

This upper limit is given support by the fact that Ga-saturated P_4 solutions do not, upon solidification at 25° , exhibit the "blackening" effect shown by the Hg- P_4 system.⁵ Further, when P_4 saturated with Hg was diluted 100 \times with more P_4 , it also failed to reveal any trace of "blackening." Since the solubility of Hg in P_4 is 0.5 mg./cc. P_4 ,⁵ it is unlikely that more than 5 μ g. of Ga dissolves per cc. of P_4 .

(2).—The lower limit of 0.01 μ g. is given by the fact that the residues mentioned above when examined spectrographically *did* reveal the 4033 Å. Ga I emission line. Owens¹⁰ found that as little as 0.025 μ g. of aluminum on such electrodes could be detected spectrographically. Assuming that gallium has the same sensitivity of detection under these conditions as aluminum, we can say that the amount of Ga per cc. of P_4 is about 0.01 μ g.

Microscopic examination (up to 900 \times) of thin sections (approx. 1 mm.² in area, under immersion oil) of solid P_4 saturated with Ga failed to reveal any distinct difference between them and those of pure solid P_4 . We estimate there is about 5×10^{-11} g. of Ga per section (*i.e.*, about 10^{-12} mole of Ga = 10^{11} atoms of Ga). This small amount if distributed evenly would be difficult to detect since the P_4 contains tiny entrapped bubbles of water and has in addition the slicing marks on its surface. One has difficulty in spotting the difference even with the Hg- P_4 system where the Hg solubility is some 1000 \times that of the Ga. Thus the size of the Ga particles present and frozen out must be below the lower detectable limit of the microscope. The possibility that the liquid Ga exists in colloidal form of particle size larger than this limit is therefore precluded.

Our earlier attempts to determine the amount of Ga were; unsuccessful; these included a micro-balance loss-in-weight procedure and the polarographic procedure of Zeltzer.¹¹ These failures were undoubtedly due to the small amount of Ga present in our P_4 samples. The use of large samples of P_4 is inadvisable due to the fire hazard in case of an accident.

The inability of the regular solution theory to predict the solubility of 0.01–0.1 μ g. Ga/ml. P_4 at 45° may be due to the extremely large differences in molar volumes of the two substances and to the metallic character of the Ga.

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Some Metal Complexes of Kojic Acid

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Introduction

There has been in progress in this Laboratory an investigation of the metal complexes of tropolone and its derivatives.^{2,3} It was found that tropolone² and the alkyltropolones^{3a} form metal complexes of much greater stability than those of β -diketones of comparable acidity. The benzotropolones^{3b} were found to form complexes whose stabilities are intermediate between the simple tropolones and the β -diketones. Several factors^{3a} were proposed as possibly contributing to the unusual stabilities of the metal tropolonates. Among these was the size of the chelate ring.

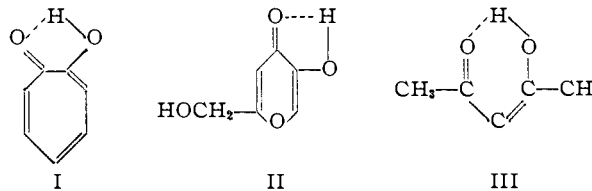
Tropolone (I) and kojic acid (II) both form five-membered chelate rings with hydrogen or a metal,

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(2) B. E. Bryant, W. C. Fernelius and B. E. Douglas, *THIS JOURNAL*, **75**, 3784 (1953).

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while acetylacetone (III), a typical β -diketone, forms a six-membered ring.



If the size of the chelate ring is the major contributing factor to the stability of the metal complexes of tropolone, it would be expected that the metal kojates would also exhibit stabilities appreciably greater than those of metal derivatives of β -diketones of comparable acidity. Since kojic acid has been shown to react with a large number of metal ions⁴ and is readily available, it was chosen as a representative compound for study.

Experimental

The kojic acid was a gift from the Corn Products Refining Company and was purified by sublimation: stout, white needles, m.p. 154 – 156° ; reported⁶ 154° .

Potentiometric titrations and calculations of constants were done as described previously.^{3a} An orange powder, m.p. $> 250^\circ$, precipitated when methanolic solutions of kojic acid and uranyl acetate were mixed. *Anal.* Found: C, 26.72; H, 2.13. *Calcd.* for $UO_2(C_6H_5O_4)_2$: C, 26.09; H, 1.83; *calcd.* for $UO_2(C_6H_5O_4)_2 \cdot 1/2 H_2O$: C, 25.66; H, 1.97. Purification was difficult because of the extremely low solubility of the material.

The negative logarithm of the acid dissociation constant (pK_D) of kojic acid in 50% aqueous dioxane was found to be 9.40. Formation constants of the metal complexes are given in Table I.

TABLE I

FORMATION CONSTANTS OF METAL KOJATES			
Metal ion	log K_1	log K_2	log K_{av}
UO_2^{++}	10.1	7.4	8.8
Cu^{++}	9.3	7.2	8.3
Zn^{++}	7.4	5.8	6.6
Ni^{++}	7.1	5.5	6.3
Co^{++}	6.8	5.2	6.0
Cd^{++}	6.6	4.7	5.7
Ca^{++}	4.4	2.7	3.6

Discussion

Calvin and Wilson⁶ demonstrated for a variety of compounds containing a carbonyl group and an hydroxyl group (so situated as to make the formation of a six-membered chelate ring possible) that there exists a linear relationship between pK_D 's for the hydrogen compounds and log k_{av} 's for the copper complexes. The hydroxy aldehydes divided themselves into three major groups classified according to the aromatic ring system of the molecule. A fourth group, forming the most stable copper derivatives, consisted of β -diketones and β -keto esters. When the pK_D of kojic acid is plotted on the same graph⁶ with the hydroxy aldehydes, β -diketones and β -keto esters, it is found that copper kojate is of the same order of stability as the copper derivatives of β -diketones and β -keto esters, but much more stable than the copper derivatives of

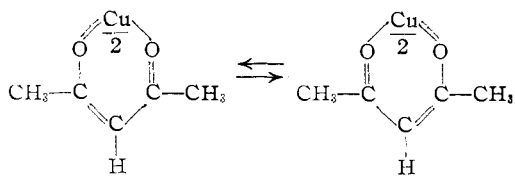
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the hydroxyaldehydes. The nickel and zinc kojates appear to be slightly more stable than the corresponding derivatives of β -diketones, but none show the unusual stability of the complexes of the simple tropolones.

Calvin and Wilson⁶ 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 views⁷ on the structure of tropolone itself indicate that in the tropolonate ion, the two oxygens should be fully equivalent. For the copper complex of tropolone⁸ it appears that there are two different types of copper-oxygen bonds in the solid material. The same type of X-ray analysis⁹ indicates that only one type of copper-oxygen bond is present in copper acetylacetonate.

Present information¹⁰ 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

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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-(ortho-phenanthroline)-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 Burgess⁵ who observed that solutions of beryllium benzoylcampor undergo a rapid mutarotation. Mills and Gotts⁶ 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 coordinated 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 benzoylacetonate was chosen for investigation.

Since bis-(benzoylacetonato)-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-(benzoylacetonato)-beryllium.—The synthesis given here is an adaptation of the method reported by

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