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Effect of Changes in the Ligand's Backbone Moiety on Formation Constants of 1:1 Nickel, Copper, Zinc, and Cadmium Chelates

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Reactions that form metal chelate compounds have received considerable attention in recent years,[1] and a large range in selectivity (with respect to ionic radius) exhibited by certain polyamino polycarboxylate ligands has afforded a ready mechanism for resolving mixtures of cations of similar charge.[2]

Recently, we reported new sets of formation constants for Ln^{3+} complexes of this kind and noted some striking differences in bonding affinities of diamino-N,N,N',N'-tetraacetates for such cations as the nature of the backbone (chain between N and N') was varied.[3-5] There was, for example, a (4×10^6)-fold difference in stabilities between 1:1 chelates formed with Gd^{3+} by (bis(2-aminoethyl) ether)-N,N,N',N'-tetraacetate (EEDTA)[6] and by (bis(3-aminopropyl) ether)-N,N,N',N'-tetraacetate (BPETA).[7]

Such results have prompted us to compare the affinities of these two ligands (and another, N,N-bis(2-aminoethyl)ethylamine-N',N',N'',N''-tetraacetate (DEATA)[8] for some divalent transition-metal ions (Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}). With regard to lanthanon chelate formation, DEATA bears a close resemblance to EEDTA, although there is a 2–5-fold attenuation in relative affinities from EEDTA to DEATA.[8]

Experimental Section

Reagents. (Bis(3-aminopropyl) ether)-N,N,N',N'-tetraacetic acid monohydrate, $O[CH_2CH_2CH_2N(CH_2COOH)_2]_2 \cdot H_2O$ (BPETA), was prepared by condensing bis(3-aminopropyl) ether with excess chloroacetate via the method described previously.[4]

N,N-Bis(2-aminoethyl)ethylamine-N',N',N'',N''-tetraacetic acid monohydrate, $CH_3CH_2N[CH_2CH_2N(CH_2COOH)_2]_2 \cdot H_2O$ (DEATA) was prepared by condensing N,N-bis(2-aminoethyl)ethylamine with excess chloroacetate via the method described just recently.[8]

Individual metal–nitrate solutions, having concentration of ca. 0.10 M, were prepared from Baker Analyzed reagents in deionized water and standardized compleximetrically by titration with standard EDTA solution.[9] An excess of acid or deficiency of anion (if any) in the individual solutions was determined by titration of the acid liberated when an aliquot of the standardized solution was passed through a small H^+-form cation-exchange column. Any deviation from a 1:2 stoichiometry was adjusted for in subsequent computations.

Apparatus. The apparatus for potentiometric determinations included a constant-temperature bath controlled at 25.00 ± 0.5 °C, an enclosed water-jacketed titration cell equipped with Beckman electrodes, and a Beckman research pH meter, calibrated to read pH_c to 0.001.

Metal–BPETA and –DEATA Chelate Formation Constants. The stability constants, $[ML]/[M^{2+}][L^{4-}]$ and $[MHL]/[M^{2+}][HL^{3-}]$, for divalent Ni, Cu, Zn, and Cd complexes with the ligands $O[CH_2CH_2C-H_2N(CH_2COO^-)_2]_2$ (BPETA) and $CH_3CH_2N[CH_2CH_2N(CH_2CO-$

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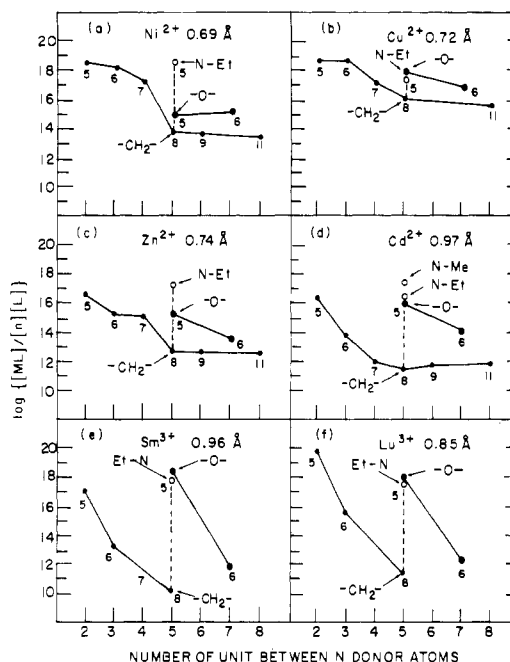

Figure 1. Comparison of the effects of ligand backbone alterations on metal chelate formation constants.

Table I. Successive Protonation Constants of BPETA, DEATA, and EEDTA at 25.0 °C and $I = 0.100$ (KNO_3)

K_n	BPETA[4] 25 °C	DEATA[8] 25 °C	EEDTA[6] 20 °C
K_1	10.03	10.44	9.47
K_2	9.88	7.42	8.84
K_3	2.65	4.00	2.76
K_4	2.3	2.8	1.8

Table II. Stability Constants of Transition-Metal BPETA and DEATA Chelate Species at 25.0 °C and $I = 0.10$ (KNO_3)

cation	BPETA[a] log K_{MHL}	log K_{ML}	DEATA log K_{MHL}	log K_{ML}	EEDTA[b] log K_{MHL}	log K_{ML}
Ni^{2+}	9.56	15.26	11.80	18.61	8.9	15.1
Cu^{2+}	11.02	16.96	10.72	17.45	12.8	18.1
Zn^{2+}	9.13	13.35	10.54	17.18	8.6	15.3
	(9.18)	(13.52)				
Cd^{2+}	8.26	13.80	9.35	16.49	9.9	16.2

[a] Values in parentheses are those of Irving and Stacey at 20 °C.[5]
[b] Values from ref 10 at 20 °C.

$O^-)_2]_2$ were determined by potentiometric measurements at 25 °C in $I = 0.10$ (KNO_3) solutions. In each case, a final series of buffer solutions was prepared (in a limited pH range) wherein the total metal and total L concentrations were equivalent and constant, and the pH (3–4.5) was altered prior to final dilution by adding different volumes of standard (carbonate-free) KOH and sufficient standard KNO_3 solution to achieve an equilibrium ionic strength of 0.100 ± 0.005). The requisite amount of KNO_3 to be added was calculated from a previous stability constant determination in each case by using a computer program described in the doctoral dissertation of Tse.[4] After equilibration overnight, the pH of each solution was read to 0.001 pH units.

The formation constants for ML and MHL were computed from each set of buffer solutions by using protonation constants determined previously, which are compared in Table I.

Results of the metal chelate formation constant determinations for BPETA and DEATA species are listed in Table II, wherein they are compared with previously reported values for BPETA[7] and EEDTA.[5]

Discussion

It is noteworthy, in the case of these cations, that the discrimination between EEDTA and BPETA is not nearly as great as the factor of ca. 10^6 noted in the case of lanthanons such as Sm^{3+}. In fact, with Ni from Ni(EEDTA) to Ni(BPETA) $\Delta \log K_{ML}$ is +0.2 instead of the −6.5 log units observed in the case of Sm. That

the relative affinities are not so dependent upon potential ring size is probably a reflection of the fact that the full heptadentate capabilities of the ligands are never called upon by the smaller cations of the d-transition series. Ni^{2+} (0.69 Å), Cu^{2+} (0.72 Å), and Zn^{2+} (0.74 Å) are all considerably smaller than the smallest lanthanon, Lu^{3+} (0.85 Å), and conveniently utilize sp^3d^2 orbitals to form hexadentate bonds having greater covalent character than is characteristic of Ln–ligand interactions. We have plotted, in Figure 1, a few of the constants available for complexes of nickel, copper, zinc, cadmium, and lanthanons with diamino tetraacetate ligands having a variety of backbones, in order to demonstrate the effect that difference in cation size has as the number of members in potential chelate rings is varied. When $(CH_2)_n$ backbones are considered, the response of cation–ligand affinity for nickel, copper, and zinc in going from a five-membered to a six-membered middle ring is small (less than a factor of 3 in the cases of Ni and Cu). In the cases of the somewhat larger Ln^{3+} cations, affinity is attenuated by a factor of 10 000 when the middle ring size is increased by one CH_2 unit in going from EDTA to PDTA. The affinity is attenuated by a factor of 500 in the case of Cd^{2+} (0.97 Å)—much more than the factor of 16 noted for zinc or the factor of 2.5 noted for nickel. Cadmium has a radius akin to that of Sm^{3+} (0.96 Å). After the polymethylene backbone has attained a length of five C atoms, virtually no further at-tenuation in affinity is observed, and it is likely that 8–11-membered rings have no tendency to form even transiently.

Note that when the central CH_2 of the pentamethylene backbone is replaced by the O atom (which is a potential electron pair donor) the affinity is enhanced more than 10^8-fold in the case of Sm^{3+} nearly 10^7-fold in the case of Lu^{3+} and about $10^{4.5}$-fold in the case of Cd^{2+}. The response to replacing CH_2 by O in the cases of Ni^{2+}, Cu^{2+}, and Zn^{2+} is much less dramatic in all cases, but still increases in the order of increasing radius (Ni < Cu < Zn).

When the central atom of the five-membered backbone is N instead of CH_2 the response (increase in affinity) toward Sm^{3+}, Lu^{3+}, and Cd^{2+} is nearly (but not quite) as large in each case as when the electron pair donor is O. Zn^{2+}, on the other hand, exhibits a 100-fold preference for N over O, and Ni^{2+} prefers the N atom over O by a factor of some 4000. Why Cu^{2+} prefers O to N is puzzling.

After the middle CH_2 is replaced by O, allowing the possibility of forming two five-membered rings, increasing the size of both rings to six members, by adding CH_2 to each ethylene segment of the EEDTA backbone (yielding BPETA), reduces the ligand affinity for lanthanons by a factor of a million or more, and for Cd^{2+} by a factor of about 90. The affinity for Zn^{2+} is decreased about 50-fold and for Cu^{2+} about 10-fold. If anything, BPETA exhibits a greater affinity for Ni^{2+} than EEDTA does.