



METAL COMPLEXES OF SCHIFF BASES DERIVED FROM DICINNAMOYLMETHANE AND AROMATIC AMINES

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Abstract

Two new Schiff bases containing olefinic linkages have been synthesized by condensing *ortho*-substituted aromatic amines with dicinnamoylmethane under specified conditions. The existence of these compounds predominantly in the intramolecularly hydrogen bonded keto-enamine form has been well demonstrated from their IR, ¹H NMR and mass spectral data. Details on the formation of their complexes with Ni(II), Cu(II) and Zn(II) and their nature of bonding are discussed on the basis of analytical and spectral data.

Key Words: Schiff base; dicinnamoylmethane; keto-enamine; metal complexes; IR spectra; ¹H NMR spectra and mass spectra.

Resumen

Dos nuevas bases de Schiff conteniendo acoplamientos olefinicos se sintetizaron por condensación de *ortho*-aminas aromáticas substituidas con dicinnamoilmethane bajo condiciones especificadas. La existencia de éstos compuestos en la forma ceto-enamina predominantemente con enlace de hidrogeno intramolecular se demuestra a partir de los espectros de IR, ^1H NMR y masas. Los detalles de la formación de sus complejos con Ni (II), Cu (II) y Zn (II) y la naturaleza de su enlace se discuten en base a los datos analíticos y espectrales.

Palabras claves: Base de Schiff; dicinnamoilmethane; ceto-enamine; complejos metálicos; espectros IR; ^1H NMR y masas.

Introduction

In recent years, there has been enhanced interest in the synthesis and characterization of transition metal complexes containing Schiff bases as ligands due to their importance as catalysts in many reactions [1-6]. The reactivity of carbonyl functions of 1,3-diketones and metal 1,3-diketonates towards amino compounds has been utilised in the synthesis of a large number of multidentate and macrocyclic ligands [7,8]. These ligand systems have evoked considerable interest because of their utility as model compounds in bioinorganic studies [9-11]. Most of the reported studies are based on 1,3-diketones in which the diketo function is directly linked to alkyl/aryl groups [12-16]. Very few reports exist [17] on Schiff bases of 1,3-diketones in which the diketo group is linked to alkenyl function. Such unsaturated 1,3-diketones constitute the major physiologically active principle (known generally as curcuminoids) of the traditional Indian medicinal plant turmeric (*Curcuma longa*, Linn, *Zingiberacea* family) and several other related spices. Curcuminoids, their synthetic analogues and their metal complexes are known to exhibit anticancer, antioxidant and anti-inflammatory activities [18-22]. In this paper we report the synthesis and characterization of Schiff bases of the unsaturated 1,3-diketone; 1,7-diphenyl-1,6-heptadiene-3,5-dione (dicinnamoylmethane) and their metal complexes.

Experimental

Methods and instruments

Carbon, hydrogen and nitrogen percentages were determined by microanalyses (Heraeus Elemental analyzer) and metal contents of complexes by AAS (Perkin Elmer 2380). The electronic spectra of the compounds were recorded in methanol solution (10^{-4} M) on a 1601 Shimadzu UV-Vis. spectrophotometer, IR spectra (KBr discs) on an 8101 Shimadzu FTIR spectrophotometer, ^1H NMR spectra (CDCl_3 or DMSO-d_6) on a Varian 300 NMR spectrometer and mass spectra on a Jeol/SX-102 mass spectrometer (FAB using Argon and *meta*-nitrobenzyl alcohol as the matrix). Molar conductance of the complexes was determined in DMF at $28 \pm 1^\circ\text{C}$ using solution of about 10^{-3} M concentration. Magnetic susceptibilities were determined at room temperature on a Guoy type magnetic balance.

Synthesis of bis(dicinnamoylmethane)o-aminophenol (H₂dcp) and bis(dicinnamoylmethane)o-aminothiophenol (H₂dct).

Dicinnamoylmethane was synthesized according to the method of Pabon [23] by the condensation of benzaldehyde with acetylacetonate-boron complex in the presence of tri(*sec*-butyl) borate and *n*-butylamine as the condensing agents. An ethanolic solution of *o*-

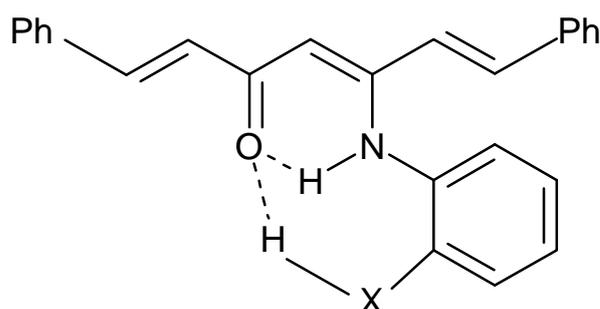
aminophenol/ *o*-aminothiophenol (0.01 mol, 20 mL) was added to a methanolic solution of dicinnamoylmethane (2.76 g, 0.01 mol, 30 mL) drop by drop with constant stirring. The mixture was refluxed on a boiling water bath for ~3 h and concentrated to half of its original volume. The crystalline precipitate formed was filtered, washed with water and recrystallized from hot methanol to get chromatographically (TLC) pure compound.

Synthesis of Cu(II), Ni(II) and Zn(II) complexes

A solution of the metal(II) acetate (0.001 mol) in minimum amount of water was added to an ethanolic solution of the ligand (0.001 mol, 20 mL) and the mixture was refluxed for ~4 h on a boiling water bath. The volume was reduced to half and the precipitated complex was filtered, washed with water, then with methanol, recrystallized from hot ethanol and dried in vacuum.

Results and Discussion

The Schiff bases **H₂dcp** and **H₂dct** are formed in good yield by the condensation of dicinnamoylmethane with *o*-aminophenol and *o*-aminothiophenol. The compounds are crystalline in nature and are soluble in common organic solvents. The elemental analytical data of the compounds (Table 1) indicate that the Schiff base formation has occurred in the 1:1 ratio as in structure **1** (Figure 1). They formed stable complexes with Ni(II), Cu(II) and Zn(II) ions. The analytical data (Table 1) together with non-electrolytic nature in DMF (specific conductance $<10\Omega^{-1}\text{cm}^{-1}$; 10^{-3} M solution) suggest $[\text{ML}(\text{OH}_2)]$ stoichiometry of the complexes. The Ni(II) and Zn(II) chelates are diamagnetic while Cu(II) complexes showed normal paramagnetic moment. The observed electronic, IR, ^1H NMR and mass spectral data of the complexes are fully consistent with structure **2** (Figure 2) in which the phenolic and amine protons are replaced by metal ion.

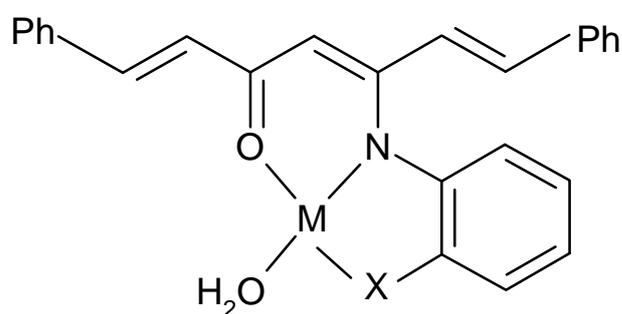


Compound	X
H₂dcp	O
H₂dct	S

Figure 1. Structure of the Schiff bases

Table 1. Physical and analytical data of **H₂dcp**, **H₂dct** and their metal complexes

Compound/ Empirical formula	Yield %	M.P. °C	Elemental Analysis: Found (Calculated) %			
			C	H	N	M
H₂dcp C₂₅H₂₁NO₂	60	135	81.88 (81.74)	5.62 (5.72)	3.71 (3.81)	-
H₂dct C₂₅H₂₁NSO	65	138	78.14 (78.33)	5.34 (5.48)	3.68 (3.66)	-
[Cu(dcp)(H₂O)] C₂₅H₂₁CuNO₃	74	276	67.36 (67.18)	4.65 (4.70)	3.07 (3.14)	14.12 (14.23)
[Cu(dct)(H₂O)] C₂₅H₂₁CuNSO₂	70	288	64.72 (64.86)	4.56 (4.54)	2.97 (3.03)	13.66 (13.73)
[Ni(dcp)(H₂O)] C₂₅H₂₁NNiO₃	68	246	67.78 (67.92)	4.70 (4.75)	3.32 (3.17)	13.09 (13.29)
[Ni(dct)(H₂O)] C₂₅H₂₁NNiSO₂	70	264	65.34 (65.54)	4.49 (4.59)	3.02 (3.06)	13.02 (12.83)
[Zn(dcp)(H₂O)] C₂₅H₂₁NO₃Zn	72	208	66.74 (66.91)	4.60 (4.68)	3.11 (3.12)	14.54 (14.58)
[Zn(dct)(H₂O)] C₂₅H₂₁NSO₂Zn	70	205	64.44 (64.60)	4.45 (4.52)	3.09 (3.01)	14.22 (14.08)



M = Ni(II), Cu(II), Zn(II)

Figure 2. Structure of the metal complexes of Schiff bases

Infrared spectra

Dicinnamoylmethane exists in the intramolecularly hydrogen bonded enol form and the carbonyl stretching band is observed at 1620 cm^{-1} [24]. The IR spectra of **H₂dcp** and **H₂dct** are characterized by the presence of a strong slightly broadened band at $\sim 1645\text{ cm}^{-1}$ assignable to cinnamoyl carbonyl. This indicates that only one of the carbonyl group is involved in the Schiff base formation. The IR spectra of the compounds show prominent bands at $\sim 1540\text{ cm}^{-1}$ and $\sim 1280\text{ cm}^{-1}$ due to NH deformation vibration and $\nu\text{C-N}$. The $1600\text{--}1650\text{ cm}^{-1}$ region of the spectra do not show any band assignable to $\nu\text{C=N}$. These together with the presence of a carbonyl band suggest the existence of the compounds in the keto-enamine form rather than in the enol-imine form [25]. The existence of strong intramolecular hydrogen bonding in the compounds is clearly indicated from the appearance of a broad band in the range $2500\text{--}3500\text{ cm}^{-1}$. In the IR spectra of the metal complexes the band at $\sim 1540\text{ cm}^{-1}$ of the free ligands disappeared. The cinnamoyl carbonyl and $\nu\text{C-N}$ of the ligands are also vanished and appeared as new bands at $\sim 1605\text{ cm}^{-1}$ and $\sim 1260\text{ cm}^{-1}$ respectively. No other prominent band is present in the $1600\text{--}1800\text{ cm}^{-1}$ region of the spectra indicating the involvement of the amine nitrogen and carbonyl oxygen in coordination with the metal ion [26]. The broad band in the region $2500\text{--}3500\text{ cm}^{-1}$ of the ligands cleared up in the spectra of all the metal complexes indicating the replacement of amine hydrogen by the metal cation during complexation. Instead, the spectra of the complexes in this region show a number of bands arising from $\nu\text{C-H}$ and vibrations due to coordinated H_2O . The low frequency region of the spectra revealed the presence of two new medium intensity bands at $\sim 420\text{ cm}^{-1}$ and $\sim 530\text{ cm}^{-1}$ due to $\nu\text{M-O}$ and $\nu\text{M-N}$ vibrations [27]. Important bands that appeared in the spectra are given in Table 2.

Table 2. Characteristic IR stretching bands (cm^{-1}) of **H₂dcp**, **H₂dct** and their metal complexes

Compound	(C=O)	(C-N)	(N-H)	(C=C) phenyl/ alkenyl	(M-N)	(M-O)
H₂dcp	1644	1284	1535	1594, 1590, 1588, 1580	-	-
[Cu(dcp)(H ₂ O)]	1604	1260	-	1592, 1588, 1585, 1582	526	425
[Ni(dcp)(H ₂ O)]	1605	1262	-	1599, 1595, 1588, 1584	528	424
[Zn(dcp)(H ₂ O)]	1603	1263	-	1598, 1594, 1590, 1585	526	422
H₂dct	1646	1280	1540	1595, 1590, 1585, 1582	-	-
[Cu(dct)(H ₂ O)]	1602	1260	-	1596, 1588, 1585, 1580	525	419
[Ni(dct)(H ₂ O)]	1606	1260	-	1598, 1595, 1590, 1586	520	428
[Zn(dct)(H ₂ O)]	1605	1262	-	1598, 1594, 1591, 1588	530	420

¹H NMR spectra

The ¹H NMR spectra of the compounds displayed a low field one proton singlet at ~δ 13.50 ppm assignable to the hydrogen bonded amine proton [28]. The phenolic OH and SH signals are observed at δ 11.16 ppm and δ 6.25 ppm respectively. The olefinic protons are observed at ~δ 7.90 and ~δ 8.00 ppm. The aryl proton signals appeared in the range δ 6.50-7.50 ppm as a complex multiplet. In the ¹H NMR spectra of the diamagnetic Ni(II) and Zn(II) complexes the low field signals due to the NH and OH/SO protons disappeared indicating the replacement of these protons by metal ion. The methine proton signal shifted appreciably to low field compared to the shift in the olefinic protons. This may be due to the aromatic character that might have been imparted to the C₃NOM ring system of the chelates by the highly conjugated groups attached to the carbonyl moiety [29]. The observed J values (~16 Hz) of the alkenyl proton signals in the free ligands and also in complexes suggest the *trans* nature. Integrated intensities of all the protons agree well with structure **2** of the complexes. The assignments of various proton signals observed are assembled in Table 3.

Table 3. ¹H NMR spectral data (δ, ppm) of **H₂dcp**, **H₂dct** and their Ni(II) and Zn(II) complexes

Compound	NH	Phenolic OH/SO	Methine	Alkenyl
H₂dcp	13.47 (1H)	11.16 (1H)	5.88 (1H)	8.13 (2H) 7.98 (2H)
[Ni(dcp)(H₂O)]	-	-	6.30 (1H)	8.18 (2H) 8.02 (2H)
[Zn(dcp)(H₂O)]	-	-	6.34 (1H)	8.16 (2H) 8.06 (2H)
H₂dct	13.54 (1H)	6.25 (1H)	5.81 (1H)	8.10 (2H) 7.88 (2H)
[Ni(dct)(H₂O)]	-	-	6.34 (1H)	8.14 (2H) 7.94 (2H)
[Zn(dct)(H₂O)]	-	-	6.26 (1H)	8.16 (2H) 7.90 (2H)

Mass spectra

The formulation of the Schiff bases as in structure **1** is clearly supported from the presence of intense molecular ion peak in the mass spectra. Other prominent peaks are due to the elimination of CO, [C₆H₅-CH=CH-C=O]⁺, tropylium ion, CH≡CH, etc., from the parent ion and subsequent fragments [30]. The FAB mass spectra of the Cu(II) complexes showed molecular ion peaks corresponding to [CuL(OH₂)₂] stoichiometry. Peaks correspond to L⁺ and fragments of L⁺ are also present in the spectra. The spectra of all the chelates contain a number of fragments containing copper in the 3:1 natural abundance of ⁶³Cu and ⁶⁵Cu isotopes (Table 4).

Table 4. Mass spectral data of H₂dcp, H₂dct and their Cu(II) complexes.

Compound	Mass spectral data (m/z)
H ₂ dcp	367, 290, 274, 264, 236, 222, 161, 145, 133, 131, 119, 77
H ₂ dct	383, 306, 280, 274, 252, 238, 229, 197, 177, 161, 149, 145, 135, 131, 120, 77
[Cu(dcp)(H ₂ O)]	448, 446, 430, 428, 371, 369, 367, 345, 343, 317, 315, 297, 292, 290, 276, 274, 264, 242, 240, 236, 222, 161, 145, 133, 131, 119
[Cu(dct)(H ₂ O)]	464, 462, 446, 444, 387, 385, 383, 361, 359, 333, 331, 308, 306, 313, 290, 280, 274, 256, 252, 240, 238, 197, 177, 161, 135, 131, 120

Electronic spectra

The UV spectra of the Schiff bases show two broad bands with maxima at ~370 nm and ~260 nm due to the various $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. The absorption maxima of the metal chelates bare close resemblance with the free ligands which indicates that no structural alteration of the ligand has occurred during complexation. However the values shifted slightly to longer wavelength indicating the involvement of the carbonyl group in metal complexation. The Cu(II) complexes showed a broad visible band, λ_{\max} at $\sim 15,000 \text{ cm}^{-1}$. This, together with the measured μ_{eff} values ($\sim 1.74 \text{ BM}$) suggests the square-planar geometry [31]. In agreement with this, spectra recorded in pyridine, a broad band centered at $\sim 11,000 \text{ cm}^{-1}$ was observed which indicates the formation of octahedral pyridine adducts. The observed diamagnetism and broad medium-intensity band at $\sim 17,500 \text{ cm}^{-1}$ in the spectra of the Ni(II) chelates suggest their square-planar geometry. In conformity, the spectra of the chelates in pyridine solution (10^{-3} M) showed three bands corresponding to configurational change to octahedral due to the association of pyridine. The three well-separated absorption bands at $\lambda_{\max} \sim 8,300$, $\sim 13,500$ and $\sim 24,500 \text{ cm}^{-1}$ correspond to the transitions; ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{F})$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{P})$ respectively.

Conclusion

Two new Schiff base ligands have been prepared by the condensation of dicinnamoylmethane with *o*-aminophenol and *o*-aminothiophenol. Analytical, IR, ¹H NMR and mass spectral data revealed a 1:1 product in which one of the carbonyl group of the diketone is involved in Schiff base formation suggesting their existence as the keto-enamine form rather than in the enol-imine form. Analytical, physical and spectral data of their Ni(II), Cu(II) and Zn(II) complexes showed the dibasic tridentate O₂N coordination involving the amino nitrogen and oxygens of the carbonyl and phenolic groups with a coordinated water molecule having the [ML(OH₂)] stoichiometry.

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