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Original scientific paper

Metal complexes of Schiff bases derived from dicinnamoylmethane and aliphatic diamines

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Abstract: Two new Schiff bases containing olefinic linkages have been synthesized by condensing aliphatic diamines with dicinnamoylmethane under specified conditions. The existence of these compounds predominantly in the intramolecularly hydrogen bonded keto-enamine form was well demonstrated by their IR, ¹H-NMR and mass spectral data. Dibasic tetradentate N₂O₂ coordination of the compounds in their [ML] complexes (M = Ni(II), Cu(II) and Zn(II)) was established on the basis of analytical and spectral data.

Keywords: Schiff base; dicinnamoylmethane; metal complexes; IR spectra; ¹H-NMR spectra; mass spectra.

INTRODUCTION

The reactivity of carbonyl functions of 1,3-diketones and metal 1,3-diketones towards amino-compounds has been employed in the synthesis of a large number of multidentate and macrocyclic ligands.¹ These ligand systems have evoked considerable interest because of their utility as model compounds in bioinorganic studies.^{2,3} Most of the reported studies are based on 1,3-diketones in which the diketo function is directly linked to alkyl/aryl groups.⁴ Very few reports exist⁵ on Schiff bases of 1,3-diketones in which the diketo group is linked to an 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. Zingiberaceae family) and several other related spices. Curcuminoids, their synthetic analogues and their metal complexes are known to exhibit anticancer, anti-oxidant and anti-inflammatory activities.^{6,7} In this paper, 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 are reported.

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EXPERIMENTAL

Methods and instruments

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

Synthesis of Schiff bases H_2ded and H_2dpd

Dicinnamoylmethane was synthesized according to the method of Pabon⁸ by the condensation of benzaldehyde with acetylacetone–boron complex in the presence of tri-*sec*-butyl borate and *n*-butylamine as the condensing agents. An ethanolic solution of 1,2-diaminoethane/1,3-diaminopropane (0.01 mol, 20 ml) was added to a methanolic solution of dicinnamoylmethane (2.76 g, 0.01 mol, 30 ml) drop by drop under constant stirring. The mixture was refluxed on a boiling water bath for ≈ 3 h and left overnight. The formed crystalline precipitate was filtered, washed with water and recrystallized from hot methanol to obtain the 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 a minimum amount of water was added to a methanolic solution of the ligand (0.001 mol, 20 ml) and the mixture was refluxed for ≈ 4 h on a boiling water bath. The precipitated complex was filtered, washed with water, recrystallized from hot ethanol and dried under vacuum.

RESULTS AND DISCUSSION

The Schiff bases H_2ded and H_2dpd were formed in good yield by the condensation of dicinnamoylmethane with 1,2-diaminoethane and 1,3-diaminopropane, respectively. The compounds are crystalline in nature and soluble in common organic solvents. The elemental analytical data of the compounds (Table I) indicate that the Schiff base formation occurred in the ratio 2:1, as shown in Fig. 1. They formed stable complexes with Ni(II) , Cu(II) and Zn(II) ions. The analytical data (Table I) together with their non-electrolytic nature in DMF (specific conductance $< 10 \Omega^{-1} \text{ cm}^{-1}$; 10^{-3} M solution) suggest 1:1 stoichiometry of the complexes. The Ni(II) and Zn(II) chelates are diamagnetic while the Cu(II) complexes showed normal paramagnetic moments. The observed electronic, IR, $^1\text{H-NMR}$ and mass spectral data of the complexes are fully consistent with the structure shown in Fig. 2.

Infrared spectra

Dicinnamoylmethane exists in the intramolecularly hydrogen-bonded enol form and the carbonyl stretching band is observed⁹ at 1620 cm^{-1} . The IR spectra of H_2ded and H_2dpd are characterized by the presence of a strong slightly

broadened band at $\approx 1660\text{ cm}^{-1}$, assignable to the cinnamoyl carbonyl. This indicates that only one of the carbonyl groups is involved in the Schiff base formation. The IR spectra of the compounds show prominent bands at $\approx 1540\text{ cm}^{-1}$ and $\approx 1280\text{ cm}^{-1}$ due to NH deformation vibration and $\nu(\text{C}-\text{N})$, respectively. The $1600\text{--}1650\text{ cm}^{-1}$ region of the spectra do not show any band assignable to $\nu(\text{C}=\text{N})$. These facts 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.¹⁰ The strong intramolecular hydrogen bonding present in the compounds is clearly indicated from the appearance of a broad band in the range $2700\text{--}3600\text{ cm}^{-1}$. In the IR spectra of the metal complexes, this broad band and the band at $\approx 1540\text{ cm}^{-1}$ of the free ligands disappeared. The cinnamoyl carbonyl and $\nu(\text{C}-\text{N})$ of the ligands also vanished and appeared as new bands at $\approx 1645\text{ cm}^{-1}$ and $\approx 1260\text{ cm}^{-1}$, respectively. No other prominent band was present in the $1600\text{--}1800\text{ cm}^{-1}$ region of the spectra, indicating the involvement of the amine nitrogen and carbonyl oxygen in the coordination with the metal ion.¹¹ The presence of two medium intensity bands at $\approx 420\text{ cm}^{-1}$ and $\approx 520\text{ cm}^{-1}$, assignable to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ in the spectra of all the complexes¹² also support the structure presented in Fig. 2. Important bands that appeared in the spectra are given in Table II.

TABLE I. Physical and analytical data of H_2ded , H_2dpd and their metal complexes

Compound/empirical formula	Yield %	M.p. °C	Found(calcd.), %			
			C	H	N	M
$\text{H}_2\text{ded}/\text{C}_{40}\text{H}_{36}\text{N}_2\text{O}_2$	72	120	83.25(83.33)	6.20(6.25)	4.84(4.86)	—
$\text{H}_2\text{dpd}/\text{C}_{41}\text{H}_{38}\text{N}_2\text{O}_2$	70	148	83.54(83.39)	6.50(6.44)	4.67(4.75)	—
$[\text{Ni}(\text{ded})]/\text{C}_{40}\text{H}_{34}\text{N}_2\text{NiO}_2$	68	236	75.64(75.86)	5.31(5.37)	4.41(4.43)	9.12(9.28)
$[\text{Ni}(\text{dpd})]/\text{C}_{41}\text{H}_{36}\text{N}_2\text{NiO}_2$	70	240	75.91(76.08)	5.64(5.57)	4.46(4.33)	8.99(9.08)
$[\text{Cu}(\text{ded})]/\text{C}_{40}\text{H}_{34}\text{CuN}_2\text{O}_2$	72	281	75.42(75.29)	5.28(5.33)	4.44(4.39)	9.86(9.97)
$[\text{Cu}(\text{dpd})]/\text{C}_{41}\text{H}_{36}\text{CuN}_2\text{O}_2$	65	276	75.68(75.51)	5.46(5.52)	4.28(4.30)	9.56(9.75)
$[\text{Zn}(\text{ded})]/\text{C}_{40}\text{H}_{34}\text{N}_2\text{O}_2\text{Zn}$	72	187	75.21(75.07)	5.44(5.32)	4.28(4.38)	10.14(10.23)
$[\text{Zn}(\text{dpd})]/\text{C}_{41}\text{H}_{36}\text{N}_2\text{O}_2\text{Zn}$	72	189	75.14(75.30)	5.61(5.51)	4.38(4.29)	9.92(10.01)

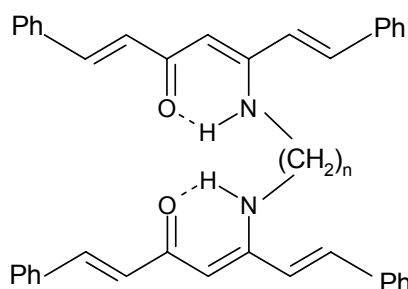
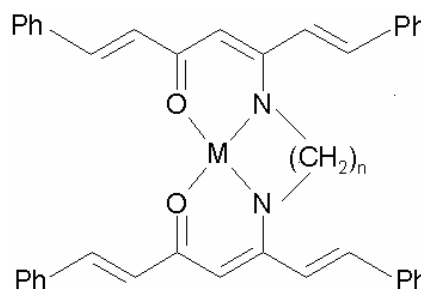
Fig. 1. Structure of the Schiff bases. For H_2ded and H_2dpd n equals 2 and 3, respectively.Fig. 2. Structure of the metal complexes of the Schiff bases. $\text{M} = \text{Ni}(\text{II}), \text{Cu}(\text{II}), \text{Zn}(\text{II})$.

TABLE II. Characteristic IR stretching bands, in cm^{-1} , of H_2ded , H_2dpd and their metal complexes

Compound	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{N})$	$\nu(\text{N}-\text{H})$	$\nu(\text{C}=\text{C})$ phenyl/ alkenyl	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
H_2ded	1666	1282	1542	1596, 1590, 1588, 1580	—	—
$[\text{Cu}(\text{ded})]$	1644	1262	—	1592, 1588, 1585, 1582	528	422
$[\text{Ni}(\text{ded})]$	1642	1265	—	1599, 1595, 1588, 1584	526	420
$[\text{Zn}(\text{ded})]$	1645	1263	—	1598, 1594, 1590, 1585	530	420
H_2dpd	1662	1280	1538	1595, 1590, 1585, 1582	—	—
$[\text{Cu}(\text{dpd})]$	1640	1260	—	1596, 1588, 1585, 1580	525	418
$[\text{Ni}(\text{dpd})]$	1641	1261	—	1598, 1595, 1590, 1586	518	428
$[\text{Zn}(\text{dpd})]$	1640	1262	—	1598, 1594, 1591, 1588	530	420

 ^1H -NMR spectra

The ^1H -NMR spectra of the compounds displayed a two proton singlet at $\approx \delta$ 13.60 ppm, assignable to hydrogen bonded amine protons.¹³ The methylene protons, methine protons and olefinic protons showed signals at the expected positions. The aryl proton signals are observed in the δ range 6.80–7.80 ppm as a complex multiplet. In the ^1H -NMR spectra of the diamagnetic $\text{Ni}(\text{II})$ and $\text{Zn}(\text{II})$ complexes, the low field amine proton signal of the ligands disappeared, indicating its replacement by the metal cation during complexation. The methine proton signals shifted appreciably to low field compared to the shift of the olefinic protons. This may be due to the aromatic character that might have been imparted to the C_3NOM ring system of the chelates by the highly conjugated groups attached to the carbonyl moiety.¹⁴ The integrated intensities of the methylene and olefinic protons agree well with structure of the complexes shown in Fig. 2. The assignments of the various proton signals observed are assembled in Table III.

TABLE III. ^1H -NMR spectral data (δ , ppm) of H_2ded , H_2dpd and their $\text{Ni}(\text{II})$ and $\text{Zn}(\text{II})$ complexes

Compound	NH	Methine	CH_2	Alkenyl
H_2ded	13.60 (2H)	5.86 (2H)	3.34 (4H)	8.13 (4H) 7.98 (4H)
$[\text{Ni}(\text{ded})]$	—	6.32 (2H)	3.37 (4H)	8.18 (4H) 8.02 (4H)
$[\text{Zn}(\text{ded})]$	—	6.30 (2H)	3.35 (4H)	8.17 (4H) 8.04 (4H)
H_2dpd	13.56 (2H)	5.83 (2H)	3.80 (4H) 2.87 (2H)	8.10 (4H) 7.88 (4H)
$[\text{Ni}(\text{dpd})]$	—	6.36 (2H)	3.84 (4H) 2.92 (2H)	8.14 (4H) 7.94 (4H)
$[\text{Zn}(\text{dpd})]$	—	6.28 (2H)	3.86 (4H) 2.94 (2H)	8.16 (4H) 7.90 (4H)

Mass spectra

The formulation of the Schiff bases as shown in Fig. 1 is clearly supported from the presence of an intense molecular ion peak in the mass spectra. Other

prominent peaks are due to the elimination of CO, $[\text{C}_6\text{H}_5\text{--CH=CH--C=O}]^+$, tropylium ion, $\text{CH}\equiv\text{CH}$, *etc.*, from the parent ion and subsequent fragments.¹⁵ The FAB mass spectra of the Cu(II) complexes showed molecular ion peaks corresponding to $[\text{CuL}]$ 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 ^{63}Cu and ^{65}Cu isotopes (Table IV).

TABLE IV. Mass spectral data of H_2ded , H_2dpd and their Cu(II) complexes

Compound	Mass spectral data (m/z)
H_2ded	576, 499, 473, 445, 431, 422, 396, 370, 354, 300, 288, 268, 164, 145, 131, 103
H_2dpd	590, 513, 487, 459, 445, 436, 410, 384, 368, 356, 342, 314, 300, 282, 178, 145, 131, 103
$[\text{Cu}(\text{ded})]$	639, 637, 576, 536, 534, 508, 506, 445, 433, 431, 422, 405, 403, 396, 375, 370, 354, 328, 300, 272, 199, 197, 169, 164, 145, 131, 103
$[\text{Cu}(\text{dpd})]$	653, 651, 590, 550, 548, 522, 520, 513, 447, 445, 436, 419, 417, 389, 368, 356, 342, 286, 282, 239, 183, 178, 145, 131, 103

Electronic spectra

The UV spectra of the Schiff bases show two broad bands with maxima at ≈ 390 and 260 nm, due to the various $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. The absorption maxima of the metal chelates bear close resemblance with those of the free ligands, which indicates that no structural alteration of the ligand occurred during complexation. However, the values are slightly shifted to longer wavelengths, indicating the involvement of the carbonyl group in metal complexation. The Cu(II) complexes showed a broad visible band, λ_{max} at ≈ 15000 cm^{-1} . This, together with the measured μ_{eff} values ($\approx 1.74 \mu_{\text{B}}$) suggests square-planar geometry.¹⁶ In agreement with this, a broad band centred at ≈ 11000 cm^{-1} was observed in the spectra recorded in pyridine, which indicates the formation of octahedral pyridine adducts. The observed diamagnetism and broad medium-intensity band at ≈ 17500 cm^{-1} in the spectra of the Ni(II) chelates suggest their square-planar geometry. In conformity with this, the spectra of the chelates in pyridine solution (10^{-3} M) showed three bands corresponding to a configurational change to octahedral due to the association of pyridine. The three well-separated absorption bands at $\lambda_{\text{max}} \approx 8200$, 13400 and 24400 cm^{-1} correspond to the transitions: $^3\text{A}_{2\text{g}} \rightarrow ^3\text{T}_{2\text{g}}$, $^3\text{A}_{2\text{g}} \rightarrow ^3\text{T}_{1\text{g}}(\text{F})$ and $^3\text{A}_{2\text{g}} \rightarrow ^3\text{T}_{1\text{g}}(\text{P})$, respectively.

CONCLUSIONS

Two new Schiff base ligands have been prepared by the condensation of dicinnamoylmethane with 1,2-diaminoethane and 1,3-diaminopropane. Analytical, IR, ^1H -NMR and mass spectral data revealed a 2:1 product in which one of the carbonyl groups of the diketone is involved in the Schiff base formation. Analytical, physical and spectral data of the $[\text{ML}]$ complexes of Ni(II), Cu(II) and

Zn(II) showed dibasic tetradentate N_2O_2 coordination involving the amino nitrogens and carbonyl oxygens. These compounds may exhibit interesting physiological properties compared to curcuminoids because of the presence of nitrogen donor sites. Studies in this direction are in progress.

ИЗВОД

МЕТАЛНИ КОМПЛЕКСИ СА ШИФОВИМ БАЗАМА ДОБИЈЕНИМ ОД ДИЦИНАМОИЛМЕТАНА И АЛИФАТИЧНИХ ДИАМИНА

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Две нове Шифове базе које садрже олефинске везе синтетисане су под одређеним условима кондензацијом алифатичних диаминa и дицинамоилметана. Показано је ИЦ, ¹H-NMR и масеним спектралним подацима да су ова једињења претежно у кето-енаминској форми, са интрамолекулском везом преко водоника. На основу аналитичких и спектралних података установљена је двобазна тетрадентатна N_2O_2 координација ових једињења у [ML] комплексима (M = Ni(II), Cu(II) and Zn(II)).

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