# 4-*N*,*N*-Di-Ethylamino-3-penten-2-one Complexes of some Metals of First Transition Series

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**Summary**: Complexes of 4-*N*,*N*-diethylamino-3-penten-2-one with Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) were synthesized and characterized. Physical characteristics, analytical data and spectroscopic studies are reported. The compounds are very stable and are obtained in good yield.

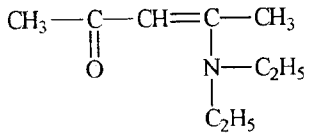
## Introduction

The chemistry of metal chelates of β-diketones [1], β-secondary amino-α,β-unsaturated ketones [2] and Schiff bases [3-7] has been fairly well studied. Chelain, *et al.*, for instance studied the successive formation of enaminoketene and arene tricarbonyl nitrogen ylide complexes during intramolecular alkyne insertions into aminocarbene complexes [8]. Copper(I) iodide promoted cyclization of enaminones having β-secondary amino group was similarly reported by Yang [9]. Romanenko *et al.*, studied the crystal structures of zinc (II) complexes with spin labelled enaminoketones of 3-imidazoline [10].

The liquid crystal properties of various 1-(alkylamino)-3-[(4″-hexyl-*trans*-cyclohexyl)-4′-phenyl] prop-1-ene-3-ones and their Cu(II) complexes were examined by Pyzuk, *et al.*, [11].

But the chemistry of metal complexes of β-tertiary amino derivatives of β-diketones has not yet been reported. The amino derivatives of β-diketones known as enaminoketones or enaminones have myriad medicinal [12], industrial [13] and analytical [14] applications. They have been used to prepare some novel pyranopyridine derivatives [15], and the reactions of 2,3-di-*O*-mesyl-lyxo-uridine with secondary amines have been used for the conversion of mesylated nucleosides to enamino nucleosides [16].

The enaminone esters have been found to exhibit histaminergic effect, uterine relaxation properties and anticonvulsant activity [12]. The enaminones have been found to improve electrodeposition of metals due to their chelating properties [13]. They have also been used to provide a convenient route for the synthesis of metal chelates of parent diketones [17]. The reactions of 4-*N*,*N*-diethylamino-3-penten-2-one with various metals to produce complexes of different characteristic colours have been, recently used for locating various cations [14]. The metal complexes of enaminones similarly can also be used to correlate the stability, structure and reactivity pattern of the metal complexes of 1,3-diketones and their amino and thio derivatives. In view of such vast significance, the preparation of the metal complexes of 4-*N*,*N*-diethylamino-3-penten-



2-one with some of metals of first transition series was initiated by the authors.

## Results and Discussion

Acetylacetone and diethylamine were condensed to get 4-*N,N*-diethylamino-3-penten-2-one using the standard method reported in literature [18]. The ligand, 4-*N,N*-diethylamino-3-penten-2-one formed complexes with transition metals such as Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) in ethanol. These compounds were obtained as solids and were characterized by elemental analysis and spectral data. The physical properties, analytical and spectral data of these compounds are given in Table 1 and 2.

Presence of nitrogen in the complexes was confirmed by Lassaigne's test and that of metal by spot test [19]. The percent of metal and nitrogen reveal that the complexes formed possessed varying coordination number 4 to 6 for the metals with oxidation state II and III, respectively. Chemical formula of the complexes is based upon elemental analysis.

Complexation of an enaminone with a metal ion is similar to protonation of the molecule and results in change in wavelength and intensity of absorption [20]. The UV spectra exhibits that there is an apparent change in wavelength of the various coordination compounds synthesized in present studies from that of the ligand (Table-2). This indicates that coordination has occured between ligand and metal ions. The infrared spectra also gives very valuable information about the structure of the compounds. A comparison of the infrared spectra of the ligand and the complexes indicates the coordination between the 4-*N,N*-diethylamino-3-penten-2-one, the ligand and metal ions. The infrared spectrum of the ligand exhibits strong characteristic peaks at 1550 and 1640 $cm^{-1}$, whereas, the corresponding iron chelate shows major bands at 1520 and 1570 $cm^{-1}$, the coablt chelate at 1510 and 1600 $cm^{-1}$, the nickel chelate at 1520 and 1615 $cm^{-1}$ the copper chelate at 1520 and 1580 $cm^{-1}$ and the zinc chelate at 1520 and 1600 $cm^{-1}$. Complexation results in a change in frequency and intensity of characteristic IR bands of the free ligand [21]. The IR spectra exhibits that there is an apparent shift in frequency and intensity of characteristic IR bands of the ligand in compounds synthesized in present studies (Table-2). The fragment O=C-CH=C-N< exhibits strong characteristic IR bands at 1550 and 1640 $cm^{-1}$. The band at 1550 $cm^{-1}$ is assigned to C = C or C-N and the band at 1640 $cm^{-1}$ is assigned to C=O by Leonard [18]. These bands have been shifted to lower frequencies on complexation. This indicates that ligand coordinates with the metal ion through N and O atoms of O=C-CH=C-N group and π-electron density of C=C double bond is also in stretch and spreads over the ring conferring aromatic behaviour to the complex. This IR pattern is identical to those studied by Collman [2] in case of chromium chelates with β-secondary amino ketones. These complexes are highly stable through cyclometallation.

Table-1: Amounts of compounds and physical properties as well as analytical data for the metal complexes of 4-*N*, *N*-diethylamino-3-penten-2-one

| Reactants | | | Product[a] | | | | Analysis %[b] | |
|---|---|---|---|---|---|---|---|---|
| Metal salt | 4-*N,N*-Diethyl amino-3-penten-2-one | Reflux time (min.) | Amount | Yield % | Colour | Melting point C° | Nitrogen | Metal |
| $FeCl_3.6H_2O$ 2.7003 g (10 m mol) | 4.65g (30 m mol) | 15 | $Fe(L)_3Cl_3$ 2.345g | 37.35 | Crimson red | 182° | 7.012 (6.692) | 9.500 (8.894) |
| $Co(CH_3COO)_2.4H_2O$ 2.4908g (10m mol) | 3.10g (20 m mol) | 20 | $Co(L)_2(CH_3COO)_2$ 1.382 g | 28.35 | Scarlet red | 174° | 5.844 (5.747) | 12.000 (12.089) |
| $Ni(CH_3COO)_2.4H_2O$ 2.4870g (10 m mol) | 3.10g (20 m mol) | 20 | $Ni((L)_2(CH_3COO)_2$ 2.900g | 59.51 | Light turquoise blue | 156° | 6.078 (5.749) | 11.750 (12.047) |
| $Cu(CH_3COO)_2.4H_2O$ 1.9955g (10 m mol) | 3.10g (20 mmol) | 20 | $Cu(L)_2(CH_3COO)_2$ 1.441g | 29.28 | Royal blue | 240° | 5.844 (5.693) | 12.500 (12.913) |
| $Zn(NO_3)_2.6H_2O$ 2.9747g (10 m mol) | 3.10g (20 m mol) | 15 | $Zn(L)_2(NO_3)_2$ 0.537g | 10.74 | White needle like crystals | 136° | 5.714 (5.604) | 13.000 (13.080) |

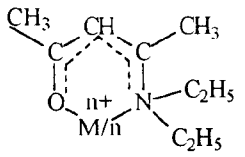
a Formula of complex is based upon elemental analysis
L = 4-*N,N*-Diethylamino-3-penten-2-one

b Calculated values are given in parentheses.

Table-2: Spectral data

| Compound | U.V[a]. $\lambda_{max}$ | Prominent IR[b] bands ν $cm^{-1}$ |
|---|---|---|
| 4-*N,N*-Di-Ethylamino-3-penten-2-one | 310 | 740s, 768w, 800s, 970s, 1020m, 1060s, 1080s, 1170s, 200s, 1220s, 1360vs, 1380vs, 1460sh, 1470vs, 1550vs, 1640s, 2820s, 2880s, 2920sh |
| $Fe(L)_3Cl_3$ | 270 | 680s, 740m, 790s, 820m, 960vs,1030vs, 1200s, 1280vs, 1380vs, 1420w, 1460vs 1520vs, 1570vs, 2350(broad), 2820vs 2880vs(sh), 3350 broad. |
| $Co(L)_2(CH_3COO)_2$ | 254 | 680w, 740w, 750m, 790s, 810vw, 950s, 1020s, 1210s,1270s, 1380m, 1400s, 1460s, 1510vs, 1600vs, 1650m, 2820vs 2880vs(sh), 3350 broad. |
| $Ni(L)_2(CH_3COO)_2$ | 281 | 690m, 710w, 750m, 790vs, 960vs, 990m, 1040vs, 1080w, 1120m, 1170w, 1220s, 1260w, 1280vs, 1320w, 1390s, 1420vs, 1475vs, 1520vs, 1615vs, 1660m, 2850vs, 2900vs (sh), 3350 (broad). |
| $Cu(L)_2(CH_3COO)_2$ | 236 | 630vw, 680m, 700m, 740s, 800vs, 950s, 980w, 1030s, 1200s, 1280vs, 1360m, 1380vs, 1420m, 1460vs, 1520vs, 1550m, (sharp) 1580vs, 2820vs, 2890vs, 3350 (broad). |
| $Zn(L)_2(NO_3)_2$ | 261 | 580vw, 680w, 710w, 730w, 750w, 800vs, 960s, 980w, 1040s, 1210s, 1280vs, 1320w, 1330w, 1380s, 1415s, 1460s, 1520vs, 1600vs, 2850vs, 2900vs, 3150 broad. |

a Measured in ethanol
b Measured in Nujol
s-strong, V-very, w- weak, m-medium, sh-shoulder



Where n = 3 for Fe (III)
and n = 2 for Co (II), Ni(II), Cu(II) and Zn(II).

## Experimental

*Materials*

BDH/E. Merck chemicals were used. Ethanol was distilled before use.

*Instrumentation*

The melting points were determined by capillary method on Gallenkamp melting point apparatus. "Registered Design No. 889339"

Infrared spectra were recorded in Nujol on a "Hitachi 270-30 infrared spectrophotometer".

U.V. spectra were recorded in ethanol on "Hitachi U-2000 spectrophotometer"

Nitrogen contents of complexes were estimated by Kjeldahl method. Metal contents were determined by Atomic Absorption Spectrophotometer "Varian AA-1275" after digesting the known amounts of samples in concentrated $HNO_3$.

*General procedure for the synthesis of complexes*

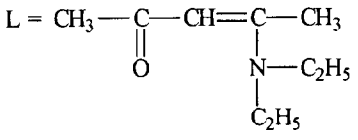
Ethanolic solutions of metal salts were taken in a three necked round bottom flask equipped with a water condenser, a separating funnel and stirring arrangement. Appropriate amounts (Table 1) of 4,-*N,N*-diethylamino-3-penten-2-one dissolved in ethanol were gradually poured into the flask through the separating funnel with constant stirring. The contents were refluxed on water bath. The reaction mixtures were then allowed to cool to room temperature. The crystals of the complexes began to appear immediately. However, the contents were allowed to stand overnight at room temperature for complete crystallization. The crystals were separated by filtration, washed with ethanol and dried to obtain the complexes (Table-1).

The synthesis of these compounds can be represented by the following general equation.

$$Mx_n + mL \longrightarrow (ML_m)\,X_n$$

where M = Fe (III), Co(II), Ni(II),Cu(II), Zn(II)

$X = Cl^-, CH_3COO^-, NO_3$



Physical properties, analytical and spectral data are given in Table 1 and 2.

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