

Formation of Mn^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} Complexes of p-substituted Benzylidene Nicotinylic Hydrazones

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Summary: Two new series of $[M(L)_2(H_2O)_2]$ and $[Mn(L)_2(H_2O)_2]Cl_2$ complexes ($M = Mn^{2+}$, Co^{2+} , Ni^{2+} and Cu^{2+} , $L =$ monoanionic bidentate ligands) have been prepared and characterised by DTA and TGA analysis. IR spectra indicated that the enolate oxygen and the C=N group are participating in complex formation in presence of metal(II) acetate, whereas the C=O group as well as the azomethine nitrogen are contributing to complex formation in presence of metal(II) chloride. Measurements of magnetic moments, ligand field and electron paramagnetic resonance spectra showed that Mn(II), Co(II) and Ni(II) exhibit octahedral geometry whereas Cu(II) ions display an axial elongated symmetry D_{4h} .

Introduction

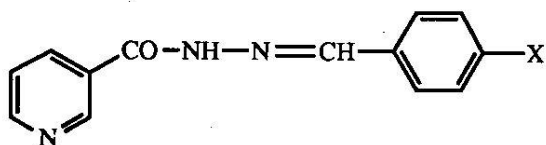
The interest in nicotinic hydrazides and their metal chelates draw the attention of many workers [1-6], yet it seems that those with arylidene derivatives drew little attention in the literature [7], so far as their structure and geometry in the solid state are concerned.

In the present investigation, it is aimed to prepared and investigate the Mn^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} chelates with p-substituted benzylidene nicotinylic hydrazones. The complexes are characterised by differential (DTA) and thermogravimetric analysis (TGA), IR, electronic and electron paramagnetic resonance (EPR) spectra as well as conductance and magnetic studies in order to throw more light on their structure and geometry.

Experimental

All compounds used in the present investigation were pure BDH products.

Nicotinic hydrazide was prepared in the same ways as that given by Struve [8]. The hydrazones were obtained by condensation of nicotinic hydrazide with p-chloro, p-bromo, or p-methoxybenzaldehyde in the usual manner. The ligands prepared have the following structural formulae:



where X = Br(L_I), Cl(L_{II}) or OCH₃ (L_{III}).

(i) Preparation of $[M(L)_2(H_2O)_2]$ Complexes

A solution of the metal (II) acetate (0.002 mole) in distilled water was added dropwise to a hot solution of the hydrazone ligand (0.004 mole) in the least amount of pure ethanol; the reaction mixture was stirred for 3 hours. The crystals obtained were filtered off, washed several times with distilled water to remove any traces of the metal ions, finally washed with diethylether and then dried in vacuo.

Preparation of $[M(L)_2(H_2O)_2]Cl_2$ Complexes

To a hot ethanolic solution of the ligand (0.004 mole) was added dropwise (0.002 mole) of metal (II) chloride, dissolved in the least amount of distilled water. The metal-ligand solutions thus obtained were refluxed on a water bath for one hour then allowed to cool. The solids separated were filtered off, washed several times with hot ethanol to ensure removing any contaminations of the unreacted metal salt or ligand, finally washed with diethylether and then dried in vacuo.

The apparatus and working procedures are the same as used previously [9,10].

Results and Discussion

Fig. 1 shows the thermal decomposition curves (TGA-DTA) of some metal (II) nicotinylic hydrazone complexes. The corresponding data of each thermal step are included in Table-1. Significant differences related to the thermal behaviour of the hydrazone complexes could be pointed out as follows:

Table-1: TGA-DTA of some p-substituted benzylidene nicotinyldiazone complexes

Lig(L) Complex	Decomposition temp °C		Thermogravimetric steps	DTA
	initial	(M-lig) core		
I [Cu(L) ₂ (H ₂ O) ₂]	150	240	up to 190°C 5.3 (5.85%)	160- 220°C
I [Cu(L) ₂ (H ₂ O) ₂]Cl ₂	145	230	up to 145°C 4.9 (5.24%)	145- 220°C
II [Cu(L) ₂ (H ₂ O) ₂]	140	225	up to 140°C 5(5.4%)	150- 215°C
III [Cu(L) ₂ (H ₂ O) ₂]	130	220	up to 130°C 5.4 (5.9%)	140- 210°C
III [Ni(L) ₂ (H ₂ O) ₂]	125	205	up to 125°C 5.5(5.96%)	130- 220°C
III [Co(L) ₂ (H ₂ O) ₂]	120	200	up to 120°C 5.4(5.95%)	130-190°C
				220-370°C
				> 370
				87.5 (87.06%)
				> 380°C
				88(88.4%)
				> 390°C
				87.6 (87.94%)
				> 395°C
				87.2 (86.97%)
				> 370°C
				87.2 (87.76%)
				> 380°C
				87.4 (87.61%)

1 - loss of coordinated H₂O

2 - thermal stability

3 - process of decomposition

4 - crystallisation and recrystallisation

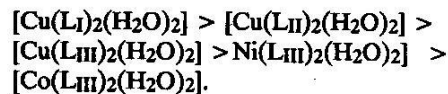
Found (% calc)

a) The upper parts of TGA curves show a small gradual loss in weight which is due to removal of coordinated water molecules from the complexes within the temperature range 120- 150°C. DTA curves, on the other hand, show differences in this region. Some are flat, others show slight exothermic trends of reactions. This may be attributed to variation in crystallinity of the samples.

b) TGA curves show by progressive heating in the temperature range from 200-240 and 370-395°C considerable loss of weights with the formation of some thermodynamically unstable intermediates which decomposes further as seen in Fig. 1. This may be attributed to a probable different stereochemical changes of the complexes. Similar conclusions were early given on studying the problem of stoichiometry of thermal decomposition of different M²⁺-complexes undergoing different stereochemical changes [11]. DTA curves show two exothermic peaks at 215- 230°C (a sharp and strong peak) and at 375- 390°C. The exothermic reactions may be discussed on the basis that two simultaneous processes could take place, namely a successive decomposition of the M²⁺-complexes and partial crystallization of an amorphous M-organic residual. It seems apparent, however, for the studied complexes the evolved energy of crystallization exceeds that required for decomposition. M-O continues to develop within temperature above the first exothermic peak.

c) The initial decomposition temperature of the complexes appears to depend largely on the M(II) ion and also to the type of the ligand used.

The thermal stability of the complexes runs in the order:



L_I is more volatile than L_{II} and L_{III} i.e. the substitution of Cl or Br group instead of OCH₃ decreases the stability.

The low conductance values of [M(L)₂(H₂O)₂] complexes (17-12 ohm⁻¹ cm² mol⁻¹ in DMF solutions, Table-2) indicate that the hydrazone ligand behaves as monoanionic ligand whereas the conductance values of [M(L)₂(H₂O)₂]Cl₂ complexes in DMF solutions 140-160 ohm⁻¹ cm² mol⁻¹ indicate the non-coordinated nature of Cl⁻ ions and also the ligands behave as neutral ones [12].

The bulk magnetic susceptibility measurements for all the solid complexes under investigation at room temperature 298 K are indicative of five unpaired electrons per Mn(II) ion $\mu_{\text{eff}} = 5.93-5.82$ B.M., three unpaired electrons per Co(II) ion $\mu_{\text{eff}} = 4.1 - 4.0$ B.M., two unpaired electrons per

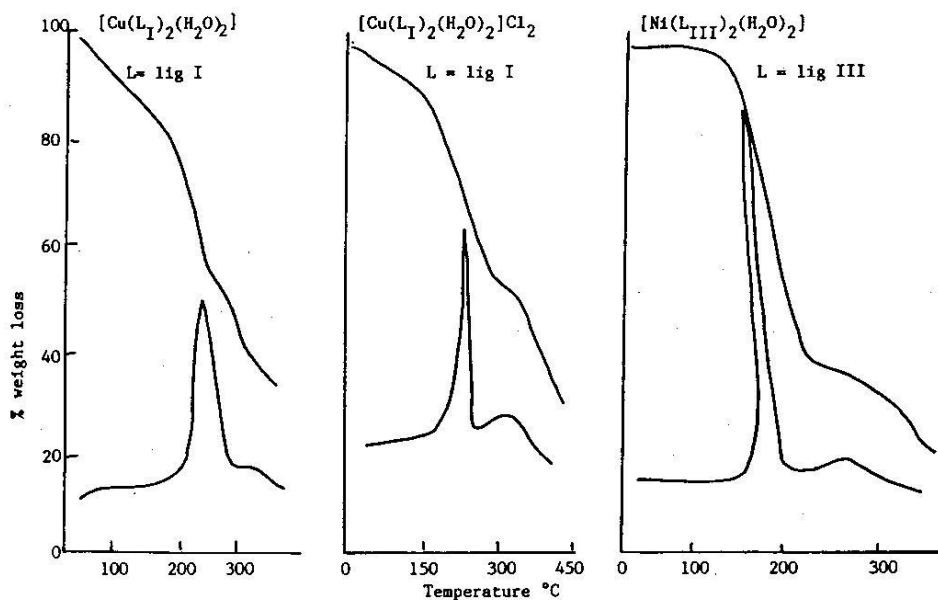


Fig.1: Representative thermogravimetric analysis of $[M(L)_2(H_2O)_2]$ and $[M(L)_2(H_2O)_2]Cl_2$ complexes.

Table-2; Conductance, magnetic moments, electronic and EPR spectra of complexes.

Lig (L)	Complex	a	b μ_{eff}	Reflectance $\lambda_{max}(nm)$	g_{eff}
I	$[Mn(L)_2(H_2O)_2]$	15	5.93	445,510	1.9732
II	$[Mn(L)_2(H_2O)_2]$	14	5.87	440,505	1.9641
III	$[Mn(L)_2(H_2O)_2]$	12	5.82	455,520	1.9612
I	$[Co(L)_2(H_2O)_2]$	13	4.1	515,645	1.9831
II	$[Co(L)_2(H_2O)_2]$	15	4.0	520,640	1.9862
III	$[Co(L)_2(H_2O)_2]$	16	4.1	525,630	1.9665
I	$[Ni(L)_2(H_2O)_2]$	14	2.85	430,550,620	silent
II	$[Ni(L)_2(H_2O)_2]$	15	2.80	440,510,525	silent
III	$[Ni(L)_2(H_2O)_2]$	14	2.97	450,540,625	silent
I	$[Cu(L)_2(H_2O)_2]$	12	1.52	620	2.0614
I	$[Cu(L)_2(H_2O)_2]Cl_2$	150	1.57	630	2.0321
II	$[Cu(L)_2(H_2O)_2]$	13	1.54	625	2.0732
II	$[Cu(L)_2(H_2O)_2]Cl_2$	160	1.57	640	2.0432
III	$[Cu(L)_2(H_2O)_2]$	17	1.53	635	2.0861
III	$[Cu(L)_2(H_2O)_2]Cl_2$	14	1.57	640	2.0463

a) $ohm^{-1} cm^2 mol^{-1}$, $10^{-3}M$ in DMF solution

b) B.M./M.

Ni(II) ion $\mu_{eff} = 2.97-2.80$ B.M. and one unpaired electron per Cu(II) ion, $\mu_{eff} = 1.57 - 1.52$ B.M., Table-2. The magnetic susceptibilities are in general lower than the moment expected which are more obvious in complexes $[M(L)_2(H_2O)_2]$ than $[M(L)_2(H_2O)_2]Cl_2$. The low moment in these complexes is due to antiferromagnetism [13] which arises *via* super exchange mechanism.

The bonding of the ligands to Mn(II), Co(II), Ni(II) and Cu(II) was investigated by comparing the IR spectra of nicotiny hydrazone complexes with those of the free ligands, one can conclude the following:

a) The spectra of the solid complexes exhibit a broad band at $3520-3460 cm^{-1}$ that could be attributed to ν_{OH} of associated water.

b) The IR spectra of $[M(L)_2(H_2O)_2]$ complexes show that ν_{OH} enolic, ν_{NH} , $\nu_{C=O}$, ν_{OH} and ν_{C-OH} bands within the range $2995-2990$, $3220-3180$, $1700-1690$, $1570-1560$ and $1090-1070 cm^{-1}$ in the spectra of the ligands disappear on complex formation. The C=N band exhibits obvious shift to lower frequency and splits into two different energies at

1605-1600 and 1645-1640 cm^{-1} indicating the existence of two C=N groups in the chelates.

c) The IR spectra of $[\text{M}(\text{L})_2(\text{H}_2\text{O})_2]\text{Cl}_2$ complexes show that the $\nu_{\text{C}=\text{O}}$ and $\nu_{\text{C}=\text{N}}$ bands within the ranges 1700-1690 and 1645-1640 cm^{-1} are shifted to lower frequency by (20-30) and (25-30) cm^{-1} respectively, whereas the ν_{NH} band still lies at nearly the same position in the spectra of free ligands (3220-3180 cm^{-1}). This indicates that C=O and C=N groups are contributing to complex formation.

d) The new bands appearing in the spectra of M(II) complexes within 485-470 and 380-370 cm^{-1} ranges are assigned to $\nu_{\text{M}=\text{O}}$ and $\nu_{\text{M}=\text{N}}$ respectively.

Thus the bond between metal (II) ions and nicotinyi hydrazone ligands can take place through covalent bonding to the enolate oxygen and coordination to one of the C=N groups in case of $[\text{M}(\text{L})_2(\text{H}_2\text{O})_2]$ complexes. In case of $[\text{M}(\text{L})_2(\text{H}_2\text{O})_2]\text{Cl}_2$ complexes the C=O and C=N groups would contribute by coordination to complex formation.

The electronic reflectance spectra of Mn(II), Co(II), Ni(II) and Cu(II) complexes were studied, the λ_{max} values are listed in Table-2. The difference in the λ_{max} values with changed metal ions is due to variation in the perturbing influence of the central metal ions on the ligand groups. The shift of the band together with the change in colour of the complexes indicates complex formation. Mn(II) complexes exhibit two absorption bands with λ_{max} situated at 440-455 and 505-520 nm. The two bands can be assigned to ${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{T}_{2\text{g}}$ (G) and ${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{T}_{1\text{g}}$ (G) Mn(II) transition respectively. Co(II) complexes exhibit two absorption bands with λ_{max} at 515-525 and 630-645 nm. These bands can be assigned to ${}^4\text{T}_{1\text{g}}(\text{P}) \rightarrow {}^4\text{T}_{1\text{g}}$ and ${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{A}_{2\text{g}}$ transitions for the d^7 system. The Ni(II) complexes exhibit two main groups of bands with λ_{max} at 430-450 and 510 - 625 nm which can be assigned to ${}^3\text{A}_{2\text{g}} \rightarrow {}^3\text{T}_{1\text{g}}(\text{P})$ and ${}^3\text{A}_{2\text{g}} \rightarrow {}^3\text{T}_{1\text{g}}(\text{F})$ transitions respectively. The Cu(II) complexes show one broad band with λ_{max} at 620-640 nm which can be assigned to ${}^2\text{E}_{\text{g}} \rightarrow {}^2\text{T}_{2\text{g}}$ transition of the Cu(II) ion.

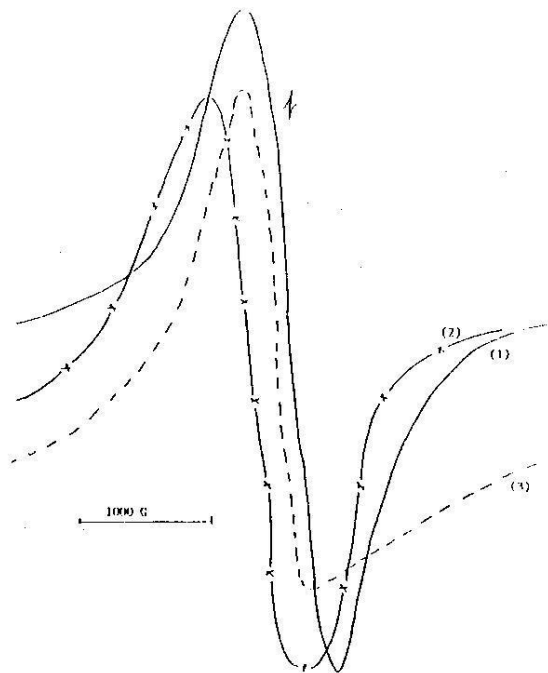
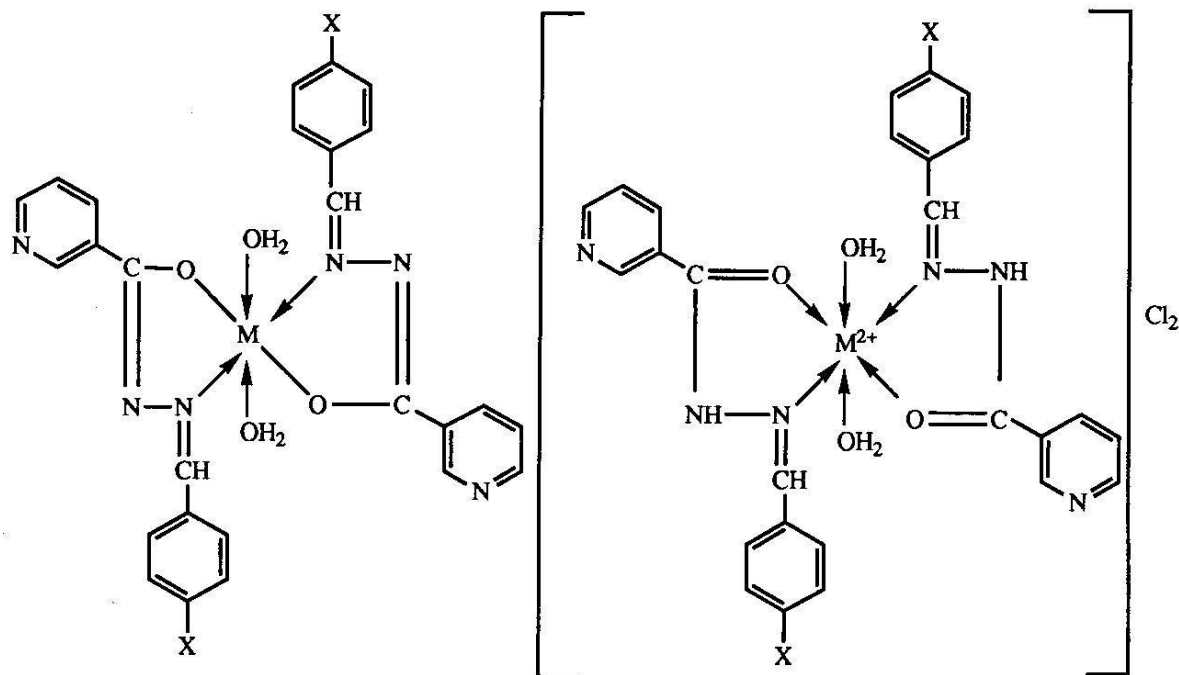


Fig.2: X-band EPR spectra of complexes (1) $[\text{Mn}(\text{L})_2(\text{H}_2\text{O})_2]$ (2) $[\text{Cu}(\text{L})_2(\text{H}_2\text{O})_2]$ (3) $[\text{Co}(\text{L})_2(\text{H}_2\text{O})_2]$

The position of λ_{max} and the shape of the bands indicate octahedral geometry for Mn(II), Co(II) and Ni(II) complexes [14,15] and a tetragonal elongation leading to a square planar geometry in extreme state [16] for Cu(II) complexes.

X-band EPR complexes measured at room temperature (298 K) exhibit an intense broad signal with no obvious hyperfine splitting (Fig.2). The g_{eff} values (Table-2) of Mn(II) or Co(II) complexes together with the shape of the EPR spectra indicate octahedral geometry around the Mn(II) or Co(II) ion. For Cu(II) complexes, the data suggest octahedral geometry with tetragonal distortion leading to a square planar geometry in extreme state.

Based on the knowledge gained from DTA, TGA, magnetic moment and conductance studies, IR, electronic and EPR spectra, the bonding between nicotinyi hydrazone and metal (II) ion can be formulated as follows:



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