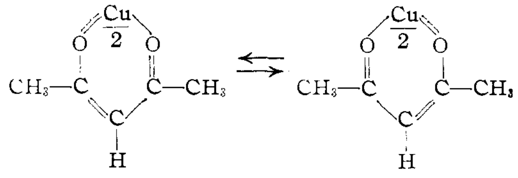
the hydroxyaldehydes. The nickel and zinc kojates appear to be slightly more stable than the corresponding derivatives of β-diketones, but none show the unusual stability of the complexes of the simple tropolones.

Calvin and Wilson[6] have pointed out that the division of the hydroxy aldehydes, β-diketones and β-keto esters into four major groups parallels the ability of the corresponding anions to distribute the negative charge between the two oxygen atoms. They have also suggested the possibility of a benzenoid resonance within the chelate ring itself, as indicated in IV.



IV.—Copper acetylacetonate.

Benzenoid resonance within the five-membered chelate rings of the metal kojates and metal tropolonates is impossible. However, present views[7] on the structure of tropolone itself indicate that in the tropolonate ion, the two oxygens should be fully equivalent. For the copper complex of tropolone[8] it appears that there are two different types of copper–oxygen bonds in the solid material. The same type of X-ray analysis[9] indicates that only one type of copper–oxygen bond is present in copper acetylacetonate.

Present information[10] indicates that the keto form of the γ-pyrones makes a large contribution to the over-all structure. In this case, the two oxygen atoms cannot bear the same partial charges, and any contribution to stability of the copper chelate by reason of equivalence of copper–oxygen bonds should be absent. This conjecture cannot be sustained by any direct evidence at this time, and its validity or invalidity can best be determined by X-ray analysis.

Since it is now known that the tropolones and kojic acid form metal complexes whose stabilities are greater than, or at least equal to, those of β-diketones of the same acidity, it is suggested that the five-membered chelate ring itself may contribute significantly to the stability of compounds of this type. Some factor other than ring size must contribute to the stability of the metal tropolonates.

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The Optical Stability of Beryllium Complexes

BY DARYLE H. BUSCH AND JOHN C. BAILAR, JR.

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The resolution of tetrahedral beryllium complexes is significant from the theoretical standpoint in view of the very small number of metal ion complexes with sp^3 or sp^3d^2 bonding which are known to involve directed valence. Among the more conclusive cases of resolution of complexes of this type are tris-(dipyridyl)-nickel(II),[1] tris-(orthophenanthroline)-nickel(II),[2] tris-(oxalato)-germanium(IV),[3] and bis-(8-quinolinolo-5-sulfonic acid)-zinc(II).[4]

The existence of optical isomers was first demonstrated for complexes of beryllium by Lowery and Burgess[5] who observed that solutions of beryllium benzoylcamphor undergo a rapid mutarotation. Mills and Gotts[6] later resolved bis-(benzoylpyruvato)-beryllium into its optical antipodes through the formation of its brucine salt. They were able to obtain an optically active solution virtually free from the alkaloid. The rotation of this solution rapidly diminished, racemization being complete in fifteen minutes.

It seems probable that the rapid racemization of bis-(benzoylpyruvato)-beryllium is associated with the presence of the strongly negative carboxyl group adjacent to one of the coördinated ketone groups. Such an arrangement leads to competition between two conjugated systems, that of the chelated enol form of the β-diketone portion of the molecule and that of the α-ketoacid. This results in a relatively unsymmetrical electronic distribution in the chelate ring and consequent instability in the complex. In order to obtain a complex of greater configurational stability, it is logical to choose an unsymmetrical chelating agent having identical donor groups coupled to no competing conjugated system. For this reason the beryllium complex of benzoylacetone was chosen for investigation.

Since bis-(benzoylacetono)-beryllium(II) is a non-electrolyte, resolution cannot be effected by the formation of diastereoisomers. However, it is possible to obtain partial resolution of the complex by an asymmetric adsorption on finely divided, optically active quartz. Inasmuch as the reliability of this technique has been verified by its use in resolutions simultaneously carried out by conventional means,[7] the results are considered to be conclusive. It should be noted that the feasibility of complete resolution by this method has not been demonstrated, although rather high rotations may be obtained in some cases.[8]

Preparation of Bis-(benzoylacetono)-beryllium.—The synthesis given here is an adaptation of the method reported by

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[1] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 2213 (1931); G. K. Schweitzer and J. M. Lee, *J. Phys. Chem.*, **56**, 195 (1952).

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[5] T. M. Lowry and H. Burgess, *J. Chem. Soc.*, **125**, 2081 (1925).

[6] W. H. Mills and R. A. Gotts, *ibid.*, 3121 (1926).

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Booth and Pierce.[9] While the earlier workers simply mixed alcoholic solutions of beryllium nitrate and benzoylacetone, the present method involves neutralization of the benzoylacetone in the presence of beryllium ion. The reaction proceeds with the dilution of the alcoholic solution by a considerable volume of water, thus facilitating crystallization of the water-insoluble product.

Five grams of benzoylacetone (0.032 mole) in 20 ml. of 95% ethanol is added to a solution of 3.3 g. of beryllium(II) nitrate 4-hydrate (0.016 mole) in 35 ml. of 95% ethanol. Thirty milliliters of 1 *N* aqueous sodium hydroxide (0.030 mole) is added dropwise to the solution while it is stirred rapidly. As the sodium hydroxide is added, crystals begin to form. After addition is complete, the solution is allowed to stand 30 minutes and then filtered. The product is washed with small amounts of alcohol and water and then dried at 110°. After recrystallization from benzene and again drying at 110°, the melting point is 210°. Booth and Pierce reported 211°. *Anal.* Calcd. for $[Be(C_{10}H_9O_2)_2]$: C, 72.45; H, 5.47. Found: C, 72.67; H, 5.58.

Partial Resolution with *d*-Quartz.—Partial resolution of bis-(benzoylacetono)-beryllium was attained by shaking 25 ml. of a benzene solution of the complex with powdered quartz for 15 minutes. The quartz was removed by filtration and the rotation read at the sodium D line using a Schmidt and Haensch Polarimeter (No. 9143). The readings given represent from six to ten settings of the instrument and are compared with a benzene blank.

Concn., %	Quartz, g.	α
0.2	1	$+0.011 \pm 0.003$
2.0	2	$+0.026 \pm 0.002$
2.0	2	$+0.019 \pm 0.004$

The racemization of the complex is slow enough to allow adequate verification of the observed rotation.

Time, hr.	Initial	1.5	5	9
α	+0.019	+0.020	+0.013	0.000

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[9] H. S. Booth and D. G. Pierce, *J. Phys. Chem.*, **37**, 59 (1933).

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The Preparation and Properties of Tin(II) Chlorofluoride

BY WM. H. NEBERGALL, GINO BASEGGIO AND JOSEPH C. MUHLER

RECEIVED JUNE 25, 1954

In connection with investigations concerning methods of preparing tin(II) fluoride[1] for use as an anticariogenic agent,[2] crystallin tin(II) chlorofluoride was found to be formed when hydrofluoric acid was added to a concentrated aqueous solution of tin(II) chloride.

Subsequent studies showed tin(II) chlorofluoride to be very effective in reducing the acid solubility of powdered human dental enamel as well as the incidence of experimental dental caries in rats.[3] Moreover the results of a clinical study involving the topical application of tin(II) chlorofluoride solutions to the erupted permanent teeth of school children[4] indicate that this compound is even more effective in reducing the incidence of new dental caries than tin(II) fluoride when solutions of the two compounds are administered at the same fluoride level.

The work reported herewith will make it possible for those who may wish to study the anticariogenic activity of tin(II) chlorofluoride to prepare samples of this compound for their own use.

Experimental

The Preparation of Tin(II) Chlorofluoride from Tin(II) Chloride and Hydrofluoric Acid.—Tin(II) chloride dihydrate, 112.8 g. (0.5 mole), was weighed into a 200-ml. polyethylene beaker and 15 g. of oxygen-free, boiling water was added to dissolve the salt. With an atmosphere of oxygen-free nitrogen maintained above the solution, it was heated to 55° on a steam-bath, and 22.5 g. (0.55 mole) of 49.6% hydrofluoric acid was slowly added to the solution. Crystals of the product formed when the mixture was allowed to cool to room temperature. The supernatant liquid was decanted and the crystals were washed three times with 95% ethanol; the alcohol was decanted after each washing. The product was dried in an evacuated desiccator over a 1:1 mixture of anhydrous calcium chloride and potassium hydroxide. The yield of the product was 21.8 g. (25%).

Anal. Calcd. for SnClF: Sn, 68.53; F, 10.97. Found: Sn, 68.7, 68.3, 68.5; F, 10.7, 10.7, 10.8.

Properties of Sn(II) Chlorofluoride.—Tin(II) chlorofluoride crystallizes as colorless prisms which melt at 185–190°. The compound dissolves in water (55% at 25°) to give solutions which are essentially clear initially; within an hour a white precipitate is formed due to hydrolysis of the salt. A 4% solution (the concentration used in topical application[4]) was found to have a *p*H of 2.0 immediately after preparation and also after standing for two hours.

X-Ray Powder Diffraction Data for Tin(II) Chlorofluoride.—In the following table are listed the interplanar spacings ("d") and the relative line intensities found to be characteristic of SnClF.

5.09 VS	2.68 M	2.27 M	1.61 M	1.39 W
3.89 VS	2.63 VW	2.19 M	1.58 M	1.34 W
3.35 VS	2.53 W	2.02 S	1.48 W	1.25 VW
3.07 M	2.44 W	1.90 M	1.45 W	1.24 VW
2.95 S (diffuse)	2.34 M	1.76 S	1.43 W	1.23 W

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[1] Wm. H. Nebergall, Joseph C. Muhler and Harry G. Day, THIS JOURNAL, **74**, 1604 (1952).

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The Orthobaric Density of Pure Nitric Acid[1]

BY S. ALEXANDER STERN AND WEBSTER B. KAY

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In the course of an investigation of the thermal decomposition of pure nitric acid, it became necessary to know accurately the orthobaric density of the pure acid between 0 and 32°. The "International Critical Tables"[2] tabulate values of the density of pure nitric acid between 5 and 30° based on a compilation of data published previous to 1927. More recent measurements, however, do not agree well with these data. Consequently, it was decided to measure the liquid density of pure nitric acid at a series of temperatures in this temperature range.

Materials.—Pure nitric acid was prepared by the reaction of 100% sulfuric acid on anhydrous potassium nitrate at 0° and under high vacuum. The nitric acid formed was collected in a container kept at the temperature of liquid nitrogen. The total acidity of the samples obtained in this manner was found, by volumetric analysis, to vary between 99.95 and 100.05%. No trace of NO_2 or of SO_3

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[1] This paper is based upon work performed under contract Number AF 33(038)-10381 with W.A.D.C., Wright-Patterson Air Force Base, Ohio.

[2] "International Critical Tables," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1928, p. 59.