only qualitative features will be discussed, taking into account the extracted percentage of the alkali cations by the crown-ether-compunds given in Table 2. The high solubility of H_2L, CoL and UO_2L in aqueous alkali solutions hindered the evaluation of their alkali metal extracting capabilities.

The binding stability of crown compounds CuL and NiL with alkali metal ions show the order $K^+ > Na^+ > Li^+$. This is the expected selectivity since the ionic radius of Li^+ is too small for this cavity and that of Na^+ perfectly fits it. The enhanced planarity of CuL and NiL fragments causes sterically suitable donor sites for forming sandwich-type 2:1 crown ether/alkali metal adducts with K^+ ions and therefore these are the most stable complexes.

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