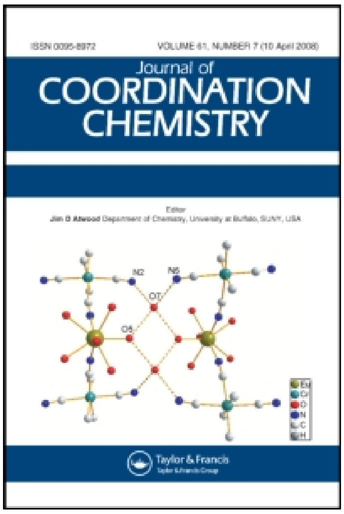

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COORDINATION OF METAL IONS BY INDOLIC ACIDS. COPPER(II) COMPLEXES OF INDOLE-3-CARBOXYLIC, -5-CARBOXYLIC, -*N*-ACETIC, AND *N*-METHYLINDOLE-2-CARBOXYLIC ACIDS

L. Strinna Erre[a]; G. Micera[a]; P. Piu[a]; A. Pusino[b]; F. Cariati[c]
[a] Istituto di Chimica Generale e Inorganica, Università di Sassari, Sassari, Italy [b] Istituto di Chimica Organica, Università di Sassari, Sassari, Italy [c] Dipartimento di Chimica Inorganica e Metallorganica and Centro C.N.R., Università di Milano, Milan, Italy

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COORDINATION OF METAL IONS BY INDOLIC ACIDS. COPPER(II) COMPLEXES OF INDOLE-3-CARBOXYLIC, -5-CARBOXYLIC, -*N*-ACETIC, AND *N*-METHYLINDOLE-2-CARBOXYLIC ACIDS

L. STRINNA ERRE, G. MICERA†, P. PIU
Istituto di Chimica Generale e Inorganica, Università di Sassari, Via Vienna 2, 07100 Sassari, Italy,
A. PUSINO
Istituto di Chimica Organica, Università di Sassari, Via Vienna 2, 07100 Sassari, Italy,
and
F. CARIATI
Dipartimento di Chimica Inorganica e Metallorganica and Centro C.N.R., Università di Milano, Via G. Venezian 21, 20121 Milan, Italy.

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Copper(II) complexes formed by indole-3-carboxylic, -5-carboxylic, -*N*-acetic and *N*-methylindole-2-carboxylic acids were prepared and characterized by means of analysis, ESR, IR and electronic spectroscopy. All the ligands yield dimeric copper(II) acetate-like complexes. In addition, *N*-methylindole-2-carboxylic acid yields hydrated monomeric complexes most likely involving bidentate carboxylate groups. Factors which may be important in favouring the adoption of monomeric or dimeric structures by these ligands are suggested.

Keywords: Indoles, carboxylates, copper, complexes, synthesis

INTRODUCTION

Interest in metal complex formation by ligands which may be involved in the transport and storage of metal ions in soil and plants apprompted us to study the coordinative properties of indolecarboxylic acids which constitute a well-known class of plant auxins.[1] The copper(II) complexes of indole-2-carboxylic, -3-acetic, -3-propanoic and -3-butanoic acids have been described in a previous paper.[2] It has been found that, as the indole-ring nitrogen atoms is never involved in metal coordination, the ligands behave as simple carboxylic acid donors giving rise to monomeric (with indole-2-carboxylic acid) or dimeric (with indole-3-acetic, -3-propanoic and -3-butanoic acids) copper(II) acetate-like complexes.

In order to understand the factors which can influence the adoption of one or another of the two structural arrangements or the conditions under which one form is favoured, we have prepared and characterized the copper(II) complexes of other indolic acids differing from each other and from those examined previously as to the position of the carboxylate group within the indolic skeleton. In this paper we report on the copper(II) complexes of the following ligands: indole-3-carboxylic (L^1H), indole-5-carboxylic (L^2H), indole-*N*-acetic (L^3H) and *N*-methylindole-2-carboxylic (L^4H) acids.

EXPERIMENTAL

Materials

Indole-3-carboxylic, -5-carboxylic and -*N*-acetic acids were purchased from EGA

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† Author for correspondence

and twice recrystallized from aqueous ethanol. *N*-methylindole-2-carboxylic acid was prepared as follows. A solution of 2.2 g (13.5 mmol) of indole-2-carboxylic acid (EGA) in 40 cm^3 of anhydrous dimethylformamide was stirred with 7 cm^3 (108.0 mmol) of methyl iodide and 12.5 g (54.0 mmol) of silver oxide at room temperature for 5 h and then filtered. A fourfold volume of chloroform was added to the filtrate and the chloroform phase washed with water and dried over sodium sulphate. Evaporation of the solution gave the methyl ester of *N*-methylindole-2-carboxylic acid (2.3 g, yield 89%). A solution of the crude ester (1.13 g, 6.0 mmol) and 6.2 cm^3 of 1 M sodium hydroxide in 20 cm^3 of 95% ethanol was allowed to stand at room temperature for 1 h. The major part of the solvent was evaporated *in vacuo*, after which 15 cm^3 of water was added. The resulting solution was cooled and acidified with hydrochloric acid. The aqueous phase was extracted with chloroform and the organic layer was washed several times with water and dried over sodium sulphate. Evaporation of the solvent yielded 0.84 g (80%) of acid which was recrystallized from benzene-light petroleum ether (white crystals, m.p. 208° (lit. 212°C[3]).

Synthesis of the complexes and physical measurements

The complexes were prepared generally by dissolving *ca* 3.0 mmol of acid and 1.5 mmol of copper(II) acetate monohydrate in water or in aqueous methanol or ethanol. After stirring at room temperature for 24 h the precipitates were filtered off, washed with water or alcohol and air-dried. $Cu(L^3)_2 \cdot 2\ CH_3OH$ was prepared from aqueous methanol. This complex is stable if stored below 0°, but at higher temperatures it is transformed into $Cu(L^3)_2$, which can be prepared directly by reaction in absolute ethanol. The reaction of L^4H with copper(II) acetate in water gives $Cu(L^4)_2 \cdot 2(3)\ H_2O$, whereas in 99.9% aqueous methanol it yields $Cu(L^4)_2 \cdot 1.5\ H_2O$. From methanolic solutions with intermediate composition, mixtures of $Cu(L^4)_2 \cdot 1.5\ H_2O$ and $Cu(L^4)_2 \cdot 2\ (3)\ H_2O$ separated. Increase of temperature or reactant concentrations favoured the formation of the former complex. By suspending $Cu(L^4)_2 \cdot 1.5\ H_2O$ in water, $Cu(L^4)_2 \cdot 2(3)\ H_2O$ was obtained. The opposite transformation was observed on suspending $Cu(L^4)_2 \cdot 2(3)\ H_2O$ in methanol. Analytical data are summarized in Table I.

Physical measurements were carried out as described previously.[2]

TABLE I
Analytical data[a] for the complexes

Compound	%C	%H	%N	%H_2O or MeOH[b]
$Cu(L^1)_2 \cdot H_2O$	53.01(53.80)	3.81(3.51)	6.68(6.97)	3.5(4.48)[c]
$Cu(L^2)_2 \cdot 1.5\ H_2O$	53.26(52.62)	3.65(3.68)	7.02(6.82)	6.5(6.57)
$Cu(L^3)_2 \cdot 2\ CH_3OH$	56.05(55.51)	5.02(5.08)	5.66(5.88)	13.5(13.45)
$Cu(L^3)_2$	58.45(58.32)	4.09(3.92)	6.52(6.80)	
$Cu(L^4)_2 \cdot 1.5\ H_2O$	53.89(54.73)	3.95(4.36)	5.93(6.38)	6.0(6.16)
$Cu(L^4)_2 \cdot 2\ H_2O$	53.07(53.63)	4.65(4.50)	5.88(6.25)	8.0(8.04)
$Cu(L^4)_2 \cdot 3\ H_2O$	51.85(51.55)	4.50(4.76)	6.15(6.01)	11.6(11.5)
$NaL^1 \cdot 1.5\ H_2O$	51.04(51.43)	3.95(4.31)	6.28(6.66)	12.5(12.86)
$NaL^2 \cdot H_2O$	53.25(53.74)	4.10(4.01)	6.57(6.96)	8.5(8.95)
$NaL^3 \cdot 3.5\ H_2O$	47.01(46.16)	5.49(5.81)	5.36(5.38)	24.0(24.23)
$NaL^4 \cdot H_2O$	55.72(55.82)	4.74(4.68)	6.19(6.51)	8.0(8.37)

[a] Calculated values in parentheses. [b] Thermogravimetric determination. [c] Weight loss overlapping with decomposition.

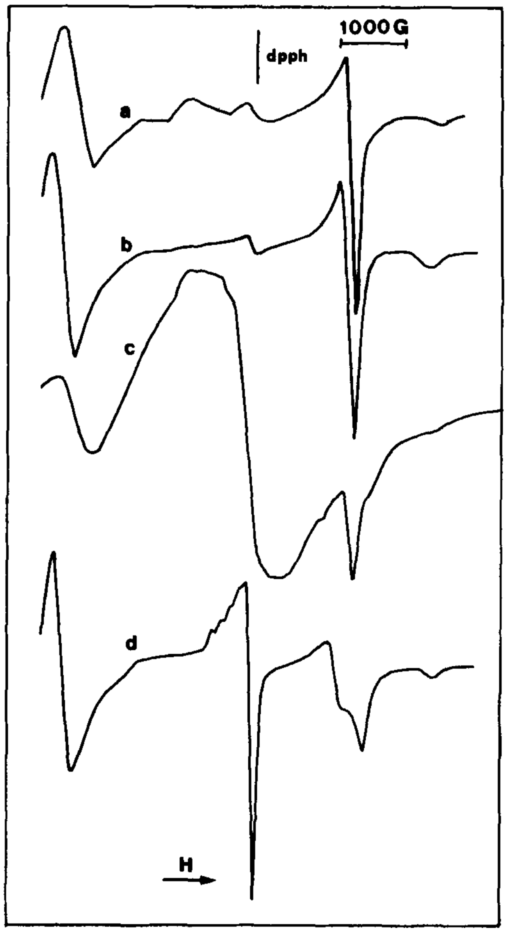

FIGURE 1 X-band ESR spectra recorded on polycrystalline samples of (a): $Cu(L^3)_2 \cdot 2\ CH_3OH$ (at 123 K); (b): $Cu(L^4)_2 \cdot 1.5\ H_2O$ (at 298 K); (c): $Cu(L^3)_2$ (at 298 K); (d): $Cu(L^3)_2$ (at 123 K).

RESULTS AND DISCUSSION

Dimeric Complexes

All the ligands yield dimeric complexes. In fact, the powder ESR spectra of $Cu(L^1)_2 \cdot H_2O$, $Cu(L^2)_2 \cdot 1.5\ H_2O$, $Cu(L^3)_2 \cdot 2\ CH_3OH$ and $Cu(L^4)_2 \cdot 1.5\ H_2O$ (Fig. 1 and Table II) are typical of binuclear copper(II) carboxylates in the triplet state and substantiate tetra-carboxylate bridged structures of the copper(II) acetate monohydrate-type. The fifth position of the copper coordination sphere must be occupied by a water molecule or, in $Cu(L^3)_2 \cdot 2\ CH_3OH$, by methanol. $Cu(L^3)_2$ is also a dimeric complex, but involves a polymeric structure as supported by the rather broad ESR resonances (Fig. 1) detected at room temperature and which may be considered indicative of interdimeric exchange transmitted *via* carboxylate bridges.[4,5]

TABLE II
Electronic and ESR data for the complexes in the solid state.

Complex	*d-d* Absorption maxima (10^3 cm^{-1})	ESR Parameters			
		$g_{\parallel}$	$g_{\perp}$	D (cm^{-1})	E (cm^{-1})
$Cu(L^1)_2 \cdot H_2O$	14.6	2.35	2.06	0.30	
$Cu(L^2)_2 \cdot 1.5\ H_2O$	14.5	2.34	2.07	0.30	
$Cu(L^3)_2 \cdot 2\ CH_3OH$	14.3	2.35	2.09	0.36	
$Cu(L^3)_2$	14.6	2.34	2.07	0.34	0.01[a]
$Cu(L^4)_2 \cdot 1.5\ H_2O$	14.1	2.37	2.07	0.34	
$Cu(L^4)_2 \cdot 2\ H_2O$	14.3	2.31	2.12		
$Cu(L^4)_2 \cdot 3\ H_2O$	14.6	2.28	2.11		
$Cu(L^4)_2 \cdot H_2O$	13.4	2.340[b]	2.067		
$Cu(L^4)_2$	13.4	2.17			

[a] Values refer to the spectrum recorded at 123 K. [b] $A_{\parallel} = 164 \times 10^{-4}$ cm^{-1}.

TABLE III
Relevant IR bands (cm^{-1}) for the ligands, sodium salts and complexes[a].

Compound	ν(NH)	ν_a(COO)	ν_s(COO)	$\Delta(\nu_a - \nu_s)$
L^1H	3310vs 3400s	1645vs	1195s	450
$NaL^1 \cdot 1.5\ H_2O$	3270br 3400s	1545s	1410mw	135
$Cu(L^1)_2 \cdot H_2O$	3270br	1565s	1425sh	140
L^2H	3360s	1665s	1205m	460
$NaL^2 \cdot H_2O$	3400mbr	1540s	1400s	140
$Cu(L^2)_2 \cdot 1.5\ H_2O$	3420s	1565s	1395s	170
L^3H		1715vs	1235s	480
$NaL^3 \cdot 3.5\ H_2O$		1585vs	1400s	185
$Cu(L^3)_2 \cdot 2CH_3OH$		1645vs	1400s	245
$Cu(L^3)_2$		1610s	1395s	215
L^4H		1680vs	1265vs	415
$NaL^4 \cdot H_2O$		1565s	1415s	150
$Cu(L^4)_2 \cdot 1.5\ H_2O$		1600s	1410s	190
$Cu(L^4)_2 \cdot 2\ H_2O$		1550s	1455s	95
$Cu(L^4)_2 \cdot 3\ H_2O$		1550s	1455m	95
$Cu(L^4)_2$		1540*m*	1415*m*	125

[a] Abbreviations: v = very; s = strong; br = broad; m = medium; w = weak; sh = shoulder.

The electronic spectra of the complexes (Table II) are similar and show *d-d* absorption maxima falling in the range expected for tetra-carboxylate copper(II) complexes with long apical bonds to *O*-donors.[6] The more relevant IR bands for these complexes, along with those for the parent acids and corresponding sodium salts, are given in Table III. It is noticeable that remarkably different $\Delta(\nu_a(COO) - \nu_s(COO))$ values are detected, the differences being attributable, in addition to the nature of the ligands, to the different extents of hydrogen-bonding involving carboxylate groups and water (or methanol) molecules or to the presence of intermolecular carboxylate bridges (in $Cu(L^3)_2$).

Monomeric Complexes

The ESR spectra of the complexes $Cu(L^4)_2 \cdot 2\ H_2O$ and $Cu(L^4)_2 \cdot 3\ H_2O$ are

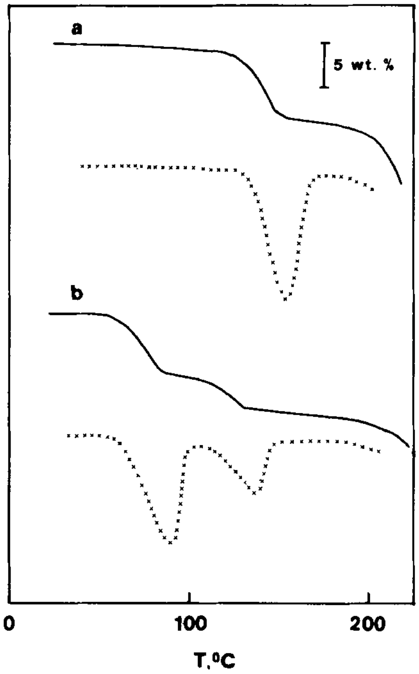

FIGURE 2 Thermogravimetric curves of (a): $Cu(L^4)_2 \cdot 2\ H_2O$ and (b): $Cu(L^4)_2 \cdot 3\ H_2O$.

supportive of monomeric structures (Table II). Taken with the energy of the *d-d* absorption maxima, the ESR parameters suggest CuO_6 chromophores having tetragonally distorted geometries. The metal coordination should involve two water molecules and two bidentate carboxylate groups behaving in an asymmetrical fashion. This conclusion is strongly supported by the IR spectra (Table III) which display $\Delta(\nu_a(COO) - \nu_s(COO))$ values consistent with bidentate coordination of carboxylate.

The thermal removal of two water molecules from $Cu(L^4)_2 \cdot 3\ H_2O$ (see the thermogravimetric curve in Fig. 2) afforded a monohydrate whose spectral parameters ($g_{\parallel}$ and $\bar{\nu}_{max}$ values higher and lower, respectively, than for the trihydrate complex) substantiate changes in the metal surrounding. As a well-resolved hyperfine parallel pattern is displayed by the powder ESR spectrum, six-coordination achieved through intermolecular bonding can be ruled out for the monohydrate complex. On the whole, it is likely that in this complex the metal is bound to two bidentate carboxylate groups and the geometry is tetrahedrally distorted. Indeed, further dehydration of the compound, while producing a broad ESR resonance indicative of dipolar exchange between paramagnetic centers, does not produce any shift of the *d-d* absorption maximum, excluding, thus, the coordination of the remaining water molecule. Based on the spectral parameters, $Cu(L^4)_2 \cdot 2\ H_2O$ is less planar than $Cu(L^4)_2 \cdot 3\ H_2O$. However, dehydration, which occurs in only one step (Fig. 2), gives rise to an anhydrous derivative similar to that obtained for $Cu(L^4)_2 \cdot 3\ H_2O$.

CONCLUSIONS

The results of this work, along those reported previously,[2] support the notion that the monomeric or dimeric nature of the copper(II) complexes formed by indolic acids is strongly dependent on the position of the carboxylic group in the indolic framework. Indeed, a carboxylic group in the 3- or 5-positions (or belonging to alkyl substituents in these positions) invariably yields dimeric acetate-like complexes. Instead, indole-2-carboxylic acid gives rise to a diaquabis (carboxylato)copper(II) complex having a monomeric structure. *N*-methyl substitution in indole-2-carboxylic acid allows both monomeric and dimeric complexes to be formed depending on the reaction temperature and the composition of the solution.

The reasons for the preference for dimeric over monomeric complex formation are not well understood. Electronic effects connected with the basicity of the carboxylate group and steric effects appear to be important.[7,8] However, in the present case, the trend observed does not parallel the order of acidity as judged from the pK_a values determined by us or reported in the literature:[9] IAA† (6.18), IBA† (6.10), IPA† (6.10), L^1H (5.56), L^2H (4.74), L^4H (4.57), ICA† (4.27) and L^3H (4.05).

Indeed, it appears that formation of monomers is strongly preferred when the carboxylic group is on the carbon atom adjacent to the ring nitrogen. A possible explanation is that factors other than steric and electronic effects can contribute to the formation of monomeric or dimeric structures. It could be suggested that, as most of copper(II) arrangements involve monodentate coordination of carboxylate, short bonds to water or another ligand are needed to complete the coordination sphere. Probably, water molecules can act as donors in the copper plane only if they are anchored to the whole structure by formation of suitable H-bonds. Such bonds, in the case of indolic acids, are possible only with the nitrogen atom and thus monomeric structures are favoured in the case of indole-2-carboxylic acids. *N*-methyl substitution hinders formation of strong H-bonds and thus the dimer is obtained in addition to the monomer. The latter case however, involves a rather uncommon bidentate coordination of the carboxylate groups.

It should be noted that the adoption of dimeric instead of monomeric structures, as an effect of the reduced ability of groups near carboxylate to participate in hydrogen-bonding, has been previously observed by us on passing from the 2,6-dihydroxybenzoate to the 2,6-dimethoxybenzoate complexes of copper(II).[10,11]

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† IAA = Indole-3-acetic acid; IBA = indole-3-butanoic acid; IPA = indole-3-propanoic acid; ICA = indole-2-carboxylic acid.