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### COORDINATION OF METAL IONS BY INDOLIC ACIDS. COMPLEXES OF INDOLE-2-CARBOXYLIC, -3-ACETIC, -3-PROPANOIC AND -3-BUTANOIC ACIDS WITH SOME DIVALENT METAL IONS

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## COORDINATION OF METAL IONS BY INDOLIC ACIDS. COMPLEXES OF INDOLE-2-CARBOXYLIC, -3-ACETIC, -3-PROPANOIC AND -3-BUTANOIC ACIDS WITH SOME DIVALENT METAL IONS

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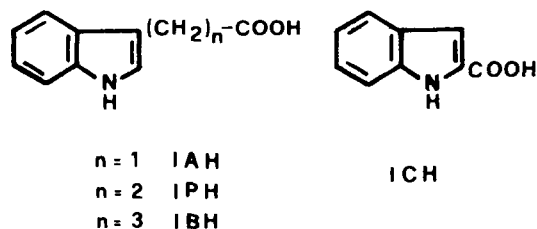
*(Received September 1, 1983; in final form October 31, 1983)*

Metal complexes of indole-2-carboxylic (ICH), -3-acetic (IAH), -3-propanoic (IPH) and -3-butanoic (IBH) acids, were prepared and characterized by means of thermal analysis, magnetic measurements, ESR, IR and electronic spectroscopy. While  $\text{Cu}(\text{IA})_2 \cdot \text{H}_2\text{O}$ ,  $\text{Cu}(\text{IP})_2 \cdot \text{H}_2\text{O}$ ,  $\text{Cu}(\text{IP})_2$  and  $\text{Cu}(\text{IB})_2$  are tetracarboxylate-bridged dimers of the copper(II) acetate monohydrate-type,  $\text{Cu}(\text{IC})_2 \cdot 2\text{H}_2\text{O}$  appears to be monomeric with the copper atom in square planar coordination involving two carboxylate groups and two water molecules. Six-coordination at the metal ions, most likely involving bidentate carboxylate groups and water molecules, is suggested for the complexes  $\text{M}(\text{IC})_2 \cdot 2\text{H}_2\text{O}$  ( $\text{M} = \text{Co}, \text{Ni}, \text{Mn}$  and  $\text{Zn}$ ). All the ligands appear to behave as simple carboxylic acids, being able to coordinate metal ions through the carboxylic groups alone.

### INTRODUCTION

Indolecarboxylic acids are natural or synthetic plant growth accelerators, whose biological activity was suggested to have a connection with metal binding in plant tissues.<sup>1</sup> Relatively limited information is available on the metal complexes of this class of ligands. Earlier work relates mainly to solution studies of binary and ternary complexes of indole-2-carboxylic and indole-3-acetic acids.<sup>1-3</sup> Lanthanide indole-3-carboxylates and some metal indole-2-carboxylates were also reported.<sup>4-6</sup> The involvement of the indole-ring nitrogen atom in coordination was always suggested, but no conclusive evidence was given.

To better understand the coordination behaviour of indolic auxins and to substantiate the feasibility of metal chelation by these ligands in soil and plants, we have undertaken a comparative study of some indolic binary and ternary complexes. This paper reports Cu(II) complexes of indole-3-acetic (IAH), -3-propanoic (IPH) and -3-butanoic (IBH) acids as well as Cu(II), Mn(II), Co(II), Ni(II) and Zn(II) complexes of indole-2-carboxylic acid (ICH).



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## EXPERIMENTAL

*Materials*

Reagent grade acids (Merck) were twice recrystallized from aqueous ethanol and dried *in vacuo*. Commercially pure metal salts (Merck) were used without further purification.

*Syntheses*

The metal complexes were prepared by mixing stoichiometric amounts of acid and metal salt (sulphate or acetate) in aqueous ethanol or methanol. The products, which precipitated out either immediately or after standing at room temperature, were filtered, washed with water and alcohol and dried *in vacuo*. The metal complexes and the sodium salts are listed in Table I.

In contrast to the other ligands, IPH gave two different copper(II) complexes depending on the solvent used.  $\text{Cu(IP)}_2 \cdot \text{H}_2\text{O}$  was obtained from aqueous methanol, whereas  $\text{Cu(IP)}_2$  precipitated from ethanolic solution. Attempts to prepare complexes of IAH, IPH and IBH with divalent metals other than copper(II) have so far been unsuccessful.

*Analytical and Physical Measurements*

Elemental analyses (C, H and N) were obtained with a Perkin-Elmer 240 B instrument. Infrared spectra were recorded with a Perkin-Elmer 683 B spectrophotometer in KBr pellets or as samples spread over NaCl plates. Thermal analyses were carried out on a Perkin-Elmer TGS-2 apparatus under nitrogen or air flow. Diffuse reflectance electronic spectra were recorded on a Beckman Acta MIV spectrophotometer. Magnetic susceptibilities were measured by using a Bruker B-MB4 Faraday system equipped with a Cahn 1000 electrobalance. X-Band ESR spectra were recorded on a Varian E-9-spectrometer.

TABLE I  
Analytical data<sup>a</sup> for the compounds.

Compound	% C	% H	% N	% H <sub>2</sub> O <sup>b</sup>
$\text{Cu(IC)}_2 \cdot 2 \text{H}_2\text{O}$	51.68(51.49)	3.89(3.84)	6.82(6.67)	8.3(8.6)
$\text{Co(IC)}_2 \cdot 2 \text{H}_2\text{O}$	52.67(52.06)	4.05(3.88)	6.77(6.74)	8.8(8.7)
$\text{Ni(IC)}_2 \cdot 2 \text{H}_2\text{O}$	52.53(52.09)	4.14(3.89)	6.70(6.75)	9.0(8.7)
$\text{Mn(IC)}_2 \cdot 2 \text{H}_2\text{O}$	52.40(52.57)	3.97(3.92)	6.98(6.81)	8.5(8.8)
$\text{Zn(IC)}_2 \cdot 2 \text{H}_2\text{O}$	51.58(51.27)	3.90(3.82)	6.51(6.64)	8.9(8.5)
$\text{Cu(IA)}_2 \cdot \text{H}_2\text{O}$	55.56(55.87)	4.50(4.22)	6.34(6.52)	4.5(4.2)
$\text{Cu(IP)}_2 \cdot \text{H}_2\text{O}$	57.84(57.69)	5.16(4.84)	6.21(6.12)	4.0(3.9)
$\text{Cu(IP)}_2$	59.78(60.06)	4.50(4.58)	6.31(6.36)	—
$\text{Cu(IB)}_2$	61.06(61.59)	5.31(5.17)	6.14(5.99)	—
$\text{NaIC} \cdot \text{H}_2\text{O}$	54.53(53.73)	3.87(4.01)	7.07(6.96)	8.5(8.9)
$\text{NaIP} \cdot \text{H}_2\text{O}$	57.77(57.64)	5.28(5.27)	6.21(6.11)	7.5(7.8)
$\text{NaIB} \cdot \text{H}_2\text{O}$	59.18(59.25)	5.66(5.80)	5.78(5.75)	7.0(7.4)
$\text{NaIA} \cdot 0.5 \text{H}_2\text{O}$	58.55(58.26)	4.28(4.40)	6.85(6.79)	4.5(4.4)

<sup>a</sup>Calculated values in parentheses.

<sup>b</sup>Thermogravimetric determination.

## RESULTS AND DISCUSSION

*Infrared spectra*

The more relevant IR bands of the acids, the sodium salts and the metal complexes are listed in Table II. The acids and the sodium salts exhibit  $\nu(\text{NH})$  vibrations in the 3470–3380  $\text{cm}^{-1}$  range, the differences between the sodium salts and the corresponding acids being attributable to different extents of inter- or intra-molecular hydrogen bonding.

In all the complexes these bands do not significantly change in position with respect to those of the free acids or of their sodium salts, thus ruling out the participation of the indole nitrogen atom in metal coordination.

The IR spectra of the  $\text{M}(\text{IC})_2 \cdot 2 \text{H}_2\text{O}$  complexes ( $\text{M} = \text{Mn}, \text{Co}, \text{Ni}$  and  $\text{Zn}$ ) are all identical to each other, giving clear evidence that the complexes have the same structure, and slightly but significantly different with respect to that of  $\text{Cu}(\text{IC})_2 \cdot 2 \text{H}_2\text{O}$ . In particular the  $\Delta\nu$  value ( $\nu_a(\text{COO}) - \nu_s(\text{COO})$ ) for  $\text{Cu}(\text{IC})_2 \cdot 2 \text{H}_2\text{O}$  is higher than for the other  $\text{M}(\text{IC})_2 \cdot 2 \text{H}_2\text{O}$  complexes. As regard to the IA, IP and IB complexes, the  $\Delta\nu$  values observed for the hydrated complexes are higher than for the anhydrous compounds.

*Magnetic, Electronic and ESR Data*

The room-temperature magnetic moments, the electronic absorption and the ESR parameters of the complexes in the solid state are summarized in Table III. The  $\text{M}(\text{IC})_2 \cdot 2 \text{H}_2\text{O}$  complexes ( $\text{M} = \text{Mn}, \text{Co}$  and  $\text{Ni}$ ) exhibit magnetic moments indicative of high-spin configurations. The electronic spectra of the Ni- and Co-complexes are typical of pseudo-octahedrally coordinated ions. The Dq values (825 and 843  $\text{cm}^{-1}$  for Ni and Co, respectively), calculated according to refs. 7 and 8, are consistent with distorted chromophores of the type  $\text{MO}_6$ .

$\text{Cu}(\text{IC})_2 \cdot 2 \text{H}_2\text{O}$ , which has a normal magnetic moment, displays a  $d-d$  absorption maximum indicative of strong tetragonal distortion at the metal ion in a chromophore

TABLE II  
More relevant IR bands ( $\text{cm}^{-1}$ ) for the ligands and complexes.

Compound	$\nu(\text{NH})$	$\nu(\text{COO})_a$	$\nu(\text{COO})_s$	$\Delta\nu$
ICH	3380 s	1725 vs	1200 vs	525
NaIC · H <sub>2</sub> O	3440 vs	1583 vs	1415 m	168
$\text{Cu}(\text{IC})_2 \cdot 2 \text{H}_2\text{O}$	3450 m	1564 s	1410 sh	154
$\text{Mn}(\text{IC})_2 \cdot 2 \text{H}_2\text{O}$	3390 m	1548 vs	1414 m	134
$\text{Zn}(\text{IC})_2 \cdot 2 \text{H}_2\text{O}$	3390 m	1548 vs	1414 m	134
$\text{Ni}(\text{IC})_2 \cdot 2 \text{H}_2\text{O}$	3390 m	1546 vs	1414 m	132
$\text{Co}(\text{IC})_2 \cdot 2 \text{H}_2\text{O}$	3390 m	1548 vs	1412 m	136
IAH	3420 vs	1715 vs	1210 s	505
NaIA · 0.5 H <sub>2</sub> O	3420 vs	1576 vs	1404 m	172
$\text{Cu}(\text{IA})_2 \cdot \text{H}_2\text{O}$	3420 vs	1606 vs	1403 m	203
IPH	3470 vs	1704 vs	1210 s	494
NaIP · H <sub>2</sub> O	3440 vs	1538 vs	1415 m	123
$\text{Cu}(\text{IP})_2 \cdot \text{H}_2\text{O}$	3435 s	1605 vs	1425 m	180
$\text{Cu}(\text{IP})_2$	3420 vs	1597 vs	1427 m	170
IBH	3420 vs	1710 vs	1210 s	500
NaIB · H <sub>2</sub> O	3410 s	1572 vs	1418 m	154
$\text{Cu}(\text{IB})_2$	3435 s	1589 vs	1424 m	165

s = strong, m = medium, v = very, sh = shoulder

TABLE III  
Magnetic, electronic and ESR data for the complexes in the solid state.

Complex	$\mu_{\text{eff}}$ (B.M.) <sup>a</sup>	Absorption Maxima ( $10^3 \text{ cm}^{-1}$ )	ESR Parameters <sup>b</sup>			
			$g_{\parallel}$	$g_{\perp}$	D ( $\text{cm}^{-1}$ )	E ( $\text{cm}^{-1}$ )
Mn(II)·2 H <sub>2</sub> O	5.98		2.01 <sup>c</sup>			
Co(II)·2 H <sub>2</sub> O	5.05	20.8 <sup>d</sup> , 15.4 sh, 12.5, 7.8				
Ni(II)·2 H <sub>2</sub> O	3.25	22.5 <sup>d</sup> , 14.6, 13.4, 8.2				
Cu(II)·2 H <sub>2</sub> O	1.93	14.6	2.30	2.10		
Cu(II)·H <sub>2</sub> O	1.50	14.4, 23.8 sh	2.39	2.11	0.34	
Cu(IP) <sub>2</sub> ·H <sub>2</sub> O	1.44	14.5, 25.3 sh	2.38	2.11	0.35	
Cu(IP) <sub>2</sub>	1.41	14.9, 25.6 sh	2.34	2.08	0.34	
Cu(II)·2 H <sub>2</sub> O	1.42	15.0, 26.3 sh	2.36	2.07	0.33	0.01

<sup>a</sup>At room temperature. <sup>b</sup>At 123 K. <sup>c</sup>Isotropic resonance. <sup>d</sup>Multiple absorption.

having four oxygen atoms in the metal plane. Indeed, the value of the absorption maximum is quite similar to those of CuO<sub>4</sub> complexes, *e.g.*, diaquabis(salicylato)copper(II) dihydrate,<sup>9,10</sup> in which the metal is bonded to two *trans*-carboxylate oxygen atoms and two water molecules in the plane and experiences weak interactions in the axial positions.

All the copper(II)-IA, -IP and -IB complexes show subnormal moments characteristic of exchange interactions between metal ions. These findings are supported by the ESR spectra (Fig. 1), which all display resonances typical of binuclear copper(II)

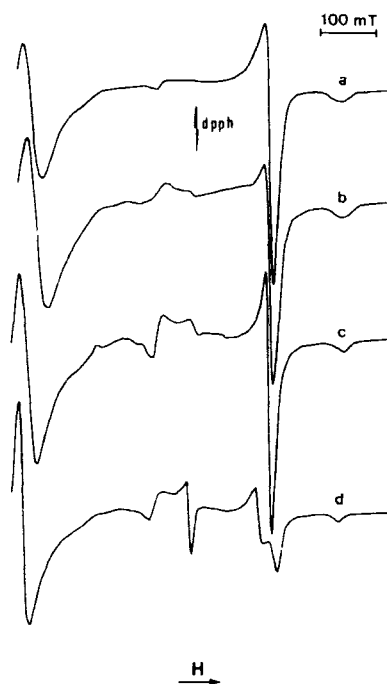


FIGURE 1 X-Band ESR spectra ( $\sim 9.16 \text{ GHz}$ ) of Cu(II)·H<sub>2</sub>O at 298 K (a), Cu(IP)<sub>2</sub>·H<sub>2</sub>O at 298 K (b), Cu(IP)<sub>2</sub> at 123 K (c) and Cu(II)·2H<sub>2</sub>O at 123 K (d).

carboxylates in the triplet state. Evidence of rhombic distortion in  $\text{Cu(IP)}_2$  is given by the splitting of the  $\text{H}_2$  resonance even though only one  $g$  value was calculated. Interestingly, at room temperature the triplet absorptions of the anhydrous  $\text{Cu(IP)}_2$  and  $\text{Cu(IB)}_2$  complexes are partly obscured by a broad resonance centered at  $g \approx 2$ , not due to monomeric impurities. Such a resonance, which vanishes as the temperature is lowered, is indicative of interdimeric exchange interactions, as is often the case with anhydrous copper(II) carboxylates.<sup>11-13</sup> The electronic spectra also are characteristic of dimeric Cu(II) carboxylates, with a  $d-d$  maximum in the 14.4–15.0 kK range and a shoulder at about 23.8–26.3 kK; these are peculiar to carboxylate-bridged dinuclear complexes.<sup>14</sup> The 'blue-shift' of the absorption maximum in the anhydrous  $\text{Cu(IP)}_2$  and  $\text{Cu(IB)}_2$  complexes indicates diminished axial interactions at the copper ion to give a more strictly planar environment than in the hydrated compounds.

The present study clearly demonstrates that, at least in the solid state, the indolic nitrogen atom has no tendency to coordinate the investigated metal ions. This is probably due to the weak basicity of the nitrogen atom. As a consequence, the indolic acids behave as simple carboxylic acid ligands even when formation of chelate complexes (see indole-2-carboxylic acid) could be expected.

Based on the experimental results, pseudo-octahedral geometry is suggested for the  $\text{M(IC)}_2 \cdot 2 \text{H}_2\text{O}$  complexes ( $\text{M} = \text{Mn, Co, Ni}$  and  $\text{Zn}$ ) with the metal ions surrounded by two water molecules and two carboxylate groups behaving in a bidentate fashion. This view is supported by both IR data, through low  $\Delta\nu$  values indicative of bidentate carboxylate groups and, to some extent for the Co- and Ni-complexes, by electronic absorption spectra consistent with  $\text{MO}_6$  chromophores.

In  $\text{Cu(IC)}_2 \cdot 2 \text{H}_2\text{O}$  the metal coordination is severely distorted towards square-planar, with water molecules and monodentate carboxylate groups as basal ligands. If present, axial interactions involve only long contacts from the remaining oxygens of the carboxylate groups which should thus behave in a strongly asymmetrical fashion. Accordingly, the  $\Delta\nu$  value increases with respect to the other  $\text{M(IC)}_2 \cdot 2 \text{H}_2\text{O}$  complexes without reaching values characteristic of monodentate carboxylate coordination. Some contribution of hydrogen bonding to the lowering of  $\Delta\nu$  cannot be ruled out.

All the  $\text{Cu(IA)}_2 \cdot \text{H}_2\text{O}$ ,  $\text{Cu(IP)}_2 \cdot \text{H}_2\text{O}$ ,  $\text{Cu(IP)}_2$  and  $\text{Cu(IB)}_2$  complexes display magnetic and ESR properties typical of carboxylate-bridged dimers.  $\text{Cu(IA)}_2 \cdot \text{H}_2\text{O}$  and  $\text{Cu(IP)}_2 \cdot \text{H}_2\text{O}$  are 'caged' dimers of the copper(II) acetate monohydrate-type, with the copper ions axially coordinated to a water molecule. The anhydrous  $\text{Cu(IP)}_2$  and  $\text{Cu(IB)}_2$  compounds can be better regarded as polymeric species due to the detection of magnetic exchange between the dimeric units. As previously observed,<sup>13</sup> such interactions are transmitted by intermolecular binding of carboxylate groups which behave as conducting bridges. Support for this view is found in the IR spectra, which compared to those of the 'caged' dimers, display lower  $\Delta\nu$  values mainly due to the shift of  $\nu_a$  to lower frequency as expected for more pronounced bidentate behaviour of carboxylate groups. In addition, such IR features have been previously observed in structurally characterized dimeric carboxylates in which intermolecular bridging occurs through carboxylate groups.<sup>15</sup> On this basis, similar arrangements may be reasonably proposed for  $\text{Cu(IP)}_2$  and  $\text{Cu(IB)}_2$ .

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