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Formation Constants of 2,3-Dihydroxy-2-hydroxymethylpropanoato (α,β,β'-Trihydroxyisobutyrato) Rare Earth Chelate Species

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Our interest in determining formation constants of chelate species formed between 2,3-dihydroxy-2-hydroxymethylpropanoate (α,β,β'-trihydroxyisobutyrate) anion (hereafter abbreviated THIB) at 0.10 ionic strength and 25 °C was aroused by disparate behaviors of 2,3-dihydroxy-2-methylpropanoate (DHIB) and 2-hydroxy-2-methylpropanoate (HIB) under these conditions. Comparing data for DHIB reported by Powell et al.[1] and those for HIB reported by Devine[2] indicates that the dihydroxycarboxylate ligand (DHIB) forms considerably stronger complexes with larger lanthanons (La–Eu) but appreciably weaker complexes with the smaller lanthanons (Tb–Lu) and yttrium than does the monohydroxycarboxylate anion (HIB). A similar effect was reported earlier by Stagg and Powell[3] in the case of HIB and THIB data obtained at a fivefold higher ionic strength, but no direct comparison of results for all three ligands under comparable conditions could be made.

Experimental Section

2,3-Dihydroxy-2-hydroxymethylpropanoic Acid (THIB). This material was synthesized from 1,3-dihydroxypropanone via 2,3-dihydroxy-2-hydroxymethylpropanenitrile and 2,3-dihydroxy-2-hydroxymethylpropanamide as described by Powell and Kulprathipanja.[4] The product melted at 117–117.5 °C and exhibited an equivalent weight of 137.0 upon titration (theoretical 136.1).

Ionization Constant of THIB. The stoichiometric ionization constant of 2,3-dihydroxy-2-hydroxymethylpropanoic acid was determined over a range of anion concentrations up to 0.0125 M at 25.0 °C and an ionic strength of 0.100 (KNO_3) as described by Powell et al.[5] in the case of 2-hydroxy-2-methylbutanoic acid. The variable ionization parameter for THIB under these conditions was $(3.764 + 34[L^-]) \times 10^{-4}$.

Stability of Rare Earth–THIB Chelate Species. The successive step-formation constants of the (1:1, 2:1, and 3:1) 2,3-dihydroxy-2-hydroxymethylpropanoatolanthanon and -yttrium chelate species were determined by conventional means[5] at 25.0 °C and $I = 0.100$ (KNO_3), using a Corning Model 101 digital electrometer. Due to a limited supply of reagent, the maximum $\bar{n}$ value achieved in our experiments never exceeded 2.2. Consequently, the values of K_1, K_2, and K_3 reported in Table I are subject to errors of 2%, 5%, and perhaps 50%, respectively. Hence, only K_1 and K_2 values are plotted in Figure 1 and only K_1/K_2 ratios (reliable to ±7%) have been reported in Table I. Trends of K_1 data for HIB and DHIB are also indicated in Figure 1 for comparison with the data for THIB.

Conclusions

It is quite clear (from the trends of 1:1 lanthanon–HIB, –DHIB, and –THIB chelate stabilities in Figure 1) that the β-OH and β'-OH groups progressively enhance affinity of the HIB moiety for the larger lanthanons (La–Eu) but attenuate its propensity to bond with smaller lanthanons (Tb–Lu). Adding the first β-OH converts HIB to a potentially tridentate ligand; and, when the cation complexed is large enough (La–Eu) and the (perhaps nine or ten) H_2O molecules in the coordination sphere are not crowded together as closely as possible so that it is feasible to accommodate all three donor O atoms of the ligand in mutually adjacent sites vacated by waters (even though the new donor O atoms cannot quite be arranged in the previous perfectly equilateral array), DHIB forms inherently stabler complexes than HIB does. Adding a β'-OH group to DHIB, on the other hand, does not convert the acid anion to a tetradentate ligand, because of the tetrahedral arrangement (of the $-CH_2OH$ groups, the –OH group, and the $-COO^-$ radical) about the α-carbon atom. Only three donor O atoms out of four can simultaneously occupy contiguous coordination sites. Rather, the presence of the fourth donor O atom enhances the ligand's ability to bond by increasing the multiplicity of tridentate bonding modes. That is, either the β-OH or the β'-OH O atom (but not both) can supplement bonding due to the α-OH and a carboxyl O.

Table I. Formation Constants of Rare Earth–THIB Chelate Species

Cation	$\bar{n}_{max}$	$10^{-2}K_1$	10^{-2}-K_2	10^{-2}-K_3	K_1/K_2	log K_1
La^{3+}	1.5	4.9	1.0	0.4	4.9	2.69
Ce^{3+}						
Pr^{3+}	1.8	9.2	1.7	0.6	5.4	2.97
Nd^{3+}	1.7	10.3	2.2	0.4	4.7	3.01
Pm^{3+}						
Sm^{3+}	1.9	12.3	2.3	0.8	5.4	3.09
Eu^{3+}	2.0	13.0	2.7	0.8	4.8	3.11
Gd^{3+}	2.0	12.2	2.6	0.8	4.7	3.09
Tb^{3+}	2.1	10.5	2.7	1.0	3.9	3.02
Dy^{3+}	2.1	10.8	2.8	1.0	3.9	3.03
Ho^{3+}	2.1	10.9	2.8	1.0	3.9	3.04
Er^{3+}	2.0	11.3	3.0	0.7	3.8	3.05
Tm^{3+}	2.2	12.1	3.3	1.1	3.7	3.08
Yb^{3+}	2.2	13.5	3.6	1.1	3.8	3.13
Lu^{3+}	2.2	14.5	3.8	1.2	3.8	3.16
Y^{3+}	1.8	8.9	2.4	0.6	3.7	2.94

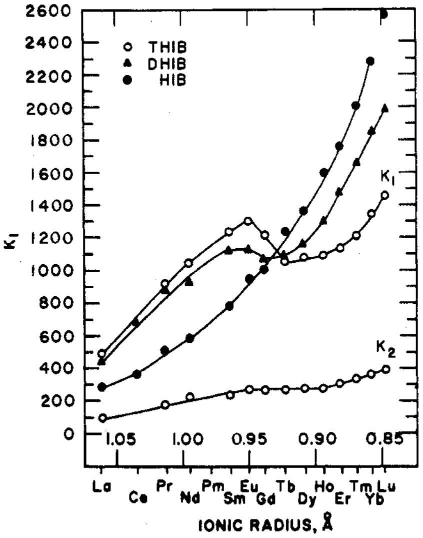

Figure 1. The effect of β-hydroxyl group donor O atoms on the ability of the α-hydroxyisobutyrate ligand to chelate cations of the lanthanide series.

As the cationic radius of lanthanons becomes smaller, one envisions a tighter, less flexible packing arrangement of O atoms (from water molecules) in the coordination sphere. Under such increasingly stringent conditions it becomes more and more difficult for three O atoms on a carbon chain to pack together in an acceptable configuration to fit the "hole" formerly occupied by three contiguous water O atoms. Furthermore, because of the closer mutual proximity of the (perhaps six) other water molecules occupying coordination sites, the "hole" cannot as readily be enlarged by pushing these other ligands aside a bit (as was possible when the cations were larger and the arrangement of (perhaps nine) donor atoms on their surfaces was less constrained). When the available "3-H_2O hole" becomes too small and cannot be stretched (by slightly displacing the remaining coordinated waters) to accommodate more than two of the three imperfectly arrayed O atoms of the organic ligand (Tb–Lu and Y), the unused (β-OH and β'-OH) O atoms have a progressively adverse inductive effect on the ability of the α-OH and carboxyl donor groups to form strong attachments. Note that the change in K_1/K_2 ratios also supports the concept of a change from bidentate to tridentate ligancy at about the radius of gadolinium. The attenuation of bidentate bonding (by β-OH O atoms) is a more regular phenomenon than the enhancement of tridentate bonding ability. The first β-OH converts the HIB moiety from a bidentate to a possibly tridentate ligand, whereas the introduction of a second β-OH only increases availability of groups which can furnish the requisite third donor O atom. Opposing this statistical effect is the fact that an unused β-OH or β'-OH O atom exerts a detrimental inductive effect on tridentate (as well as on bidentate) bonding.

In a previous paper[2] it was shown that adding one β-CH_3 group to DHIB (designated DHMP in that article) to give 2,3-dihydroxy-2-methylbutanoic acid (DHMB) enhanced the affinity of the ligand for lanthanons whenever the anion functioned tridentately (e.g., with Pr–Eu) but decreased the affinity when the anion exhibited bidentate attachment. Thus a β-CH_3 has a positive effect on the ability of a β-OH to be utilized but a negative (probably steric as opposed to inductive) effect when the β-OH is unused. We propose to investigate the rare earth bonding behaviors of ligand anions derived from 2,3-dihydroxy-2,3-dimethylbutanoic, 2,3-dihydroxy-2-hydroxymethylbutanoic, 2,3-dihydroxy-2-(1-hydroxyethyl)-butanoic, and other highly substituted acids, if these acids can be synthesized in sufficient amounts. It appears that none of these more complex reagents has been prepared to date and that synthesis of at least some of them (in good yield) might prove to be a formidable task.

Registry No. La(THIB)$_3$, 57606-49-2; Pr(THIB)$_3$, 57606-50-5; Nd(THIB)$_3$, 57606-51-6; Sm(THIB)$_3$, 57606-52-7; Eu(THIB)$_3$, 57606-53-8; Gd(THIB)$_3$, 57606-54-9; Tb(THIB)$_3$, 57606-55-0; Dy(THIB)$_3$, 57606-56-1; Ho(THIB)$_3$, 57606-57-2; Er(THIB)$_3$, 57606-58-3; Tm(THIB)$_3$, 57606-59-4; Yb(THIB)$_3$, 57606-60-7; Lu(THIB)$_3$, 57606-61-8; Y(THIB)$_3$, 57606-62-9.

References and Notes

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A Bonding Model for Transition Metal–Sulfur Dioxide Complexes[1]

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Sir:

The bonding of the nitrosyl ligand in transition metal complexes has recently been a topic of considerable interest and a general molecular orbital model has been proposed which accounts for the geometry of the M–NO moiety (linear or bent) in terms of the number of d electrons in the system and the transition metal coordination polyhedron.[2] The central theme for the model is developed around the existence in the isolated NO^+ ligand of a σ orbital and degenerate π* orbitals which, when the ligand is attached to a transition metal in a linear fashion, produces a strong interaction with d_{z^2} (z = M–N–O axis) and the d_{xz}, d_{yz} orbitals, respectively. The resulting molecular orbital scheme contains a σ-type antibonding orbital (z^2, σ*) and a degenerate (in a molecule with a threefold or higher symmetry axis) pair of antibonding π* orbitals [(π*, d_{xz}) and (π*, d_{yz})]. If they lie sufficiently close to one another in energy, the two sets of orbitals (σ*, π*) will interact strongly upon bending the nitrosyl group to give stabilized and destabilized orbitals of the same symmetry (a') and a little perturbed orbital of different symmetry (a''). If the lowest of these orbitals is at least partially filled, the conformation with a bent nitrosyl will be stabilized. Previous authors have pointed out that the approach outlined above is applicable to other ligands, including SO_2,[3,7] with bonding characteristics similar to those of NO^+. It has not been emphasized, however, that the SO_2 ligand not only has orbitals of the proper symmetry and energy to fit into the framework of this model but also has the requisite structural credentials; i.e., it exhibits both planar and pyramidal coordination about the sulfur atom in its transition metal complexes (see Table I).[4-10]

Table I. Known Structures of Compounds with Terminal M–SO_2 Moieties

Compd	Coordination type	No.[b] of d electrons	M–S dist, Å	Angle between M–S vector and SO_2 plane,[a] deg
[Ru(NH_3)$_4$$SO_2$-Cl[4]	Octahedral	6	2.072 (3)	180
CpMn(CO)$_2$-SO_2[5]	Octahedral	6	2.037	180
IrCl(CO)SO_2-(Ph_3P)$_2$[6]	Tetragonal pyramidal	8	2.49 (1)	121.5 (1.5)
RhCl(CO)SO_2-(Ph_3P)$_2$[7]	Tetragonal pyramidal	8	2.450 (2)	120.3 (3)
(Ph_3P)$_3$PtSO_2[8,9]	Tetrahedral	10	2.36 (3)	120.3 (3)
(Ph_3P)$_2$Pt-(SO_2)$_2$[17]	Tetrahedral	10	2.45 (1)	117.0 (3)

[a] See text. [b] Nitrosyl is considered to be NO^+.

Table II. Model Systems Investigated for L_nIrA (A = NO, SO_2)

L	n	A	Geometry	Position of A	d^6, d^8, d^{10} [a]
Cl	4	SO_2	Square pyramidal	Axial	p, b, –
Cl	4	SO_2	Trigonal bipyramidal	Axial	p, p, –
Cl	4	SO_2	Trigonal bipyramidal	Equatorial	p, b, –
Cl	5	SO_2	Octahedral		p, b, –
Cl	2	SO_2	Trigonal planar		p, b, b
Cl	3	SO_2	Square planar		p, b, b
Cl	3	SO_2	Trigonal pyramidal	Axial	p, b, b
Cl	3	SO_2	Tetrahedral		–, –, b
Cl	3	NO	Tetrahedral		–, –, b
CO	3	SO_2	Tetrahedral		–, –, p
CO	3	NO	Tetrahedral		–, –, p

[a] p denotes planar M–SO_2 or linear M–NO; b denotes bent.

We report here the results of some extended Hückel molecular orbital calculations on L_nM–A complexes (A = NO, SO_2) performed with a version of Hoffmann's program which uses Slater-type double-ζ orbitals.[2b] In order to allow a direct comparison between NO and SO_2 complexes we have used the structural and H_{ii} values from ref 2b with the following additions: for the S(3s) and S(3p) orbitals, H_{ii} = −20.77 and −11.63 eV, respectively, with a Slater exponent of 2.05, S–O = 1.45 Å, O–S–O = 114°, and Ir–S = 2.49 Å. The model systems examined are shown in Table II.

Two approaches to understanding the bonding in L_nMNO complexes have proven to be especially useful. (1) The perturbations of the transition metal d orbitals by the NO ligand are introduced first and the splittings produced by the