

$S^*(\text{Np}^{\text{VII}}, \text{Hg}_2^{2+}) - S^*(\text{Np}^{\text{VII}}, \text{VO}_2^{2+}) = 61 \text{ cal mol}^{-1} \text{ deg}^{-1}$ ; the two activated complexes presumably have the same formal charge. See K. D. Watkins, J. C. Sullivan, and E. Deutsch, *Inorg. Chem.*, **13**, 1712 (1974).

(19)  $S^\circ(\text{CrO}_2\text{Np}^{4+})$  can be estimated from data on the activation process<sup>2</sup>  $\text{Co}^{3+} + \text{CrO}_2\text{Np}^{4+} + \text{H}_2\text{O} = [\text{CrONpOCoOH}^{6+}] + \text{H}^+$ :  $S^\circ(\text{CrO}_2\text{Np}^{4+}) - \Delta S^\ddagger - S^\circ(\text{Co}^{3+}) - S^\circ\text{H}_2\text{O} = -125 - 2 + 72 - 17 = -72 \text{ cal mol}^{-1} \text{ deg}^{-1}$ .

Contribution from Ames Laboratory—USAEC and the Chemistry Department, Iowa State University, Ames, Iowa 50010

## Formation Constants of 2,3-Dihydroxy-2-methylpropanoate and 2,3-Dihydroxy-2-methylbutanoate Rare Earth Chelate Species

J. E. POWELL,\* J. L. FARRELL, and S. KULPRATHIPANJA

Received August 6, 1974

AIC40540J

The consecutive step formation constants of the 1:1, 2:1, and 3:1 chelate species formed by interaction of 2,3-dihydroxy-2-methylpropanoate and 2,3-dihydroxy-2-methylbutanoate anions (separately) with the trivalent lanthanon and yttrium cations were determined potentiometrically at an ionic strength of 0.100 (KNO<sub>3</sub>) and 25.0°. The results indicate that these dihydroxycarboxylate ligands exhibit a tridentate character in bonding to the lighter (larger) lanthanons (La–Sm) but bond only bidentately to the heavier (smaller) lanthanons (Ho–Lu) and to yttrium. The dentate character appears to change gradually from tridentate to bidentate as the lanthanon radius diminishes from that of samarium to that of holmium.

### Introduction

Various investigators have measured the formation constants of consecutive chelate species formed by yttrium and the trivalent rare earth cations with the presumably bidentate ligand anions derived from various  $\alpha$ -hydroxycarboxylic acids (glycolate and lactate,<sup>1–6</sup>  $\alpha$ -hydroxyisobutyrate,<sup>2,4,7–9</sup> and other homologs of the hydroxyacetate anion<sup>8,10–14</sup>).

Grenthe<sup>15</sup> has determined the structures of solid heavy rare earth glycolates (hydroxyacetates) of the composition  $\text{Ln}(\text{HOCH}_2\text{COO})_3 \cdot 2\text{H}_2\text{O}$  (where Ln = Tb, Dy, Ho, Er, Tm, Yb, or Lu) from X-ray intensity data. He reported two non-equivalent eight-coordinated metal atoms in the structure, located on twofold axes. One metal ion is coordinated to eight O atoms furnished by four hydroxyacetate ligands, forming a discrete (distorted dodecahedral) anionic complex; the other is coordinated to eight O atoms furnished by two hydroxyacetate anions and four water molecules, forming a discrete (distorted dodecahedral) cationic complex. The anionic and cationic entities are joined by hydrogen bonds.

The anhydrous  $\text{Gd}(\text{HOCH}_2\text{COO})_3$  and  $\text{Eu}(\text{HOCH}_2\text{COO})_3$  species,<sup>16</sup> on the other hand, involve nine-coordinated metal ions.<sup>17,18</sup> The coordination polyhedra are of the tricapped trigonal-prism type. All three ligands are bonded as chelates, with the hydroxy O atoms in the equatorial (tricapped) positions and one of the carboxyl O atoms of each ligand at a corner position of the trigonal prism (two at one end and one at the other). The three remaining corners of the trigonal prism are occupied by (unchelated) O atoms furnished by glycolate ligands which are chelated to neighboring lanthanons.

From the above-determined structures in crystalline materials and stability data,<sup>3</sup> it may be inferred that the hydroxyacetate ligand exhibits predominantly bidentate character in bonding to lanthanons in aqueous media as well. It also appears safe to presume that the hydroxyl O atoms of homologous (alkyl-substituted hydroxyacetate) ligands are generally involved in five-membered ring formation with rare earth metal ions. In solution, the various  $\text{Ln}(\text{HOCH}_2\text{COO})_3 \cdot n\text{H}_2\text{O}$  species probably exist in monomeric form with two to four molecules of water in the coordination sphere, depending on the radius of the particular  $\text{Ln}^{3+}$  ion. However, Grenthe<sup>19</sup> and Larson<sup>20</sup> earlier suggested that the glycolate chelate ring might be formed *via* a water molecule between the hydroxyl O atom and the cation. The latter suggestion should not be taken too seriously, since it involves

a seven-membered ring not indicated by subsequent crystallographic studies. Jones and Choppin,<sup>21</sup> on the basis of formation constants and thermodynamic data, concluded that the conceivable six-membered chelate ring does not form in the case of  $\beta$ -hydroxypropionate lanthanon complexes, although the strain involved in forming a six-membered ring ought not to exceed by much that involved in forming five-membered ring systems.

Two striking effects are observed in complex formation constants reported for species formed between rare earth cations and simple carboxylic acid anions (e.g., acetate,<sup>22</sup> propionate,<sup>23</sup> and isobutyrate<sup>7</sup>), as well as with  $\beta$ -hydroxypropionate,<sup>21</sup> methoxyacetate,<sup>23</sup> and most (not too sterically hindered)  $\alpha$ -hydroxycarboxylate homologs.<sup>3,8,13</sup> They are the "gadolinium break" and a rather abrupt decline in  $K_1/K_2$  ratios as the lanthanon radius decreases beyond that of  $\text{Sm}^{3+}$ . In the case of acetate<sup>22</sup> and propionate<sup>23</sup> chelate species, the  $K_1/K_2$  ratio gradually decreases from about 5 to ca. 2.5 (from  $\text{Eu}^{3+}$  to  $\text{Dy}^{3+}$ ). In the case of 1-hydroxycyclopentane-carboxylate (HCPC) complexes,<sup>14</sup> the  $K_1/K_2$  ratio changes from about 4.9 to 3.3, and with 2-hydroxy-2-methylbutanoate (HMB) species,<sup>13</sup> the change is from about 6.0 to 4.0. Powell and coworkers<sup>13,14</sup> have cited the statistical ratio theory of Bjerrum.<sup>24</sup> They have concluded that such changes in the  $K_1/K_2$  ratios correspond to a change from tridentate to bidentate liganacy in the case of  $\alpha$ -hydroxycarboxylate anions combining with a nine-coordinate (tricapped trigonal prism) hydrated lanthanon. It is just as possible that such ratio changes signal a change from tridentate liganacy on more highly coordinated lanthanons (say 10 or 9) to bidentate liganacy on cations of lower coordination number (say 9 or 8).

The statistical ratio argument immediately raises the question as to how a simple carboxylate anion such as acetate can function bidentately (or how  $\alpha$ -hydroxycarboxylates can function tridentately) in bonding to the larger rare earth cations. It has been suggested that the second carboxyl oxygen of the ligand is simply hydrogen bonded to a water molecule that occupies a coordination site, rather than occupying a coordination site itself.<sup>13</sup> A tenuous bond of this kind would affect the statistical ratio by blocking access to an additional site without causing any large anomaly in the overall chelate stability trend.

It occurred to us that introduction of an alternate donor atom, as in 2,3-dihydroxycarboxylate anions, should permit

**Table I.** Formation Constants of Lanthanum and Yttrium 2,3-Dihydroxy-2-methylpropanoate Chelate Species ( $25^\circ$ ;  $I = 0.100$ )

| Ln(III) | $K_1$                  | $K_2$                | $K_3$                | $K_1/K_2$ | $K_2/K_3$ |
|---------|------------------------|----------------------|----------------------|-----------|-----------|
| La      | 446 <sup>a</sup> (441) | 74 <sup>a</sup> (81) | 16 <sup>a</sup> (12) | 6.0 (5.5) | 5 (6)     |
| Ce      | 683 (690)              | 112 (113)            | 24 (27)              | 6.1 (6.1) | 5 (4)     |
| Pr      | 887 (864)              | 154 (154)            | 27 (29)              | 5.7 (5.6) | 6 (5)     |
| Nd      | 922 (995)              | 152 (170)            | 31 (32)              | 6.1 (5.9) | 5 (5)     |
| Sm      | 1115 (1157)            | 218 (221)            | 44 (41)              | 5.1 (5.2) | 5 (5)     |
| Eu      | 1123 (1146)            | 254 (233)            | 46 (34)              | 4.5 (4.9) | 6 (7)     |
| Gd      | 1067 (1046)            | 235 (235)            | 48 (47)              | 4.6 (4.5) | 5 (5)     |
| Tb      | 1084 (1108)            | 242 (238)            | 43 (52)              | 4.5 (4.6) | 6 (5)     |
| Dy      | 1165 (1205)            | 251 (266)            | 47 (47)              | 4.6 (4.5) | 5 (6)     |
| Ho      | 1299 (1263)            | 279 (273)            | 61 (53)              | 4.7 (4.6) | 5 (5)     |
| Er      | 1479 (1428)            | 323 (309)            | 65 (61)              | 4.6 (4.6) | 5 (5)     |
| Tm      | 1657 (1624)            | 363 (354)            | 67 (72)              | 4.6 (4.6) | 5 (5)     |
| Yb      | 1848 (1828)            | 384 (377)            | 66 (66)              | 4.8 (4.8) | 6 (6)     |
| Lu      | 1984 (1925)            | 402 (394)            | 71 (78)              | 4.9 (4.9) | 6 (5)     |
| Y       | 1134 (1034)            | 276 (223)            | 54 (47)              | 4.1 (4.6) | 5 (5)     |

<sup>a</sup> The first listed  $K_1$  values are estimated to be reliable to  $\pm 2\%$  of the value reported;  $K_2$  to  $\pm 5\%$ ;  $K_3$  to  $\pm 20\%$ . The values in parentheses were actually obtained earlier by means of pH measurements with the Beckman Research pH meter and are considered to be slightly less reliable than the first listed values obtained with the more stable Corning instrument.

direct occupancy of a third coordination site by ligand O atoms and that this more direct bonding mode would be reflected by a significantly enhanced chelate stability. As with the more tenuous hydrogen-bonded case, lanthanide contraction ought eventually to inhibit the ligand's ability to exhibit tridentate liganacy, but the effect on the trend in chelate stabilities should be much more dramatic. While an -OH group in the 3 position should enhance chelate stability when it is bound, it ought to have an adverse inductive (and/or steric) effect when the ligand is attached only bidentately.

Recent development of efficient synthetic procedures for preparing 2,3-dihydroxy-2-methylpropanoic acid<sup>25</sup> and the higher melting diastereomer of 2,3-dihydroxy-2-methylbutanoic acid<sup>26</sup> have made it feasible to investigate the bonding of such potentially tridentate ligands to the lanthanons.

### Experimental Section

**2,3-Dihydroxy-2-methylpropanoic Acid.** This material was prepared via the acetol cyanohydrin-2,3-dihydroxy-2-methylpropanamide route reported by Powell, *et al.*,<sup>25</sup> and was found to melt sharply at  $104.0\text{--}104.5^\circ$  in agreement with the melting point reported by Glattfeld and Sherman.<sup>27</sup>

**2,3-Dihydroxy-2-methylbutanoic Acid.** This reagent was prepared by the acetoin cyanohydrin-2,3-dihydroxy-2-methylbutanamide route described by Powell, *et al.*,<sup>26</sup> and was found to melt at  $109\text{--}110^\circ$  in good agreement with the melting point of the high-melting diastereomer reported by various investigators.<sup>28-30</sup>

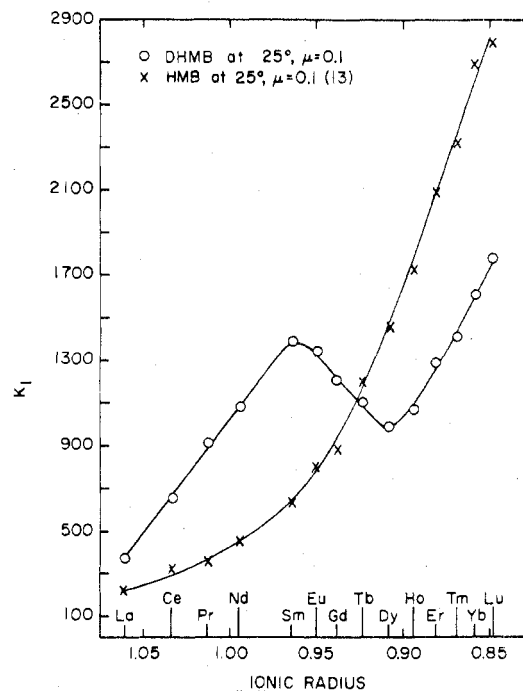
**Ionization Constants of the Acids.** The stoichiometric ionization constants of 2,3-dihydroxy-2-methylpropanoic and 2,3-dihydroxy-2-methylbutanoic acids were determined over a range of anion concentrations up to  $0.02\text{ M}$  at  $25.0^\circ$  and an ionic strength of  $0.100$  ( $\text{KNO}_3$ ) as described by Powell, *et al.*,<sup>13</sup> in the case of 2-hydroxy-2-methylbutanoic acid. The variable ionization parameters under these conditions were found to be  $(2.65 - 1.4[\text{L}^-]) \times 10^{-4}$  and  $(3.06 - 5.2[\text{L}^-]) \times 10^{-4}$ .<sup>31</sup>

**Stability Constants of Chelate Species.** The individual step formation constants of the various lanthanum and yttrium 2,3-dihydroxy-2-methylpropanoate (DHMP) and 2,3-dihydroxy-2-methylbutanoate (DHMB) chelate species were determined<sup>31</sup> by a standardized potentiometric method used previously in this laboratory<sup>13</sup> at  $25.0^\circ$  and an ionic strength of  $0.100$  ( $\text{KNO}_3$ ). The pH measurements were determined to  $0.001$  unit by means of a Corning Model 101 digital electrometer in the case of both ligands. An independent set of determinations was made in the case of the 2,3-dihydroxy-2-methylpropanoate chelate species using a Beckman Research pH meter. Summaries of the individual data sets obtained through a four-parameter least-squares computation on the IBM 360/60 system are given in Tables I and II.

**Table II.** Formation Constants of Lanthanum and Yttrium 2,3-Dihydroxy-2-methylbutanoate Chelate Species ( $25^\circ$ ;  $I = 0.100$ )

| Ln(III) | $K_1$            | $K_2$           | $K_3$           | $K_1/K_2$ | $K_2/K_3$ |
|---------|------------------|-----------------|-----------------|-----------|-----------|
| La      | 373 <sup>a</sup> | 60 <sup>a</sup> | 10 <sup>a</sup> | 6.2       | 6         |
| Ce      | 651              | 100             | 14              | 6.5       | 7         |
| Pr      | 903              | 142             | 21              | 6.4       | 7         |
| Nd      | 1082             | 166             | 24              | 6.5       | 7         |
| Sm      | 1393             | 210             | 28              | 6.6       | 7         |
| Eu      | 1342             | 300             | 40              | 4.5       | 7         |
| Gd      | 1204             | 227             | 37              | 5.3       | 6         |
| Tb      | 1099             | 224             | 36              | 4.9       | 6         |
| Dy      | 995              | 229             | 15 (?)          | 4.4       | 15 (?)    |
| Ho      | 1065             | 222             | 22 (?)          | 4.8       | 10 (?)    |
| Er      | 1288             | 241             | 39              | 5.3       | 6         |
| Tm      | 1401             | 292             | 53              | 4.8       | 6         |
| Yb      | 1616             | 355             | 52              | 4.6       | 7         |
| Lu      | 1769             | 382             | 60              | 4.6       | 6         |
| Y       | 817              | 175             | 27              | 4.7       | 6         |

<sup>a</sup>  $K_1$  values are estimated to be reliable to  $\pm 2\%$  of the value reported;  $K_2$  to  $\pm 5\%$ ;  $K_3$  to  $\pm 20\%$ , except as noted by (?).



**Figure 1.** Formation constants of 1:1 lanthanum 2,3-dihydroxy-2-methylbutanoate and lanthanum 2-hydroxy-2-methylbutanoate chelate species as a function of decreasing radius of the lanthanum. The supporting electrolyte in both cases was  $\text{KNO}_3$ .

### Discussion

$K_1$  values for analogous lanthanum DHMB and HMB (2-hydroxy-2-methylbutanoate) chelate species are plotted for comparison in Figure 1 vs. the crystal ionic radius of the Ln(III) cation. These data most clearly reveal the expected transition from tridentate liganacy to bidentate liganacy that occurs with diminishing cationic radius (lanthanide contraction) in the case of DHMB. In concert with this stability anomaly, the  $K_1/K_2$  ratio drops from an average value of about 6.5 (La-Sm) to 4.7 (Dy-Lu). It is significant that  $K_1/K_2$  for HMB species changes by about the same amount (6.0 to 4.0) although the  $K_1$  vs. radius plot for this ligand is fairly smooth. Similar trends are also apparent in the lanthanum-DHMP data, although the stability change is not as dramatic as in the case of DHMB and the  $K_1/K_2$  ratio change is somewhat less (5.8 to 4.6). See Table I and Figure 2. The effect of  $\beta$ -OH substitution on the HMB skeleton is to enhance greatly the affinity of the ligand for lanthanons large enough to accept the additional donor O atom. However, when the lanthanum

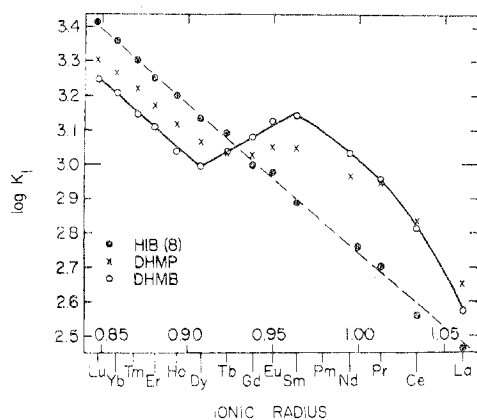


Figure 2. Comparison of the logarithms of the formation constants of 1:1 lanthanide chelate species formed with 2-hydroxy-2-methylpropanoate, 2,3-dihydroxy-2-methylpropanoate, and 2,3-dihydroxy-2-methylbutanoate anions.

cannot accommodate its O atom, the effect of the  $\beta$ -OH group is to attenuate the donor ability of the  $\alpha$ -OH and carboxyl O atoms.

Comparison of  $K_1$  values for lanthanide-DHMB species with those for DHMP reveals that adding a methyl radical at the OH-substituted  $\beta$ -position of DHMP (giving DHMB) involves two factors: a favorable inductive effect and a detrimental steric effect. At the optimum radius associated with Sm(III), the affinity of the ligand for the lanthanide is some 20% greater with DHMB than with DHMP. The fact that the stability curves converge and cross over at Ce suggests that the terminal methyl group perhaps interferes in some way as the radius of the lanthanide increases (and the number of water molecules in the primary hydration sphere possibly increases by 1, *i.e.*, from 9 to 10 or from 8 to 9). When both hydroxyl O atoms and one of the carboxyl O atoms occupy contiguous coordination sites in either a bicapped Archimedes antiprism or a tricapped triangular prism array, their centers approximate an equilateral triangle. Because of the chirality of the particular diastereomer of 2,3-dihydroxy-2-methylbutanoic acid (the 2*S*,3*R* and 2*R*,3*S* pair of optical isomers) under consideration, the methyl groups are of necessity *cis* with regard to a somewhat out-of-plane five-membered  $-\text{O}-\text{C}-\text{C}-\text{O}-\text{Ln}-$  ring. If the centers of the O atoms are moved apart (as in fitting a larger triangular array of coordination sites) the proximate methyl groups are pushed closer together, introducing a strain.

It is clear that, in the portion of the stability sequence where bidentate liganacy occurs solely, the terminal methyl group of DHMB is detrimental rather than instrumental in bond formation. Since the methyl group's potentially favorable inductive effect is far removed from the bonding  $\alpha$ -OH and carboxyl O atoms, its principal effect, when the  $\beta$ -OH O atom is unbonded, seems to be an undesirable steric effect. If it is supposed that bidentate liganacy exhibited by the DHMP and DHMB anions is due to involvement of the  $\alpha$ -OH O atom and one carboxylate O atom in a nearly planar five-membered  $-\text{O}-\text{C}-\text{C}-\text{O}-\text{Ln}-$  ring, it is possible for the H atom of the  $\beta$ -OH group to participate in a six-membered ring by hydrogen bonding to the other carboxylate O atom. It may be argued that this hydrogen bond is inherently stronger in the case of DHMB than with DHMP, because of the tendency of the two methyl groups in DHMB to repel each other and assume naturally the requisite *trans* configuration with regard to the proposed  $-\text{O}-\text{C}-\text{C}-\text{C}-\text{O}-\text{H}-$  ring. This should shorten the hydrogen bond in the case of DHMB to the detriment of the carboxyl  $-\text{O}-\text{Ln}-$  bond of the metal chelate ring. Such an argument gains some support when it is noted that the ionization constants of isobutyric,  $\alpha$ -hydroxyisobutyric, 2,3-di-

Table III. Stoichiometric Ionization Constants of Some Organic Acids of Interest, at 25° and  $I = 0.100$  (Unless Indicated Otherwise)

| Acid | Media            | $K_a$                               | Ref       |
|------|------------------|-------------------------------------|-----------|
| IB   | $\text{NaClO}_4$ | $2.30 \times 10^{-5}$ (0.5 M)       | 7         |
| HIB  | $\text{NaClO}_4$ | $(1.63 - 1.5 [L^-]) \times 10^{-4}$ | 8         |
| DHMP | $\text{KNO}_3$   | $(2.65 - 1.4 [L^-]) \times 10^{-4}$ | This work |
| DHMB | $\text{KNO}_3$   | $(3.06 - 5.2 [L^-]) \times 10^{-4}$ | This work |
| HDMB | $\text{NaClO}_4$ | $1.71 \times 10^{-4}$               | 12        |

Table IV. Comparison of the Formation Constants of the 1:1 Heavier Lanthanide (Dy-Lu) and Yttrium Chelate Species of 2,3-Dihydroxy-2-methylbutanoate (DHMB) and 2-Hydroxy-2,3-dimethylbutanoate (HDMB)

| $\text{Ln}^{3+}$ | $K_1(\text{LnDHMB})$ | $K_1(\text{LnHDMB})^{12}$ |
|------------------|----------------------|---------------------------|
| Dy               | 995                  | 1030                      |
| Ho               | 1065                 | 1130                      |
| Er               | 1288                 | 1180                      |
| Tm               | 1401                 | 1370                      |
| Yb               | 1616                 | 1590                      |
| Lu               | 1769                 | 1650                      |
| Y                | 817                  | 920                       |

hydroxy-2-methylpropanoic, and 2,3-dihydroxy-2-methylbutanoic acids increase in that order. (See Table III.) It is seen from this sequence that the availability of an  $\alpha$ -OH for hydrogen bonding to a carboxyl O atom attenuates the H-O bond of the carboxyl group considerably and that the additional availability of a  $\beta$ -OH for further hydrogen bonding (to the other carboxyl O atom) increases this trend. If one argues that these are purely inductive effects (transmitted along the carbon chain), then one cannot explain why it is that the added  $\beta$ -methyl group also causes attenuation (rather than enhancement) of the carboxyl H-O bond.

On the other hand, it can be seen that substituting either a  $\beta$ -OH or  $\beta$ -CH<sub>3</sub> group (or both) on the third C atom of 2-hydroxy-2-methylpropanoate (HIB) increases the length and flexibility of the chain ( $\text{H}-\text{O}-\text{C}-\text{C}-\text{O}-$  or  $\text{H}-\text{C}-\text{C}-\text{C}-\text{O}-$ ) to permit the terminal H atom to collide with (and thus interfere with the anion's bonding to) a proton or  $\text{Ln}^{3+}$  cation. Certainly, the ionization constant sequence (HIB < DHMP < DHMB) and the stability constant sequences for the smaller lanthanides (Dy-Lu) and yttrium 1:1 chelate species (HIB > DHMP > DHMB) agree with this possibility. However, while DHMB and 2-hydroxy-2,3-dimethylbutanoate (HDMB) exhibit bidentate 1:1 lanthanide chelate stability sequences from Dy through Lu that are nearly coincident (Table IV), the ionization constants of the acids are disparate ( $3.06 \times 10^{-4}$  and  $1.71 \times 10^{-4}$ , respectively). It appears logical, from the DHMB and HDMB data, that collision of the terminal -OH or -CH<sub>3</sub> with a large cation may be more important in weakening the bond to  $\text{Ln}^{3+}$ , whereas hydrogen bonding of the  $\beta$ -OH H atom to a carboxyl O atom may be the principal factor which attenuates bonding of the DHMB anion to a smaller proton.

Whatever the reason, the decrements in ligand affinity attributable to the addition of first an -OH and then a -CH<sub>3</sub> group to the end of the 2-hydroxy-2-methylpropanoate ligand are remarkably uniform from Lu through Dy (Figure 2). The unusual trends in chelate stability noted thereafter with DHMP and DHMB ligands are readily rationalized on the basis of relative differences in the abilities of the two anions to bond tridentately *via* the  $\beta$ -OH donor O. These are due first to the favorable inductive effect of the added methyl group and then to an unfavorable steric factor arising from the *cis* configuration of the two -CH<sub>3</sub> groups in the metal chelate ring (of DHMB). Therefore, we are led to the following predictions:

1. It is conjectured that the low-melting diastereomer of DHMB (the 2*S*,3*S* and 2*R*,3*R* pair of optical isomers, which cannot be obtained by the cyanohydrin synthesis from acetoin<sup>26</sup>) would yield a  $\text{Ln}(\text{DHMB})^{2+}$  stability sequence that

would parallel rather than cross under the Ln(DHMP)<sup>2+</sup> sequence between Sm and Lu.

2. Adding a second methyl group to the third carbon atom of our ligand (to give 2,3-dihydroxy-2,3-dimethylbutanoate) should enhance its affinity when it exhibits tridentate liganacy with lanthanons that are neither too large nor too small (Pr through Gd) but should further decrease the affinity of the bidentate ligand associated with smaller lanthanons (Dy–Lu) and yttrium. That is, the additional inductive effect of a second close-by –CH<sub>3</sub> group on the β-OH O atom should make DHDMB a better donor than DHMB when conditions are optimum for tridentate attachment, but its added bulk ought to cause the end of the anion to collide more frequently with a hydrated metal cation whenever the ligand binds only bidentately. The “club” effect of a terminal HO(CH<sub>3</sub>)<sub>2</sub>C– group should be similar to that encountered with the (CH<sub>3</sub>)<sub>3</sub>C– group of 2-hydroxy-2,3,3-trimethylbutanoate (HTMB), so that the formation constant sequences from Dy through Lu for Ln-(DHDMB)<sup>2+</sup> and Ln(HTMB)<sup>2+</sup> species should nearly coincide, as do those for Ln(DHMB)<sup>2+</sup> and Ln(HDMB)<sup>2+</sup>.

3. If the favorable positioning of the β-OH H atom in DHMB for hydrogen bonding to a carboxyl O is the reason for the increase in the acid ionization from DHMP to DHMB, then this trend may reverse itself with DHDMB, due to an attenuated ability of the latter ligand to rotate (or twist) about the 2–3 bond in the carbon chain. The acid ionization in the case of DHDMB might conceivably drop to a value coincident with that of 2-hydroxy-2,3,3-trimethylbutanoic acid, which has been determined in this laboratory to be about  $1.14 \times 10^{-4}$  at 25° and  $I = 0.10$  (NaClO<sub>4</sub>). This prediction, however, is subject to some reservations (in the event that the opposite inductive effects of the HO– and CH<sub>3</sub>– are capable of being transmitted along a three-carbon chain to the carboxyl O atom). Certainly, the ionization constant of DHDMB will be found to be less than that of DHMP ( $2.65 \times 10^{-4}$  at 25° and  $I = 0.100$ ) but not less than that of HTMB.

**Registry No.** DHMP, 21620-60-0; DHMB, 40634-99-9; La, 7439-91-0; Ce, 7440-45-1; Pr, 7440-10-0; Nd, 7440-00-8; Sm,

7440-19-9; Eu, 7440-53-1; Gd, 7440-54-2; Tb, 7440-27-9; Dy, 7429-91-6; Ho, 7440-60-0; Er, 7440-52-0; Tm, 7440-30-4; Yb, 7440-64-4; Lu, 7439-94-3; Y, 7440-65-5.

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Contribution from the Department of Chemistry,  
University of North Dakota, Grand Forks, North Dakota 58201

## Metal Atom Reactions with Fluorocarbons. VI. Complexes of Halogenated Benzenes with Vanadium(0) and Chromium(0). Effects of Strongly Electron-Withdrawing Substituents, Particularly Trifluoromethyl Groups

KENNETH J. KLABUNDE\* and HOWARD F. EFNER

Received February 4, 1974

AIC40081M

Vapors of vanadium and chromium were cocondensed with arene substrates to yield bis(arene)vanadium(0) and -chromium(0) complexes. A number of halogenated arenes were studied as ligands, and trifluoromethyl substitution enhanced the air stability of the complexes considerably. The presence of two trifluoromethyl groups (1,3- or 1,4-bis(trifluoromethyl)benzene) caused the preparation of the complexes to fail in the case of vanadium, but in the case of chromium extremely air- and temperature-stable complexes were formed in good yields. However, infrared studies suggested that the ring-metal bonding is weaker in bis(1,4-bis(trifluoromethyl)benzene)chromium(0) than in bis(benzene)chromium(0).

### Introduction

The technique of cocondensing free metal atoms with organic substrates at low temperature has proven to be a viable method of synthesizing many new as well as known organometallic complexes.<sup>1–6</sup> A considerable amount of effort in this area has been on the use of chromium atoms for the synthesis of bis(arene)chromium(0) complexes. Timms<sup>7</sup> was the first to report the production of bis(benzene)chromium(0) itself using the metal atom technique, and Skell,<sup>3</sup> Timms,<sup>2b</sup> Lagowski,<sup>8</sup>

and their coworkers have all reported on the use of chromium atoms for synthesis of a number of substituted sandwich complexes. Recently, molybdenum, tungsten,<sup>3b</sup> and titanium<sup>5</sup> atoms have also been employed for synthesis of arene π complexes. We have also been working in this area for quite some time<sup>9,10</sup> and have been mainly concerned with polyhalogenated benzene complexes with chromium as well as vanadium. In this paper we report on the synthesis, properties, and spectra of a series of bis(arene) complexes with vanadium