Studies involving Mixed-donor Macrocyclic Ligands. A Comparative Study of the Influence of Medium Effects on the Stabilities of Complexes of Co^{II}, Ni^{II}, and Cu^{II} with 14- to 16-Membered O_2N_2-Donor Macrocycles

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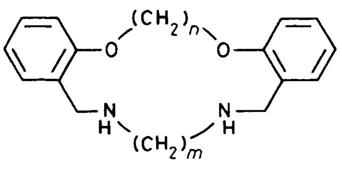
The effect of change of background electrolyte and solvent from 95% methanol (I = 0.1 mol dm^{-3}, NEt_4ClO_4 or NMe_4Cl) to 65% ethanol (I = 0.1 mol dm^{-3}, NMe_4NO_3) on the stability constants of a series of complexes of Co^{II}, Ni^{II}, and Cu^{II} with 14- to 16-membered O_2N_2-macrocycles has been investigated. The present study does not substantiate the results of a previous study, in which the latter conditions were employed, when it was proposed that a different stability order occurs for the complexes of the 14- and 16-membered macrocycles than reported for these complexes in 95% methanol (I = 0.1 mol dm^{-3}, NMe_4Cl). Instead, it was found that the same stability order is maintained no matter which of the above conditions is employed for the measurements. In the case of the nickel(II) complexes, the stability increases from the 14- to the 16-membered ring in accordance with the previous prediction that the fit of the latter ring is nearly ideal for high-spin Ni^{II}.

The strong binding of the cyclic and bicyclic polyether macrocyclic ligands for the alkali- and alkaline-earth metal ions has been well documented;[1] however such ligands generally yield very weak complexes with transition-metal ions. Nevertheless, incorporation of donor atoms other than oxygen in the backbone of polyether ligands tends to increase considerably their affinity for the latter ions. For example, it has been demonstrated in previous studies that the O_2N_2-donor ligands L^1—L^4, incorporating 14- to 17-membered macrocyclic rings, form stable complexes with a range of transition (and post-transition) metal ions.[2—4] Thus, these ligands give metal complexes of the type $[NiCl_2(macrocycle)]$ which have pseudo-octahedral co-ordination geometries;[5,6] the *trans*-planar arrangement of the macrocycle in complexes of this type has now been demonstrated by a number of *X*-ray diffraction studies.[7]



	n	m
L^1	2	2
L^2	2	3
L^3	3	3
L^4	4	3

Using a recently developed procedure for estimating the 'fit' of a metal ion for a macrocyclic ligand (based on *X*-ray data), it was concluded that the 16-membered ring (L^3) provides the optimum hole size for nickel along this series.[8] This conclusion has also been supported by molecular mechanics calculations.[2] In agreement with this, the respective thermodynamic stabilities of the nickel chloride complexes of L^1—L^4 have been shown previously to increase from the 14- to the 16-membered ring species and then decrease for the 17-membered ring complex.[6] The complex of L^3 also corresponds to the maximum kinetic stability along the series.[9] Thus, both the thermodynamic and kinetic evidence supports the contention that the 16-membered ring is close to ideal for Ni^{II} in these pseudo-octahedral complexes. Although it is expected that substitution of other anionic ligands for chloride in the axial co-ordination positions of the above complexes will have some influence on the in-plane co-ordination of the macrocycle, we were nevertheless somewhat surprised by a report[10] in which the log *K* values (obtained in 65% ethanol; I = 0.1 mol dm^{-3}, NMe_4NO_3) for the nickel complexes of L^1 and L^3 were quite different to our previously reported values determined in 95% methanol (I = 0.1 mol dm^{-3}, NMe_4Cl).[6] Surprisingly, for the study in nitrate media the complex of the 14-membered system was reported to be more than an order of magnitude more stable than the complex of the 16-membered ring. This apparent reversal in stability order was suggested by the authors to reflect, to a large degree, the different anionic ligands present in the respective studies. Similarly, the values reported for the copper(II) and cobalt(II) complexes of these ligands in nitrate media were quite different (see later) to the values obtained by us in the presence of chloride ion.[3,4]

In view of this, we have undertaken further log *K* determinations for the complexes of Ni^{II}, Co^{II}, and Cu^{II} with L^1—L^4 in the presence of the 'non-co-ordinating' perchlorate anion (I = 0.1 mol dm^{-3}, NEt_4ClO_4) in 95% methanol as well as determining (and in the case of L^1 and L^3, redetermining) the stabilities of the complexes of Ni^{II} and Cu^{II} under similar conditions to those used in the previously mentioned study, that is in 65% ethanol with I = 0.1 mol dm^{-3} (NMe_4NO_3). All values are compared with those originally reported by us in chloride media.[3,4,6]

Experimental

The ligands L^1—L^4 were prepared and characterized as described previously.[11] Care was taken to isolate the required monomeric product, L^1, from any dimeric product that formed during the condensation.[12] The ligand protonation constants and the log K values for the metal complexes in 95% methanol ($I = 0.1$ mol dm^{-3}, NEt_4ClO_4) were determined as reported previously;[6] the present values represent the mean of at least three (and up to eight) independent determinations at different metal and/or ligand concentrations; precipitation of complex or hydrolysis products prevented the collection of a full set of titration data in a number of cases. The related values for this solvent mixture, but with $I = 0.1$ mol dm^{-3} (NMe_4Cl), have been reported previously.[3,4,6] (In most cases, the latter are mean values from separate determinations in each of the authors' laboratories.)

For the determinations in 65% ethanol (35 cm^3 of water made up to 100 cm^3 with ethanol), the system was calibrated (to yield E° and pK_w values) by a similar procedure to that used for the studies in 95% methanol; this involved titration of a solution containing HNO_3 (4×10^{-3} mol dm^{-3}) and recrystallized NMe_4NO_3 ($I = 0.1$ mol dm^{-3}) with standardized NMe_4OH in 65% ethanol. This differed from the calibration procedure used by Wang and Chung[10] who employed NBS buffers in water and corrected the pH values for the use of 65% ethanol.

The log K values were calculated using the program KONST;[13] a range of data was also processed by MINIQUAD[14] and/or SUPERQUAD.[15] All programs yielded values for a given system which were identical within experimental error.

Cobalt(II) yielded weak complexes; a precipitate (probably a hydroxy species) tended to form before appreciable amounts of complexation had occurred and the corresponding log K values are of low accuracy. For the complexes of Ni^{II} and Cu^{II} the degree of interference due to precipitation varied from one system to the next.

As is generally the case, equilibria for Co^{II} and Cu^{II} were established quickly while for Ni^{II} longer equilibration times were required.

Table 1. Protonation constants (log K^H values) for L^1—L^3 in different media at 25 °C

	0.1 mol dm^{-3}, NMe_4NO_3 (65% EtOH)		0.1 mol dm^{-3} NEt_4ClO_4 (95% MeOH)		0.1 mol dm^{-3} NMe_4Cl[a] (95% MeOH)	
Ligand	K_1^H	K_2^H	K_1^H	K_2^H	K_1^H	K_2^H
L^1	8.31(5)	4.96(5)[b]	9.27(1)	5.14(2)	9.19	5.40
L^2	8.86(2)	6.36(2)	9.85(4)	6.78(4)	9.81	6.82
L^3	9.08(2)	6.50(2)[c]	10.03(3)	6.83(4)	10.07	7.09

[a] Values from ref. 6. [b] Values quoted in ref. 10 for this (L^1) system are $K_1^H = 9.22(5)$ and $K_2^H = 5.38(6)$. [c] Values quoted in ref. 10 for this (L^3) system are $K_1^H = 9.95(4)$ and $K_2^H = 7.03(6)$.

Table 2. The log K values for complexes of Co^{II}, Ni^{II}, and Cu^{II} with L^1—L^3 in different media at 25 °C

Medium ($I = 0.1$ mol dm^{-3})	Ligand	Co^{II}	Ni^{II}	Cu^{II}
NMe_4NO_3 (65% EtOH)	L^1	*ca.* 3[a]	4.2(2)[b]	7.60(5)[c]
	L^2	*ca.* 3	4.7(2)	6.8(2)
	L^3	3.1(3)[d]	4.85(2)[e]	7.15(20)[f]
NEt_4ClO_4 (95% MeOH)	L^1	*ca.* 3	3.43(2)	7.73(1)
	L^2	<3.6	4.76(3)	7.29(2)
	L^3	4.10(6)	4.97(5)	7.09(3)
NMe_4Cl (95% MeOH)[g]	L^1	<4.5	3.7(2)	8.2(1)
	L^2	<4.5	5.4(1)	7.2(1)
	L^3	<4.5	5.8(1)	7.7(1)

[a] Value quoted in ref. 10, 5.66(12). [b] Value quoted in ref. 10, 6.46(13). [c] Value quoted in ref. 10, 9.27(11). [d] Value quoted in ref. 10, 5.21(15). [e] Value quoted in ref. 10, 5.74(12). [f] Value quoted in ref. 10, 8.35(12). [g] Values taken from refs. 3,4, and 6.

Results and Discussion

Macrocycle Protonation Constants.—The protonation constants K_1^H and K_2^H, where $K_1^H = [HL^+]/[L][H^+]$ and $K_2^H = [H_2L^{2+}]/[HL^+][H^+]$, were obtained potentiometrically by titration of the respective ligands in the presence of an excess of acid with the appropriate tetra-alkylammonium hydroxide solution.

A summary of the protonation constants for different media obtained in our present and previous studies is given in Table 1. Clearly, the values for L^1 and L^3 in 65% ethanol ($I = 0.1$ mol dm^{-3}, NMe_4NO_3) are quite different to those reported by Wang and Chung (see footnote to Table 1).[10] Although some variation might be expected because of the different calibration procedures used (arising from variation in the standard state), we are unable to explain the generally large discrepancies that occur between our results and those of the above-mentioned authors.

Metal Complex Stability Constants.—Table 2 lists the log K values obtained in the present study for Co^{II}, Ni^{II}, and Cu^{II} with L^1—L^3 alongside the results reported by us previously for chloride media. As for the protonation constants, the log K results for L^1 and L^3 in 65% ethanol ($I = 0.1$ mol dm^{-3}, NMe_4NO_3) do not agree with those reported by Wang and Chung.[10] Once again, some variation in the two sets might occur because of the different calibration procedures used. In this case, the log K values would be expected to be displaced by regular amounts reflecting the presence of different standard states. However, the differences are far from regular and we are unable to offer an explanation for this. Nevertheless, the trends in our values for this (65% ethanol) system agree with those observed by us for 95% methanol using either NMe_4Cl or NEt_4ClO_4 as the background salt (Table 2).

For each system the individual constants follow the expected Irving–Williams order of $Co^{II} < Ni^{II} < Cu^{II}$.[16] As mentioned already, the values obtained for the respective cobalt(II) complexes are not of high accuracy. Because of this, it is inappropriate to comment on stability trends for the complexes of this ion except to note that the values are all low. For Cu^{II}, regardless of the anion or solvent, the complexes show no definite peak as the macrocycle ring size increases from 14- to 16-membered. This lack of ring-size discrimination has previously been ascribed, at least for some complexes, to the copper ion lying slightly above the hole of the macrocycle and towards an axial ligand such that a five-co-ordinate (distorted square pyramidal) geometry is attained.[3] An *X*-ray study of $[CuL^2Cl]ClO_4$ confirms that such a structure occurs in the solid state in this case. Since there is a tendency for the copper ion not to occupy completely the macrocyclic cavity in these complexes, it is not surprising that clear ring-size effects are not observed in the log K studies.

For the complexes of Ni^{II}, it is of particular interest that the maximum stability for each system occurs at the 16-membered ring complex no matter which tetra-alkylammonium salt or solvent mixture is used (Figure). This is in accordance with our earlier prediction that this ring is nearly ideal for high-spin nickel. Nevertheless, from the Figure it is apparent that the *relative* values within each set of results do vary somewhat as the solvent and/or background salt is changed. This is not unexpected since, for example, the solvating power of 65% ethanol (dielectric constant approximately 40 at 25 °C) will differ from that of 95% methanol (dielectric constant, 35.4);[17]

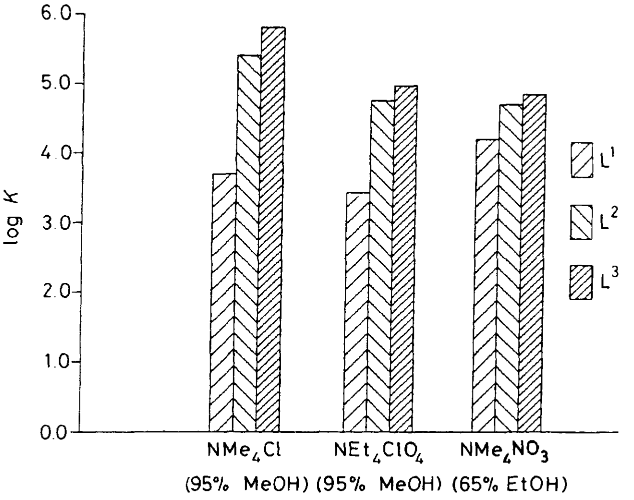


Figure. The log *K* values for the nickel(II) complexes of L^1—L^3, illustrating that the same relative stability order is maintained in different media; in all cases $I = 0.1$ mol dm^{-3}

solvation terms will undoubtedly affect the respective free energies but the magnitude of the contribution is likely to be variable. In any case, the anion present in the three systems ranges from the strongly co-ordinating chloride ion, through nitrate, to perchlorate with its weak binding properties. As a consequence, the competition between solvent and anion for the respective axial co-ordination sites will also be expected to vary considerably from one system to the next.

Acknowledgements

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