

agreement of magnetic moments of the two complexes and the existence of crystallographically nonequivalent water molecules in the tetrahydrate along with the close similarity in color and cleavage between these complexes suggest that two molecules of water in the tetrahydrate can be replaced with two urea molecules to form the bisurea dihydrate without affecting appreciably the two-dimensional network structure involving copper atoms.

Copper(II) formate monourea shows a subnormal magnetic moment of 1.08 B.M., indicating the presence of paired copper atoms as in the crystals of copper(II) acetate monohydrate.¹ It is presumed that in this binuclear complex, copper atoms are bridged in pairs by four formate groups with two urea molecules occupying the terminal positions. This is interesting because unlike other copper(II) carboxylates,⁹ copper(II) formate and its stable derivatives are known to show moments^{7,10} close to the theoretical spin-only moment of 1.73 B.M. for one unpaired electron except in dioxane solution.^{4,11}

(9) R. L. Martin and H. Waterman, *J. Chem. Soc.*, 2545 (1957); M. Kondo and M. Kubo, *J. Phys. Chem.*, **62**, 1558 (1958); O. Asai, M. Kishita, and M. Kubo, *ibid.*, **63**, 96 (1959).

(10) G. A. Barclay and C. H. L. Kennard, *J. Chem. Soc.*, 3289 (1961).

(11) R. L. Martin and A. Whitley, *ibid.*, 1394 (1958).

All the urea complexes of copper(II) acetate and higher homologs studied show typically subnormal magnetic moments equal to 1.40 ± 0.03 B.M. The values are close to the moments of anhydrous copper(II) *n*-alkanoates and hydrated ones.^{2,6,9} Undoubtedly, urea molecules in the monourea complexes occupy the same positions about copper atoms as do water molecules in the crystals of copper(II) acetate monohydrate. In fact, it has been found by X-ray crystal analysis¹² that pyridine can replace water in the latter compound without affecting the characteristic binuclear structure involving copper atoms. Probably, oxygen atoms rather than nitrogen atoms of urea molecules are directly coordinated on copper atoms.¹³

The observed subnormal magnetic moments of copper(II) *n*-alkanoate hemiureas indicate the presence of paired copper atoms in crystals. It is unlikely that $\text{Cu}_2(\text{C}_n\text{H}_{2n+1}\text{CO}_2)_2 \cdot (\text{NH}_2)_2\text{CO}$ is the structural unit composing the crystals, because it is not probable that copper atoms have vacant coordination sites, whereas oxygen and nitrogen atoms of urea exist in the crystals without participating in coordination.

(12) G. A. Barclay and C. H. L. Kennard, *ibid.*, 5244 (1961).

(13) R. B. Penland, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **79**, 1575 (1957).

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Magnetic Moments of Copper(II) Salicylate, Copper(II) Benzoate, and Some Related Compounds

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Received August 13, 1963

Copper(II) salicylate tetrahydrate and anhydrous copper(II) salicylate can be obtained in two different crystal modifications, in one of which the magnetic moment per copper atom is normal whereas in the other it is subnormal. Copper(II) benzoate trihydrate shows a normal magnetic moment in spite of the close distance of approach and bridging arrangement of copper atoms in crystals. Anhydrous copper(II) benzoate forms three different modifications, each characterized by its color, magnetic moment, and X-ray powder patterns. The addition compounds of copper(II) benzoate with benzoic acid, ethanol, and urea show subnormal magnetic moments characteristic of some crystalline copper(II) carboxylates having the binuclear structure of copper atoms.

Introduction

On the basis of their magnetic moments at room temperature, copper(II) compounds can be classified into two main groups. A great majority of these compounds show normal moments (1.8–2.0 Bohr magnetons), indicating the absence of any appreciable spin coupling between unpaired electrons belonging to copper atoms. On the other hand, a number of copper(II) compounds have been reported to show moments considerably smaller than the spin moment 1.73 B.M. for one unpaired electron (subnormal moments approximately equal to 1.4 B.M. or less). Some copper(II) carboxylates^{1,2} and the so-called tricoordinated copper(II) complexes³ belong to this category. Obviously, some

kind of spin interaction either of a direct nature or of a super-exchange type must be responsible for the subnormal moments. In fact, it has been shown by X-ray crystal analysis that in copper(II) acetate monohydrate,⁴ copper atoms are bridged in pairs by four acetate groups to form dimer molecules in which the Cu–Cu

(1) B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956); R. L. Martin and H. Waterman, *ibid.*, 2545 (1957); R. L. Martin and A. Whitley, *ibid.*, 1394 (1958); R. L. Martin and H. Waterman, *ibid.*, 1359, 2960 (1959).

(2) M. Kondo and M. Kubo, *J. Phys. Chem.*, **62**, 468, 1558 (1958); O. Asai, M. Kishita, and M. Kubo, *ibid.*, **63**, 96 (1959); M. Inoue, M. Kishita, and M. Kubo, *Acta Cryst.*, **16**, 699 (1963); M. Kishita, M. Inoue, and M. Kubo, *Inorg. Chem.*, **3**, 237 (1964).

(3) M. Kishita, Y. Muto, and M. Kubo, *Australian J. Chem.*, **10**, 386 (1957), **11**, 309 (1958); M. Kubo, Y. Kuroda, M. Kishita, and Y. Muto, *ibid.*, **16**, 7 (1963).

(4) J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **6**, 227 (1953).

distance is as short as 2.64 Å. On the other hand, acetylacetonemono(*o*-hydroxyanil)copper(II),⁵ a typical example of the so-called tricoordinated copper(II) complexes, forms dimer molecules in which two copper atoms are located at the ends of a diagonal (3.00 Å. in length) of a square with two oxygen atoms occupying other corners.

Accordingly, one is led to suppose that subnormal magnetic moments for copper(II) compounds are indicative of the close distance of approach of copper atoms in crystals. Copper(II) salicylate tetrahydrate presents an exception to this rule. The observed moment is subnormal,⁶ whereas X-ray crystal analysis⁷ has revealed the absence of any paired copper atoms in the crystal. Copper(II) benzoate trihydrate⁸ deserves particular attention, because X-ray analysis has indicated that neighboring copper atoms are 3.15 Å. distant from each other and are linked by two oxygen atoms and one Cu-O-C-O-Cu bridge of *syn-syn* arrangement. Therefore, we have prepared copper(II) salicylate, copper(II) benzoate, and various derivatives thereof for the study of their magnetic behavior.

Preparation of Materials

Copper(II) Salicylate Tetrahydrate.—The pale blue modification was prepared by essentially the same method as that employed by Hanic and Michalov.⁷ The blue-green modification was prepared as follows. The aforementioned copper(II) salicylate tetrahydrate and an equimolar amount of salicylic acid were dissolved in as small an amount of ethanol as possible. A small quantity of water was added plus a minimum amount of acetone to avoid the formation of a precipitate. When the solution was cooled to 0°, blue-green plate crystals separated. Alternatively, the ethanol solution of salicylic acid and the aqueous solution of copper(II) acetate were mixed and cooled to obtain the same sample. This compound is fairly stable as long as it is kept in a refrigerator. It gradually loses water of crystallization in air at room temperature. Recrystallization from water yielded the pale blue tetrahydrate.

Anal. Calcd. for $\text{Cu}(\text{C}_6\text{H}_4\cdot\text{OH}\cdot\text{CO}_2)_2\cdot 4\text{H}_2\text{O}$: C, 41.0; H, 4.4; Cu, 15.5; H_2O , 17.6. Found: Pale blue: C, 41.0; H, 4.6; Cu, 15.6. Blue-green: C, 41.7; H, 4.6; Cu, 15.7; H_2O , 17.2. The analysis of carbon and hydrogen in the latter modification was made on a dehydrated sample, which was found to be identical with the green modification of anhydrous copper(II) salicylate described below.

Anhydrous Copper(II) Salicylate.—The pale blue tetrahydrate gave two different anhydrous compounds depending on the method of dehydration. The brown modification was obtained when the tetrahydrate was dehydrated at room temperature over phosphorus pentoxide or by heating rapidly up to 85°. The blue-green modification was obtained when the pale blue tetrahydrate was heated to 85° very slowly and maintained at that temperature until no further weight decrease took place. The green modification resulted when the blue-green tetrahydrate was dehydrated by gradual heating or by allowing it to stand over phosphorus pentoxide at room temperature until the weight became constant. Anhydrous copper(II) salicylate was obtained in a powder form.

Anal. Calcd. for $\text{Cu}(\text{C}_6\text{H}_4\cdot\text{OH}\cdot\text{CO}_2)_2$: C, 49.7; H, 3.0; Cu, 18.8. Found: Brown: C, 49.2; H, 3.1; Cu, 18.6.

Blue-green: C, 48.9; H, 3.3; Cu, 19.0. Green: C, 49.2; H, 3.3; Cu, 18.8.

Copper(II) Benzoate Trihydrate.—This compound was prepared from aqueous solutions of copper(II) sulfate and sodium benzoate by the diffusion method in exactly the same manner as for single crystals studied by X-rays.^{8,9}

Anal. Calcd. for $\text{Cu}(\text{C}_6\text{H}_5\text{CO}_2)_2\cdot 3\text{H}_2\text{O}$: C, 46.6; H, 4.5; Cu, 17.6; H_2O , 15.0. Found: C, 46.5; H, 4.5; Cu, 17.7; H_2O , 15.5.

Anhydrous Copper(II) Benzoate.—The α modification was formed when the trihydrate was dehydrated in a vacuum desiccator at 95° over phosphorus pentoxide. Pale greenish blue powders were obtained. The β modification resulted when the monoethanol derivative described below was heated in air at 90°. Ethanol escaped and blue-green crystalline powders remained. The γ modification was prepared when copper(II) benzoate monoethanol was boiled in carbon tetrachloride for 1–2 hr. Blue-green crystalline powders were obtained.

Anal. Calcd. for $\text{Cu}(\text{C}_6\text{H}_5\text{CO}_2)_2$: C, 55.0; H, 3.3; Cu, 20.8. Found: α : C, 54.1; H, 3.4; Cu, 20.5. β : C, 54.5; H, 3.3; Cu, 20.8. γ : C, 53.9; H, 3.4; Cu, 20.6.

Copper(II) Benzoate Mono(benzoic acid).—Sodium benzoate (1.4 g.) was dissolved in a 0.1 N hot aqueous solution (50 ml.) of benzoic acid. When the solution was slowly dropped into a hot aqueous solution (30 ml.) of copper(II) sulfate pentahydrate (1 g.), fine blue-green precipitates were formed. After being warmed over a water bath for a while, they were filtered off while the solution was still warm and washed with hot water.

Anal. Calcd. for $\text{Cu}(\text{C}_6\text{H}_5\text{CO}_2)_2\cdot \text{C}_6\text{H}_5\text{CO}_2\text{H}$: C, 58.9; H, 3.8; Cu, 14.8. Found: C, 58.6; H, 3.8; Cu, 14.5.

Copper(II) Benzoate Monoethanol.—A solution of copper(II) acetate (0.6 g.) in ethanol (80 ml.) was mixed with a solution of benzoic acid (0.8 g.) in the same solvent (25 ml.). When the mixture was left to stand in a refrigerator at about 6°, green needle-like crystals separated. They readily lost ethanol in air.

Anal. Calcd. for $\text{Cu}(\text{C}_6\text{H}_5\text{CO}_2)_2\cdot \text{C}_2\text{H}_5\text{OH}$: $\text{C}_2\text{H}_5\text{OH}$, 13.1; Cu, 18.0. Found: $\text{C}_2\text{H}_5\text{OH}$, 13.5; Cu, 17.9. Elementary analysis was performed for carbon and hydrogen after ethanol was removed (see preparation of anhydrous copper(II) benzoate, β modification).

Copper(II) Benzoate Monourea.—A concentrated solution of urea in methanol was added dropwise to methanol saturated with copper(II) benzoate monoethanol until the concentration of urea amounted to 1–2%. When the mixture was left to stand in a sealed vessel, fine green crystals separated.

Anal. Calcd. for $\text{Cu}(\text{C}_6\text{H}_5\text{CO}_2)_2\cdot (\text{NH}_2)_2\text{CO}$: C, 49.2; H, 3.9; Cu, 17.4. Found: C, 49.3; H, 4.1; Cu, 17.1.

Magnetic Measurements and Results

Magnetic susceptibility was determined at room temperature^{2,3,10} by means of a Gouy magnetic apparatus provided with a semimicrobalance and an electromagnet capable of yielding a field of about 23,000 oersteds with 10 mm. separation between pole pieces. From the observed susceptibilities, the magnetic moments were evaluated per copper atom. Corrections were made for the diamagnetic susceptibilities of salicylic acid (-75×10^{-6} per mole), benzoic acid (-70×10^{-6}), ethanol (-34×10^{-6}), urea (-34×10^{-6}), and water (-13×10^{-6}). Here, the diamagnetic susceptibilities enclosed in parentheses are available in the literature,¹¹

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(6) J. Ploquin, *Bull. Soc. Chim. France*, **18**, 757 (1951).

(7) F. Hanic and J. Michalov, *Acta Cryst.*, **13**, 299 (1960).

(8) H. Koizumi, K. Osaki, and T. Watanabé, *J. Phys. Soc. Japan*, **18**, 117 (1963).

(9) F. Ephraïm and A. Pfister, *Helv. Chim. Acta*, **8**, 374 (1925).

(10) M. Kondo, M. Kishita, M. Kimura, and M. Kubo, *Bull. Chem. Soc. Japan*, **29**, 305 (1956); M. Kondo and M. Kubo, *J. Phys. Chem.*, **61**, 1648 (1957).

(11) G. Foëx, "Constantes Sélectionnées, Diamagnétisme et Paramagnétisme," Masson, Paris, 1957.

TABLE I
MAGNETIC SUSCEPTIBILITIES PER GRAM (C.G.S., E.M.U.) AND
MAGNETIC MOMENTS (BOHR MAGNETONS) OF COPPER(II)
SALICYLATE, COPPER(II) BENZOATE, AND SOME RELATED
COMPOUNDS^a

Compounds	Temp., °C.	$\chi_g \times 10^4$	μ , B.M.	
Cu(II) salicylate·4H ₂ O	pale blue	22	3.32	1.92
	blue-green	24	1.65	1.45
Cu(II) salicylate	brown	25	3.89	1.87
	blue-green	25	2.01	1.41
	green	25	2.12	1.44
Cu(II) benzoate·3H ₂ O		18	3.67	1.87
		18	3.65	1.72
Cu(II) benzoate	α	18	2.66	1.49
	β	18	2.28	1.40
	γ	18	1.85	1.41
Cu(C ₆ H ₅ CO ₂) ₂ ·C ₆ H ₅ CO ₂ H	18	1.48	1.40	
Cu(C ₆ H ₅ CO ₂) ₂ ·C ₂ H ₅ OH	18	1.89	1.40	
Cu(C ₆ H ₅ CO ₂) ₂ ·(NH ₂) ₂ CO	18	1.85	1.41	

^a The moments are calculated for the particular temperature listed and are not expected to be constant, especially for the compounds showing a subnormal moment.

except for the susceptibility of salicylic acid, which was calculated from that of benzoic acid and Pascal's constant for an oxygen atom. Utmost precaution was taken to avoid possible contamination by ferromagnetic impurities in samples. The observed values were not altered by repeated purification. The results are shown in Table I.

Discussion

Ploquin⁶ has determined the magnetic susceptibility of copper(II) salicylate tetrahydrate, which yields a magnetic moment per copper atom equal to about 1.44 B.M. This subnormal magnetic moment apparently contradicts the results of a complete X-ray crystal analysis carried out by Hanic and Michalov.⁷ It has been shown that planar centrosymmetric molecules Cu(C₆H₄·OH·CO₂)₂·2H₂O are linked in the structure by a system of hydrogen bonds in which two remaining water molecules also take part. The shortest Cu-Cu distance is equal to 3.728 Å. There are no pairs of copper atoms of close distance of approach in the crystals. Therefore one would expect a normal magnetic moment of about 1.9 ± 0.1 B.M. In fact copper(II) salicylate tetrahydrate prepared in accordance with the method employed by Hanic and Michalov (pale blue modification) shows a moment equal to 1.92 B.M., indicating the presence of separate rather than paired copper atoms in crystals in agreement with the results of X-ray analysis.

Accordingly, we were led to suppose that there should be at least two magnetically different crystal modifications of copper(II) salicylate tetrahydrate unless Ploquin's value is incorrect. Unfortunately, Ploquin does not describe the method of preparation of his sample in detail. Therefore, we have tried various methods of preparation and finally succeeded in obtaining a sample supposedly identical with Ploquin's but differing from the aforementioned tetrahydrate in its color, crystal habit, and magnetic moment (blue-green modification).

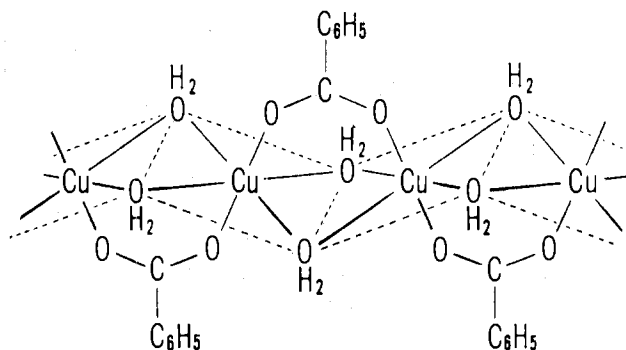


Fig. 1.—Copper atoms linked by water molecules and benzoate groups in copper(II) benzoate trihydrate.

The existence of two modifications of copper(II) salicylate tetrahydrate has suggested the possible formation of magnetically different modifications for anhydrous copper(II) salicylate also. Therefore, we have tried various methods of synthesis and obtained three kinds of samples differing from one another in their color. One of them (brown modification) shows a normal moment, whereas the moments of two others are subnormal. Although chemical analysis indicated the anhydrous nature of these three samples, it is not certain that they are free from being contaminated with magnetically different modifications. The magnetic moments of the blue-green and green samples are slightly different from each other. However, it is difficult to conclude that they represent two different crystallographically uniform chemical species, since the X-ray powder patterns taken by a Norelco X-ray diffractometer bore a close resemblance to each other with respect to the main maxima and minima. However, there is no doubt that at least two magnetically different modifications exist for anhydrous copper(II) salicylate.

X-Ray crystal analysis carried out by Koizumi, *et al.*,⁸ on a single crystal of copper(II) benzoate trihydrate has shown that in this crystal neighboring copper atoms are 3.15 Å. distant from each other and are bridged by two oxygen atoms and one Cu-O-C-O-Cu link to form linear chains [Cu·C₆H₅CO₂·2H₂O]_n, shown in Fig. 1 with [H₂O·C₆H₅CO₂]_n intervening between them. In view of the close distance of approach and bridging arrangement of copper atoms, one would expect the presence of spin interaction between copper atoms. However, we have observed a normal magnetic moment 1.87 B.M. per copper atom. This is the first instance of crystalline copper(II) compounds ever reported to have a short Cu-Cu distance and a normal magnetic moment at room temperature. At the present stage of development of the theory of superexchange interactions, it is difficult to explain why spin interaction is apparently negligible in this crystal. Therefore, we merely point out some structural features possibly responsible for reducing magnetic couplings, postponing a final conclusion until sufficient knowledge is accumulated on the magnetic behavior of various copper(II) compounds having different types of crystal structure. In the first place, copper atoms

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 1.50 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 Waterman¹ 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.

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Complexes of the Trivalent Rare Earths with Isobutyrate, α -Hydroxyisobutyrate, and α,β,β' -Trihydroxyisobutyrate Ligands¹

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Received July 15, 1963

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

(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.

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 acetate⁴⁻⁶ and glycolate^{2,3} both exhibit discontinuities in plots of stability constant *vs.* atomic number in the Eu-Gd-Tb region. The rare earth propionate⁷ 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.

(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.