

Synthesis and spectral characterization of naphthyldihydrazones derived from some 1,3-dicarbonyl compounds and their Ni(II), Cu(II) and Zn(II) complexes

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The coupling of tetrazotised 1,8-diaminonaphthalene with 1,3-dicarbonyl compounds [acetylacetone, methylacetoacetate and acetoacetanilide] yielded a new series of tetradentate ligand systems. Analytical, IR, ¹H NMR and mass spectral data indicate that the compounds exist in the intramolecularly hydrogen bonded dihydrazone form. Dibasic tetradentate N₂O₂ coordination of these compounds in their [ML] complexes [M = Ni(II), Cu(II) and Zn(II)] has been established on the basis of analytical and spectral data. The Ni(II) and Zn(II) chelates are diamagnetic while Cu(II) complexes showed normal paramagnetic moment.

Keywords: Naphthyldihydrazones; Metal complexes; IR spectra; ¹H NMR; Mass spectra

1. INTRODUCTION

Coupling of aryldiazonium salt on active methylenic compounds is of technical importance as a general method for the synthesis of yellow dyes and pigments [1]. The introduction of an areneazo group at the 2-position of 1,3-diketones raises the possibility of azo-hydrazone tautomerism [2, 3]. Aryl hydrazones have been used for analytical purposes [4], in the determination of metal ions [5], and some of their derivatives have been used in bacteriological and histological investigations [6]. Several applications of substituted azo compounds depend on their ability to form complexes with metal ions [7]. The factors that influence the structure and tautomeric behavior of the azo compounds and formation, structure and stability of their metal complexes are all important in determining their use not only in dye stuff industry but also in analytical and synthetic chemistry [8, 9]. However structural aspect of many of these products and their metal derivatives do not received as much attention as they deserve. In continuation of our studies on arylazo derivatives of 1,3-dicarbonyl compounds and their metal complexes [2, 10-17], we report here the synthesis and characterization of a new series of naphthyldihydrazones obtained by the coupling of tetrazotised 1,8-diaminonaphthalene with the active methylene group of three 1,3-dicarbonyl compounds: acetylacetone, methylacetoacetate and acetoacetanilide. Typical metal complexes of these compounds were also synthesized and characterized.

2. EXPERIMENTAL

2.1. Methods, instruments and materials

Carbon, hydrogen and nitrogen contents were determined by microanalyses (Heraeus Elemental analyzer from RSIC, Central Drug Research Institute, Lucknow, India and Catalysis division, Department of Chemistry, Indian Institute of Technology, Chennai, India) and metal contents of complexes by AAS (Perkin Elmer 2380 spectrometer). The electronic spectra of the compounds in methanol (10^{-4} mol/L) were recorded 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 ($\sim 10^{-3}$ mol L^{-1}) at room temperature (301 ± 1 K). Magnetic susceptibilities were determined at room temperature on a Guoy type magnetic balance, Sherwood Scientific Ltd., England, at room temperature using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as standard. 1,8-Diaminonaphthalene, methanol, urea and metal acetates were of AR grade, purchased from Merck, Germany.

2.2. Synthesis of naphthyldihydrazones, H_2tnp , H_2tnm and H_2tnb

1,8-Diaminonaphthalene (0.04 mol) was tetrazotised as reported [18]. After destroying the excess nitrous acid with urea, the tetrazonium salt solution was added drop by drop with stirring to a methanolic solution of the 1,3-dicarbonyl compound (0.08 mol, 50 mL). Concentrated sodium acetate solution was simultaneously added to control the pH of the solution around 6. The precipitate formed was filtered, washed with cold water and recrystallized from hot ethanol to get chromatographically pure (TLC) material.

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

A solution of the metal salt (0.01 mol) in minimum amount of water was added to a solution of the ligand in 1:1 dioxan-methanol mixture (0.01 mol, 25 mL). The mixed solution was refluxed on a boiling water bath for ~ 12 h. The pH of the solution was maintained around 8 by adding LiOH as the deprotonating agent [19]. The volume was reduced to half and cooled in an ice bath. The crystals formed were filtered, washed with water, recrystallized from hot dioxan and dried in vacuum.

2.3.2. Determination of magnetic susceptibility

A thin cylindrical glass tube, filled with the sample is vertically suspended from the beam of a balance in draught free enclosure in such a way that its lower end lies between the poles of an electromagnet. The weight of the sample is determined with the field off and with the field on. Corrections for diamagnetism of the constituents were made using Pascal's constants [20]. The effective magnetic moments were calculated using the formula $\mu_{\text{eff}} = 2.83 \times [\chi_{\text{M}} \cdot T]^{1/2} \times 9.274 \times 10^{-24}$ Am^2 where χ_{M} is the corrected molar susceptibility and T is the room temperature.

3. RESULTS AND DISCUSSION

Elemental analytical data of the naphthyldihydrazones (Table 1) indicate that coupling between tetrazotised 1,8-diaminonaphthalene and 1,3-dicarbonyl compounds has occurred in the 1:2 ratio. All the compounds are crystalline in nature and are soluble in common organic solvents. 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 $< 10 \text{ } \Omega^{-1} \text{ cm}^{-1}$; 10^{-3} M solution) suggest

[ML] 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 are in conformity with Fig. 1 of the naphthyldihydrazones and Fig. 2 of their complexes.

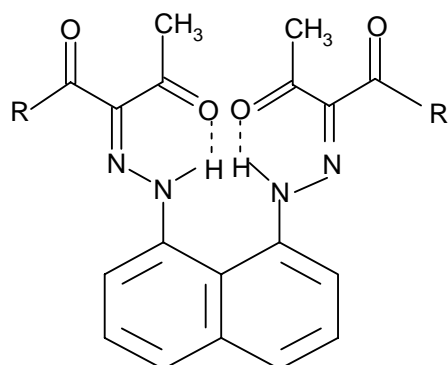


Fig. 1. Structure of the naphthyldihydrazones, H_2tnp ($\text{R} = -\text{CH}_3$), H_2tnm ($\text{R} = -\text{OCH}_3$) and H_2tnb ($\text{R} = -\text{NHC}_6\text{H}_5$).

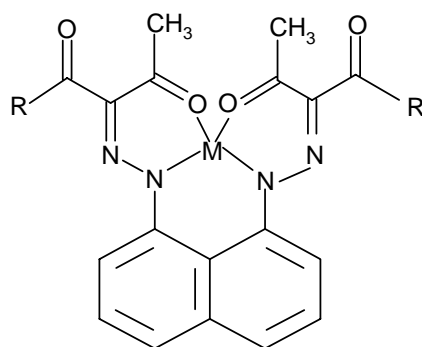


Fig. 2. Structure of the metal complexes of naphthyldihydrazones, $\text{M} = \text{Ni(II)}$, Cu(II) , Zn(II) .

3.1. Infrared spectra

The IR spectra of H_2tnp , H_2tnm and H_2tnb in the $1600\text{--}1800\text{ cm}^{-1}$ region showed strong bands at 1678 cm^{-1} , 1722 cm^{-1} and 1668 cm^{-1} due to the stretching of free acetyl, ester and amide carbonyls respectively [12]. The spectra also showed a strong band at $\sim 1630\text{ cm}^{-1}$ and a medium intensity band at $\sim 1620\text{ cm}^{-1}$ assignable to the stretching of intramolecularly hydrogen bonded acetyl carbonyl and $\text{C}=\text{N}$ vibrations [21, 22] of compounds as in Fig. 1. The broad band in the range $2500\text{--}3500\text{ cm}^{-1}$ indicates the existence of strong intramolecular hydrogen bonding in these compounds [13].

In the spectra of all the complexes the free carbonyl and $\text{C}=\text{N}$ bands remained almost unaffected indicating their non-involvement in complexation. However the band due to the hydrogen bonded acetyl carbonyl at $\sim 1630\text{ cm}^{-1}$ of all the ligands disappeared and instead a new strong band appeared at $\sim 1570\text{ cm}^{-1}$ assignable to the stretching of metal bonded carbonyl group. The spectra showed several medium intensity bands in the range $1580\text{--}1600\text{ cm}^{-1}$ due to various $\text{C}=\text{C}$ vibrations. The broad band in the range $2500\text{--}3500\text{ cm}^{-1}$ of the ligands disappeared in the spectra of all the complexes and bands due to various $\nu\text{C-H}$ vibrations appeared in the region. This strongly supports the replacement of the chelated protons of the ligands by metal ion as in Fig. 2. The complexes of H_2tnb showed a band at 3380 cm^{-1} due to NH group of anilide. A prominent band present at $\sim 1525\text{ cm}^{-1}$ of the ligands due to $\nu\text{N-H}$ vibration disappeared in the spectra of all the complexes indicating the replacement of the hydrazone NH protons by metal ion.

Table 1. Physical and analytical data of H₂tnp, H₂tnm, H₂tnb and their metal complexes.

| Compound/ Empirical formula | Yield % | M.P. °C | μ_{eff} Am ² | Elemental Analysis: Found (Calculated) % | | | |
|---|------------|---------|---------------------------------------|---|----------------|------------------|------------------|
| | | | | C | H | N | M |
| H ₂ tnp C ₂₀ H ₂₀ N ₄ O ₄ | 75 | 170 | - | 63.11 (63.16) | 5.24 (5.26) | 14.72 (14.73) | - |
| H ₂ tnm C ₂₀ H ₂₀ N ₄ O ₆ | 70 | 160 | - | 58.20 (58.25) | 4.83 (4.85) | 13.62 (13.59) | - |
| H ₂ tnb C ₃₀ H ₂₆ N ₆ O ₄ | 65 | 190 | - | 67.52 (67.42) | 4.90 (4.87) | 15.71 (15.73) | - |
| [Ni(tnp)] C ₂₀ H ₁₈ N ₄ NiO ₄ | 70 | >300 | - | 55.01 (54.96) | 4.12 (4.12) | 12.84 (12.82) | 13.34 (13.44) |
| [Ni(tnm)] C ₂₀ H ₁₈ N ₄ NiO ₆ | 72 | >300 | - | 51.24 (51.20) | 3.83 (3.84) | 11.92 (11.95) | 12.50 (12.53) |
| [Ni(tnb)] C ₃₀ H ₂₄ N ₆ NiO ₄ | 75 | >300 | - | 61.02 (60.94) | 4.02 (4.06) | 14.28 (14.22) | 10.02 (9.94) |
| [Cu(tnp)] C ₂₀ H ₁₈ CuN ₄ O ₄ | 65 | 215 | 16.4 x 10 ⁻²⁴ | 54.30 (54.36) | 4.11 (4.08) | 12.64 (12.68) | 14.35 (14.39) |
| [Cu(tnm)] C ₂₀ H ₁₈ CuN ₄ O ₆ | 70 | >300 | 16.2 x 10 ⁻²⁴ | 50.72 (50.68) | 3.72 (3.80) | 11.84 (11.83) | 13.48 (13.42) |
| [Cu(tnb)] C ₃₀ H ₂₄ CuN ₆ O ₄ | 75 | >300 | 16.6 x 10 ⁻²⁴ | 60.52 (60.45) | 4.02 (4.03) | 14.14 (14.10) | 10.60 (10.67) |
| [Zn(tnp)] C ₂₀ H ₁₈ N ₄ O ₄ Zn | 68 | >300 | - | 54.10 (54.13) | 4.03 (4.06) | 12.70 (12.63) | 14.80 (14.74) |
| [Zn(tnm)] C ₂₀ H ₁₈ N ₄ O ₆ Zn | 70 | >300 | - | 50.54 (50.49) | 3.72 (3.79) | 11.72 (11.78) | 13.78 (13.75) |
| [Zn(tnb)] C ₃₀ H ₂₄ N ₆ O ₄ Zn | 65 | >300 | - | 60.32 (60.26) | 4.04 (4.02) | 14.10 (14.06) | 11.02 (10.94) |

That the hydrazone nitrogens and the intramolecularly hydrogen bonded carbonyl oxygens are involved in complexation is clearly evident from the appearance of two additional medium intensity bands at ~420 cm⁻¹ and ~550 cm⁻¹ assignable of $\nu_{\text{M-O}}$ and $\nu_{\text{M-N}}$ vibrations [23] in the spectra of complexes. Important bands that appeared in the spectra are given in Table 2.

Table 2. Characteristic IR stretching bands (cm⁻¹) of H₂tnp, H₂tnm, H₂tnb and their metal complexes.

| Compound | Free (C=O) | Chelated (C=O) | (C=N) | (M-N) | (M-O) |
|--------------------|------------|-------------------|-------|-------|-------|
| H ₂ tnp | 1678 | 1632 | 1618 | - | - |
| [Cu(tnp)] | 1675 | 1574 | 1612 | 552 | 426 |
| [Ni(tnp)] | 1672 | 1568 | 1614 | 548 | 428 |
| [Zn(tnp)] | 1670 | 1565 | 1615 | 556 | 425 |
| H ₂ tnm | 1722 | 1628 | 1622 | - | - |
| [Cu(tnm)] | 1718 | 1575 | 1617 | 545 | 430 |
| [Ni(tnm)] | 1718 | 1568 | 1618 | 530 | 420 |
| [Zn(tnm)] | 1720 | 1564 | 1616 | 530 | 420 |
| H ₂ tnb | 1668 | 1630 | 1615 | - | - |
| [Cu(tnb)] | 1670 | 1570 | 1610 | 560 | 428 |
| [Ni(tnb)] | 1662 | 1572 | 1614 | 548 | 425 |
| [Zn(tnb)] | 1665 | 1567 | 1612 | 558 | 418 |

3.2. ^1H NMR spectra

The ^1H NMR spectra of the naphthyldihydrazones are characterized by the presence of a low field two proton signal in the range of $\sim\delta 15$ ppm due to N–H...O=C group [13,24,25]. The methyl protons of acetyl groups show signals in the range of $\sim\delta 2.5$ ppm. The aromatic protons appear in the range $\delta 7$ -8 ppm as a complex multiplet. The integrated intensities of all the signals agree well with the Fig. 1 of the compounds. In the ^1H NMR spectra of the diamagnetic Ni(II) and Zn(II) complexes, the low field signal due to the chelated hydrogens disappeared [26] indicating the replacement of hydrazone protons by metal ion during complexation [13, 27]. The close resemblance of the spectra of the complexes and ligands indicate that no structural alteration of the ligands have occurred during complexation. The NH proton signals of anilide group of H₂tnb remain unaltered in the spectra of their complexes indicating their non-involvement in complexation. Integrated intensities of all other protons agree well with the Fig. 2 (Table 3) of the complexes.

Table 3. ^1H NMR spectral data (δ , ppm) of H₂tnp, H₂tnm and H₂tnb and their Ni(II) and Zn(II) complexes.

| Compound | CH ₃ CO | RCO | Naphthyl | NH |
|--------------------|--------------------|--------------|---------------------|---------------------------------|
| H ₂ tnp | 2.51 (6H, s) | 2.34 (6H, s) | 7.14 - 7.87 (6H, m) | 15.42 (2H, s, br) |
| H ₂ tnm | 2.50 (6H, s) | 3.36 (6H, s) | 7.12 - 7.95 (6H, m) | 15.35 (2H, s, br) |
| H ₂ tnb | 2.49 (6H, s) | | 7.05–8.12* (m) | 15.33 (2H, s, br) 11.68 (2H, s) |
| [Ni(tnp)] | 2.56 (6H, s) | 2.38 (6H, s) | 7.10 - 7.82 (6H, m) | - |
| [Zn(tnp)] | 2.52 (6H, s) | 3.34 (6H, s) | 7.14 - 7.92 (6H, m) | - |
| [Ni(tnm)] | 2.47 (6H, s) | | 7.08–8.02* (m) | 11.62 (2H, s) |
| [Zn(tnm)] | 2.50 (6H, s) | 2.33 (6H, s) | 6.98 - 7.77 (6H, m) | - |
| [Ni(tnb)] | 2.48 (6H, s) | 3.38 (6H, s) | 7.04 - 7.90 (6H, m) | - |
| [Zn(tnb)] | 2.52 (6H, s) | | 7.12–7.96* (m) | 11.66 (2H, s) |

* due to anilide and naphthyl groups

3.3. Mass spectra

The formulation of the compounds as in Fig. 1 is clearly supported from the presence of intense molecular ion peak in the mass spectra. The appearance of a peak at m/z 155 indicates that cleavage occurs first at one of the N–N bonds followed by the scission of the second N–N bond. Since peaks due to the elimination of N₂ [28,29], a characteristic feature of the azo tautomer, has not been observed in the mass spectra indicate the existence of the compounds in the hydrazone form.

The formation of other important peaks is due to the elimination of CH₃CO, RCO, etc. from the molecular ion or subsequent fragments. The FAB mass spectra of the Cu(II) complexes showed molecular ion peaks of appreciable intensity corresponding to [CuL] stoichiometry. Peaks corresponding to the elimination of CH₃CO, RCO, dicarbonyl moieties etc. from the molecular ion 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 H₂tnp, H₂tnm, H₂tnb and their Cu(II) complexes.

| Compound | Mass spectral data (m/z) |
|--------------------|---|
| H ₂ tnp | 380, 337, 294, 268, 251, 208, 155 |
| H ₂ tnm | 412, 369, 353, 326, 310, 294, 284, 267, 251, 208, 155 |
| H ₂ tnb | 534, 491, 448, 414, 371, 328, 294, 251, 208, 182, 155, 120, 92 |
| Cu(tnp) | 443, 441, 400, 398, 380, 357, 355, 337, 334, 332, 314, 312, 271, 269, 251, 208, 155 |
| Cu(tnm) | 475, 473, 432, 430, 416, 414, 412, 389, 387, 373, 371, 369, 357, 355, 347, 345, 314, 312, 330, 328, 271, 269, 251, 208, 155 |
| Cu(tnb) | 597, 595, 554, 552, 534, 511, 509, 477, 475, 434, 432, 391, 389, 357, 355, 314, 312, 271, 269, 245, 243, 182, 155, 120, 92 |

3.4. Electronic spectra

The UV spectra of the naphthyldihydrazones show two absorption maxima at ~380 nm and ~250 nm due to the various n→π* and π→π* transitions. In complexes these absorption maxima shifted appreciably to low wave numbers. The Cu(II) complexes showed a broad visible band, λ_{max} at ~15,000 cm⁻¹. This, together with the measured μ_{eff} values (Table 1) suggests the square-planar geometry [30]. The observed diamagnetism and broad medium-intensity band at ~17,600 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 [30]. The three well-separated absorption bands at λ_{max} 8,200, 13,500 and 24,300 cm⁻¹ correspond to the transitions ³A_{2g} → ³T_{2g}; ³A_{2g} → ³T_{1g}(F) and ³A_{2g} → ³T_{1g}(P), respectively.

4. CONCLUSION

A new series of tetradentate ligand systems have been prepared by the coupling of tetrazotised 1,8-diaminonaphthalene with acetylacetone, methylacetoacetate and acetoacetanilide. Analytical, IR, ¹H NMR and mass spectral data revealed a 1:2 product in which one of the carbonyl groups of the dicarbonyl compound is involved in intramolecular hydrogen bonding with one of the hydrazone nitrogens. Analytical, physical and spectral data of their [ML] complexes with Cu(II), Ni(II) and Zn(II) showed the dibasic tetradentate N₂O₂ coordination involving one of the hydrazone nitrogens and carbonyl oxygens.

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