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Spectral characterization and synthesis of Knoevenagel condensate ligand β -ketoanilide and its transition metal (II) complexes

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Abstract

New type of Knoevenagel condensate ligand derived from cinnamaldehyde and β-ketoanilide (acetoacetanilide) and some of its transition metal (II) complexes have been synthesized. The structural features have been determined from their microanalytical, magnetic susceptibility, IR, UV-Vis, 'H NMR, ESR and mass spectral data. An octahedral geo-metry is assigned for the synthesized complexes. The Knoevenagel condensate β -ketoanilide acts as bidentate ligand. These complexes show lower conductance values, supporting their non-electrolytic nature. The monomeric nature of the complexes was confirmed from their magnetic susceptibility values. The cyclic voltammetric technique has been used to find out the anodic and cathodic peak potentials of the copper and nickel complexes.

Keywords: Knoevenagel condensate, β-ketoanilide, transition metal complexes

Introduction

Properties of the metal chelates of β–diones [1, 3] have stimulated research in these interesting compounds that find a variety of laboratory uses and many industrial application [4, 6]. Studies of transition metal complexes of β -diketones have been well established. Several ligands derived from β -diketones are also known to form metal complexes. These ligands derived from β -diketones have been employed for the preparation of new complexes. The β -diketone ligands are considered as potential ligands due to their enolising ability. Complex formation is conceived by replacement of the enolic proton by metal ion, commonly in the bidentate fashion. Condensation of β -diketones with aldehyde was first carried out by Knoevenagel and Arnors [7] to prepare 3-arylidene 2,4-pentanediones and many Knoevenagel condensates in high yield and pure form have also been reported [8, 10], The effect of substitution on these ligands in the position 3 on the tautomeric equilibria has been investigated by NMR spectroscopy [11], 3-Salicylidene-2,4-pentanediones and the related compounds were used as chelating agents with many transition metal ions [12, 14]. The Knoevenagel condensation of substituted benzylidenes with active methylene compounds were perfonned very efficiently using Ultrastable Y zeolite as heterogeneous catalyst [15].

The optimum conditions to prepare some knoevenagel condensates and their metal complexes with transition metals [16]. A bidentate ligand, from cinnamaldehyde and acetylacetone and its copper (II) complex has been reported [17], in general, the anilides and aldehydes are biologically important. The literature survey reveals that there is no work on the Knoevenagel condensate β -ketoanilide and its metal complexes. Hence, it is thought worthwhile to synthesize and characterize the above ligand and its copper (II), nickel (II), cobalt (II) and zinc (II) complexes by elemental analysis, thermogravimetry, magnetic susceptibility, IR, NMR and mass spectral studies.

Materials and Methods

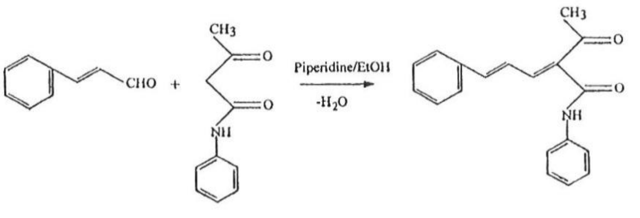
The chemicals and solvents used for the preparation of ligands and complexes were Merck products. Spectroscopic grade solvents were used for spectral studies. Microanalytical data, ^{1}H NMR and FAB mass spectra of the compounds were performed at the Regional Sophisticated Instrunientation Centre, Central Drug Research Institute, Lucknow U.P. (India), (RSIC, CDRI). The fast atom bombardment mass spectrum of the complex was recorded on a JEOL SX 102/DA-6000 mass spectrometer and data system using Argon/Xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature. *m*-Nitrobenzylalcohol (NBA) was used as the matrix. The IR spectra of the samples were recorded on a Perkin Elmer 783 spectrophotometer in the 4000-200 cm^{-1} range using KBr as solvent. The UV Vis spectra were recorded on a Shimadzu UV-1601 spec trophotometer. The X-band ESR spectra of the complexes were recorded in DMSO at 300 K and 77 K at IIT, Mumbai using TCNE (tetracyanoethylene) as the g-marker. Magnetic susceptibility measurements of the complexes were carried out using a Gouy balance. CuSO, was used as calibrant. Electrochemical studies were carried out using EG & G Princeton Applied Research Potentiostat/Galvanostat Model 273A, controlled by M 270 software. Cyclic voltammetric measurements were performed us-ing a glassy carbon working electrode, platinum wire auxillary electrode and an Ag/AgCl reference electrode. Tetrabutylammonium perchlorate (TBAP) was used as the supporting electrolyte. All solutions were purged with for 30 min prior to each set of experiments. Molar conductances of the complexes were measured in MeCN solution using a Systronic conductivity bridge type 305.

Synthesis of Knoevenagel condensate β-ketoanilide: Condensation of acetoacetanilide with cinnamaldehyde was performed by heating equimolar amounts (10 mmol) under reflux in 50 ml ethanol, in the presence of 5 drops of piperidine as catalyst for not less than 10 h (until the solution becomes dark brown). The solution was then cooled, the condensed product was separated by adding 5 ml of benzene and 30 ml of petroleum ether (40 - 60 ºC) The yellow colour solid Knoevenagel condensate β-ketoanilide (3-cinnamalideneacetoacetanilide) was isolated by filtration, washed and recrystallised from ethanol to constant melting point (103 ºC) yield 2.59 g, 89%.

Synthesis of complexes: The Co^{II}, Ni^{II}, CuII and Zn^{II} complexes of the above ligand were prepared by the following general procedure: A solution containing (2.91 g, 10 mmol) the ligand in 30 ml of ethanol was added to an ethanolic solution of 10 mmol of $CoCl_2.2H_2O/NiCl_2.6H_2O/CuCl_2.2H_2O/ZnCl_2$. The mixtures were refluxed for 3 h, cooled to room temperature and concentrated to one third by evaporating the solvent. The complexes were then isolated by filtration, extensively washed with doubly distilled water, recrystallised from acetone and air dried.

Results and Discussion

The Knoevenagel condensate was prepared via condensation of acetoacetanilide (10 mmol) and cinnamaldehyde (10 mmol) in the presence of piperidine as a catalyst according to the following Scheme-1.



Scheme 1

Table 1: Physical and analytical data of the synthesized complexes.

Compd.	Colour	Melt/dec.pt (ºC)	Found					Formula weight (Calcd.)	Λ_M (Ω^{-1} cm^{-1}) $mol^{-1} \times 10^{-3}$)	μ_{eff} (B.M.)
			M	C	H	N	Cl			
$C_{19}H_{17}NO_2$	Yellow	105	-	77.86 (78.33)	5.95 (5.88)	4.21 (4.80)	-	291..33	-	-
$[CuL\ (H_2O)_2Cl_2$	Blue	256	13.50 (13.76)	49.20 (49.41)	4.44 (4.58)	2.86 (3.03)	15.27 (15.35)	461.82	18.71	1.81
$[NiL(H_20)_2Cl_2]$	Green	310	13.14 (12.84)	50.58 (49.93)	4.78 (4.63)	3.15 (3.06)	15.48 (15.53)	456.97	16.35	3.24
$[CoL(H_20)_2Cl_2]$	Pink	205	12.98 (12.88)	51.05 (49.91)	4.60 (4.63)	2.97 (3.06)	15.53 (15.50)	457.19	9.40	4.86
$[ZnL(H_2o)_2Cl_2]$	Colourlesss	261	14.33 (14.10)	51.53 (49.22)	4.51 (4.56)	3.09 (3.02)	15.34 (15.29)	463.63	13.25	-

Table 2: Electronic absorption spectral data of the synthesized complexes.

Compd./ Complex	Absorption (cm^{-1})	Transition	Solvent	Geometry
Ligand	40000	INCT	CH_3CN	-
	28653	INCT	-	-
$[CuL(H_20)_2Cl_2]$	41450	INCT	-	-
	14388	$^2T_2g \rightarrow {}^2E_g$	CH_3CN	Distorted octahedral
	42372	INCT	-	-
$[NiL\ (H_2O)_2Cl_2]$	25974	$^3A_{2g} \rightarrow {}^3T_{1g}$ (p)	-	-
	15290	$^3A_{2g} \rightarrow {}^3T_{1g}$ (F)	CH_3CN	octahedral
	13605	$^3A_{2g} \rightarrow {}^3T_{2g}$	-	-
	42850	INCT	-	-
$[CoL\ (H_2O)_2Cl_2]$	19569	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	CH_3CN	Octahedral

The resulting compound was characterized by elemental analysis (Table-1), IR, mass, UV-Vis (Table-2) and ^1H NMR spectral data. All the synthesized compounds were coloured and air stable. The elemental analyses were found to be in good agreement with the calculated data (Table-1) of the ligand and its metal complexes. The chloride ions present in the complexes were estimated according to the Volhard's method. The magnetic susceptibility values of the complexes indicate that they are mononuclear. The low conductance values of the chelates support their non-electrolytic nature.

Mass and ^1H NMR spectra: The FAB-mass spectra of the ligand and its zinc complex were recorded. The ligand shows molecular ion peak at 291 m/z and the zinc complex shows molecular ion peak at 463 m/z. Both the ligand and the complex show the base peak at 177 *m/z* which indicates the presence of acetoacetanilide moiety. The prominent peak found at 71 *m/z* is due to the presence of two chlorine atoms, which is the evidence for the proposed structure of the complex. This is also supported by the FAB mass spectra of the other complexes.

The ^1H NMR spectrum of the ligand recorcded in $CDCL_3$ shows a singlet at δ 2.7 due to the methyl proton, two multiplets, one at δ 7.3 due to the -CH=CH-CH=group and another at δ 7.6 due to phenyl group. One singlet observed at the downfield region δ 8.5 is due to the –NH proton. The zinc complex shows the following peaks: δ 2.5 (singlet), δ 6.9 (multiplet), δ 7.5 (multiplet) and δ 8.3 (singlet). These observations confirm the coordination of the ligand to the metal.

IR spectra: The IR spectra provide valuable information regarding the nature of the functional group attached to the metal ion. The ligand shows broad and strong band at 3359 cm^{-1} assigned to NH stretching frequency. A weak absorption peak at 2919 cm^{-1} is assigned to CH_3 stretching vibration. The two bands ca. 1600 and 1495 cm^{-1} correspond to C = C ring stretching vibration. The ligand also shows two sharp bands at 1710 and 1623cm^{-1} which are assigned to the stretching frequencies of the carbonyl and amide carbonyl groups respectively. The observed downfield shifts, going from the free ligand to metal complexes suggest neutral ketonic coordination of carbonyl and amide carbonyl groups to the metal ions.

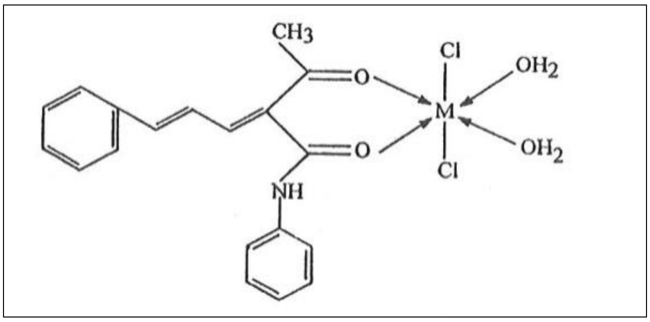
The 3440-3000 cm^{-1} region of the spectra of all the complexes shows broad bands, which may be due to the coordinated water molecules associated with the complexes. All the complexes exhibit only one band due to v (M - Cl) at ca. 350cm^{-1} which indicates that the chlorine atoms are present in trans position.

The thermogravimetric analysis of the metal complexes was measured from ambient temperature upto 800 ºC at a heating range of 10ºC min^{-1}. It is apparent that the coordinated water molecules are 2 in the 1: 1 complex. The results obtained are in good agreement with the theoretical ones (Table-3).

Table 3: Thermal analytical data of the complexes Wt. loss (%) (coord. water).

Complexes	Wt. Loss (%) (Coord. water)		
	Temp. range (ºC)	Calcd.	Observed
Cobalt	165-190	7.88	7.65
Nickel	180-210	7.88	7.70
Copper	155-175	7.26	7.50

Electronic absorption spectra: Electronic absorption spectra serve as a useful tool to distinguish between the squareplanar, octahedral and tetrahedral geometries of the complexes. The absorption regions, assignments and the proposed geometry of the complexes are given in Table-2. From this, it is concluded that an octahedral geometry has been proposed around the metal atom. These facts were also confirmed from their magnetic moment values as expected for octahedral geometry. In the case of diamagnetic zinc complex, only charge transfer transition was seen around 41892 cm^{-1}. The suggested structural formulae of the complexes may be represented as follows:



ESR spectral studies: The ESR spectrum of the copper complex, recorded in DMSO solution at 77 K and the data are given in Table-4. The spectrum of the copper complex at 300 K gives one intense absorption band in the high field region and is isotropic due to tumbling motion of the molecule. However, this complex in frozen state shows four well-resolved peaks, three peaks with low intensities in the low field region and one intense peak in the high field region. The magnetic moment of the complex (1.8 B.M.) indicates that the complex, is mononuclear.

Table 4: ESR spectal data of the copper complex in DMSO solution at 300 and 77K.

$A_{\parallel}$ cm^{-1}	170.4 × 10^{-4}	$A_{\perp}$ cm^{-1}	45 × 10^{-4}	α^2	0.8505
$g_{\parallel}$	2.3150	$g_{\perp}$	2.06	β^2	0.7169
A_{iso} cm^{-1}	76.66 × 10^{-4}	g_{iso}	2.056	γ^2	0.5098

This fact was also evident from the absence of a half field signal, observed in the spectrum at 1600 G due to the $m_s = \pm 2$ transition, ruling out any Cu-Cu interaction [18, 19]. The spin Hamiltonian parameters of the complexes are given in Table-4. From the observed value, it is clear that g || >$g_{\perp}$ perp >2.00 and A || >A which suggests that the in octahedral geometry and the unpaired electron lies predominantly in the $d_{x^2-y^2}$ or bital [20]. Molecular orbital coefficients, α^2 (covalent in-plane σ-bonding) and β^2 (covalent in-plane π-bonding), were calculated and it is found that $\alpha^2 > \beta^2$which shows that the σ -bonding is more covalent than that of the in-plane π -bonding [21]

Redox studies: The cyclic voltammogram of the copper complex was recorded in CH_3CN solution containing 0.1 *M* TBAP as supporting electrolyte (scan rate 100 mV s^{-1}) at 300 K in the potential range +1.0 to 1.4 V. It shows three reduction peaks in the cathodic direction and three oxidation peaks in the anodic direction. The observed peaks at E_{pc} = 0.046V and E_{Pa} =0.104 V is due to the formation of Cu^{III} / Cu^{II} couple. The ratio of i_{pc} /i_{pa} =50.00 μA/68.75 μA = 0.72 for this couple indicates the quasi-reversible nature of the couple. The other two couples, observed at E_{pc} = -0.905 V, E_{Pa} =-0.247 V and and E_{Pa} =-0.976 are assigned as CuIII / Cu^{I} and Cu^{I} / Cu^{0} respectively.

The cyclic voltammetric behaviour of nickel (II) complex has been studied in CH_3CN solution between +0.2 to -0.8 V vs Ag/AgCl. It shows two peaks at cathodic side in the negative region and two peaks in anodic region. One couple observed in this voltammogram at E_{pc} = 0.728 V and E_{Pa} = 0.646 is the formation of and Ni^{II}/Ni^{III}. The cathodic to anodic peak current ratio i_{pc} /i_{pa} of this couple [Ni^{II}/Ni^{III}] indicates the quasi-reversible nature of the couple.

References

1. Nagar S, Bohra R, Mehrotra RC. Indian Journal of Chemistry, Section A,2002:41:2288–2293.
2. Prasad RN, Agrawal M, Sharma S. Indian Journal of Chemistry, Section A,2004:43:337–340.
3. Funk RL, Fitzgerald JF, Olmstead TA, Para KS, Wos JS. Journal of the American Chemical Society,1993:115:8849–8852.
4. Zheng H, Swager TM. Journal of the American Chemical Society,1994:116:761–764.
5. Petrukhin OM, Kalichkin SV, Kolycheva NV, Korolkova OV, Ozerov RP, Tsirelson VG. Russian Journal of Inorganic Chemistry,1988:33:859–862.
6. Sievers RE, Turnispeed SB, Huang L, Laglante AF. Coordination Chemistry Reviews,1993:128:285–288.
7. Rahman AV, Qurash MA. Science International (Lahore),1993:8:331–334.
8. Knoevenagel E, Arnot R. Chemische Berichte,1904:37:4499–4502.
9. Chandra V, Prasad S. Journal of the Indian Chemical Society,1976:53:857–862.
10. Kawato T, Kanatomi H, Demarav Y, Murase T. Bulletin of the Chemical Society of Japan,1975:48:882–885.
11. Yamashita M, Watanabe Y, Mitsudo T, Takegami Y. Bulletin of the Chemical Society of Japan,1978:51:835–838.

12. Masahik C, Akira Y, Yasuko Y, Hisashi T. Chemical & Pharmaceutical Bulletin,1975:23:507–510.
13. Kailash D. Transition Metal Chemistry,1975:1:73–76.
14. Abdul Samath S, Raman M, Raman N, Jeayasubramanian K, Ramalingam SK. Transition Metal Chemistry,1992:17:3–6.
15. Wang QL, Yudao M, Bojun Z. Synthetic Communications,1997:27:4107–4110.
16. Issa YM, Hegazy WH. Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry,2000:30:1731–1735.
17. Veeraraj A, Sami P, Raman N. Proceedings of the Indian Academy of Sciences - Chemical Sciences,2000:112:515–518.
18. Sharma AL, Singh IO, Singh MA, Singh HR, Kadam HR, Bhide MK, *et al*. Transition Metal Chemistry,2001:26:532–536.
19. Hathaway BJ, Tomlinson AAG. Coordination Chemistry Reviews,1970:5:1–4.
20. Fernandes C, Parrilha GL, Lessa JA, Santiago LJM, Kanashiro MM, Boniolo FS, *et al*. Inorganica Chimica Acta,2006:353:3167–3170.
21. Natarajan C, Sheela CD, Athappan P, Murugesan R. Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry,1992:22:827–830.