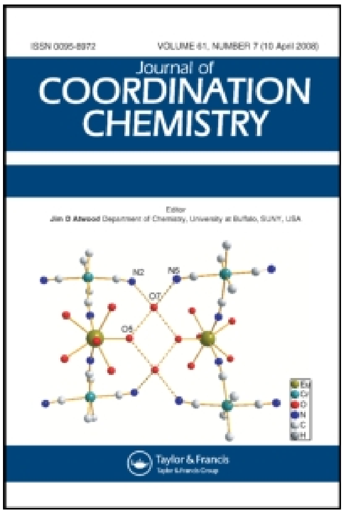

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Note

COMPLEX FORMATION BETWEEN SOME DI- AND TERVALENT HEAVY METAL CATIONS AND DIAZA CROWN ETHERS AND CRYPTANDS IN AQUEOUS SOLUTION

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The complexation of some di- and tervalent heavy metal cations in aqueous solution with diaza crown ethers and cryptands has been studied using pH-metric titrations. The macrobicyclic cryptands form more stable complexes with these cations compared with diaza crown ethers. The size of the cavity also influences the stability of the complexes formed. In contrast to EDTA only ion-dipole and covalent interactions between the ligands and the cations take place. Thus, it is not surprising that the complex stabilities of the diaza crown ethers and the cryptands with heavy metal cations are smaller than the stabilities of the cation EDTA complexes.

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

INTRODUCTION

The ability of diaza crown ethers and cryptands to form stable complexes with several divalent and monovalent heavy metal cations is well known.[1–3] The complexation of tervalent heavy metal cations with noncyclic ligands

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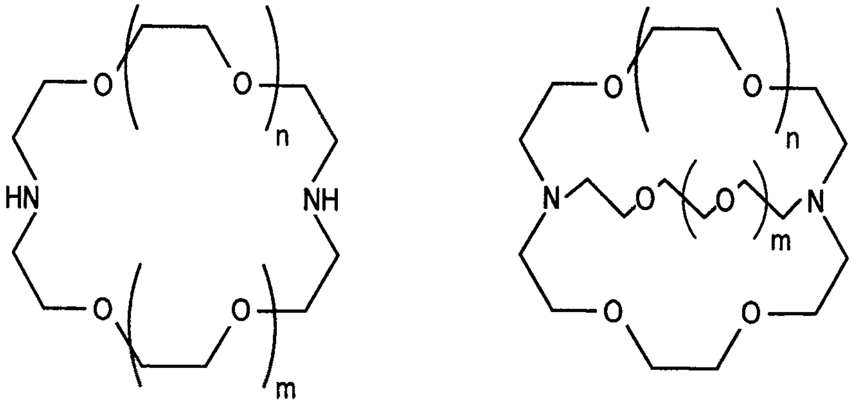

n=0, m=1:(21)

n=1, m=1:(22)

n=0, m=0:(211)

n=0, m=1:(221)

n=1, m=1:(222)

FIGURE 1 Chemical structures of the diaza crown ethers and cryptands used in this work.

like ethylene diamine tetraacetic acid (EDTA) has also been studied extensively.[4–6] By analogy to EDTA, tetraaza macrocycles with carboxymethyl groups have also been used to complex cations like Ga^{3+} and Fe^{3+}.[7,8]

Surprisingly, no stability constants for the complex formation of diaza crown ethers and cryptands with tervalent cations, *e.g.*, Al^{3+} and Cr^{3+}, have been reported in the literature. It seems improbable that these ligands would not form complexes with the mentioned cations in aqueous solution. We therefore decided to determine stability constants for complex formation with these cations. The stability constants for the complexation of some other divalent heavy metal ions with diaza crown ethers and cryptands have already been remeasured and reported.[9]

EXPERIMENTAL

The diaza crown ethers (21) and (22) and the cryptands (211), (221) and (222) (all Merck) were used without further purification. The salts $MnCl \cdot 4H_2O$ (Merck), $Al(ClO_4)_3 \cdot 9H_2O$ (Johnson Matthey), $Ga(NO_3)_3 \cdot 9H_2O$ (Heraeus), $CrCl_3$ (Merck), $Cr(ClO_4)_3 \cdot 6H_2O$ (Johnson Matthey), $FeCl_3$ (Merck), $Fe(ClO_4)_3$ (Alfa), $(C_2H_5)_4NClO_4$ (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 tetramethylammonium hydroxide (0.06 mol dm^{-3}) was titrated into 20 cm^3 of an aqueous solution containing the ligand (0.01 mol dm^{-3}), the salt (0.01 mol dm^{-3}) and hydrochloric acid or perchloric acid (0.04 mol dm^{-3}). The ionic strength was kept constant during the titrations by supporting electrolyte (tetraethylammonium perchlorate) at 0.05 mol dm^{-3}. The titration was automatically performed using a Metrohm Dosimat 665 and a pH-electrode (Metrohm 6.0203.100). After each addition of tetramethylammonium hydroxide the potential was recorded after 15 minutes to be sure that equilibrium had been reached. Some titrations were performed where each potential change was recorded after 30 minutes. The stability constants calculated from both titration curves are identical.

In the case of Fe^{3+}, instead of hydrochloric acid and $FeCl_3$, perchloric acid and $Fe(ClO_4)_3$ was used. With the chloride anion no stability constants could be calculated from the titration curves. No effect of the anion upon the calculated stability constant was observed in the case of Cr^{3+}. Titrations with Al^{3+} were also performed with perchloric acid.

Stability constants K, for complex formation with the diaza crown ethers and cryptands with cations were calculated using the protonation constants, K_1 and K_2, of the ligands.[10] The mathematical treatment of the measured potential values has already been described.[9]

RESULTS AND DISCUSSION

The determined stability constants for the complexation of some di- and trivalent metal cations by diaza crown ethers and cryptands in aqueous solution are summarized in Table I together with data for EDTA. No values of stability constants of these cations with diaza crown ethers and cryptands are available from the literature.

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

Cation	*Ligand*					
	EDTA[a]	(21)	(22)	(211)	(221)	(222)
Mn^{2+}	13.9	4.0	2.7	5.3	5.4	3.9
Al^{3+}	16.5	9.3	9.4	12.9	11.3	10.6
Ga^{3+}	21.0	12.7	12.8	15.2	14.9	13.7
Cr^{3+}	23.4	9.1	9.2	11.4	11.8	9.9
Fe^{3+}	24.1	13.0	13.0	17.3	16.2	13.3

[a] From Refs. 4–6.

All stability constants with EDTA are much higher than with diaza crown ethers and cryptands. This is not surprising because in complex formation with EDTA electrostatic and covalent interactions take place between cations and ligand. In contrast to complex formation of these cations with neutral ligands only ion-dipole and additional covalent interactions are responsible for the stability of the complexes formed.

The stability constants of the aza crown ethers (21) and (22) with the different cations are nearly constant. This is explained by the flexible structure of the aza crown ethers which allows interactions of the donor atoms with the cations although the cation is too small for the ring size of the aza crown ether. The bicyclic cryptands form more stable complexes with the heavy metal cations than the monocyclic diaza crown ethers. Thus the three dimensional cavity of the cryptands has an influence on the complex stabilities. Increasing cavity size of the cryptands (211) to (222) leads to weaker interactions with the donor atoms as shown by decreasing stability constant. As the radii of the cations[11] examined are smaller than the radii of the ligands[12] used, the cryptand (211) forms the most stable complexes with all cations.

For a given ligand the stabilities of the heavy metal cation complexes vary by several order of magnitudes. The differences in the complex stabilities of these cations with mono- and bicyclic ligands may be used for separation processes.

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