Thermodynamic Stabilities of Cobalt(II), Nickel(II), and Copper(II) Complexes of O_2N_2-Donor Macrocyclic Ligands

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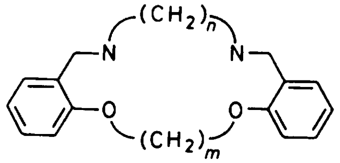
Co-ordination compounds formed between two O_2N_2-donor macrocyclic ligands, one 14-membered (L^1) and one 16-membered (L^2), and H^+, Co^{2+}, Ni^{2+}, and Cu^{2+} in 65% ethanol have been studied potentiometrically at 25.0 °C and $I = 0.10$ mol dm^{-3} [$N(CH_3)_4NO_3$]. For each of these ligands the formation constants of the bivalent metal ions follow the Irving–Williams order of stability. For each of the bivalent metal ions the stabilities follow the macrocyclic ring-size sequence 16 < 14. It can be deduced that an alternating sequence of five- and six-membered chelate rings increases complex stability.

The intense interest recently generated in macrocyclic ligands stems from the extraordinary stability of their metal complexes and their peculiar ability to bind selectively certain cations in preference to others. The thermodynamic stabilities of nickel(II) and copper(II) complexes of a series of O_2N_2-donor macrocyclic ligands of type (I) in the presence of chloride ion have recently been studied.[1,2] For nickel(II) complexes in the presence of chloride ion, a clear correlation between macrocyclic hole size and thermodynamic stability has been observed. In the 14- to 17-membered unsubstituted ligand series, maximum stability is reached at the 16-membered ring.[1] In marked contrast to the behaviour of nickel(II), no well defined relationship between macrocycle ring size and thermodynamic stability was observed for copper(II).[2] As already mentioned by Lindoy and co-workers,[2–4] the presence of chloride ion in the background electrolyte solution strongly promotes the formation of [CuLCl]$^+$, [NiLCl]$^+$, and [$NiLCl_2$], where L is an O_2N_2-donor ligand of type (I).

In order to avoid the formation of the five- or six-co-ordinated adduct, the thermodynamic stabilities of cobalt(II), nickel(II), and copper(II) complexes of L^1 (I; $n = m = 2$) and L^2 (I; $n = m = 3$) in the absence of halide ion have been studied. The results obtained are significantly different from those in the presence of chloride ion.



(I) n = 2 or 3
m = 2 or 3

Table. Equilibrium constants for the macrocyclic systems in 65% ethanol at 25.0 ± 0.1 °C and $I = 0.1$ mol dm^{-3} [$N(CH_3)_4NO_3$]

	log (protonation constant)		log (stability constant)		
Ligand	K_1^H	K_2^H	Co^{2+}	Ni^{2+}	Cu^{2+}
L^1	9.22 ±0.05	5.38 ±0.08	5.68 ±0.12	6.46 ±0.13	9.27 ±0.11
L^2	9.95 ±0.04	7.03 ±0.06	5.23 ±0.15	5.74 ±0.12	8.35 ±0.12

Experimental

Materials.—The macrocyclic ligands L^1 and L^2 were prepared by using the literature procedures.[5,6] They were 99.9% pure as determined by titration with standard base. The solutions of transition-metal ions were standardized by titration with ethylenediaminetetra-acetate. All other chemicals used were of GR grade from Merck or Fluka.

Measurements.—For pH measurements a Radiometer PHM 64 equipped with a GK 2401 B combined electrode was used. The pH was standardized with NBS buffers and the readings were corrected to give the hydroxide-ion concentration. The hydrogen-ion concentration in 65% ethanol solution [$I = 0.10$ mol dm^{-3}, $N(CH_3)_4NO_3$] was calculated from $-\log[H^+] = pH - 0.19$.[7] Appropriate aliquots of standard solutions of ligand or ligand and metal ion were titrated with a standard tetramethylammonium hydroxide solution. In all titrations the ionic strength was maintained relatively constant by using 0.10 mol dm^{-3} $N(CH_3)_4NO_3$ as supporting electrolyte. The solutions were protected from air by a stream of 65% ethanol-saturated prepurified nitrogen and were maintained at 25.0 ± 0.1 °C during measurements. The equilibrium constants were calculated using the program KONST.[8]

Results and Discussion

Protonation Constants for the Macrocycles.—Owing to the very low solubility of the unprotonated free ligand in water, the bulk of the studies were performed using 65% ethanol as solvent. The values of the protonation constants of these ligands are listed in the Table.

For each of these macrocyclic ligands, the value of the protonation constant K_2^H is significantly less than that of K_1^H as might have been expected on the basis of both statistical factors and of electrostatic repulsion between the hydrogen ion and the protonated ligand.[9] In general, the electrostatic repulsion between protonated amine groups of a macrocyclic ligand is much larger than those of the analogous open-chain ligand. The large differences between K_1^H and K_1^H of L^1 and L^2 lend support to this view. For each stage of protonation, the constants K_1^H and K_2^H lie in the order $L^2 > L^1$. This sequence can be related to the different inductive effects of the constituent groups in the ligands. The values of K_1^H and K_2^H

of L^2 are all lower than the corresponding constants of trimethylenediamine,[10] and those of L^1 are all lower than the corresponding constants of ethylenediamine,[10] in accord with the large base-weakening effect of the neighbouring *o*-alkoxy phenyl group.[11]

Compositions of the Complexes.—Job's method of continuous variations was adopted for the determination of the compositions of the complexes. The results indicated that cobalt(II), nickel(II), and copper(II) form 1 : 1 complexes with each of these macrocyclic ligands.

Stability Constants.—The log K_f values for the cobalt(II), nickel(II), and copper(II) complexes of L^1 and L^2 are listed in the Table. For each of these ligands, the formation constants of the bivalent metal ions follow the expected Irving–Williams order of $Co^{II} < Ni^{II} < Cu^{II}$.[12] For each of the transition-metal ions, the K_f values indicate that the stabilities follow the order $L^2 < L^1$, *i.e.* the macrocyclic ring-size sequence 16 < 14.

It is interesting to compare the protonation constants and stability constants for the transition-metal complexes of L^1 and L^2. The value of $K_1^HK_2^H$ for L^2 is about 200 times larger than the corresponding value for L^1, while the value of K_f for $[NiL^2]^{2+}$ is about 5 times smaller than the corresponding constant for $[NiL^1]^{2+}$. In addition to the effect of the basicity of the ligand, hole-size considerations based on crystallographic data also suggest that the 16-membered macrocycle provides the fit of lowest strain for nickel(II).[3] On the other hand, the girdle strains among linked consecutive chelate rings [13] strongly disfavour the formation of transition-metal complexes with the 16-membered macrocyclic ligand L^2. The relative stabilities shown in the Table reflect mainly the steric constraints among the four linked six-membered rings of $[ML^2]^{2+}$ which are relieved by the presence of the two middle five-membered rings in the L^1 complexes. Analogous to the transition-metal complexes of the linear quadridentate ligands *N,N′*-bis(3-aminopropyl)propane-1,3-diamine and *N,N′*-bis(β-carbamoylethyl)trimethylenediamine,[14–16] the extremely large strain in the consecutive six-membered chelate rings significantly hinders the formation of $[ML^2]^{2+}$ and an alternating sequence of five- and six-membered rings increases complex stability.[16,17] It is worthwhile to note that with nickel(II) in the presence of chloride ion, the stability reaches a peak for the 16-membered ring complex in 95% methanol.[1] This is in marked contrast to the behaviour in the absence of chloride ion.

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