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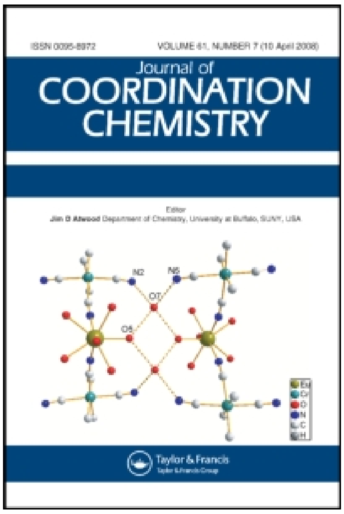

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COMPETITIVE NMR STUDY OF THE COMPLEXATION OF SOME ALKALINE EARTH AND TRANSITION METAL IONS WITH 12-CROWN-4, 15-CROWN-5 AND BENZO-15-CROWN-5 IN ACETONITRILE SOLUTION USING THE LITHIUM-7 NUCLEUS AS A PROBE

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COMPETITIVE NMR STUDY OF THE COMPLEXATION OF SOME ALKALINE EARTH AND TRANSITION METAL IONS WITH 12-CROWN-4, 15-CROWN-5 AND BENZO-15-CROWN-5 IN ACETONITRILE SOLUTION USING THE LITHIUM-7 NUCLEUS AS A PROBE

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^{7}Lithium NMR measurements were used to determine the stoichiometry and stability of Li^+ complexes with 12-crown-4, 15-crown-5 and benzo-15-crown-5 in acetonitrile solution. A competitive ^{7}Li NMR technique was also employed to probe the complexation of Mg^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} ions with the same crown ethers. In all cases, the stability of the resulting 1:1 complexes was found to decrease in the order 15-crown-5 > benzo-15-crown-5 > 12-crown-4. Ca^{2+} and Cd^{2+} ions formed the most stable complexes in the series.

Keywords: Competitive ^{7}Li NMR; Alkaline earth; Transition metals; Crown ethers; Stability; Acetonitrile

INTRODUCTION

Since the discovery of crown ethers by Pedersen [1], studies of these ligands and their interaction with a wide variety of cations, anions and neutral guests have become a major field of research that is still expanding [2–5]. Structural, spectroscopic, electrochemical, kinetic and thermodynamic

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*Corresponding author.

properties of macrocyclic complexation have been studied [2] and detailed thermodynamic and kinetic data for different crown ether complexes obtained by a variety of methods in various solvent media are reported [3–5]. Crown ethers contain central hydrophilic cavities ringed with electronegative O, N or S binding atoms and exterior frameworks exhibiting hydrophobic behaviour allowing them to solubilize different ionic species in non-aqueous solvents or in membrane media [2]. Because of their pronounced selectivity and extraction efficiency, macrocyclic crown ethers have been extensively used as suitable neutral carriers for selective transport through liquid membranes [6–8] and for constructing membrane-selective electrodes for different metal ions [9–11]. Information about the selectivity and stability of metal ion complexes with macrocyclic ligands are of special importance in the development of new methods for their selective removal, concentration, purification and determination from their mixtures.

During the past decade, we have developed some competitive spectrophotometric [12–16], polarographic [17, 18] and potentiometric [19] methods to probe the thermodynamics and kinetics of complexation of a variety of crown ether-metal ion systems which possess no spectrophotometric or electrochemical properties under the experimental conditions used. In this paper, we employed ^{7}Li NMR as a very sensitive probe to study the complexation of Mg^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} ions with 12-crown-4, 15-crown-5 and benzo-15-crown-5 in acetonitrile solution by a competitive technique. It should be noted that the cations used have unsuitable NMR properties such as low receptivity, high quadropole moment, insensitive chemical shifts, *etc.*

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EXPERIMENTAL

Reagent grade crown ethers 12-crown-4 and 15-crown-5 (both from Merck) were used as received. Benzo-15-crown-5 and lithium perchlorate (both from Merck) were purified and dried using previously reported methods [20, 21]. The nitrate salts of all other cations used were of highest purity available from Fluka and used without any further purification except for vacuum drying over P_2O_5. Spectroscopic grade acetonitrile (Merck) was used as solvent.

All nuclear magnetic resonance measurements were made on a JEOL FX90Q FT-NMR spectrometer with a field strength of 21.13 kG. At this field, ^{7}lithium resonates at 33.74 MHz. A 4.0 M aqueous LiCl solution was used as external reference and the reported ^{7}lithium chemical shifts refer to this solution. The paramagnetic (downfield) shift from the reference is designated as being positive. The concentration of all cation solutions used was 0.005 M. All chemical shift measurements were carried out at a probe temperature of 27.0 ± 0.1°C.

RESULTS AND DISCUSSION

The ^7Li chemical shifts were determined as a function of crown/Li^+ ion in acetonitrile solution, in the absence of the M^{2+} ions, and the resulting mole ratio plots are shown in Figure 1. In all cases studied, only one resonance

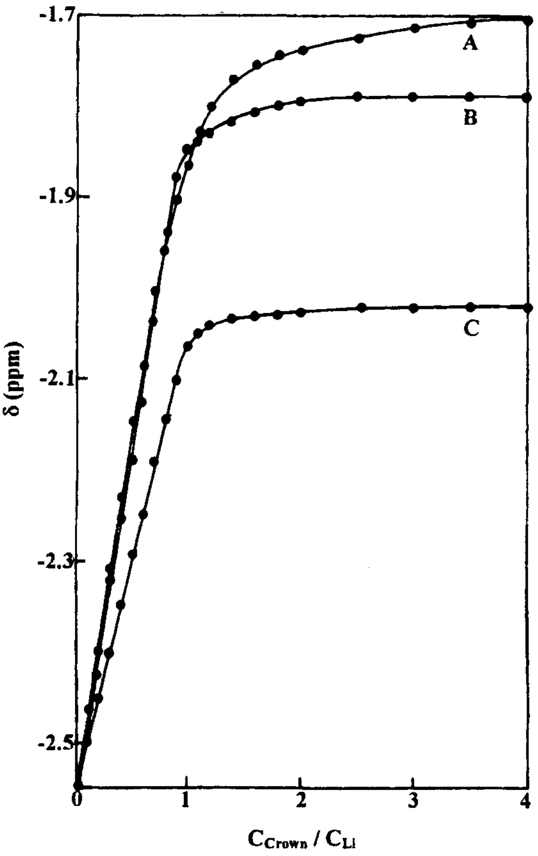

FIGURE 1 Lithium-7 chemical shifts as a function of crown/Li^+ mole ratio in acetonitrile at 27°C for 12-crown-4 (A), 15-crown-5 (B) and benzo-15-crown-5 (C).

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line for the Li^+ ion was observed irrespective of the crown/Li^+ mol ratio. In general, if the mean lifetime for the exchange of the metal ion between the free and complexed sites is smaller than $\sqrt{2}/\Delta\nu$ ($\Delta\nu$ is the difference between the characteristic resonance frequencies of the two sites in hertz), only one population-average resonance is observed (see Fig. 3).

As is seen from Figure 1, in all three cases, addition of the crown ether to the Li^+ ion solution causes an almost linear paramagnetic chemical shift which begins to level off at mol ratios greater than unity. The slope of the corresponding mole ratio plots changes sharply at the point where the ligand-to-cation mol ratio is equal to one, emphasizing the formation of a fairly stable 1:1 complex.

The formation constants of 1:1 Li^+-crown complexes, K_{Li}, were calculated from the variation of ^7Li chemical shift with the crown/Li^+ mol ratio. It has been shown that, in the cases where there is fast exchange between free and complexed metal ions, the observed chemical shift of the resulting single NMR signal is given by [22] (1),

$$\begin{aligned}\delta_{obs} = \{[&(K_{Li}C_{Li} - K_{Li} - K_{Li}C_{Crown} - 1)\\ &+ (K_{Li}^2C_{Crown}^2 + K_{Li}^2C_{Li}^2 - 2K_{Li}^2C_{Crown}C_{Li}\\ &+ 2K_{Li}C_{Crown} + 2K_{Li}C_{Li} + 1)^{1/2}]\\ &(\delta_{Li} - \delta_{Li\text{-}Crown})/2K_{Li}C_{Li}\} + \delta_{Li\text{-}Crown} \qquad (1)\end{aligned}$$

where C_{Crown} and C_{Li} are the analytical concentrations of the crown ether and lithium ion, respectively, and δ_{Li} and $\delta_{Li\text{-}Crown}$ are the respective chemical shifts of the free and complexed Li^+ ion. The non-linear least-squares curve fitting program KINFIT [23] was used to evaluate K_{Li} and $\delta_{Li\text{-}Crown}$ values.

A sample computer fit of the ^7Li chemical shift-mole ratio data is shown in Figure 2A, and the calculated log K_f values are given in Table I. It is seen that there is a satisfactory agreement between the formation constants obtained for the Li^+-crown complexes in acetonitrile with those previously reported in the literature.

The data given in Table I clearly indicate that the stability of Li^+ complexes decrease in the order 15-crown-5 > benzo-15-crown-5 > 12-crown-4. Obviously, the consonance between the ionic size of Li^+ and the size of the macrocyclic ring is an important factor in determining the stabilities of the metal ion crown ether complexes [2, 3]. According to Pedersen and Frensdorff [24], the cavity sizes of 15-crown-5 and 12-crown-4 are 1.7–2.2 Å and 1.2-1.5 Å, respectively. Lithium ion, with an ionic diameter of

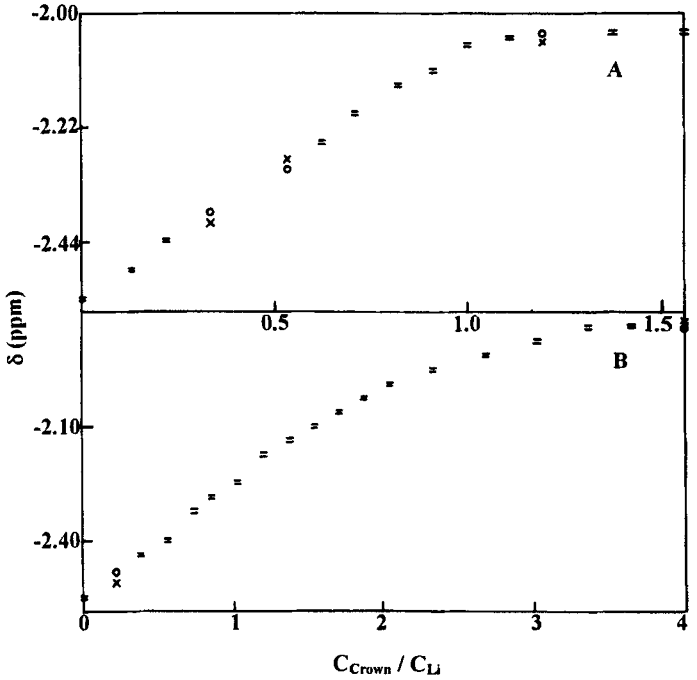

FIGURE 2 Computer fit of lithium-7 chemical shift *versus* benzo-15-crown-5/Li^+ mol ratio in acetonitrile at 25°C in the absence (A) and presence (B) of Cu^{2+} ions: (×) experimental point; (o) calculated point; (=) experimental and calculated points are the same within the resolution of the plots.

TABLE I Formation constants of metal ion complexes with different crown ethers in acetonitrile at 27°C

	log K_f		
Cation	*12-crown-4*	*Benzo-15-crown-5*	*15-crown-5*
Li^+	3.91 ± 0.04	4.56 ± 0.02	4.76 ± 0.03
	4.25[a]	4.46[b]	4.73[c]
Mg^{2+}	4.14 ± 0.04	4.48 ± 0.03	4.74 ± 0.03
Ca^{2+}	4.36 ± 0.03	5.11 ± 0.05	5.41 ± 0.04
Co^{2+}	2.64 ± 0.04	3.09 ± 0.04	3.56 ± 0.08
Ni^{2+}	3.05 ± 0.06	3.56 ± 0.02	3.72 ± 0.05
Cu^{2+}	3.28 ± 0.04	3.91 ± 0.03	4.27 ± 0.03
Zn^{2+}	2.76 ± 0.05	3.44 ± 0.04	3.82 ± 0.05
Cd^{2+}	4.17 ± 0.07	4.79 ± 0.05	4.92 ± 0.03

[a] Ref. [36], [b] Ref. [37], [c] Ref. [38].

1.72 Å [25] seems to have the best fitting conditions for the cavities of 15-crown-5 and benzo-15-crown-5; thus, they form more stable Li^+ complexes than 12-crown-4, which has a small cavity. On the other hand, the

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presence of a benzo group in benzo-15-crown-5 would cause a significant decrease in the stability of the resulting complex, as compared with Li^+-15-crown-5. This behaviour could be due to some combination of the electron withdrawing effect of the benzo group, which weakens the electron-donor ability of the ring oxygens, and the reduced flexibility of the macrocycle, which prevents the molecule wrapping itself around the cation [17].

It is well known that, because of their low receptivities and high quadropole moments, most alkaline earth and transition metal nuclei cannot be accurately used in NMR studies of their macrocyclic complexes [26]. Thus, in this study, ^7Li NMR was used as a very sensitive probe [19, 20, 27–30] to investigate the complex formation of Mg^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} ions with the crown ethers. Variation of ^7Li chemical shift in the presence of equimolar concentrations of different M^{2+} ions as a function of crown/Li^+ for various crown ethers in acetonitrile was obtained. Typical spectra are shown in Figure 3 and resulting chemical shift-mol ratio plots are illustrated in Figures 4–6.

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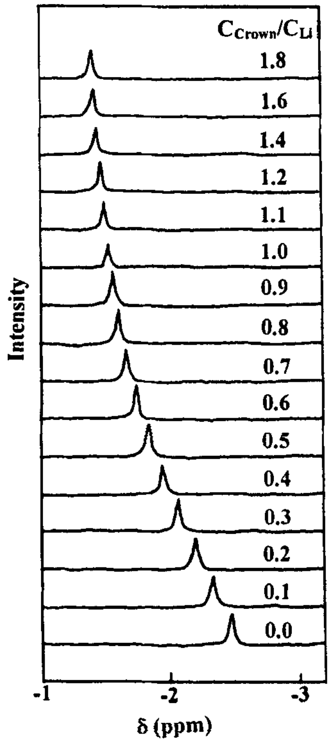

FIGURE 3 Lithium-7 NMR spectra of 12-crown-4 at various crown/Li^+ mol ratios in acetonitrile at 27°C in the presence of Ni^{2+} ions.

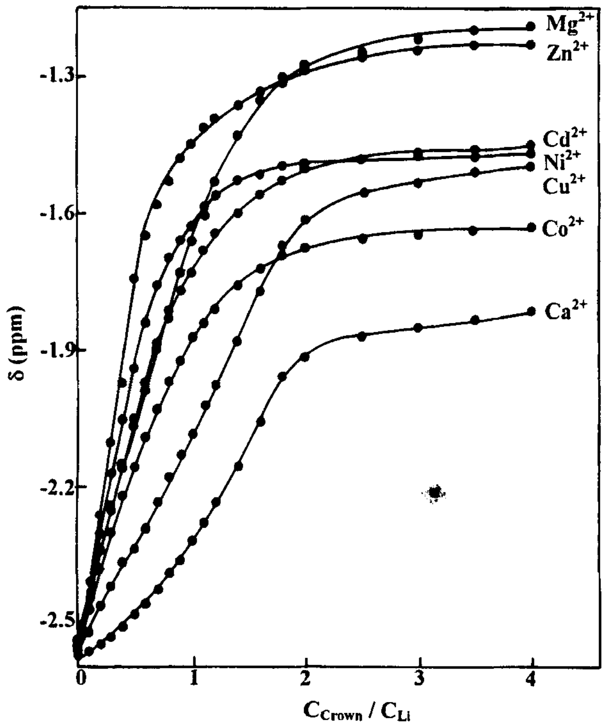

FIGURE 4 Lithium-7 chemical shifts as a function of 12-crown-4/Li^+ mol ratios in acetonitrile at 27°C in the presence of M^{2+} ions.

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Unlike cases involving the formation of 1:1 Li^+-crown complexes (Fig. 1), in which the change in chemical shift with ligand/metal ion mol ratio is quite linear at mol ratios < 1, mol ratio plots in Figures 4–6 show a curved relationship for $0 <$ crown/$Li^+ < 2$. However, in all cases, a plateau is reached for mol ratios > 2, due to the quantitative formation of 1:1 complexes of the crown ethers with both Li^+ and M^{2+} ions. It is interesting to note that, in many cases, the mol ratio plots show a distinct inflection point at a crown/Li^+ mol ratio of about 1, most probably due to significant differences in the formation constants of the Li^+-crown and M^{2+}-crown complexes in solution.

The competitive complexation equilibria, where only the 1:1 complexes of Li^+ and M^{2+} ions are formed are shown in (2) and (3).

$$Li^+ + \text{Crown} = \text{LiCrown}^+ \quad K_{Li} = [\text{LiCrown}^+]/[Li^+][\text{Crown}] \qquad (2)$$

$$M^{2+} + \text{Crown} = \text{MCrown}^{2+} \quad K_M = [\text{MCrown}^{2+}]/[M^{2+}][\text{Crown}] \qquad (3)$$

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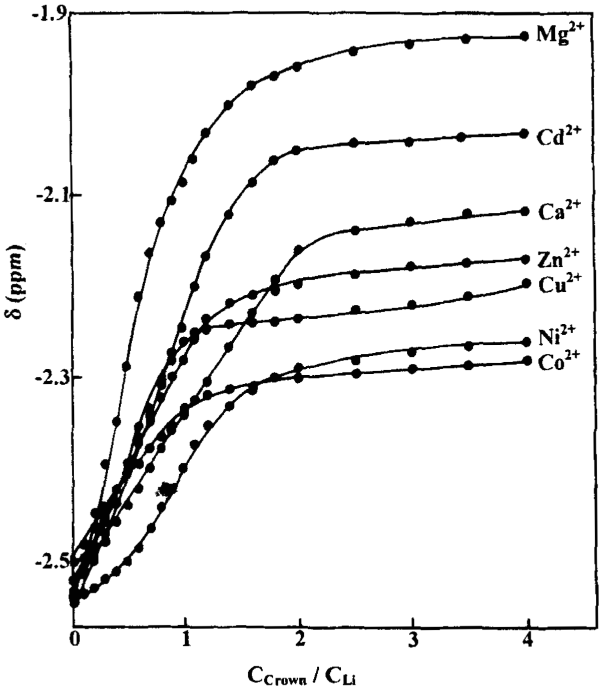

FIGURE 5 Lithium-7 chemical shifts as a function of 15-crown-5/Li^+ mol ratios in acetonitrile at 27°C in the presence of different M^{2+} ions.

The free crown concentration is obtained from Eq. (4), [13]

$$K_{Li}K_M[\mathrm{Crown}]^3 - \{K_{Li}K_M(C_{\mathrm{Crown}} - C_{Li} - C_M) - K_{Li} - K_M\}[\mathrm{Crown}]^2 - \{K_{Li}(C_{\mathrm{Crown}} - C_{Li}) + K_M(C_{\mathrm{Crown}} - C_M) - 1\}[\mathrm{Crown}] - C_{\mathrm{Crown}} = 0 \quad (4)$$

where C_{Crown}, C_{Li} and C_M are the analytical concentrations of the crown ether, Li^+ ion and M^{2+} ion, respectively. In this case, the observed ^7Li NMR chemical shift is obtained from the following Eq. (5), [22]

$$\delta_{\mathrm{obs}} = P_{Li}\delta_{Li} + P_{\mathrm{LiCrown}}\delta_{\mathrm{LiCrown}} \quad (5)$$

where P_{Li} and P_{LiCrown} are the mol fractions of the free and complexed lithium ion, respectively. By substitution from Eq. (2) and the mass balance equation $C_{Li} = [Li^+] + [\mathrm{LiCrown}^+]$, Eq. (5) can be written as (6),

$$\delta_{\mathrm{obs}} = \{\delta_{Li} + \delta_{\mathrm{LiCrown}}[\mathrm{Crown}]K_{Li}\}/\{1 + K_{Li}[\mathrm{Crown}]\} \quad (6)$$

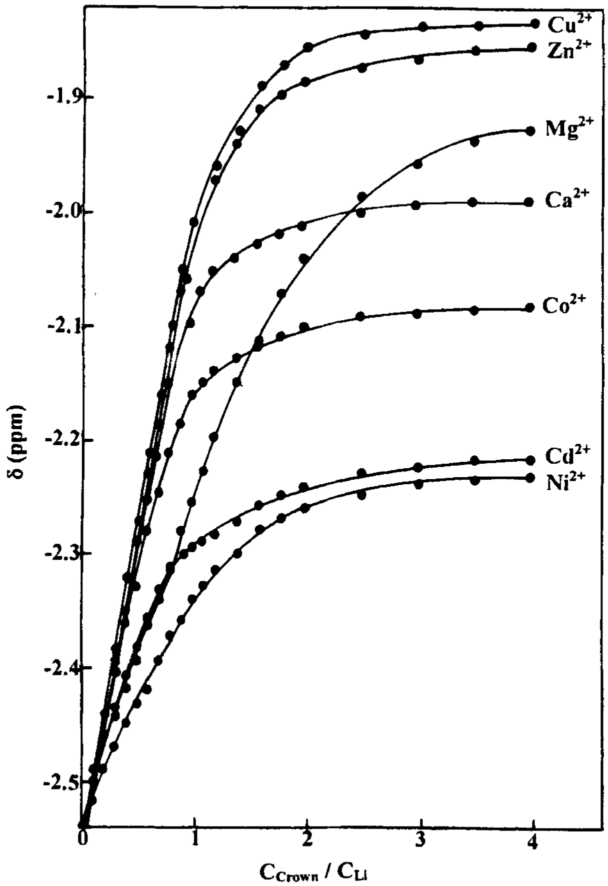

FIGURE 6 Lithium-7 chemical shifts as a function of benzo-15-crown-5/Li^+ mol ratios in acetonitrile at 27°C in the presence of different M^{2+} ions.

K_M values were evaluated by obtaining the free crown ether concentration, [Crown], from Eq. (4) and fitting the chemical shift-mol ratio data to Eq. (6), by using the KINFIT program.

A sample computer fit of the data are shown in Figure 2B and the resulting $\log K_f$ values are included in Table I. Our assumption of the 1:1 stoichiometry for both Li^+-crown and M^{2+}-crown complexes seems reasonable in the light of fair agreement between the observed and calculated chemical shifts [3, 5].

From the data given in Table I, it is immediately obvious that, in the case of all M^{2+} ions, the stability sequence of M^{2+}-crown ether complexes is similar to that observed for the Li^+ ion complexes (*i.e.*,

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15-crown-5 > benzo-15-crown-5 > 12-crown-4). As expected, Ca^{2+} and Cd^{2+} ions with ionic sizes 2.00 and 1.90 Å, respectively [25], and increased cationic charges, form more stable crown ether complexes than the Li^+ ion. The stability of other M^{2+}-crown complexes is lower than that of the corresponding Li^+-ion complexes. The increased ionic solvation of these cations, not only due to their considerable charge density enhancement, but, also, in the case of transition metal ions as soft acids [31], because of their strong soft – soft interactions with acetonitrile as a soft base [31, 32], seems to be the dominant factor in determining the diminished stability of their complexes.

It is interesting to note that in the case of all complexes with metal ions of the first transition series, the stability of the resulting complexes decreases in the order $Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+}$. This sequence follows the Irving–Williams order [33] which generally holds for equilibrium constants of different complexes of metal ions of first transition series [12, 34, 35].

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