Synthesis and Magnetic Characterization of some Cu(II) Complexes of Cinnamic Acids

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Abstract

Metal complexes of cinnamic (CA), *o*-hydroxycinnamic acid (*o*-CA), *o*-nitro (*o*-NCA) and *m*-nitrocinnamic acid (*m*-NCA) were prepared and characterized by means of magnetic measurements, ESR, electronic spectroscopy and thermal analysis.

Introduction

Cinnamic acids are widely distributed in biological tissues in higher plants and have been detected in culture solutions from lignin decomposed by white-rot fungi [1–4]; furthermore they have been demonstrated to be active in tests for auxin activity [5]. For organic acids it is possible that they may increase the availability of insoluble forms of plants nutrients and can be involved in the downward movements of metals [6].

Due to our interest in the metal complexes of growth factors and metabolic inhibitors [7–10], to understand better the coordination behaviour and to substantiate the feasibility of metal chelation in soil and plants, we have examined the copper(II) cinnamic, *ortho*-hydroxycinnamic, *ortho*-nitro and *meta*-nitro cinnamic acids complexes for which relatively limited information is available [11–13].

Experimental

Elemental analyses (C, H, N) were obtained with a Perkin-Elmer 240 B instrument.

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 M-IV spectrophotometer.

Magnetic susceptibilities were measured at room temperature by using a Bruker B-MB4 Faraday system equipped with a Cahn 1000 electrobalance, with $[HgCo(SCN)_4]$ as calibrant and corrected for diamagnetism with the appropriate Pascal constants.

X-band ESR spectra of polycrystalline samples at 298 and 123 K, were obtained using a Bruker ER 2200-SRC spectrometer. The magnetic parameters were derived by standardization with diphenylpicrylhydrazyl.

Synthesis

Reagent acids (Sigma) and pure metal salts (Fluka) were used without further purification.

The metal complexes were prepared by mixing stoichiometric amounts of acids or their potassium salts, and metal salt (copper(II) acetate, chloride or sulphate) in water, aqueous methanol or aqueous THF (tetrahydrofuran). The products, which were either precipitated out immediately or after standing at room temperature, were filtered. The metal complexes are listed in Table I.

TABLE I. Analytical Data[a] for the Compounds

Compound		%C	%H	%N	Thermogravimetric determination
[Cu(CA)(OH)]	(I)	47.60(47.47)	3.57(3.51)		
$[Cu(CA)_2]$	(II)	60.22(60.41)	4.00(3.91)		
$[Cu(o\text{-}CA)_2]\cdot 2CH_3OH$	(III)	52.5(52.92)	4.71(4.85)		15.0(14.5)[b]
$[Cu(o\text{-}NCA)_2]\cdot H_2O$	(IV)	46.4(46.4)	3.10(3.00)	5.81(6.01)	3.80(3.86)[c]
$[Cu(m\text{-}NCA)_2]\cdot 2H_2O$	(V)	44.7(44.6)	3.00(3.10)	5.75(5.79)	8.00(7.72)[c]

[a] Calculated values in parentheses. [b] $\%CH_3OH$. [c] $\%H_2O$.

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TABLE II. Magnetic, Electronic and ESR Data for the Complexes in the Solid State

Compound	Absorption maxima (10^3 cm^{-1})	μ_{eff} (BM)[a]	ESR parameters at 123 K		
			$g_\parallel$	$g_\perp$	D (cm^{-1})
I	14.7	2.17	1.9[b]		
II	15.0	1.5	2.36	2.03	0.34
III	14.5	1.5	2.39	2.07	0.34
IV	14.4	1.65	2.37	2.09	0.34
			(Parameters for the mononuclear species $g_\parallel = 2.27; g_\perp = 2.06; A_\parallel = 150$ G)		
V	14.6	1.6	2.34	2.08	0.34

[a] At room temperature. [b] Isotropic resonance.

Results and Discussion

Magnetic, electronic and ESR data for the complexes in the solid state are summarized in Table II, and ESR spectra of polycristalline samples of complexes **II**, **III**, **IV** and **V** at 123 K are shown in Fig.1.

Complex **I** has a magnetic moment at 293 K of 2.17 BM, above that expected for a magnetically dilute copper(II) compound. Other hydroxo-carboxylates copper(II) complexes show quite similar magnetic features [14–17] also suggesting the existence of Cu(II)–Cu(II) interactions in a polymeric structure. In addition the complete insolubility of **I** in common organic solvents is consistent with the presence of a polymeric structure.

The ESR spectra of complex **I** only showed resonance at a position typical of mononuclear copper(II) (*ca.* 300 mT), but exhibited a considerably broader line shape than that of the mononuclear complex [18] and showed the apparent g value unusually low (1.9), not showing features helpful in supporting the suggestion of a spin triplet ground state.

Complexes **II**, **III**, **IV** and **V** show the subnormal magnetic moments, characteristic of exchange interactions between metal ions, and these findings are clearly supported by the ESR spectra which all display resonances typical of binuclear copper(II) carboxylates like copper(II) acetate monohydrate [19, 20] in the triplet state.

These spectra consist of a moderately strong absorption at *ca.* 30–40 mT, an absorption of varying intensity at $g \sim 2$, a strong absorption at *ca.* 460 mT and a weak absorption at *ca.* 560–600 mT. Using these measured positions and the available literature methods [21–27], we find the values for $g_\parallel$, $g_\perp$, and D in agreement with those found for binuclear copper(II) carboxylate complexes.

The resonance at $g \sim 2$ is due to non-dimeric (doublet species) copper(II); the proof that this line is not a part of the triplet spectrum is based on the fact that the intensity of the line increases with decreasing temperature.

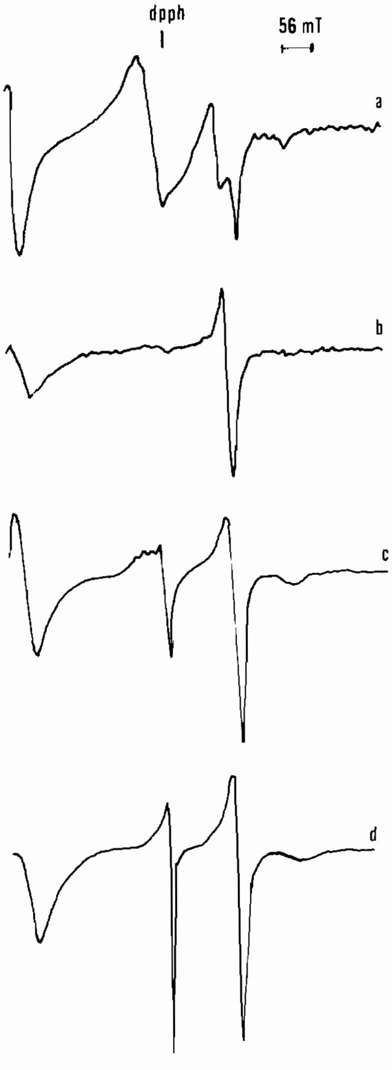

Fig. 1. X-Band ESR spectra of (a) **II**, (b) **III**, (c) **IV**, and (d) **V** complexes at 123 K.

The absorptions at the highest and lowest magnetic fields are associated with the parallel direction. The ESR spectrum of complex **II** shows splitting of the $H_\perp$ resonance, even though only one g value was calculated. Also the diffuse reflectance spectra are characteristic of Cu(II) carboxylates with d–d maximum in $14400 \div 15000$ cm^{-1} (Table II). The 'blueshift' of the absorption maximum in complex **II** indicates diminished axial interaction at the copper ion to give a more strictly planar environment than in the other compounds.

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References

1 M. E. K. Henderson, *Nature (London) 175,* 634 (1955).
2 M. E. K. Henderson, *J. Gen. Microbiol., 16,* 686 (1957).
3 H. Ishikawa, V. J. Schubert and F. F. Nord, *Arch. Biochem. Biophys., 100,* 131 (1963).
4 V. Vancura, *Plant Soil, 21,* 231 (1964).
5 A. Jönsson, in W. Ruhland (ed.), 'Handbuch der Pflanzenphysiologie', Vol. XIV, Springer, Berlin, 1961, p. 966.
6 A. Schatz, *J. Agr. Food Chem., 11,* 112 (1963).
7 F. Demartin, M. Manassero, L. Naldini and M. A. Zoroddu, *Inorg. Chim. Acta, 77,* L213 (1983).
8 L. Naldini, M. A. Cabras, M. A. Zoroddu, F. Demartin, M. Manassero and M. Sansoni, *Inorg. Chim. Acta, 88,* 45 (1984).
9 L. Naldini, M. A. Zoroddu, F. Demartin and M. Manassero, *Inorg. Chim. Acta, 89,* L1 (1984).
10 G. Micera. L. Naldini, L. Strinna Erre, M. A. Zoroddu and F. Cariati, *Inorg. Chim. Acta, 97,* 58 (1985).
11 J. Ploquin, *J. Bull. Soc. Chim., 18,* 757 (1951).
12 N. Kumar and A. K. Suri, *J. Indian Chem. Soc., 58(8),* 738 (1981).
13 A. Petron, E. Vrachnon-Astra and D. Katakis, *Inorg. Chim. Acta, 39,* 161 (1980).
14 R. Whyman, W. E. Hatfield and C. S. Fountain, *Inorg. Chim. Acta, 1,* 430 (1967).
15 D. A. Edwards and J. W. White, *J. Inorg. Nucl. Chem., 40,* 1335 (1978).
16 M. M. Bèlombe and M. A Novotny, *Inorg. Chem., 19,* 2470 (1980).
17 M. M. Bèlombe, *Bull. Chem. Soc. Jpn., 52,* 3424 (1979).
18 M. Kimura, S. Suzuki, W. Mori and A. Nakahara, *Inorg. Chim. Acta, 56,* 83 (1981).
19 M. Kato, H. B. Jonassen and J. C. Fanning, *Chem. Rev., 64,* 99 (1964).
20 P. de Meester, S. R. Fletcher and A. C. Skapski, *J. Chem. Soc., Dalton Trans.,* 2575 (1973).
21 J. Lewis, F. E. Mabbs, L. K. Royston and V. R. Smail, *J. Chem. Soc. A,* 291 (1969).
22 J. R. Wasson, C. I. Shyr and C. Trapp, *Inorg. Chem., 7,* 469 (1968).
23 J. Catterick and P. Thornton, *Adv. Inorg. Chem. Radiochem., 20,* 291 (1977).
24 R. W. Jotham, S. F. A. Kettle and J. A. Mabbs, *J. Chem. Soc., Dalton Trans.,* 427 (1972).
25 C. Oldham, *Prog. Inorg. Chem., 10,* 223 (1968).
26 G. F. Kokoszka and R. W. Duerst, *Coord. Rev., 5,* 209 (1970).
27 W. Harrisson, S. Rettig and J. Trotter, *J. Chem. Soc., Dalton Trans.,* 1852 (1972).