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# Thermodynamic and Spectroscopic Properties in Aqueous Solutions of Pentadentate Macrocyclic Complexes

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The complexes of two pentadentate macrocycles containing N, S, and O (A = 1-oxa-7,10-dithia-4,13-diazacyclopentadecane and B = 1-oxa-4,13-dithia-7,10-diazacyclopentadecane) and the open-chain analogue of B (L = 8-oxa-2,14-diaza-5,11-dithiapentadecane) with the cations $Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Zn^{2+}$, $Ag^+$, $Cd^{2+}$, and $Pb^{2+}$ have been studied in aqueous 0.1 M NaClO₄ solutions at 25 °C, by potentiometry, calorimetry, and UV–visible spectroscopy. The three ligands form 1:1 complexes with all the cations studied. The protonation constants of the ligands and the overall stability constants of the 1:1 complexes are given, together with the complexation enthalpies and entropies of some of the 1:1 complexes of B and L. The stability constants of the protonated and binuclear species, when they are formed, are also given. It is found that the following occur: (i) Selectivity corresponding to the general Irving–Williams rule is displayed by both macrocycles. (ii) The magnitude of the macrocyclic effect, displayed by B with respect to L, is strongly dependent on the nature of the cation. (iii) In the case of $Cu^{2+}$, for which there is a strong macrocyclic effect, the thermodynamic origin of the macrocyclic effect is equally enthalpic and entropic. For $Pb^{2+}$, which displays no macrocyclic effect, the enthalpic and entropic contributions are both zero. (iv) The difference in the heteroatom positions in the macrocycles A and B leads to nonnegligible variations of the complex stabilities, which also depend upon the nature of the cation. The molecular structures in the solid state, as well as the electronic spectra in the solid state and in aqueous solution of the nickel, copper, and silver complexes of A and B, suggest a possible correlation between structure and stability. The ligand field parameters $Dq$ for the octahedral Ni(II) complexes are found equal to 1740 cm⁻¹ for A and 1800 cm⁻¹ for B. The nephelauxetic ratio is very low for both macrocycles ($\beta = 0.50$) as could be expected for sulfur donor ligands.

## Introduction

Thermodynamics in solution of macrocyclic complexes has received continuously increasing interest during the last 10 years and has been extensively studied, principally with respect to macrocyclic polyethers[2] and polyamines.[3-18] But "mixed" macrocycles, containing nitrogen, oxygen, and/or sulfur donor atoms have been considerably less investigated. No data on the stability of macrocyclic complexes containing three different heteroatoms N, S, and O could be found in the literature before our work.

We report here the results of our potentiometric, spectrophotometric, and calorimetric studies in aqueous solution of the complexes of a new class of mixed N, S, and O pentadentate macrocycles. These were synthesized for the first time by one of us[19] and we have already published preliminary results,[20-23] as well as some crystal structure determinations.[22-26]

The two macrocycles investigated, A = 1-oxa-7,10-dithia-4,13-diazacyclopentadecane and B = 1-oxa-4,13-dithia-7,10-diazacyclopentadecane, are represented in Figure 1, together with the linear secondary diamine L = 8-oxa-2,14-diaza-5,11-dithiapentadecane, which is the open-chain homologue of the macrocycle B. The stabilities of the complexes of these three ligands with the transition- and heavy-metal cations $Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Zn^{2+}$, $Ag^+$, $Cd^{2+}$, and $Pb^{2+}$ have been investigated potentiometrically, in aqueous 0.1 M NaClO₄ media, at 25 °C.

Our interests in the study consisted mainly in the search for eventual complexation selectivities and in the investigation of the influence of the heteroatom positions in the cycle upon the complex structures and stabilities. We also wished to investigate the so-called "macrocyclic effect", the enhancement of stability of a metallic macrocyclic complex with respect to the corresponding noncyclic chelate,[3] by comparing the stabilities of the various complexes of the macrocycle B to those of its acyclic analogue. The enthalpies of formation of some of the complexes were determined calorimetrically, in order to evaluate the relative contributions of the enthalpic and entropic origins of the macrocyclic effect. These are much debated and seem to vary with the nature of both the cation and the ligand.[3-18] Moreover, the electronic spectra of the nickel(II) octahedral complexes in solution enabled us to determine the ligand field parameters $Dq$ and the nephelauxetic ratios $\beta$.

The results reported here are brought together for comparison with the recent thermodynamic studies of the complexes of two other pentadentate macrocyclic ligands: the pentaamine 1,4,7,10,13-pentaazacyclopentadecane or [15]-aneN₅[17] and the 1,7,10-trioxa-4,13-diazacyclopentadecane or [2.1] (Figure 2). The latter has been studied by two of us in the general framework of the study of the stability in various solvents of polyoxadiaza macrocycles.[27,28] It is analogous to A but with the S(7) and S(10) atoms replaced by oxygen atoms.

## Experimental Section

**Reagents.** The macrocycles A and B were prepared and purified as described elsewhere.[19] The aqueous solutions of ligand perchlorate, obtained by adding a slight excess of HClO₄ to the free ligand, were

Table I. Protonation Constants and Overall Stability Constants of the Complexes of A, B, and L

| cations | complexes | | logarithms of the constants | | |
| --- | --- | --- | --- | --- | --- |
| | | | A | B | L |
| $H^+$ | $HZ^+$ | $\log K_1$ | $8.60 \pm 0.10$ | $8.86 \pm 0.12$ | $9.84 \pm 0.01$ |
| | $H_2Z^{2+}$ | $\log K_2$ | $7.55 \pm 0.06$ | $5.21 \pm 0.08$ | $9.06 \pm 0.04$ |
| $Cu^{2+}$ | $CuZ^{2+}$ | $\log \beta_{101}$ | $11.55 \pm 0.20$ | $13.26 \pm 0.08$ | $9.15 \pm 0.04$ |
| | $CuHZ^{3+}$ | $\log \beta_{111}$ | | | $14.63 \pm 0.40$ |
| $Ni^{2+}$ | $NiZ^{2+}$ | $\log \beta_{101}$ | $7.98 \pm 0.16$ | $8.06 \pm 0.02$ | $4.78 \pm 0.04$ |
| | $NiZ_2^{2+}$ | $\log \beta_{102}$ | | | $7.96 \pm 0.12$ |
| $Co^{2+}$ | $CoZ^{2+}$ | $\log \beta_{101}$ | $5.42 \pm 0.06$ | $5.22 \pm 0.02$ | $<1.5$ |
| | $CoZ_2^{2+}$ | $\log \beta_{102}$ | | | $8.22 \pm 0.06$ |
| $Zn^{2+}$ | $ZnZ^{2+}$ | $\log \beta_{101}$ | $5.09 \pm 0.02$ | $4.43 \pm 0.04$ | $5.61 \pm 0.1$ |
| | $ZnZ_2^{2+}$ | $\log \beta_{102}$ | | $7.91 \pm 0.10$ | $10.81 \pm 0.10$ |
| $Pb^{2+}$ | $PbZ^{2+}$ | $\log \beta_{101}$ | $5.67 \pm 0.06$ | $6.78 \pm 0.02$ | $7.49 \pm 0.04$ |
| | $PbHZ^{3+}$ | $\log \beta_{111}$ | | | $14.11 \pm 0.32$ |
| $Cd^{2+}$ | $CdZ^{2+}$ | $\log \beta_{101}$ | $6.53 \pm 0.01$ | $7.13 \pm 0.02$ | $4.40 \pm 0.03$ |
| $Ag^+$ | $AgZ^+$ | $\log \beta_{101}$ | $8.95 \pm 0.40$ | $9.91 \pm 0.08$ | $7.32 \pm 0.05$ |
| | $AgHZ^{2+}$ | $\log \beta_{111}$ | $14.15 \pm 0.50$ | $15.22 \pm 0.06$ | $15.13 \pm 0.06$ |
| | $Ag_2Z^{2+}$ | $\log \beta_{201}$ | $12.21 \pm 0.80$ | $12.6 \pm 2.2$ | $10.19 \pm 0.24$ |
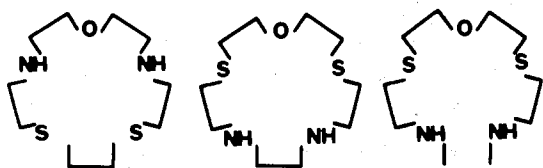


Figure 1. Pentadentate macrocyclic and linear pentadecanes studied in this work. From left to right: A, B, L.



(a)  (b)
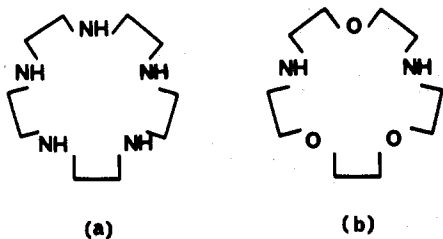
Figure 2. Some cyclopentadecanes studied in other works (ref 16, 26, and 27): (a) 1,4,7,10,13-pentaazacyclopentadecane or [15]aneN₅, (b) 1,7,10-trioxa-4,13-diazacyclopentadecane or [2.1].

flushed with argon in order to avoid any carbonation and then filtered and diluted to the desired concentrations (about $5 \times 10^{-3}$ M). The ionic strength was kept constant and equal to 0.1 M by addition of $NaClO_4$ (Fluka, recrystallized from water). The base for the titrations was NaOH, prepared in carbonate-free water and standardized against potassium biphthalate.

The $Na^+$ ions, in the concentrations used, do not interact with any of the ligands studied: the titration curves of the ligands with tetramethylammonium hydroxide, in 0.1 M tetraethylammonium perchlorate solutions, are the same as in 0.1 M sodium perchlorate solutions, and the protonation constants calculated in both cases are exactly the same.

The metallic perchlorate stock solutions (about 0.3 M) were prepared as follows: The commercial chemicals were dissolved without any further purification in 0.1 M $NaClO_4$ solutions for $Ni^{2+}$ and $Ag^+$ (Fluka), $Co^{2+}$ (Koch-Light), and $Cd^{2+}$ (Alfa-Ventron). For $Pb^{2+}$, $Zn^{2+}$, and $Cu^{2+}$, the perchlorate solutions were directly prepared by action of perchloric acid on a slight excess of metallic oxide, followed by filtration. All stock solutions were standardized by complexometric methods,[29] except for $Ag^+$ solutions, which were standardized by gravimetric titrations.

**Potentiometric Titrations.** The protonation constants of the ligands and the formation constants of the complexes were determined potentiometrically, at 25 °C. The base was added with a 1-mL Gilmont microburet to 10 mL of a solution of either the ligand perchlorate with $HClO_4$ in known excess or a mixture of ligand perchlorate and metallic perchlorate in variable amounts with a known excess of $HClO_4$.

The titrations were carried out in a thermostated glass cell (25 ± 0.05 °C), under an atmosphere of argon. The concentrations of free hydrogen ions, $[H^+]$, were measured with a Beckman combined glass

electrode ref. 39501, connected to a TACUSSEL ISIS 20000 pH meter. As $KClO_4$ is insoluble in water, the electrolyte of the reference electrode compartment (saturated KCl) was replaced by a mixed 0.01 M NaCl–0.09 M $NaClO_4$ solution, saturated with AgCl. The electrode standardization was made at $-\log [H^+] = 2$, with a solution of $10^{-2}$ M HCl–$9 \times 10^{-2}$ M $NaClO_4$. As the junction potential varies exponentially with $-\log [H^+]$, the following correction relationship was used:

$$-\log [H^+]_{real} = -\log [H^+]_{measd} + a + b[H^+]_{measd}$$

$a$ and $b$ were determined by measuring $-\log [H^+]_{measd}$ for the following solution of $[H^+]_{real} = 10^{-3}$ ($10^{-3}$ M HCl, $9 \times 10^{-3}$ M NaCl, $9 \times 10^{-2}$ M $NaClO_4$).

**Calculation of the Stability Constants.** Approximate values of the step by step protonation constants of the ligands, $K_1$ and $K_2$, were obtained from the slope and intercept of the least-squares fit to the equation

$$\frac{\bar{p}}{(\bar{p} - 1)[H^+]} = K_1 K_2 \frac{2 - \bar{p}}{\bar{p} - 1}[H^+] - K_1$$

where $\bar{p}$ is the average number of protons bound to each ligand molecule. The values thus obtained were refined either by using the computer program SCOGS[30] or by the least-squares procedure based on recalculation of $[OH^-]$, as described in one of our previous papers.[20] Both refinement procedures gave the same final values.

Approximate values of the overall formation constants of the complexes were first obtained from the formation curves, by standard graphical methods, and then refined by the program SCOGS on a UNIVAC 1110. During the refinement procedure, the protonation constants $K_1$ and $K_2$ were kept constant. For each determination, at least three experiments were performed, with different metal/ligand concentration ratios. The data for each experiment were treated first separately, to check self-consistency. All the data were then used simultaneously, in order to get a precise value.

**Calorimetric Measurements.** These were carried out at 25 °C, with a LKB 8700 calorimeter using 25-mL cells. The procedures used, as well as the calculations, have been described in a previous paper.[23]

**Spectroscopic Measurements.** Spectra of complexes in solution and in the solid state were recorded respectively on a Cary 17D spectrophotometer, using 1-mm cells, or on a Cary 14 spectrophotometer.

**Results**

Table I gives the values of the step by step protonation constants $K_1$ and $K_2$ of the ligands A, B, and L, as well as the overall formation constants $\beta_{ijk}$ of the complexes of the three ligands with the various cations studied, according to the equation

$$iM^{n+} + jH^+ + kZ \rightleftharpoons (M_iH_jZ_k)^{(in+j)+} \tag{1}$$
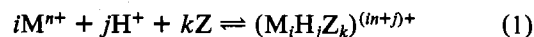
with Z = A, B, or L and $n = 1$ or 2. The given precisions $\pm 2\sigma$ ($\sigma$ being the standard deviations computed by SCOGS) correspond to the 95% confidence intervals of the constants.

The results show that the *macrocyclic ligands* A and B form a complex of 1:1 stoichiometry of general formula $MZ^{n+}$ with *all* the studied cations. In the case of $Ag^+$ and $Zn^{2+}$, additional complexes are observed: for $Ag^+$, the protonated species $AgHZ^{2+}$ and the binuclear species $Ag_2Z^{2+}$; for $Zn^{2+}$, the 1:2 complex $ZnB_2^{2+}$. Protonated and binuclear silver(I) complexes are frequently observed with open-chain polyamines;[32-34] however, we have not observed them in our study of the macrocyclic diamine [2.1].[27] The complex $ZnB_2^{2+}$ is, as far as we know, the only example of a 1:2 stoichiometry for a macrocyclic complex of a transition-metal cation. This stoichiometry has only been mentioned for the complex formed between $K^+$ and the benzo-15-crown-5, which has a sandwich type structure.[35] The open chain ligand L has a more pronounced tendency than those of the macrocyclics to form complexes other than the 1:1 variety: for $Cu^{2+}$ and $Pb^{2+}$ protonated complexes are observed; and for $Ni^{2+}$, $Co^{2+}$, and $Zn^{2+}$ complexes of 1:2 stoichiometry. For $Ag^+$, L, as well as A and B, forms $AgL^+$, $AgHL^{2+}$, and $Ag_2L^{2+}$.

## Discussion

**Protonation of the Ligands and Complexes.** Table I shows that the *protonation constants* $K_1$ and $K_2$ of the macrocycles A and B are smaller than those of the open-chain ligand L, yet quite different from one another.

For L, log $K_1$ and log $K_2$, 9.84 and 9.06, respectively, are of the same order of magnitude as the two first protonation constants of the open-chain pentaamine 3,6,9-triazaundecane-1,11-diamine, commonly named tetren (9.68 and 9.10 from Paoletti and Vacca,[36] 10.36 and 9.65 from Moss, Lin and Rorabacher[37]). The difference between $K_1$ and $K_2$ is similar for both ligands (log $K_1$ − log $K_2$ = 0.6–0.8). For the macrocycles A and B, $K_1$ and $K_2$ are clearly smaller than the two first protonation constants of the cyclic pentaamine [15]aneN$_5$ (log $K_1$ = 10.85 and log $K_2$ = 9.65 from ref 16) and, for B, $K_2$ is even smaller than the third protonation constant of [15]aneN$_5$: log $K_3$ = 6.00.[16] With respect to the cyclic polyoxadiamine [2.1] (log $K_1$ = 8.76 and log $K_2$ = 8.04 from ref 27), A and B display quite similar $K_1$ values but significantly lower $K_2$ values. These observations can be explained by electrostatic interactions,[16,38] the second proton being repulsed by the first one. This electrostatic effect acts more strongly when the protonation sites are closer.

In the open-chain ligands, the protonation sites are remote enough so that nearly no interaction can take place between the two protons. This leads to similar values of two protonation constants. In A and B, the second protonation is hindered by the vicinity of the first protonated site. This effect is more marked in B where the two amine groups are separated by only one ethylene bridge. Therefore the difference of the constants (log $K_1$ − log $K_2$) is greater in B (3.65) than in A (1.05).

Upon protonation of [15]andN$_5$, the second proton is expected to bind to the nitrogen atom which is the most remote from the first protonated one, i.e., in a position identical with that of the second protonated nitrogen of A: consequently, the difference between log $K_1$ and log $K_2$ is similar in both cases, 1.20 and 1.05, respectively. On the other hand, the third protonation site of [15]aneN$_5$ must necessarily be adjacent to an already protonated one, as is the second protonation site of B. This explains why the value of log $K_1$ − log $K_2$ for B (3.65) is the same as that of log $K_2$ − log $K_3$ for [15]aneN$_5$ (9.65 − 6.00 = 3.65). This electrostatic effect may also explain the difference between log $K_2$ and log $K_1$ for A and [2.1], even though they have similar values for $K_1$. This difference is much greater for [2.1] than for A, which may be attributed to the better electrostatic screening of the second proton by the sulfur atoms of A than by the oxygen atoms of [2.1].

The open-chain ligand L gives *protonated complexes* with the cations $Cu^{2+}$, $Pb^{2+}$, and $Ag^+$, whereas the macrocyclic

ligands A and B only give protonated complexes with $Ag^+$. The easier protonation of the complexes of L is due, at least in part, to the fact that L has larger protonation constants than the macrocycles, leading to a more difficult competition between the cation $M^{n+}$ and $H^+$. For the macrocyclic pentaamine [15]aneN$_5$, protonated complexes of $Cu^{2+}$, $Pb^{2+}$, $Zn^{2+}$, and $Cd^{2+}$ have been found,[17] whereas the macrocyclic tri- and tetraamines, as A and B, give no protonated complexes (except for [15]aneN$_4$, which has a very large ring size). The cyclic polyoxadiamine [2.1], as well, gives no protonated complexes. This important difference between the [15]aneN$_5$ and the other macrocyclic pentadecanes A, B, and [2.1] can be, at least partly, accounted for by the fact that the ligand protonation constants are much higher for [15]aneN$_5$ than for the three other ligands. Another explanation for the ease of protonation of the copper(II) complex of [15]aneN$_5$ has been put forward by Kodama and Kimura: one of the five nitrogens bound to the copper atom would occupy an axial position in the octahedral complex and, due to the Jahn–Teller tetragonal distortion, it would be more remote from the central $Cu^{2+}$ ion than the four equatorial nitrogens, and thus, more easily protonated. Nevertheless, this explanation, which is quite logical for a $d^9$ ion, can no longer be put forward for $Pb^{2+}$, $Zn^{2+}$, or $Cd^{2+}$ ions for which no Jahn–Teller effect exists.

**Macrocycle Selectivity.** Comparison of the $\beta_{101}$ values of the 1:1 complexes of ligands A and B shows that, for both ligands, the copper(II) complexes are more stable than the nickel(II) ones which, themselves, are markedly more stable than those of cobalt(II), zinc(II), and lead(II).

The stability sequence observed for each ligand agrees with the Irving–Williams rule, according to which the stability of the high-spin complexes of divalent cations of the first transition series increases, from $Mn^{2+}$ to $Cu^{2+}$ and, after, decreases for $Zn^{2+}$: $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$. The same stability order is observed for the linear ligand L and the stability differences are, in this case, comparable to those observed for A or B. In consequence, the selectivities displayed by the ligands A and B are not specific properties of their macrocyclic character but only reflect the quite general Irving–Williams rule.

**Macrocyclic Effect.** The stability difference between the macrocyclic 1:1 complexes of B and the corresponding complexes of the linear ligand L, or macrocyclic effect, can be measured by the quantity

$$\Delta\beta = \log \beta_{101}(\text{macr}) - \log \beta_{101}(\text{lin})$$

This corresponds to a difference in complexation free energy $\delta(\overline{\Delta G_c})$ such that

$$\delta(\overline{\Delta G_c}) = \overline{\Delta G_c}(\text{macr}) - \overline{\Delta G_c}(\text{lin}) = -\Delta\beta/RT$$

The free energy term $\delta(\Delta G_c)$ can be in turn decomposed into two terms

$$\delta(\overline{\Delta G_c}) = \delta(\overline{\Delta H_c}) - T\delta(\overline{\Delta S_c})$$

where $\delta(\overline{\Delta H_c}) = \overline{\Delta H_c}(\text{macr}) - \overline{\Delta H_c}(\text{lin})$ is the enthalpic contribution to the macrocyclic effect and $\delta(\overline{\Delta S_c}) = \overline{\Delta S_c}(\text{macr}) - \overline{\Delta S_c}(\text{lin})$ is the entropic contribution.

Comparison of the log $\beta_{101}$ values for the complexes $MB^{n+}$ and $ML^{n+}$, in Table I, shows that there are a strong macrocyclic effect for the cations $Cu^{2+}$, $Ni^{2+}$, and $Co^{2+}$, for which $\Delta\beta$ is respectively 4.11, 3.28, and >3.7, a moderate macrocyclic effect for $Cd^{2+}$ and $Ag^+$, for which $\Delta\beta$ = 2.73 and 2.59, respectively, and no macrocyclic effect at all for the $Pb^{2+}$ and $Zn^{2+}$ complexes, for which the complexes of L are even slightly more stable than those of B. It is clear that the macrocycle B gives rise to a macrocyclic effect depending on the nature of the cation. The magnitude of the macrocyclic effects displayed by B is slightly lower than the magnitude of the

**Table II.** Complexation Thermodynamic Functions $\overline{\Delta G_c}$, $\overline{\Delta H_c}$, and $\overline{\Delta S_c}$ of $Cu^{2+}$ and $Pb^{2+}$ with B and L and Enthalpic $(\delta(\overline{\Delta H_c}))$ and Entropic $(\delta(\overline{\Delta S_c}))$ Contributions to the Macrocyclic Effect $(\delta(\overline{\Delta G_c}))$

| cations | thermodynamic functions | ligands | | | |
| --- | --- | --- | --- | --- | --- |
| | | $B^a$ | $L^a$ | $[15]aneN_5^b$ | $tetren^b$ |
| $Cu^{2+}$ | $-\overline{\Delta G_c}$, kJ mol$^{-1}$ | 75.5 ± 0.1 | 52.1 ± 0.2 | 164.9 | 130.6 |
| | $-\overline{\Delta H_c}$, kJ mol$^{-1}$ | 52.4 ± 1.1 | 40.0 ± 3.1 | 137.5 | 104.5 |
| | $\overline{\Delta S_c}$, J K$^{-1}$ mol$^{-1}$ | 77.4 ± 4.2 | 40.9 ± 11.3 | 92.0 | 87.8 |
| | $T\overline{\Delta S_c}$, kJ mol$^{-1}$ | 23.1 ± 1.2 | 12.2 ± 3.4 | 27.4 | 26.1 |
| | $\delta(\overline{\Delta G_c})$, kJ mol$^{-1}$ | | −23.4 | 34.3 | |
| | $\delta(\overline{\Delta H_c})$, kJ mol$^{-1}$ | | −12.4 | 33.0 | |
| | $\delta(\overline{\Delta S_c})$, J K$^{-1}$ mol$^{-1}$ | | 36.5 | 4.2 | |
| | $T\delta(\overline{\Delta S_c})$, kJ mol$^{-1}$ | | 10.9 | 1.3 | |
| $Pb^{2+}$ | $-\overline{\Delta G_c}$, kJ mol$^{-1}$ | 38.6 | 42.7 | 97.8 | 56.7 |
| | $-\overline{\Delta H_c}$, kJ mol$^{-1}$ | 39.8 | 39.9 | 41.8 | 38.0 |
| | $\overline{\Delta S_c}$, J K$^{-1}$ mol$^{-1}$ | −4.0 | 9.4 | 188.1 | 62.7 |
| | $T\overline{\Delta S_c}$, kJ mol$^{-1}$ | −1.2 | 2.8 | 56.0 | 18.7 |
| | $\delta(\overline{\Delta G_c})$, kJ mol$^{-1}$ | | 4.1 | 41.1 | |
| | $\delta(\overline{\Delta H_c})$, kJ mol$^{-1}$ | | 0.1 | 3.8 | |
| | $\delta(\overline{\Delta S_c})$, J K$^{-1}$ mol$^{-1}$ | | −13.4 | 125.4 | |
| | $T\delta(\overline{\Delta S_c})$, kJ mol$^{-1}$ | | −4.0 | 37.3 | |

$^a$ This work. $^b$ Kodama and Kimura's data for [15]aneN$_5$ and tetren have been added, for comparison purposes. From ref 17.

macrocyclic effects observed with polyamines. For instance, the copper(II) complexes of [12]aneN$_4$ and [15]aneN$_5$ display macrocyclic effects which are respectively measured by $\Delta\beta$ = 4.6[14] and 5.5.[15]

The question of the thermodynamic origin of the macrocyclic effect has been widely discussed. The first studies, some 10 years ago, dealt mainly with $Cu^{2+}$ and $Ni^{2+}$ tetraamine complexes. The results obtained with the [14]aneN$_4$ seemed to verify Margerum's hypothesis according to which the macrocyclic effect should arise mainly from a favorable enthalpic contribution $(\delta(\overline{\Delta H_c}) < 0)$ due to the fact that macrocyclic ligands are less solvated than open-chain ones.[3-5] In this perspective, the macrocyclic effect should be independent from the cation. In their further study of other 12- to 15-membered tetraamine copper complexes, Fabbrizzi, Paoletti, and co-workers showed that the relative contributions of the entropic and enthalpic terms can vary with the ligand.[10]

Recent studies, involving other cations such as $Zn^{2+}$, $Pb^{2+}$, $Cd^{2+}$, and $Ag^+$, and other ligands such as the macrocyclic tri- and pentaamines[10,11,14-18] have given a large variety of diverse results, which show the following.

(i) For a given ligand, the extent of the macrocyclic effect depends on the nature of the cation; for instance, the stability differences between the complexes of [15]aneN$_5$ and tetren, measured by Kodama and Kimura,[17] are $\Delta\beta$ = 5.5 for $Cu^{2+}$, 5.1 for $Cd^{2+}$, 4.0 for $Zn^{2+}$, 3.7 for $Hg^{2+}$, and 7.4 for $Pb^{2+}$. We have also noted a strong cation dependence, although not the same one.

(ii) For a given ligand, the relative contributions of the enthalpic and entropic terms to the macrocyclic effect can vary with the nature of the cation or, for a given cation, with the nature of the ligand. For instance, for the pentaamine [15]aneN$_5$, it was found that the macrocyclic effect is mainly due to a favorable enthalpic term with $Cu^{2+}$ $(\delta(\overline{\Delta H_c})) = -33.3$ kJ mol$^{-1}$ and $\delta(\Delta S_c) = 4.2$ J K$^{-1}$ mol$^{-1}$) and to a favorable entropic term with $Pb^{2+}$, $Hg^{2+}$, $Zn^{2+}$, and $Cd^{2+}$ (for $Pb^{2+}$, $\delta(\Delta H_c) = -3.8$ kJ mol$^{-1}$ and $\delta(\Delta S_c) = 125$ J K$^{-1}$ mol$^{-1}$). To the contrary, for the $Cu^{2+}$ complex of the tetraamine [12]aneN$_4$, the macrocyclic effect is mainly due to a strong entropic contribution $(\delta(\overline{\Delta S_c}) = 132$ J K$^{-1}$ mol$^{-1})$, the enthalpic contribution being even unfavorable $(\delta(\overline{\Delta H_c}) = 13.8$ kJ mol$^{-1})$.

The comparison of our results with those of Kodama and Kimura's study of [15]aneN$_5$ shows essential differences concerning the $Pb^{2+}$ and $Zn^{2+}$ complexes. We find that these

complexes are more stable with the open-chain ligand L than with B, whereas they find a strong macrocyclic effect with [15]aneN$_4$; respectively $\Delta\beta$ = 7.4 and 4.0. Thus, in the present state of the research about the macrocyclic effect, it seems impossible to draw any general conclusion from the various results obtained.

In order to estimate what is the relative importance of the enthalpic and entropic contributions in the two extreme cases encountered, namely, the case of $Cu^{2+}$, giving rise to a strong macrocyclic effect, and the case of $Pb^{2+}$, giving rise to no macrocyclic effect at all, we have determined the complexation enthalpies $\overline{\Delta H_c}$ of the 1:1 complexes of $Cu^{2+}$ and $Pb^{2+}$ in aqueous 0.1 M NaClO$_4$ solutions, at 25 °C, calorimetrically.[21] Our results, which are summarized in Table II, show that *the macrocyclic effect displayed by the copper complex is equally due to favorable enthalpic and entropic contributions.* The situation is thus different from that of the copper complex of the pentaamine [15]aneN$_5$ where the enthalpic contribution is by far the major contribution to the macrocyclic effect (for comparison facilities, the data on [15]aneN$_5$ and tetren, measured by Kodama and Kimura,[17] have been added in Table II). Our results concerning the *lead complexes* show that, in this case, the absence of macrocyclic effect is not due to a fortuitous balance between enthalpic and entropic contributions which would cancel each other but to the fact that *both enthalpic and entropic terms are negligible.* For the pentaamine lead complexes, the enthalpic contribution is also nearly equal to zero but there is an enormous favorable entropic term.

The complexation thermodynamic functions listed in Table II show also that the copper(II) complexes of B and L, as well as those of the pentadecane pentaamines, are both enthalpy and entropy stabilized. The relative contribution of the enthalpy term to the free energy is about the same for both complexes (70–77%). On the other hand, the lead complexes of B and L are both essentially enthalpy stabilized, with very small negative entropy terms even disfavoring the complexation of $Pb^{2+}$ with B. For lead, the situation is different from that displayed by the pentaamines, for which the entropy contribution to the stability is important, 57 and 33% for the macrocyclic and linear pentaamines, respectively. It is quite remarkable that the complexation enthalpies of B, L, [15]-aneN$_5$, and tetren with $Pb^{2+}$ are nearly equal.

As recently discussed by Lehn and his co-workers,[39] there are many factors contributing to the enthalpies of complexation. In the absence of further experimental data, it is difficult to evaluate the contribution of each one. Presumably,
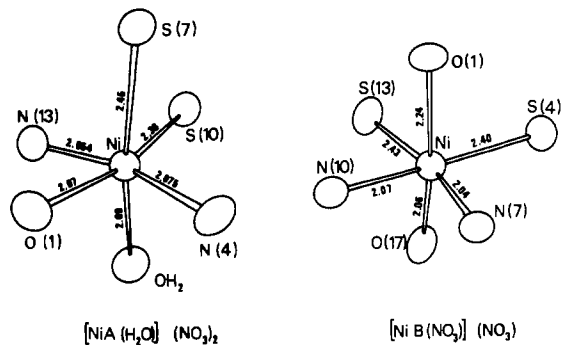
**Figure 3.** Molecular structures of [NiA(H₂O)](NO₃)₂ and [NiB(NO₃)](NO₃) (with bond lengths in Å).

**Table III.** Electronic Spectra of NiA²⁺ and NiB²⁺ in Aqueous Solution[a]

| band | transition | NiA²⁺ | | NiB²⁺ | |
|------|-----------|-------|---|-------|---|
| | | $\bar{\nu}$, cm⁻¹ | $\epsilon$ | $\bar{\nu}$, cm⁻¹ | $\epsilon$ |
| $\nu_1$ | $^3A_{2g}(F) \rightarrow \,^3T_{2g}(F)$ | 17 400 | 1.08 | 18 000 | 1.30 |
| $\nu_2$ | $^3A_{2g}(F) \rightarrow \,^3T_{1g}(F)$ | 26 900 | 1.65 | 27 500 | 3.64 |
| $\nu_3$ | $^3A_{2g}(F) \rightarrow \,^3T_{1g}(P)$ | 33 100 | 7.08 | 33 300 | 6.36 |

[a] $\bar{\nu}(\nu_1) = 10Dq$.

the variations in nature and energy of the bonds between the cation and either the ligand or the solvent, the effects of ligand solvation, and the changes in ligand conformation upon complexation play major roles in complexation enthalpies. The complexation entropies, too, depend on many factors, namely, the hydration entropies of the metal cation and of the ligand, the changes in ligand internal entropy, and the changes in total number of particles and in translational entropy.[39] Which one is the factor responsible for the great difference in complexation entropies between the "mixed" pentadentate and pentaamine ligands is, for the moment, impossible to tell.

## Influence of the Heteroatom Positions. Correlation between Structure and Stability

The $\beta_{101}$ values of the complexes of A and B, listed in Table I, show that the variation of the heteroatom positions in the macrocycles leads to nonnegligible variations of the complex stabilities for a given cation. Copper exhibits the greatest stability difference, the B copper complex being 50 times more stable than the A one. For silver, the B complex is about 10 times more stable than the A one and, for nickel, the stabilities are identical.

Five of the complexes studied in solution have been studied by X-ray diffraction in the solid state: namely, [NiA-(H₂O)](NO₃)₂[22] and [NiB(NO₃)](NO₃)[24] (which, in solution, are noted NiA²⁺ and NiB²⁺), [AgA](SCN)[23] and [AgB](SCN),[20] and [CuB](ClO₄)₂.[21]

(1) The two *nickel complexes*, for which we find identical stabilities in aqueous solutions, have similar structures in the solid state. The cations [NiA(H₂O)]²⁺ and [NiB(NO₃)]⁺, in the solid state, consist of a nickel atom in an octahedral environment, bound to the five heteroatoms of the macrocycle and to an oxygen atom (from H₂O in the A complex and from a NO₃⁻ anion in the B complex). The bond lengths are the same in both complexes, with a slight increase of the Ni–O(1) bond length in [NiB(NO₃)]⁺, as shown in Figure 3.

We have verified that, in aqueous 0.1 M NaClO₄ solutions, the NiA²⁺ and NiB²⁺ complexes have similar electronic spectra and thus, probably, similar molecular structures. The spectra, reported in Table III, consist of three absorption bands, which are characteristic of octahedral nickel(II) complexes. It is likely that, in aqueous solution, the sixth coordination site is, in both complexes, occupied by the oxygen atom of a solvent
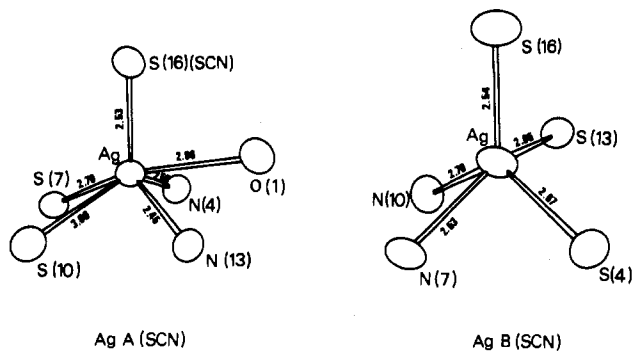


**Figure 4.** Molecular structures of AgA(SCN) and AgB(SCN) (with bond lengths in Å).

molecule. An analysis of the spectra shows that the macrocycles A and B have to be placed at the end of both the spectrochemical and nephelauxetic series: (i) the crystal field parameters $Dq$, calculated from the position of the d–d transition band ($\nu_1$), are respectively equal to 1740 and 1800 cm⁻¹, which are very high values for octahedral nickel(II) complexes, usually characterized by $Dq$ values between 650 and 1300 cm⁻¹; (ii) the Racah parameter $B$, calculated from the expression $B = (1/15)(\nu_2 + \nu_3 - 3\nu_1)$, is equal, in both cases, to 520 cm⁻¹, and the corresponding nephelauxetic ratio $\beta = B/B_0$ (with $B_0$, free-ion Racah parameter of Ni²⁺, equal to 1030 cm⁻¹) is equal to 0.50, a very low value, as could be expected for sulfur donor ligands.[40]

(2) The two *silver complexes*, which do not have identical stabilities in aqueous solution, do not have similar structures in the solid state. The radiocrystallographic studies of [AgA](SCN) and [AgB](SCN) show a significant difference in the interaction between the silver atom and the oxygen atom O(1) of the macrocycles (Figure 4): in [AgA](SCN), the Ag–O(1) distance is 2.9 Å, markedly larger than the sum of the silver atom ionic radius and the oxygen van der Waals radius, thus corresponding to an electrostatic contact between the silver and the oxygen heteroatom.[23] But in [AgB](SCN), the distance Ag–O(1) is much larger, 3.7 Å, and the oxygen heteroatom is, in this case, not bonded to silver.

With silver complexes, it is not possible, as with nickel or copper ones, to get structural information in solution from the electronic spectra. But if we assume that, in aqueous solution, as in the solid state, the oxygen heteroatom O(1) of the macrocyclic ring is closer to the silver atom in the A complex than in the B complex, the conformation change upon complexation would be more important for A than for B. A greater conformation entropy loss upon complexation for A than for B would lead to a higher stability constant for the B complex, what is actually experimentally observed.

(3) The two *copper complexes* display the greatest stability difference in solution but, in this case, we cannot compare their molecular structures in the solid state, as only the structure of CuB²⁺ has been established.[21] Nevertheless, the significant differences displayed by their electronic spectra in aqueous solution probably reflect some differences in their structures in solution. In solid [CuB](ClO₄)₂, the copper atom, which lies inside the macrocyclic cavity, is pentacoordinated, bound to the five heteroatoms of the macrocycle. Its surrounding is octahedral, the two nitrogen and two sulfur donor atoms lying in the equatorial plane and the O(1) atom in an axial position, the second axial position remaining vacant (Figure 5). As shown in Table IV, the electronic spectrum of solid [CuB](ClO₄)₂ can be decomposed into four Gaussian curves.

In nitromethane solutions, the spectrum of the complex is the same as in the solid state, whereas it is different in aqueous 0.1 M NaClO₄ solutions, where it consists of only three, well-separated Gaussian curves (Table IV). It is probable that,
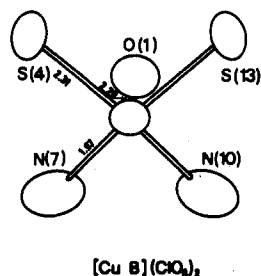
[Cu B](ClO₄)₂

**Figure 5.** Molecular structure of [CuB](ClO₄)₂ (with bond lengths in Å).

**Table IV.** Gaussian Decomposition of the Electronic Spectra of the Copper(II) Macrocyclic Complexes[a]

| band | CuB²⁺ solid $\bar{\nu}$, cm⁻¹ | CuB²⁺ solution $\bar{\nu}$, cm⁻¹ | $\epsilon$ | CuA²⁺ solution $\bar{\nu}$, cm⁻¹ | $\epsilon$ |
|---|---|---|---|---|---|
| $\nu_1$ | 18 500 | 17 500 | 315 | 16 400 | 140 |
| $\nu_2$ | 25 800 | | | | |
| $\nu_3$ | 30 000 | 29 400 | 7700 | 31 700 | 3000 |
| $\nu_4$ | 37 000 | 38 000 | 2030 | 38 000 | 1250 |

[a] Positions and heights of the Gaussian curve maxima, respectively, in cm⁻¹ and L mol⁻¹ cm⁻¹.

in aqueous solution, the complex cation is six-coordinate, as its electronic spectrum displays the spectral characteristics of acentric six-coordinate copper(II) complexes, namely, one d–d transition band near 16,000 cm⁻¹ of molar intensity equal to several hundred L cm⁻¹ mol⁻¹.[40] Two octahedral structures in solution can be considered: one with the O(1) atom of the ligand in an axial position, as in solid [CuB](ClO₄)₂, the second axial site being occupied by the oxygen atom of a water molecule; the other structure with no bonding of the O(1) atom to the copper, both axial positions being occupied by H₂O molecules. The first structure seems more improbable than the second one, as the Jahn–Teller tetrahedral distortion of the octahedron would lengthen the axial Cu–O(1) bond to such an extent that the ligand would have a highly strained conformation, which is not in agreement with the high stability and the favorable complexation enthalpy observed.

The spectrum of CuA²⁺ in solution is different from that of CuB²⁺: it also consists of three Gaussian curves, but these are strongly overlapping, displaced with respect to those of CuB²⁺, are broader, and are of half-intensity (Table IV). These differences may be related to structural differences in solution and account for the stability differences observed.

It would be of interest to continue this study for other cations in order to see if similar structures of the complexes of A and B lead to identical stabilities or, when differences in stability are observed, if they may be accounted for by structural differences.

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