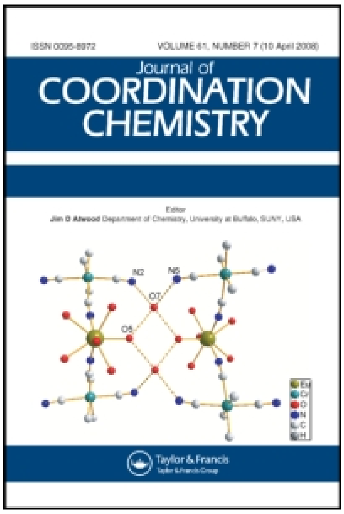

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H. -J. Buschmann[a]; E. Cleve[a]; E. Schollmeyer[a]
[a] Deutsches Textilforschungszentrum Nord-West e.V, Krefeld, Germany

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COMPLEX FORMATION BETWEEN HEAVY METAL CATIONS AND DIAZA CROWN ETHERS AND CRYPTANDS IN AQUEOUS SOLUTION

H.-J. BUSCHMANN*, E. CLEVE and E. SCHOLLMEYER

Deutsches Textilforschungszentrum Nord-West e.V., Frankenring 2, D-47798 Krefeld, Germany

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Complexation of some heavy metal cations in aqueous solution by diaza crown ethers and cryptands has been studied using pH-metric titrations. In most cases, macrobicyclic cryptands form more stable complexes than diaza crown ethers. The size of the cavity also influences the stability of the complexes formed.

Keywords: cryptands; diaza crown ethers; complexes; stability constants; heavy metals

INTRODUCTION

The ability of diaza crown ethers and cryptands to form stable complexes with heavy metal cations is well known.[1–2] Surprisingly few values of stability constants have been reported in the literature.[3–10] To now, the number of published stability constants with heavy metal cations is much smaller as compared with alkali and alkaline earth cations.

For a number of heavy metal cations only upper or lower limits of stability constants with diaza crown ethers and cryptands in aqueous solution have been reported.[3–6] In some cases, published values do not agree very well. We therefore decided to determine stability constants for complex formation with these cations. This work was done in continuation of the redetermination of the reactions of diaza crown ethers and cryptands with protons[11] and with alkali and alkaline earth cations[12] in aqueous solution.

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* Author for correspondence.

EXPERIMENTAL

The diaza crown ethers (21) and (22) and the cryptands (211), (221) and (222) (all Merck) were used without further purification. The salts $TlClO_4$ (ICN), $Pb(NO_3)_2$ (Fluka), $Co(ClO_4)_2 \cdot 6H_2O$ (Alfa), $Ni(NO_3)_2 \cdot 6H_2O$ (Alfa), $Cu(ClO_4)_2 \cdot 6H_2O$ (Alfa), $Zn(ClO_4)_2 \cdot 6H_2O$ (Alfa), $Cd(NO_3)_2 \cdot 4H_2O$ (Fluka), $(C_2H_5)_4NClO_4$ (Fluka), and $(CH_3)_4NOH$ (Fluka) were of the highest purity commercially available.

All stability constants were determined by pH-metric titrations. A solution of one ligand (1×10^{-2} mol dm^{-3}), one salt (1×10^{-2} mol dm^{-3}) and hydrochloric acid (2.5×10^{-2} mol dm^{-3}) was titrated with a solution of tetramethylammonium hydroxide (3×10^{-2} mol dm^{-3}). Ionic strength was kept constant with tetramethylammonium perchlorate (5×10^{-2} mol dm^{-3}). The pH-values were measured using a glass electrode (Metrohm 6.0203.100) with internal reference.

The stability constant, K, for the complex formation of the diaza crown ethers and cryptands with cations is calculated using the following equation with protonation constants K_1 and K_2 and the total concentrations of the salt c_M and of the ligand c_L: with $a = 1 + K_1[H^+] + K_1K_2[H^+]^2$, $b = K_1[H^+] + 2K_1K_2[H^+]^2$ and $c = C_{H+} - {}_{OH-} - [H^+]\,[OH^-]$; c_{H+} is the total concentration of the acid, C_{OH-} of the base. The actual concentration of free protons, $[H^+]$ is calculated from the measured potential by means of the Nernst equation and the actual concentration of hydroxyl ions $[OH^-]$ is obtained using the ionic product of water under the given experimental conditions. Values of the protonation constants of the ligands used have been published recently.[11]

$$K = \frac{b \cdot C_L - a \cdot c}{b \cdot C_M} \cdot \frac{b}{c}$$

RESULTS AND DISCUSSION

The determined stability constants and corresponding data from the literature for the complexation of some heavy metal cations by diaza crown ethers and cryptands in aqueous solution are summarized in Table I. Most values taken from the literature are in good agreement with the values obtained in this study. With the ligands (21) and (22), a few discrepancies are found. However, these are caused by the use of other protonation constants for these ligands.[4]

The complexes with diaza crown ethers are normally less stable when compared with those of the cryptands. Values of stability constants for both diaza crown ethers are, with few exceptions, of the same order of magnitude for a given cation. In contrast, the cavity size of the cryptands influences the stability of the

TABLE I Stability constants (K in dm^3/mol) for the reaction of some heavy metal cations with macrocyclic and macrobicyclic ligands in aqueous solution at 25° C (ionic radii,[9] cavity radii[10])

ligand	*21*	*22*	*211*	*221*	*222*
cation	*(r = 0.9 Å)*	*(r = 1.4 Å)*	*(r = 0.8 Å)*	*(r = 1.1 Å)*	*(r = 1.4 Å)*
Pb^{2+} (r = 0.94 Å)	5.6 5.85 [a]	6.6 6.90 [a] 7.01 [c]	7.4 7.93 [a]	12.1 13.12 [a]	12.5 12.72 [a] 12.36 [c] 12.0 [g]
Co^{2+} (r = 0.57 Å)	3.8 5.05 [a] 5.22 [b]	3.7 ≤2.5 [a] 3.25 [b]	4.5 ≤4.7 [a]	4.6 5.40 [a]	2.8 ≤2.5 [a]
Ni^{2+} (r = 0.69 Å)	3.3 4.05 [a] 3.73 [b]	3.2 ≤2.5 [a] 3.43 [b] ≥2.5 [d]	4.5 ≤4.5 [a]	4.4 4.28 [a]	4.4 ≤3.5 [a]
Cu^{2+} (r = 0.62 Å)	6.9 7.17 [a] 8.15 [b]	6.2 6.18 [a] 7.59 [b]	8.1 7.78 [a]	7.6 7.56 [a]	7.1 6.81 [a]
Zn^{2+} (r = 0.75 Å)	4.9 5.34 [b]	3.0 3.19 [a] 4.31 [b]	6.0 ≤5.3 [a]	4.6 5.41 [a]	2.8 ≤2.5 [a]
Cd^{2+} (r = 0.80 Å)	6.2 6.46 [a]	4.9 5.31 [a] 5.59 [b] 5.25 [e]	5.3 ≤5.5 [a]	9.3 10.04 [a]	7.4 7.10 [a] 6.8 [e]
Tl^{+} (r = 1.50 Å)	2.2	2.3	5.1	7.0 6.8 [f]	6.2 5.5 [e] 6.4 [f] 6.3 [g] 6.4 [h]

[a] Ref. 3, [b] Ref. 4, [c] Ref. 5, [d] Ref. 6, [e] Ref. 7, [f] Ref. 8, [g] Ref. 9, [h] Ref. 10, Results are significant to the last figure.

complexes formed. However, if the cation radius is much smaller than the cavity of the smallest cryptand (211), then the stability of the complexes is independent of the cavity size, *e.g.* Ni^{2+} and Cu^{2+}.

For a given ligand the stabilities of the cation complexes show large differences. Thus, cryptands are able to complex heavy metal cations selectively. In contrast to alkali and alkaline earth cations, the selectivity of the ligands does not only depend on the size of the cations.

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References

[1] R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen and D. Sen, *Chem. Rev.*, **85**, 271 (1985).
[2] R.M. Izatt, K. Pawlak, J.S. Bradshaw and R.L. Bruening, *Chem. Rev.*, **91**, 1721 (1991).
[3] F. Arnaud-Neu, B. Spiess and M. Schwing-Weill, *Helv. Chim. Acta*, **60**, 2633 (1977).
[4] E. Luboch, A. Cygan and J.F. Biernat, *Inorg. Chim. Acta*, **68**, 201 (1983).
[5] S. Kulstad, L.A. Malmsten, *J. Inorg. Nucl. Chem.*, **4**, 1299 (1981).
[6] G. Anderegg, *Helv. Chim. Acta*, **64**, 1790 (1981).
[7] G. Anderegg, *Helv. Chim. Acta*, **58**, 1218 (1975).
[8] P. Gresser, D.W. Boyd, A.M. Albrecht-Gary and J.P. Schwing, *J. Am. Chem. Soc.*, **102**, 651 (1980).
[9] J.-M. Lehn, J.P. Sauvage, *J. Am. Chem. Soc.*, **97**, 6700 (1975).
[10] E.L. Yee, J. Tabib and M.J. Weaver, *J. Electroanal. Chem.*, **96**, 241 (1979).
[11] H.-J. Buschmann, C. Carvalho, E. Cleve, G. Wenz and E. Schollmeyer, *J. Coord. Chem.*, **31**, 347 (1994).
[12] H.-J. Buschmann, E. Cleve and E. Schollmeyer, *J. Coord. Chem.*, in press.
[13] R.D. Shannon and C.T. Prewitt, *Acta Crystallogr.*, **B25**, 925 (1969).
[14] R.D. Shannon and C.T. Prewitt, *Acta Crystallogr.*, **B26**, 1046 (1970).
[15] J.-M. Lehn, *Struct. Bonding (Berlin)*, **16**, 1 (1973).