are linked to form a one-dimensional chain structure instead of forming separate pairs of copper atoms as in copper(II) acetate monohydrate or acetylacetonemono-(o-hydroxyanil)copper(II). Secondly, neighboring copper atoms are bridged by two oxygen atoms in water molecules rather than by two oxygen atoms each bonded to an aromatic ring as in the tricoordinated copper(II) complex. Lastly, these two copper atoms and two bridging oxygen atoms do not lie on a single plane, whereas they are coplanar in the tricoordinated copper(II) complex.

We have tried to prepare hydrated copper(II) benzoate showing a subnormal moment. However, unlike the case with copper(II) salicylate, all our efforts have been unsuccessful. We already have found[2,12] that urea forms addition compounds with copper(II) carboxylates more readily than water does and that the resulting addition compounds show subnormal moments. Therefore, we have prepared the addition compounds of copper(II) benzoate with urea, ethanol, and benzoic acid. As anticipated, their moments were found to be subnormal.

From copper(II) benzoate trihydrate (normal moment), we could obtain an anhydrous salt showing a

(12) M. Kishita and M. Kubo, *Naturwissenschaften*, **49**, 230 (1962).

normal moment (α modification), whereas copper(II) benzoate monoethanol (subnormal moment) gave the β modification showing a subnormal moment of 1.49 B.M., in agreement with Ploquin's value of 1.5$_0$ B.M.[6] A somewhat more elaborate method yielded the γ modification. The observed moment, 1.40 B.M., is smaller than the foregoing one by as much as about 0.1 B.M., which is definitely beyond the range of experimental error. This suggested that the β modification might be a mixture of the α and the γ modification. However, the X-ray powder patterns of the β modification taken by means of a Norelco X-ray diffractometer consist of a number of sharp peaks, none of which agrees with those of the α or of the γ modification: no broad peaks indicative of amorphous nature of the sample were observable. Thus, we are led to conclude that three different modifications exist for anhydrous copper(II) benzoate.

Martin and Waterman[1] already have reported that anhydrous copper(II) formate can be obtained in three different modifications, each of which is characterized by its color, magnetic moment, and X-ray diffraction patterns. The present investigation offers additional examples of copper(II) compounds of one and the same chemical formula capable of existing in magnetically different crystal modifications.

Contribution from the Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa

Complexes of the Trivalent Rare Earths with Isobutyrate, α-Hydroxyisobutyrate, and α,β,β'-Trihydroxyisobutyrate Ligands[1]

By W. R. Stagg and J. E. Powell

Complexes of the trivalent rare earths with the ligands isobutyrate, α-hydroxyisobutyrate, and α,β,β'-trihydroxyisobutyrate have been studied at 25° and an ionic strength of 0.5 *M*. The isobutyrate complexes were very weak compared to the other two series of complexes. It was found that the α-hydroxyisobutyrate complexes were less stable than the corresponding α,β,β'-trihydroxyisobutyrate complexes of the light rare earths, but the relative stabilities were reversed for the heavier rare earths. It was postulated that a change in coordination of the α,β,β'-trihydroxyisobutyrate ligand was responsible for this inversion.

Introduction

Recently, complexes of the trivalent rare earths with α-hydroxyisobutyrate have been reported.[2,3] The rare earth–α-hydroxyisobutyrate complexes exhibit a more or less regularly increasing stability with increasing atomic number and this property makes the ligand a useful eluent for ion-exchange elution chromatographic separation of rare earth mixtures. It was

desirable to see if addition of hydroxyl substituents to the α-hydroxyisobutyrate skeleton would enhance the stabilities of the complexes and hence improve separation factors for ion-exchange work.

Rare earth complexes of acetate[4–6] and glycolate[2,3] both exhibit discontinuities in plots of stability constant *vs.* atomic number in the Eu–Gd–Tb region. The rare earth propionate[7] and lactate[2,3] complexes do likewise. The α-hydroxyisobutyrate complexes do not demonstrate this phenomenon and it was of interest to see if the isobutyrate complexes did or not.

(1) Contribution No. 1333. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. This report is based upon a Ph.D. dissertation by W. R. Stagg and submitted to the Iowa State University of Science and Technology, Ames, Iowa, 1963.

(2) G. R. Choppin and J. A. Chopoorian, *J. Inorg. Nucl. Chem.*, **22**, 97 (1961).

(3) J. E. Powell, R. H. Karraker, R. S. Kolat, and J. L. Farrell, "Complex Systems of the Rare Earth Metals with Glycolate, Lactate, and α-Hydroxyisobutyrate Ligands," paper presented at the Third Rare Earth Research Conference, Clearwater, Florida, April 21–24, 1963.

(4) A. Sonesson, *Acta Chem. Scand.*, **12**, 165 (1958).

(5) A. Sonesson, *ibid.*, **12**, 1937 (1958).

(6) R. S. Kolat and J. E. Powell, *Inorg. Chem.*, **1**, 293 (1962).

(7) G. S. Paul, "A Study of the Rare Earth Metal Propionate Complexes," unpublished M.S. thesis, Iowa State University of Science and Technology, Ames, Iowa, 1963.

Complexes of lanthanum, yttrium, and all of the trivalent rare earths except promethium with the ligands isobutyrate, α-hydroxyisobutyrate, and α,β,β'-trihydroxyisobutyrate have been studied at an ionic strength of 0.5 M (NaClO$_4$) and a temperature of 25°. The stoichiometric stability constants representing the equilibria

$$B + nA \rightleftharpoons BA_n \qquad n = 1, 2, \ldots$$

have been evaluated.   These constants are given by

$$\beta_n = \frac{[BA_n]}{[B][A]^n}$$

where B represents the metal ion and A represents the ligand.

Experimental

Rare Earth Perchlorate Solutions.—All rare earths except cerium and europium were obtained as oxides from the rare earth separation group of the Ames Laboratory and were assayed at 99.9% purity.   Europium oxide (99.9%) was obtained from the Michigan Chemical Corporation, Saint Louis, Michigan.   The oxides were dissolved in a slight excess of perchloric acid, the solutions were evaporated to dryness to effect a slight pyrohydrolysis, and the residues were redissolved in distilled water.   Aliquots of the resulting solutions were then titrated with dilute perchloric acid, using a pH meter as an indicator, and the end point was found by means of a Gran plot.[8]   The solutions were then adjusted to this equivalence point pH.   Cerium(III) perchlorate (99.9%) was obtained from Lindsay Chemical Division of American Potash and Chemical Corporation, West Chicago, Illinois.   Approximately 0.5 M stock solutions of the rare earths were prepared.   The excess acid in the cerium solution was determined by titration with standard base using a Gran plot. The solutions were standardized both by oxalate precipitation and by the method of Fritz, *et al.*[9]

Isobutyrate Buffer.—Matheson Coleman and Bell isobutyric acid was fractionally distilled and a fraction from the middle of the distillate used to prepare an approximately 1:1 buffer with standard NaOH.   The acid concentration in the buffer was determined by titration of aliquots with standard base.   The sodium salt concentration was made 0.500 M.

α-Hydroxyisobutyrate Buffer.—α-Hydroxyisobutyric acid (Eastman Organic Chemicals No. 3025) was purified by recrystallizing it from a benzene–diethyl ether mixture and then boiling the crystals in water with activated carbon.   After filtering, the acid solution was standardized against standard base and a 1:1 buffer was prepared with standard NaOH.   The sodium salt concentration was made 0.500 M.

α,β,β'-Trihydroxyisobutyrate Buffer.—α,β,β'-Trihydroxyisobutyric acid was prepared by the method of Coleman and Glattfeld,[10] recrystallized from acetone, and analyzed by titration with standard base.   A 1:1 buffer was prepared by mixing a weighed amount of the acid with an appropriate amount of standard NaOH to give a solution with a sodium salt concentration of 0.500 M.

Other Reagents.—Sodium perchlorate (G. Frederick Smith, anhydrous) was purified by passing an approximately 1 M solution of it through a sodium-form cation exchanger.   This solution was standardized by passing aliquots through a hydrogen-form cation exchanger and titrating these with standard base.   A 1.000 × 10^{-3} M perchloric acid solution was prepared by dilution with CO$_2$-free distilled water from standard perchloric acid and sufficient sodium perchlorate to make the ionic strength of the

(8) G. Gran, *Analyst*, **77**, 661 (1952).

(9) J. S. Fritz, J. E. Abbink, and M. A. Payne, *Anal. Chem.*, **33**, 1381 (1961).

(10) H. M. Coleman and J. W. E. Glattfeld, *J. Am. Chem. Soc.*, **66**, 1183 (1944).

TABLE I

LOGARITHMS OF STABILITY CONSTANTS OF THE RARE EARTH ISOBUTYRATE COMPLEXES

Metal	log β$_1$	log β$_2$
La	1.64	2.16
Ce	1.79	2.32
Pr	1.92	3.18
Nd	1.98	3.10
Sm	2.05	3.30
Eu	1.98	3.10
Gd	1.87	3.28
Tb	1.82	2.84
Dy	1.74	2.57
Ho	1.70	2.92
Er	1.69	2.59
Tm	1.69	2.28
Yb	1.78	3.10
Lu	1.81	2.32
Y	1.60	2.71

solution 0.5 M.   This solution was subsequently used in an argon atmosphere as a pH standard.

Technique.—The experimental method of Fronaeus[11] was used. A 50-ml. sample containing 0.004 M rare earth and sufficient sodium perchlorate to give an ionic strength of 0.5 M was titrated with 5 ml. of the appropriate buffer solution.   Since the buffer had the same ionic strength as the solution being titrated, variations in ionic strength were due only to complex formation. The titrations were carried out in a thermostated titration cell at 25.00 ± 0.5°.   A Beckman Model 76 expanded scale pH meter with a glass indicator electrode and a saturated calomel reference electrode was used to measure the hydrogen ion concentration in the sample.   The KCl in the reference electrode was replaced with NaCl to avoid interference from KClO$_4$ in the fiber junction. The instrument was standardized against the 0.001 M perchloric acid solution prior to each titration so that the negative logarithm of the hydrogen ion concentration could be read directly from the meter.

Calculations.—The total ligand concentration, the free ligand concentration, a, the total metal concentration, and the mean ligand number, $\bar{n}$, were required for computation of the β_n values. These were derived from the known stoichiometry of the solutions and the observed hydrogen ion concentrations.   Equations for computation   of these quantities for monobasic acids are easily derived and need not be given here.   The stability constants were computed on an IBM 7074 computer using a weighted least squares program patterned after that of Sullivan, *et al.*[12] The β_n values were initially approximated from the data ($\bar{n}$, a) by Bjerrum half-$\bar{n}$ method[13] and the weight factors computed from these.   Second approximations to the β_n values were then calculated and the process was repeated until successive cycles gave a change of less than one part per thousand in each β_n.

Results

The results of the experiments are tabulated in Tables I, II, and III.   Low values of $\bar{n}$ permitted computation of only two constants for the isobutyrate complexes and for some of the α-hydroxyisobutyrate complexes.   The standard deviation in each parameter was computed by means of an adequate program on the IBM 7074 computer.   Generally, the standard deviation amounted to from 1 to 5% of the numerical

(11) S. Fronaeus, "Komplexsystem hos kopper," Gleerupska Universitets-Bok-handeln, Lund, 1948.

(12) J. C. Sullivan, J. Rydberg, and W. F. Miller, *Acta Chem. Scand.*, **13**, 2023 (1959).

(13) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, p. 36.
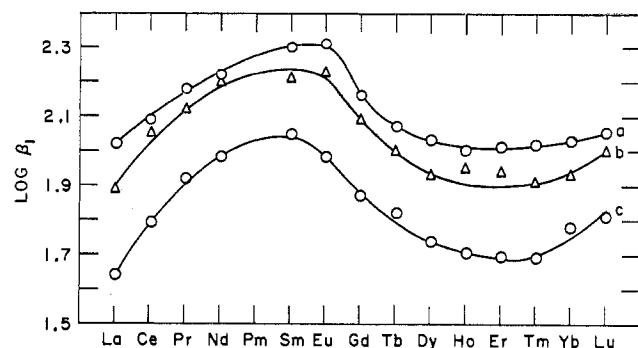
Fig. 1.—Logarithms of the first stability constants of some rare earth complexes: a, acetate[5]; b, propionate[6]; c, isobutyrate, this work.
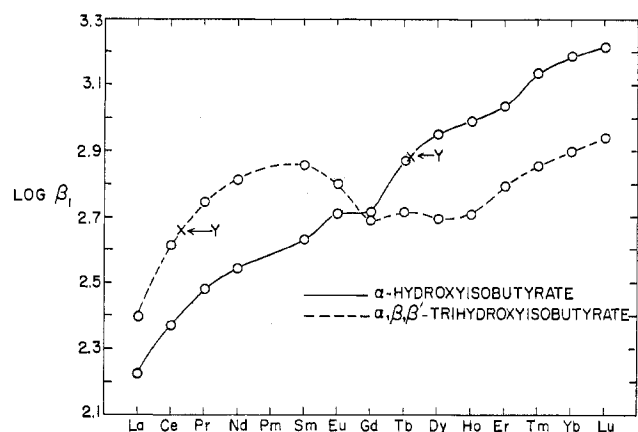

Fig. 2.—Logarithms of the first stability constants of the rare earth α-hydroxyisobutyrate and αβ,β,'-trihydroxyisobutyrate complexes.

TABLE II

LOGARITHMS OF STABILITY CONSTANTS OF THE RARE EARTH
α-HYDROXYISOBUTYRATE COMPLEXES

Metal	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$
La	2.22	3.67	...
Ce	2.37	4.01	...
Pr	2.48	4.12	...
Nd	2.54	4.32	...
Sm	2.63	4.60	...
Eu	2.71	4.92	5.91
Gd	2.71	4.97	6.01
Tb	2.87	5.21	6.19
Dy	2.95	5.32	7.16
Ho	2.98	5.42	7.41
Er	3.03	5.54	7.56
Tm	3.13	5.62	7.84
Yb	3.18	5.76	8.02
Lu	3.21	5.85	8.21
Y	2.88	5.32	6.75

value of the individual β. Since these deviations merely reflect errors in internal consistency of the twenty or more data points used to compute each parameter and are considerably smaller than the more realistic maximum possible errors, they are not given here. The reader is referred instead to the doctoral dissertation of Stagg,[1] wherein the individual standard errors are reported. By varying the input data within their estimated maximum limits of error using the Dy–THIB data, it was ascertained that the possible errors

TABLE III

LOGARITHMS OF STABILITY CONSTANTS OF THE RARE EARTH
α,β,β'-TRIHYDROXYISOBUTYRATE COMPLEXES

Metal	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$
La	2.40	3.88	4.90
Ce	2.61	4.45	5.98
Pr	2.75	4.69	6.15
Nd	2.81	4.62	6.36
Sm	2.86	5.07	6.51
Eu	2.80	5.00	6.45
Gd	2.69	4.99	6.41
Tb	2.71	4.88	6.58
Dy	2.66	4.87	6.37
Ho	2.71	4.89	6.22
Er	2.79	4.83	6.57
Tm	2.85	4.97	6.51
Yb	2.90	5.07	6.50
Lu	2.94	5.19	6.90
Y	2.65	4.67	5.26

in β_1, β_2, and β_3 might be as great as $\pm 10\%$, $\pm 25\%$, and $\pm 50\%$, respectively, when a three-parameter system was considered. The possible errors for a two-parameter system, such as that assumed in the case of dysprosium isobutyrate, were estimated to be $\pm 25\%$ for β_1 and $\pm 50\%$ for β_2.

Experiments were run to determine whether polynuclear complexes were present in significant concentrations by varying the metal ion concentration fivefold. The constants obtained from these experiments were well within the previously quoted error limits for values obtained with the 0.004 M nominal metal ion concentration.

The variation in ionic strength mentioned earlier was shown to be insignificant by an experiment in which the initial ionic strength of the sample was decreased by 5%. This was slightly greater than the maximum variation which might be expected. The resultant β_n values were within the limits of error of those at an initial ionic strength of 0.5 M.

The acid ionization constants determined in this work were $(2.30 \pm 0.03) \times 10^{-5}$ for isobutyric acid, $(1.76 \pm 0.01) \times 10^{-4}$ for α-hydroxyisobutyric acid, and $(5.15 \pm 0.07) \times 10^{-4}$ for α,β,β'-trihydroxyisobutyric acid at 25° and an ionic strength of 0.5 M (NaClO$_4$).

Discussion

Log β_1 values for the isobutyrate complexes are shown as curve c in Fig. 1. They may be compared qualitatively to the acetate data[6] (curve a) and the propionate data[7] (curve b), both of which were taken at 20° and an ionic strength of 0.1 M. No explanation seems readily apparent for the sinusoidal behavior of these stability constants.

The α-hydroxyisobutyrate data compare favorably with those of Powell, *et al.*,[3] and Choppin and Choporian[2] at different temperatures and ionic strengths. Log β_1 values for the α-hydroxyisobutyrate complexes and the α,β,β'-trihydroxyisobutyrate complexes are shown in Fig. 2. One can see that the two curves cross in the region around gadolinium. The reason for

this is not completely clear. However, one might speculate about the cause using the empirical rules of Cobble[14] for estimating the entropies of complex ions. If one metal–ligand bond in a complex of a polydentate ligand were broken and the site were then occupied by a water molecule, the resultant entropy change would account for about -0.59 unit of log β_n. This

(14) J. W. Cobble, *J. Chem. Phys.*, **21**, 1451 (1953).

would be sufficient to account for the inversion in the relative stabilities of the two series of complexes. A change in the dentate character of the α,β,β'-trihydroxy-isobutyrate ligand seems plausible.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASSACHUSETTS

The Crystal and Molecular Structure of Bis(dipivaloylmethanido)zinc(II)[1]

BY F. A. COTTON[2] AND J. S. WOOD

A single crystal, three-dimensional X-ray study of bis(dipivaloylmethanido)zinc(II) has been carried out. The results confirm an earlier deduction from space group requirements that the metal atoms lie at positions of $\bar{4}$ symmetry and are thus in "tetrahedral" (strictly D_{2d}) complexes. The space group also requires that each chelate ring be precisely symmetrical. The important bond lengths and angles in the chelate ring (standard deviations in parentheses) are: Zn–O, 1.962 (0.007) Å.; C–O, 1.274 (0.012) Å.; C–C, 1.405 (0.012) Å.; $\angle$ OZnO, 94.7° (0.6); $\angle$ OCC, 125.8° (1.1); $\angle$ CCC, 127.0° (2.8). The remaining $\angle$ OZnO angles are 114.2° (0.6). These dimensions are compared with those in some other β-ketoenolate complexes. The considerable distortion of the immediate environment of the cobalt atom, in the isostructural cobalt(II) complex, from perfect tetrahedral symmetry can be considered as an important cause of the somewhat anomalous characteristics of the visible absorption spectrum of that compound.

Introduction

Interest in the molecular structures of β-ketoenolate complexes of metal ions in this laboratory has mainly centered around those of Co(II),[3,4] Ni(II),[5–7] and Cu(II)[8] and has been generated chiefly in the attempt to understand the electronic structures and bonding and thus to interpret the electronic spectra of such compounds. While acetylacetonates themselves have been most frequently studied, the dipivaloylmethane derivatives have played a crucial role in understanding Co(II) and Ni(II) β-ketoenolate complexes and continue to offer novel and even unique opportunities for study of such compounds. It has been, or will become, necessary, in order to exploit these opportunities properly, to have precise knowledge of the crystal and molecular structures of these compounds and thus a program of X-ray crystallographic investigation has been undertaken. A future paper will report on the isomorphous Cu(II) and Ni(II) compounds, which contain planar molecules. This paper reports the structure of the Zn(II) compound, which is isomorphous[3] with that of Co(II). It has already been reported[3] that the space group and unit cell contents of these compounds appear to require that the molecules have D_{2d} (or, roughly, "tetrahedral") structures and some of the consequences

of that for the Co(II) compound have been discussed.[3,4] The complete X-ray study described here fully confirms the earlier report and provides fairly precise values for the various interatomic distances and bond angles. We elected to make this study on the zinc compound chiefly because of its greater convenience both in the preparation and the preservation of single crystals.

Experimental

Single crystals in the form of square prisms with pyramidal ends, or distorted octahedral exhibiting faces of the form {111} (crystal class 4/mmm), were prepared by slow sublimation under vacuum at $\sim$90° by Dr. Roger Soderberg. Using a crystal mounted along the prism axis, precession photographs were taken with Mo Kα radiation. The unit cell was found to be tetragonal with the following dimensions: $a = 10.67 \pm 0.01$ and $c = 21.76 \pm 0.015$ Å. The following systematic absences were observed: for hkl, $h + k + l \neq 2n$; for $hk0$, $h(k) \neq 2n$; $00l$, $l \neq 4n$. These uniquely fix the space group as I4$_1$/a (No. 88). The corresponding cobalt compound was found to be isomorphous (virtually indistinguishable precession photographs) with unit cell dimensions of $a = 10.67$ and $c = 21.87$ Å. The density (by flotation) was found to be 1.15 ± 0.02 g./cm.^{3}. Taking the molecular weight as 431.4, the calculated value of Z is 3.99 ± 0.07. The density of the cobalt compound was measured as 1.13 ± 0.02 g./cm.^{3} giving for Z, 3.98 ± 0.07.

Intensities were recorded photographically by the equiinclination Weissenberg method, using a crystal about $0.5 \times 0.5 \times 0.7$ mm. and Cu Kα radiation. Layers $hk0$ and $h0l–h6l$ were recorded using the multiple film technique and the intensities estimated visually by comparison with a set of timed exposures of a reflection from the same crystal. No corrections were made for absorption in view of the low value of the absorption coefficient ($\mu = 13.7$ cm.$^{-1}$). Absorption corrections for a spherical specimen at 0 and 45° differ by less than 4%. It was calculated that *ca.* 500 independent reflections are accessible with Cu Kα radia-

(1) Supported by the United States Atomic Energy Commission.
(2) Alfred P. Sloan Foundation Fellow.
(3) F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, **84**, 872 (1962).
(4) F. A. Cotton and R. H. Soderberg, *Inorg. Chem.*, **3**, 1 (1964).
(5) J. P. Fackler, Jr., and F. A. Cotton, *J. Am. Chem. Soc.*, **82**, 5005 (1960).
(6) F. A. Cotton and J. P. Fackler, Jr., *ibid.*, **83**, 2818 (1961).
(7) J. P. Fackler, Jr., and F. A. Cotton, *ibid.*, **83**, 3775 (1961).
(8) J. P. Fackler, Jr., and F. A. Cotton, *Inorg. Chem.*, **2**, 97, 102 (1963).