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Copper(II) complex of 3-cinnamalideneacetylacetone: Synthesis and characterisation

A VEERARAJ, P SAMI and N RAMAN*
Department of Chemistry, VHNSN College, Virudhunagar 626 001, India

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Abstract. A bidentate ligand derived from cinnamaldehyde and acetylacetone and its copper(II) complex have been synthesized and characterized by elemental analysis, UV-Vis, IR, ESR and magnetic susceptibility measurements. Magnetic susceptibility measurements, ESR and electronic spectral data indicate the presence of six coordinated Cu(II) ion. The ligand and complex are tested for antibacterial activity against *Pseudomonas aeroginosa*. They are found to show the antibacterial activity.

Keywords. *b*-Diketones; Knoevenagel condensate; electron spin resonance; *Pseudomonas aerogenosa*; *Caesalpinia bonducella*.

1. Introduction

The study of the transition metal complexes of *b*-diketones have been well established [1]. Several ligands derived from *b*-diketones are also known to form metal complexes. These ligands derived from *b*-diketones have been employed for the preparation of new complexes. The *b*-diketone ligands are considered as potential ligands due to their enolising ability. But being incapable of enolisation, the condensates have not perhaps been considered earlier as potential ligands towards transition metal ions. As compared to the metal *b*-diketone complexes, less work has been reported on metal complexes of *b*-diketone condensates. Therefore, it is thought worthwhile to synthesise a Knoevenagel condensate by the condensation of cinnamaldehyde and acetylacetone and prepare its Cu(II) complex with a view to study their spectral, magnetic and antibacterial activity. Understanding the structure and bonding of this complex help in designing and synthesizing some novel and more stable condensates of this type.

2. Experimental

AnalaR grade chemicals were used for the preparation of the complexes. The solvents were purified as per the procedure given in the literature [2].

2.1 *Preparation of 3-cinnamalideneacetylacetone (Cinac)*

Cinnamaldehyde (0·1 M) was added to acetylacetone (0·1 M) taken in a beaker with continuous stirring. The mixture was allowed to cool at room temperature and then piperidine (0·001 M) was added to it drop by drop with constant stirring. Stirring was

*For correspondence

continued for further 10 min. Then the mixture was kept in the refrigerator for 48 h. After that the mixture was extracted with chloroform and 5% hydrochloric acid. The mixture was vigorously shaken in a separating funnel. The organic layer consists of 3-cinnamalideneacetylacetone and excess chloroform. The bottom layer was eluted and dried by magnesium sulphate to remove any water. The excess chloroform was distilled out. The ligand was collected as orange yellow semisolid and preserved in a dessicator.

2.2 *Preparation of copper complex [Cu(cinac)]*

The procedure reported[3] for the preparation of [Cu(salacac)] was used with slight modification. In a typical procedure, a mixture of Cinac (0·01 M) and 3 drops of piperidine in chloroform (50 ml) was gradually added to a suspension of hydrated copper acetate (0·01 M) in chloroform (50 ml) and stirred in a round bottomed flask. The mixture was then boiled under reflux (2–3 h) until it became clear and then dark green. Upon concentration of the solution to one-third volume followed by the addition of petroleum ether (100 ml) and subsequent cooling at 0°C for 2 h, a bluish green coloured solid was precipitated. This product was removed by filtration, washed with 50% (V/V) ethanol–acetone mixture, dried and recrystallised from ethanol. The C, H contents of the complex was estimated through microanalysers. The metal content of the complex was estimated gravimetrically.

2.3 *Antibacterial test method*

NCCLS approved standard nutrient agar was used as a medium for testing the susceptibility of microorganisms to the antibacterial agents.

For testing the antibacterial activity of the ligand (cinac), complex [Cu(cinac)] and that of the oil of *Caesalpinia bonducella*, a well diffusion method[4] was used. In a typical procedure a well was made on the agar medium inoculated with *Pseudomonas aeroginosa*. The well was filled up with the test solution of appropriate concentration using a micropipette. The test medium was incubated for 24 h at 37°C. During this period the test solution was diffused into the plate and affected the growth of the inoculated *Pseudomonas aeroginosa*. A zone was developed on the plate. The radius of the zone is the measure of the antibacterial activity.

A bulk of 0·1 mM solution of cinac and [Cu(cinac)] were prepared by using DMSO as solvent and were used in our investigation. The antibacterial activity of cinac, [Cu(cinac)] were tested for two different doses (4 µl and 6 µl). The oil extracted from *Caesalpinia bonducella* seed was used without any dilution.

2.4 *Physical measurements*

The UV-Vis spectra of the ligand and complex in the range 200–1100 nm were recorded on a Shimadzu model 160 UV-Vis spectrophotometer. The IR spectra of ligand and complex were recorded in the range of 4000–200 cm^{-1} in a Perkin-Elmer model 783 IR spectrophotometer using KBr disc method. ESR spectra were recorded on a Varian E-109, X-band spectrometer equipped with 100 kHz field modulation both at room temperature and liquid nitrogen temperature using methanol as solvent. Magnetic susceptibility measurements were carried out by employing Gouy method at the room temperature on powder sample of the complex. Copper sulphate was used as calibrant.

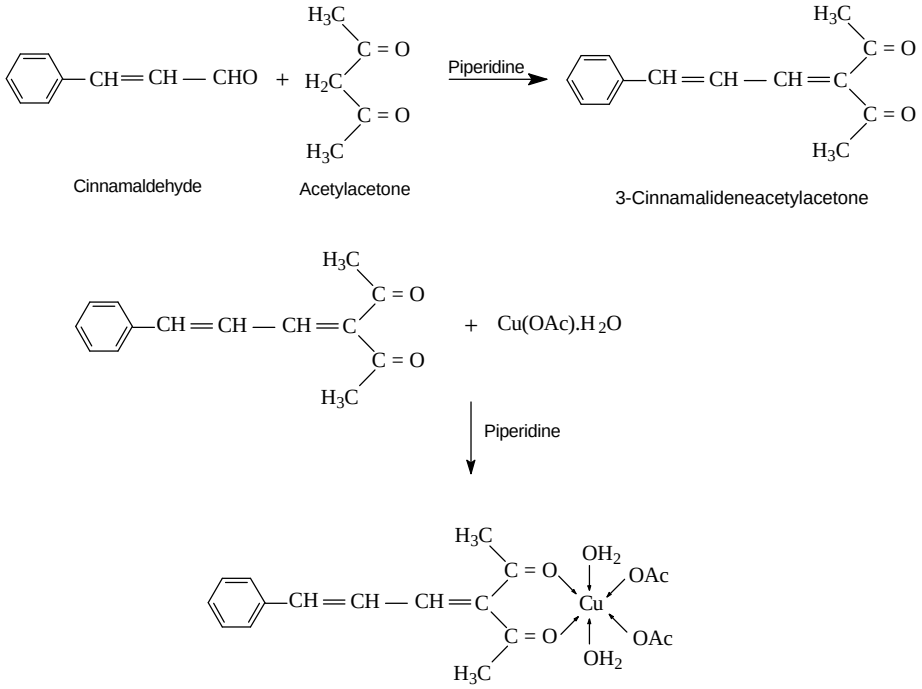
3. Results and discussion

The complex, [Cu(cinac)] is bluish green in colour, non-hygroscopic, amorphous, air and photo stable powder. The observed conductance (3·2 mho cm^2 mol^{-1}) and magnetic moment (1·8 BM) values suggest a monomeric 1:1 ligand to copper(II) acetate ratio for the complex molecule. The results obtained from microanalytical measurements and metal estimation data confirm the stoichiometry of the complex and suggest the formation of the complex as per the scheme 1.

The nature of the complex is further characterized by IR, UV-Vis and ESR spectra.

3.1 *IR studies*

The IR $g_{C=O}$ of the complex and related systems have been collected in table 1. The complex spectrum shows three prominent peaks in the region 1610–1410 cm^{-1}. The bands at 1610(sh) and 1590 cm^{-1} are assigned as $g_{C=O}$ and $g_{C=C}$ vibrations respectively [5,6]. The observed downfield shift, going from free ligand to metal complex $g_{C=O}$, suggests neutral ketonic coordination of carbonyl groups to the metal (table 1). The band at 3220 cm^{-1} for the complex ascertains the presence of coordinated water molecule [10]. Further the thermal analysis shows that the complex loses two water molecules at 170°C. This suggests the presence of two coordinated water molecules in the complex [11]. The IR stretching frequency observed at 1410 cm^{-1} in the complex has been attributed to the presence of acetate group. Hence, the proposed structure for the complex is as given in scheme 1. Furthermore, the presence of peak around 500 cm^{-1} for the complex is indicative of Cu–O stretching vibrations [3].



Scheme 1.

Table 1. Shift of $g_{(C=O)}$ frequencies (cm^{-1}) upon metal ion coordination in *b*-diketones.

Complex type	$g_{(C=O)}$ (cm^{-1}) Free ligand g_1	$g_{(C=O)}$ (cm^{-1}) Coordinated ligand g_2	Δγ (g_1–g_2)	Reference
Simple enolic, e.g. anionic coordination of (acac)	1730	1560	140	7, 8
Simple ketonic, e.g. neutral coordination of (acac)	1730	1720	10	8, 9
Conjugated ketonic, e.g. neutral (benac)	1705	1660	45	3
Title conjugated ketonic, e.g. neutral (cinac)	1700	1610	90	Present work

3.2 *UV-Visible studies*

The ligand Cinac shows a single band at 30,300 cm^{-1} characteristic l_{max} obtained from numerical calculations based on Woodward–Fieser calculation [12]. This confirms the structure of the ligand as given in chart 1.

The complex [Cu(cinac)] shows a broad band at 13,850 cm^{-1} and a sharp band at 41,490 cm^{-1}. Disappearance of the band characteristic of the ligand Cinac at 30,300 cm^{-1} and appearance of a new band at 13,850 cm^{-1} confirm the effective coordination of the ligand with Cu^{2+} ion and thereby the formation of the complex.

The *d–d* band at 13,850 cm^{-1} for [Cu(cinac)] is attributed to the d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$ electronic transition. Observation of this *d–d* transition suggests a tetragonally elongated octahedral geometry [13,14] around Cu^{2+} in [Cu(cinac)]. Further, the results are also supported by ESR studies.

3.3 *ESR studies*

The ESR spectrum of methanol solution of [Cu(cinac)] measured at X-band frequency at 300 and 77 K is given in figure 1. The 300 K spectrum (figure 1a) shows an isotropic pattern, which is expected for Cu^{2+} in solution. But the spectrum for the frozen solution (figure 1b) shows usual anisotropic pattern as expected for a powder sample. The *g* and *A* tensors evaluated are given in table 2. ESR data of [Cu(cinac)] with related systems are also collected in table 3 for the sake of comparison.

The observation of $g_{\|}$ and $g_{\perp}$ for [Cu(cinac)] suggests that the system is axially symmetric [15]. In axial spectra the *g*-values are related by the expression [16],

$$G = g_{\|} - 2/g_{\perp} - 2. \quad (1)$$

For [Cu(cinac)] $g_{\|} = 2{\cdot}3305 > g_{\perp} = 2{\cdot}0756$ and the fact that $G = 4{\cdot}3$ suggests the local tetragonal axes are aligned parallel with unpaired electrons in $d_{x^2-y^2}$ orbital [15,17]. The ESR parameters coincide well with the other related systems (table 3). This suggests the geometry of the complex as tetragonally elongated octahedron belonging to the D_{4h} point group.

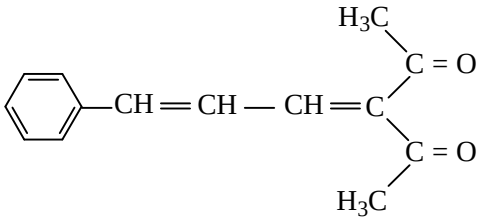


Chart 1.

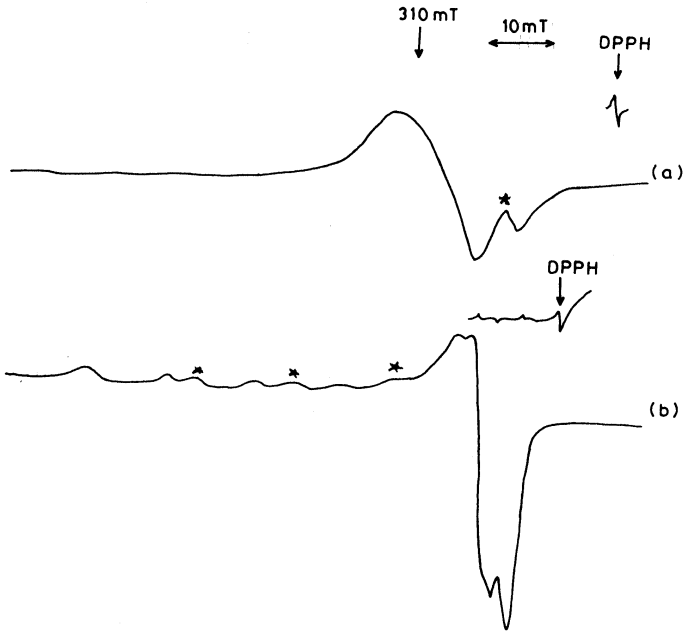


Figure 1. X-band ESR spectrum of [Cu(cinac)] measured in methanol at (**a**) 300, and (**b**) 77 K. (*Corresponds to unidentified Cu species.)

For the tetragonally elongated octahedral Cu(II) complex the g and A tensors are given by the usual axially symmetric spin Hamiltonian.

$$\mathsf{H} = b\,[g_{\|}\,(B_zS_z) + g_{\perp}\,(B_xS_x + B_yS_y) + A_{\|}\,(S_zI_z) + A_{\perp}\,(S_xI_x + S_yI_y)]. \quad (2)$$

We have used simplified molecular orbital theory [19] to calculate the molecular orbital coefficients (bonding coefficients) and a^2, b^2 and g^2. These bonding coefficients and spin orbit coupling constants were calculated using the following expressions [20],

$$g_{\|} = 2{\cdot}0023 - 8l\,(a^2b^2)/\Delta E, \quad (3)$$

$$g_{\perp} = 2{\cdot}0023 - 2l\,(a^2g^2)/\Delta E, \quad (4)$$

Table 2. ESR spectral data of [Cu(cinac)].

	g tensor		A_{63} ($\times 10^{-4}$ cm^{-1}), Cu	
Temperature (K)	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$
300	g_{iso} = 2·1645		A_{iso} = 41·27*	
77	2·3305	2·0756	171·6	21·70

*Value calculated from linewidth

Table 3. ESR spin Hamiltonian parameters of some Cu(II) complexes having D_{4h} effective symmetry.

Complex	$g_{\parallel}$	$g_{\perp}$	Reference
$Cu(H_2O)_4 (HCO_2)_2$	2·3500	2·0600	13
$Cu(NH_3)_4(SCN)_2$	2·2370	2·0560	18
$Cu(H_2O)_4(UO_2)_2(AsO_4)_2\ 4H_2O$	2·3554	2·0676	17
$Cu(NH_3)_4(NO_2)_2$	2·2340	2·0520	17
$[Cu(cinac)](H_2O_2)_2 (OAc)_2$	2·3305	2·0756	Present work

$$A_{\parallel} = P\{[-a^2(4/7 + k)]-2\,l\,a^2[4b^2/\Delta E + 3g^2/14\Delta E a^2]\}, \quad (5)$$

$$A_{\perp} = P\{[a^2(2/7-k)] - [22\,l(a^2g^2/14\Delta E)]\}. \quad (6)$$

Hence l is the spin orbit coupling constant which is –828 cm^{-1} for free Cu^{2+} ion and ΔE is the energy difference between electronic energy states.

The bonding parameters for [Cu(cinac)] are found to be a^2 = 0·9219, b^2 = 0·7803 and g^2 = 0·7013. The extent of departure of these coefficients from unity measures the extent of delocalisation of the metal electrons due to metal–ligand bonding. a^2 measures *s*-bonding [21], b^2 measures out-of-(*xy*)plane *p*-bonding and g^2 measures in-(*xy*)plane *p*-bonding. In the present case, the a^2 value (0·9219) indicates the slight ionic nature of the metal–ligand *s*-bonding. The deviation from unity in b^2 and g^2 values indicates the presence of considerable out-of-plane and in-plane *p*-bonding contribution in metal ligand *p*-bonding. The spin orbit coupling constants [22] $l_{\parallel}$ (–789·87 cm^{-1}) and $l_{\perp}$ (–785·12 cm^{-1}) suggest greater contribution from out-of-(*xy*)plane *p*-bonding than from in-plane *p*-bonding. Thus, ESR study of the copper complex has provided supportive evidence to the optical results.

4. Antibacterial studies

The complex was screened *in vitro* for its antibacterial activity against the gram-negative bacteria *Pseudomonas aerogenosa* using the diffusion method [4]. The antibacterial activity of the ligand was comparable with that of the medicinal oil *Caeselpinia bonducella*. The activity of the complex was higher than that of the ligand as well as of the oil. This identification strongly suggests the enhancement of antibacterial activity as a function of chelation.

Acknowledgements

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