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Chelate Stability Constants of *N*-(*o*-Hydroxybenzyl)iminodiacetic Acid (HBIDA) with Yttrium and Lanthanoid Ions

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Chelate stability constants of *N*-(*o*-hydroxybenzyl)iminodiacetic acid with yttrium and some lanthanoid ions (M^{3+}) were determined by the potentiometric method at 25 °C and at an ionic strength of 0.1 with potassium nitrate. The computation of the titration data indicated that four kinds of complexes, ML, ML_2^{3-}, $M(HL)^+$, and $M(HL)_2^-$ (except for thulium and lutetium) were formed on each metal ion and the values of the stability constants increased with the increase of atomic number of the element. The values found for the stability constants of yttrium complexes are between those for gadolinium and terbium ions.

It has been reported that *N*-(*o*-hydroxybenzyl)-iminodiacetic acid (HBIDA, H_3L) is a tetradentate chelating ligand in which the phenolic oxygen, in addition to the iminodiacetate group, can coordinate to metal ions such as iron(III), copper(II), nickel(II), zinc(II), and cobalt(II), and their stability constants have also been reported.[1] However, no stability constants have been reported on the HBIDA complexes with lanthanoid and yttrium ions. The chelate stability constants of many amine-*N*-polycarboxylic acids[2] including iminodiacetic acid (IDA)[3] with trivalent lanthanoid ions including yttrium have now been measured to understand the factors which influence the formation and stability of the lanthanoid ion complexes.[4]

It is interesting to study the complexes formation of the ligands which have phenolic oxygen as an additional coordination site such as HBIDA with lanthanoid ions. Accordingly, complex formation of HBIDA with lanthanoid ions has been investigated and their stability constants discussed in comparison with those for IDA and other amine-*N*-polycarboxylic acids.

Experimental

The HBIDA employed was synthesized according to Harris et al.[1] The crude product was recrystallized more than five times from water, and the purity of the final product was checked by elemental analyses, NMR spectrum and molecular weight determination by alkalimetry. The stock solutions of the metal ions were prepared from analytical grade metal nitrates or oxides and were standardized by direct EDTA titration using the appropriate indicator.[5] The 35 cm^3 of the solution containing 0.1 mmol of HBIDA and 0.05 mmol of metal ion was titrated with 0.1 M (1 M=1 mol dm^{-3}) carbonate-free potassium hydroxide solution, and the free hydrogen ion concentration was measured with a Denkikagaku Keiki IOC-10 pH meter by a procedure similar to that described in a previous report.[6] During the titrations, the solutions were kept under a nitrogen atmosphere, at 25±0.5 °C and at an ionic strength of 0.1 with potassium nitrate.

The ultraviolet absorption spectra of the 2×10^{-4} M of ligand solutions were measured at $p[H^+]=11—12.5$ in 1 cm-length quartz cell using a Shimadzu UV-180 spectrophotometer. During the measurements, the sample solutions were kept at 25±0.5 °C and at an ionic strength of 0.1 with potassium nitrate.

Results and Discussion

From the titration data of the ligand in the absence of metal ion, the two final protonation constants were calculated directly using a computer program SUPERQUAD.[7] The first protonation constant was determined by the spectrophotometric method. The following values; $\log K^H_1=11.94$, $\log K^H_2=8.15$, and $\log K^H_3=2.34$, were obtained, respectively. These values were in good agreements with those reported by Harris et al.[1] and were used in the calculations of the stability constants of the metal complexes

The titration data for the 1:2 metal to ligand systems were also analyzed by the use of the same program. The computer calculations indicated the formation of the following complexes, ML, ML_2^{3-}, MLH^+, and $ML_2H_2^-$ (except for thulium and lutetium) and evaluated the values of their stability constants. The results are summarized in Table 1, in which β functions are defined as follows.

$$\beta_1 = [ML]/[M^{3+}][L^{3-}], \quad \beta_2 = [ML_2^{3-}]/[M^{3+}][L^{3-}]^2,$$
$$\beta_{M(LH)} = [M(LH)^+]/[M^{3+}][LH^{2-}] \quad \text{and}$$
$$\beta_{M(LH)_2} = [M(LH)_2^-]/[M^{3+}][LH^{2-}]^2.$$

The value of the stability constant of the 1:1 HBIDA complexes, $\log \beta_1$, increases with an increase in the atomic number of the lanthanoid ions, starting from the first element (11.65 for lanthanum) to the last element (14.87 for lutetium) as shown in Table 1. This stability trend suggests that the HBIDA belongs to the ligand of the first group according to Moeller et al.[4] who have pointed out that the ligand such as IDA and nitrilotriacetic acid (NTA) belonged to the first group. NTA is a well known tetradentate ligand which coordinates to a metal ion with three carboxylate-oxygen atoms and an amino-nitrogen atom, and its stability constants with lanthanoid ions have been reported.[8] The stability constants for the 1:1 HBIDA

Table 1. The Stability Constants, β_n and $\beta_{M(LH)_n}$ (n=1, 2), of HBIDA Complexes of Lanthanoid and Yttrium Ions (25 °C, I=0.1 with KNO_3)

Metal ions	log β_1[a]	log β_2	log $\beta_{M(LH)}$	log $\beta_{M(LH)_2}$
Y	13.63(0.01)	24.17(0.01)	5.85(0.02)	12.32(0.03)
La	11.65(0.02)	19.67(0.01)	4.95(0.03)	10.87(0.03)
Ce	12.01(0.05)	20.76(0.01)	5.45(0.05)	11.48(0.04)
Pr	12.21(0.04)	21.20(0.01)	5.63(0.03)	11.76(0.04)
Nd	12.46(0.04)	21.98(0.01)	5.80(0.03)	11.86(0.04)
Sm	13.08(0.06)	23.16(0.01)	5.77(0.04)	12.32(0.06)
Eu	13.42(0.02)	23.93(0.01)	5.95(0.03)	12.40(0.04)
Gd	13.55(0.01)	24.13(0.01)	5.82(0.03)	12.23(0.04)
Tb	13.88(0.01)	24.73(0.01)	5.87(0.04)	12.45(0.06)
Dy	14.07(0.01)	25.18(0.01)	5.91(0.03)	12.51(0.04)
Ho	14.14(0.02)	25.30(0.01)	5.97(0.04)	12.48(0.10)
Er	14.30(0.01)	25.93(0.01)	6.22(0.02)	12.20(0.12)
Tm	14.48(0.01)	26.48(0.04)	6.40(0.02)	
Yb	14.54(0.01)	26.67(0.03)	6.44(0.02)	12.59(0.09)
Lu	14.87(0.01)	27.76(0.01)	6.71(0.02)	

a) Values in parentheses are standard deviations.

complexes are higher than those for the NTA complexes, the increments being 1.29 with the lanthanum- and 2.38 with the lutetium complex, in log unit.

On the other hand, the values for the stability constants of the 1:1 HBIDA complexes are about twice as large as those of the 1:1 IDA complexes, in log unit.[3] Since IDA binds to a metal ion as a tridentate ligand in the 1:1 normal complexes, the increase in the stability constants of the HBIDA is likely to be due to the tetradentate nature of the ligand. Such a coordination has been reported on some divalent metal complexes, such as with nickel(II) and zinc(II).[1]

As to the overall stability constants of the 1:2 metal to ligand complexes of HBIDA, log β_2, the value also increases with an increase in the atomic number of the elements, starting from lanthanum (19.67) to lutetium (27.76). It was found from these values that the second stepwise stability constants $K_{ML_2}=[ML_2^{3-}]/[ML][L^{3-}]$ were in a range of 8.02 (lanthanum) to 12.89 (lutetium) in log unit. Such an increase in the values of the second stepwise constants of the 1:2 complexes with an increase in atomic number of lanthanoid ions is common to the complexes by complexane-type or related ligands. Such a trend has been also found in the values of the second stepwise stability constants of the 1:2 metal to IDA complexes in which no steric hindrance due to the coordinated ligands has been found.[3] This suggests that no steric hindrance occurs between the two ligands in the 1:2 HBIDA complexes as in the case of the IDA complexes.[3] The corresponding value for the 1:2 yttrium complex is found in between those for gadolinium and terbium as in the case of the 1:1 complex.

The stability constant of the protonated 1:1 HBIDA complex, log $\beta_{M(LH)}$, also increases with the increase in the atomic number of the element. The value for the yttrium complex is again found in lie between the values for the gadolinium and terbium complexes as in the case of the nonprotonated complexes. These values are smaller than those of the 1:1 IDA complexes, indicating that, in the protonated 1:1 metal to HBIDA complex, the phenolate oxygen is not involved in the coordination, but is protonated to form a free phenol group. Eventually, HBIDA is likely to behave as tridentate ligand.

Concerning the overall stability constant of the protonated 1:2 HBIDA complex, the values for log $\beta_{M(LH)_2}$ are higher than those of the 1:2 IDA complexes for the lighter lanthanoid group.[3] However, the increments decrease with an increase in the atomic number of the elements; both values become almost same at holmium, then, the values for the IDA complex becoming higher than those for the HBIDA only after the erbium complex. These results suggest that the diprotonated 1:2 HBIDA complexes of the lighter lanthanoid ions are unusually stable, if one remembers that the stabilities of the protonated 1:1 HBIDA complexes are lower than those of the 1:1 IDA complexes. The second stepwise stability constant of the diprotonated 1:2 HBIDA complex ($K_{M(LH)_2}=[M(LH)_2^-]/[M(LH)^+][LH^{2-}]$) was found to be 5.92 in log units at lanthanum from Table 1. This value is higher by 0.97 log units than the value for the first constant. The value for the second stepwise constant becomes smaller with the increasing atomic number of the lanthanoid elements, but it is still in a similar level of the first ones at erbium and at ytterbium. These rather high values for the overall stability constants of the diprotonated 1:2 HBIDA complex seem to be exceptional, if one remembers that the second stepwise stability constant does not generally exceed that of the first one. In the case of the transition metal complexes of HBIDA, the values for the second stepwise stability constants are 65.0 and 63.1 per cent of the first ones, for cobalt(II) and zinc(II), respectively. Thus,

the unusually high values for the diprotonated 1:2 HBIDA complex are peculiar to the lanthanoid ions, and may be partly due to hydrogen bonding between two free phenol groups of the coordinated HBIDA. In the case of the transition metal complexes, the ionic radii are too small to allow the formation of such hydrogen bonding.

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