NOTES

Complexing Behavior of Kojic Acid with Metal Ions. III. Infrared Studies of Bivalent Metal-Kojate Chelates*

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In previous studies, the interaction of bivalent magnesium, manganese and tervalent iron ions with kojic acid in aqueous media has been investigated and the corresponding stability constants evaluated.[1,2] However, the majority of the bivalent first-transition metals do not yield the corresponding soluble kojate chelates in aqueous solutions. Therefore, most of the potentiometric studies aiming to obtain chelate stability constants have been carried out in dioxane-water media.[3,4] The stability of these kojate chelates with respect to the bivalent metals has been found to follow the sequence:

$$\mathrm{Cu(II)} > \mathrm{Zn(II)} > \mathrm{Ni(II)} \sim \mathrm{Mn(II)} \sim \mathrm{Co(II)}$$

It is interesting to note that a zinc ion forms a much more stable chelate than do nickel, cobalt and manganese ions in the kojate chelate system. In addition, the comparable stability of the manganese chelates with the corresponding nickel and cobalt chelates is rather unexpected.

In order to investigate the structural change in the ligand molecule brought about through its coordination to the metal ions and the correlation of the structural change with the stability sequence, infrared spectral measurements of the kojate chelates of copper(II), zinc(II), nickel(II) and cobalt(II) have been performed in the present study. The absorption peaks of interest for these metal chelates are listed in Table I for the sake of comparison. The absorption spectra obtained for the zinc, nickel and cobalt chelates were almost identical with each other, and slightly different from that for the copper chelate. The most significant difference among these two types of metal chelates (zinc, nickel, cobalt; copper) is the OH-stretching vibration appeared in the region ranging 3200—2400 cm^{-1}. Another difference is observed in the range between 905 and 850 cm^{-1}, where the copper chelate gives three

TABLE I. SIGNIFICANT PEAKS IN THE INFRARED SPECTRA OF SOME METAL-KOJATE CHELATES

Kojic acid	Cu(II)-kojate	Zn(II)-kojate	Ni(II)-kojate	Co(II)-kojate	Assignment
3290 m	3175 m, b				O–H str. (CH_2OH)
	3090 m	3085 m	3085 m	3090 m	
3215 m, b					O–H str. (phenol)
	2680 w	2760 w	2755 w	2760 w	OH str. (H-bonded)
		2610 w, b	2590 w, b	2590 w, b	
		2440 w	2440 w	2450 w	
1710 w					C=O str.
1668 s	1635 s	1634 s	1634 s	1635 s	
1640 s					C=C str.
1621 s	1580 s	1572 s	1570 s	1570 s	
1591 s	1535 s	1540 s	1540 s	1550 s	
865 s	895 m	905 m	905 m	905 m	
	876 w				
	867 m				

s: strong; m: medium; w: weak; b: broad

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[1] Y. Murakami, This Bulletin, **35**, 52 (1962).

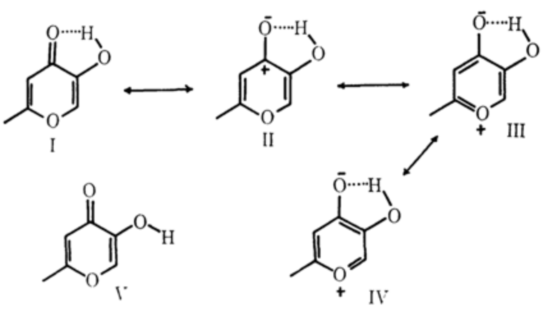
[2] Y. Murakami, *J. Inorg. Nucl. Chem.*, **24**, 679 (1962).

[3] B. E. Bryant and W. C. Fernelius, *J. Am. Chem. Soc.*, **76**, 5351 (1962).

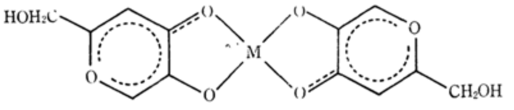
[4] H. Kido, W. C. Fernelius and C. G. Haas, Jr., *Anal. Chim. Acta*, **23**, 116 (1960).

absorption peaks while the other chelates give only one significant peak. In view of the spectral shift of the OH vibrations for the metal chelates from that of the ligand alone, it seems that the stronger hydrogen bonding is secured through metal coordination. In addition, the zinc, nickel and cobalt chelates seem to contain some sorts of hydrogen bonding stronger than that in the corresponding copper chelate, since the former chelate species demonstrated several absorption peaks in the range between 2800 and 2400 cm^{-1}, where the latter chelate does not show any significant peak. Moreover, the nearly-identical spectral behavior among the zinc, nickel and cobalt chelates seems to suggest that these chelates possess coordinate bonds of nearly identical characters.

The following four resonance structures (I—IV) may be drawn for kojic acid:



The absorption bands which appear at 1710 and 1668 cm^{-1} are most likely due to the non-hydrogen-bonded (cf. structure V) and to the hydrogen-bonded carbonyl vibrational modes (cf. structures I—IV) respectively. When kojic acid forms a complex with a metal ion (as is illustrated by structure VI), the former mode disappears and the latter shifts to lower frequencies. The other significant bands, appearing at 1640, 1621 and 1591 cm^{-1} in the free kojic acid, are assigned to the C=C stretching modes. These bands also were observed to shift to lower frequencies through the formation of metal coordinate bonds. These shifts of C=O and C=C bands to lower frequencies seem to indicate that the contribution of resonance structures of the II, III and IV types, in which a hydrogen atom is replaced by a metal ion, becomes greater as metal coordinate bonds are formed. The resonance interaction involving structures II, III and IV tends to delocalize olefinic and carbonyl π-electrons over both γ-pyron and chelate rings, thus decreasing the double-bond character of olefinic and carbonyl bonds.



VI

The infrared spectral data do not provide any significant correlation with the stability sequence among these bivalent metal kojate chelates. Thus, some further studies are needed to clarify the problems of the stability order.

Experimental

The kojic acid used was a product of the Nutritional Biochemical Corporation, U. S. A., and was purified by sublimation in vacuo: m. p. 156—156.6°C. All the kojate complexes used in this work were prepared by standard methods described in the literature. The analyses are listed in Table II.

TABLE II. ANALYSES OF METAL-KOJATE CHELATES

Chelate	Carbon,* %	Hydrogen,* %
$Cu(C_6H_5O_4)_2$	41.19 (41.68)	3.23 (2.92)
$Zn(C_6H_5O_4)_2$	41.04 (41.46)	3.20 (2.90)
$Ni(C_6H_5O_4)_2$	41.08 (42.28)	3.23 (2.96)
$Co(C_6H_5O_4)_2$	41.89 (42.25)	3.03 (2.95)

* Calculated values for the specified formula are given in parentheses.

The infrared spectra of the kojate chelates were measured by the Nujol mull method with a Koken Model DS-301 Spectrophotometer equipped with sodium chloride optics.