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1-Naphthylazo derivatives of some 1,3-dicarbonyl compounds and their Cu(II), Ni(II) and Zn(II) complexes

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Abstract: The coupling of diazotized 1-aminonaphthalene with 1,3-dicarbonyl compounds (acetylacetone, methylacetoacetate and acetoacetanilide) yielded a new series of bidentate ligand systems (HL). Analytical, IR, ¹H-NMR and mass spectral data indicate that the compounds exist in the intramolecularly hydrogen bonded keto-hydrazone form. With Ni(II), Cu(II) and Zn(II), these potential monobasic bidentate ligands formed [ML₂] type complexes. The IR, ¹H-NMR and mass spectral data of the complexes are consistent with the replacement of the chelated hydrazone proton of the ligand by a metal ion, thus leading to a stable six-membered chelate ring involving the hydrazone nitrogen and the hydrogen bonded carbonyl oxygen. The Ni(II) and Zn(II) chelates are diamagnetic, while the Cu(II) complexes are paramagnetic. In the metal complexes of the naphthylazo derivatives of acetylacetone and methylacetoacetate, the acetyl carbonyl is involved in coordination, whereas in the chelates of the naphthylazo derivative of acetoacetanilide, the anilide carbonyl is bonded with the metal ion.

Keywords: naphthylhydrazones; Cu(II), Ni(II) and Zn(II) complexes; IR, mass and NMR spectra.

INTRODUCTION

Coupling of 1,3-dicarbonyl compounds with the electrophile aryldiazonium ion provides the synthetic basis for a large number of technically important dye-stuffs.¹ These arylazo derivatives have gained considerable importance in recent years because of their application in the laboratory as acid-base, redox, metallochromic and other indicators,^{2–4} as stains for bacteriological and histological investigations,^{3–6} in the study of acid-base equilibrium and acidity constant values^{3,7} and in the preparation of a large number of biologically important hete-

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rocyclic compounds.⁸ Many variations in the dicarbonyls as well as the diazonium salt have been studied in attempts to improve the colour, solubility and stability of the resulting dyes.⁹ The patent literature discloses seemingly endless combination of these arylazodicarbonyls and their metal complex dyestuffs. However, the structural aspect of many of these products and their metal derivatives has received only scant attention. In continuation of studies on arylazo derivatives of 1,3-dicarbonyl compounds and their metal complexes,^{10–15} the synthesis and characterization of 1-naphthylazo derivatives of three 1,3-dicarbonyl compounds: acetylacetone, methylacetoacetate and acetoacetanilide, is reported herein. Typical Cu(II), Ni(II) and Zn(II) complexes of these compounds were also synthesized and characterized.

EXPERIMENTAL

Methods, instruments and materials

The carbon, hydrogen and nitrogen contents were determined by microanalyses (Heraeus elemental analyzer from CDRI, Lucknow, India) and the metal contents of the complexes by AAS (Perkin Elmer 2380). The electronic spectra of the compounds in methanol (10^{-4} mol/L) were recorded 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 ($\approx 10^{-3}$ mol/L) at 28 ± 1 °C. The magnetic susceptibilities were determined at room temperature on a Guoy type magnetic balance. Corrections for diamagnetism of the constituents were realised using Pascal's constants.¹⁶

Acetylacetone, methylacetoacetate, acetoacetanilide, 1-aminonaphthalene, methanol, urea and metal acetates used were of Merck AR grade, Germany.

Synthesis of naphthylhydrazones, Hnaa, Hnma and Hnan

1-Aminonaphthalene was diazotized as reported.¹⁷ After destroying the excess nitrous acid with urea, the diazonium salt solution (0.010 mol) was added drop wise with stirring to an ice-cold methanolic solution of the required 1,3-dicarbonyl compound (0.010 mol, 50 mL). Concentrated sodium acetate solution was simultaneously added to maintain the pH of the solution at around 6. The formed precipitate was filtered, washed with cold deionized water and recrystallized from hot ethanol to obtain chromatographically pure material (TLC – silica gel, chloroform).

Synthesis of the Ni(II), Cu(II) and Zn(II) complexes

A solution of the metal salt (0.010 mol) in a minimum amount of water was added to a solution of the ligand in methanol (0.020 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 the addition of sodium acetate. The volume was reduced to half and the remaining solution cooled in an ice bath. The formed crystals were filtered, washed with water, recrystallized from hot ethanol and dried under vacuum.

RESULTS AND DISCUSSION

The elemental analytical data of the naphthylhydrazones (Table I) indicate that coupling between diazotized 1-aminonaphthalene and the 1,3-dicarbonyl compounds occurred in a 1:1 molar ratio. All the compounds were crystalline in nature and were soluble in common organic solvents. They formed stable complexes with Ni(II), Cu(II) and Zn(II) ions. Their analytical data (Table I) together with their non-electrolytic nature in DMF (specific conductance $< 10 \text{ S cm}^{-1}$; 10^{-3} M solution) suggest $[\text{ML}_2]$ stoichiometry of the complexes. The Ni(II) and Zn(II) chelates were diamagnetic, while Cu(II) complexes showed normal paramagnetic moments (μ_{eff} , 1.75–1.80 μ_{B}). The observed electronic, IR, $^1\text{H-NMR}$ and mass spectral data are in conformity with the structures of Hnaa and Hnma and of their complexes given in Figs. 1 and 2, respectively. The analytical and spectral data of Hnan and its complex are in agreement with the structure given Figs. 3 and 4, respectively. These data of the compounds are discussed separately.

TABLE I. Physical and analytical data of Hnaa, Hnma, Hnan and their metal complexes

Compound	Yield %	M.p. °C	Elemental analysis: Found (Calculated), %			
			C	H	N	M
Hnaa ^a , C ₁₅ H ₁₄ N ₂ O ₂	80	110	70.71 (70.87)	5.44 (5.51)	11.08 (11.02)	–
Hnma ^b , C ₁₅ H ₁₄ N ₂ O ₃	75	140	66.80 (66.67)	5.17 (5.19)	10.45 (10.37)	–
Hnan ^c , C ₂₀ H ₁₇ N ₃ O ₂	80	150	72.67 (72.51)	5.12 (5.14)	12.71 (12.69)	–
[Ni(naa ^d) ₂], C ₃₀ H ₂₆ N ₄ NiO ₄	70	270	63.59 (63.75)	4.62 (4.60)	9.84 (9.92)	10.34 (10.40)
[Ni(nma ^d) ₂], C ₃₀ H ₂₆ N ₄ NiO ₆	72	204	60.24 (60.33)	4.33 (4.36)	9.28 (9.38)	9.92 (9.83)
[Ni(nan ^d) ₂], C ₄₀ H ₃₂ N ₆ NiO ₄	75	210	66.91 (66.79)	4.42 (4.45)	11.54 (11.69)	8.12 (8.17)
[Cu(naa ^d) ₂], C ₃₀ H ₂₆ CuN ₄ O ₄	65	190	63.30 (63.21)	4.51 (4.57)	9.64 (9.83)	11.25 (11.16)
[Cu(nma ^d) ₂], C ₃₀ H ₂₆ CuN ₄ O ₆	70	180	59.72 (59.84)	4.32 (4.32)	9.26 (9.31)	10.48 (10.56)
[Cu(nan ^d) ₂], C ₄₀ H ₃₂ CuN ₆ O ₄	75	200	66.52 (66.34)	4.36 (4.42)	11.54 (11.61)	8.60 (8.78)
[Zn(naa ^d) ₂], C ₃₀ H ₂₆ N ₄ O ₄ Zn	68	182	63.10 (63.00)	4.53 (4.55)	9.70 (9.80)	11.50 (11.44)
[Zn(nma ^d) ₂], C ₃₀ H ₂₆ N ₄ O ₆ Zn	70	160	59.54 (59.66)	4.32 (4.31)	9.19 (9.28)	10.78 (10.84)
[Zn(nan ^d) ₂], C ₄₀ H ₃₂ N ₆ O ₄ Zn	65	180	66.32 (66.17)	4.44 (4.41)	11.50 (11.58)	9.02 (9.01)

^a1-naphthylazo(acetylacetone); ^b1-naphthylazo(methylacetoacetate); ^c1-naphthylazo(acetoacetanilide); ^dnaa, nma, nan = deprotonated ligands

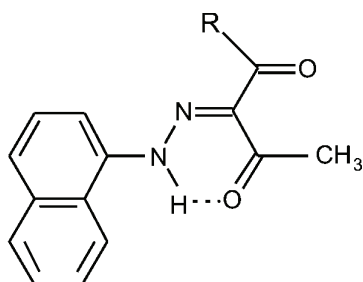


Fig. 1. Structure of Hnaa and Hnma; R = $-\text{CH}_3$ and $-\text{OCH}_3$ for Hnaa and Hnma, respectively.

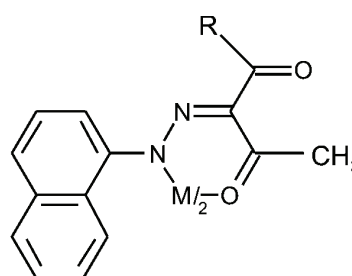


Fig. 2. Structure of the metal complexes of Hnaa and Hnma (M = Ni(II), Cu(II), Zn(II)).

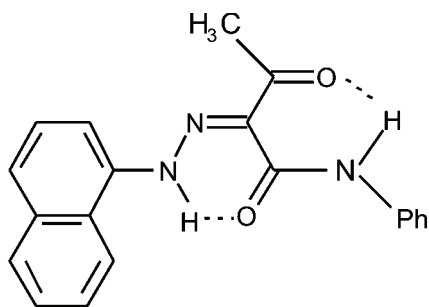


Fig. 3. Structure of Hnan.

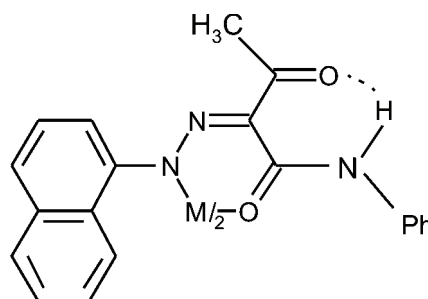


Fig. 4. Structure of the metal complexes of Hnan (M = Ni(II), Cu(II), Zn(II)).

Characterization of Hnaa, Hnma and their complexes

IR Spectra. The IR spectra of Hnaa and Hnma in the 1600–1800 cm^{-1} region both showed strong bands at 1678 and 1722 cm^{-1} due to the stretching of the free acetyl and ester carbonyls, respectively.^{13,14} The spectra also showed a strong band at $\approx 1630 \text{ cm}^{-1}$ and a medium intensity band at $\approx 1620 \text{ cm}^{-1}$, assignable to the stretching of intramolecularly hydrogen bonded acetyl carbonyl and C=N vibrations, respectively^{18,19} (Fig. 1). The broad band in the range 2500–3500 cm^{-1} indicates the existence of strong intramolecular hydrogen bonding in these compounds. In the spectra of all the complexes, the free carbonyl and C=N bands remained almost unaffected, suggesting that they were not involved in the coordination. However, the band due to the hydrogen bonded acetyl carbonyl at $\approx 1630 \text{ cm}^{-1}$ of the ligands disappeared and a new strong band assignable to the stretching of a metal bonded carbonyl group appeared at $\approx 1570 \text{ cm}^{-1}$. The spectra showed several medium intensity bands in the range 1580–1600 cm^{-1} due to various C=C vibrations. The broad band in the range 2500–3500 cm^{-1} of the ligands disappeared in the spectra of all the complexes and bands due to various $\nu(\text{C-H})$ vibrations appeared. This strongly supports the replacement of the chelated proton of the ligands by a metal ion, as shown in Fig. 2. The prominent band present at $\approx 1525 \text{ cm}^{-1}$ of the ligands, due to $\nu(\text{N-H})$ vibration, disappeared in the spectra of all the complexes as the consequence of the replacement of the hydrazone NH proton with a metal ion. The hydrazone nitrogen and the intramolecularly hydrogen bonded carbonyl oxygen participate in coordination, as evidenced by the two additional medium intensity bands at ≈ 420 and $\approx 550 \text{ cm}^{-1}$, assignable to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ vibrations, respectively,²⁰ in the spectra of the complexes. Important bands in the IR spectra are given in Table II.

$^1\text{H-NMR}$ Spectra. The $^1\text{H-NMR}$ spectra of Hnaa and Hnma are both characterized by the presence of a low field, two proton signal at $\approx \delta 15$ ppm due to the N-H \cdots O=C group.^{21,22} The integrated intensities of all the signals agree well with the representation of the compounds given in Fig. 1. In the $^1\text{H-NMR}$ spectra of the diamagnetic Ni(II) and Zn(II) complexes, the low field signal due to the

TABLE II. Characteristic IR stretching bands (cm^{-1}) of Hnaa, Hnma, Hnan and their metal complexes (abbreviations as in Table I)

Compound	Free (C=O)	Chelated (C=O)	(C=N)	(M-N)	(M-O)
Hnaa	1678	1632	1618	–	–
[Ni(naa) ₂]	1675	1574	1612	562	428
[Cu(naa) ₂]	1672	1568	1614	548	428
[Zn(naa) ₂]	1670	1565	1615	550	425
Hnma	1722	1628	1615	–	–
[Ni(nma) ₂]	1718	1575	1617	545	432
[Cu(nma) ₂]	1718	1568	1618	534	420
[Zn(nma) ₂]	1720	1564	1616	530	420
Hnan	–	1645, 1635	1620	–	–
[Ni(nan) ₂]	–	1562, 1635	1618	560	426
[Cu(nan) ₂]	–	1568, 1635	1614	548	425
[Zn(nan) ₂]	–	1556, 1635	1616	558	420

chelated hydrogen disappeared, indicating the replacement of the hydrazone proton with a metal ion during coordination.²³ The positions of the methyl proton signals indicate that the acetyl carbonyl is involved in the coordination. The integrated intensities of all other protons are in agreement with the schematic view presented in Fig. 2 (Table III).

TABLE III. ¹H-NMR spectral data (δ / ppm) of Hnaa, Hnma, Hnan and their Ni(II) and Zn(II) complexes (abbreviations as in Table I)

Compound	CH ₃ CO	RCO	Naphthyl	NH
Hnaa	2.56 (3H, <i>s</i>)	2.44 (3H, <i>s</i>)	7.14–7.87 (7H, <i>m</i>)	15.82 (1H, <i>s, br</i>)
[Ni(naa) ₂]	2.86 (6H, <i>s</i>)	2.38 (6H, <i>s</i>)	7.10–7.82 (14H, <i>m</i>)	–
[Zn(naa) ₂]	2.90 (6H, <i>s</i>)	2.33 (6H, <i>s</i>)	6.98–7.77 (14H, <i>m</i>)	–
Hnma	2.48 (3H, <i>s</i>)	3.88 (3H, <i>s</i>)	7.12–7.95 (7H, <i>m</i>)	15.05 (1H, <i>s, br</i>)
[Ni(nma) ₂]	2.82 (6H, <i>s</i>)	3.84 (6H, <i>s</i>)	7.14–7.92 (14H, <i>m</i>)	–
[Zn(nma) ₂]	2.88 (6H, <i>s</i>)	3.82 (6H, <i>s</i>)	7.04–7.90 (14H, <i>m</i>)	–
Hnan	2.65 (3H, <i>s</i>)	7.05–8.12 ^a (<i>m</i>)		15.85 (1H, <i>s, br</i>), 11.78 (1H, <i>s</i>)
[Ni(nan) ₂]	2.67 (6H, <i>s</i>)	7.08–8.02 ^a (<i>m</i>)		11.62 (2H, <i>s</i>)
[Zn(nan) ₂]	2.62 (6H, <i>s</i>)	7.02–8.12 ^a (<i>m</i>)		11.66 (2H, <i>s</i>)

^aDue to anilide and naphthyl groups

Mass spectra. The formulation of the compounds as in Fig. 1 is clearly supported by the presence of an intense molecular ion peak in the mass spectra. Since peaks due to the elimination of ArN₂,^{24,25} a characteristic feature of the azo tautomer, were not observed in the mass spectra indicates the existence of the compounds in the hydrazone form. Other important peaks resulted from 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 [CuL₂] stoichiometry. Peaks correspond-

ing to the elimination of CH_3CO , RCO , dicarbonyl moieties *etc.* from the molecular ion were also present in the spectra. The spectra of all the chelates possess a number of fragments containing copper in the natural 3:1 abundance of the ^{63}Cu and ^{65}Cu isotopes (Table IV).

TABLE IV. Mass spectral data of Hnaa, Hnma, Hnan and their Cu(II) complexes (abbreviations as in Table I)

Compound	<i>m/z</i>
Hnaa	254, 211, 168, 142, 127
Hnma	270, 227, 211, 168, 142, 127
Hnan	331, 288, 211, 168, 142, 127
[Cu(naa) ₂]	571, 569, 528, 526, 485, 483, 442, 440, 429, 427, 399, 397, 386, 384, 318, 316, 287, 285, 254, 244, 242, 211, 201, 199, 142
[Cu(nma) ₂]	603, 601, 560, 558, 517, 515, 544, 542, 485, 483, 461, 459, 442, 440, 402, 400, 399, 397, 343, 341, 334, 332, 319, 317, 270, 168, 142
[Cu(nan) ₂]	725, 723, 682, 680, 639, 637, 633, 631, 605, 603, 583, 581, 497, 495, 485, 483, 441, 439, 395, 393, 355, 353, 343, 341, 331, 288, 168, 127, 120

Electronic spectra. The UV spectra of Hnaa and Hnma show two absorption maxima at ≈ 380 nm and ≈ 250 nm due to various $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. In the spectra of the complexes, these absorption maxima were shifted to appreciably lower wave numbers. The Cu(II) complexes had a broad visible band with a maximum at ≈ 15000 cm^{-1} . This fact, together with the μ_{eff} values (1.75–1.80 μ_{B}) were ascribed to the square-planar geometry of the complexes. The observed diamagnetism and the broad medium-intensity band at ≈ 17600 cm^{-1} in the spectra of the Ni(II) chelates also suggested their square-planar geometry. Moreover, the spectra of the chelates in pyridine solution (10^{-3} mol/L) showed three bands corresponding to a configurational change to octahedral due to the association of pyridine.²⁶

Characterization of Hnan and its complexes

IR Spectra. The IR spectrum of Hnan in the 1650 – 1800 cm^{-1} region had no band assignable to free carbonyl groups. However, there were two strong bands at 1645 and 1635 cm^{-1} due to the stretching of intramolecularly hydrogen bonded anilide and acetyl carbonyl groups, respectively.^{13,14} There was also a medium intensity band at 1620 cm^{-1} , assignable to the C=N stretching vibration.^{18,19} The broad band in the range 2500 – 3200 cm^{-1} indicates the existence of strong intramolecular hydrogen bonding in the compound, as shown in Fig. 3. In the spectra of all the complexes, the acetyl carbonyl and C=N bands remained almost unaffected, indicating that they were not involved in the coordination. However, the band due to the hydrogen bonded anilide carbonyl at 1645 cm^{-1}

disappeared and instead a new strong band appeared at $\approx 1560\text{ cm}^{-1}$, assignable to the stretching of a metal bonded carbonyl group. The spectra showed several medium intensity bands in the range $1580\text{--}1600\text{ cm}^{-1}$ due to various C=C vibrations. As in the spectrum of the ligand, the complexes showed a band at 3380 cm^{-1} due to the NH group of the anilide moiety in their structure. A prominent band present at 1528 cm^{-1} in the spectrum of the ligand due to the hydrazone $\nu(\text{N-H})$ vibration was absent in the spectra of all the complexes. These indicate that the hydrazone NH proton had been replaced by the metal ion, while the anilide NH proton remained unchanged. It is evident that the hydrazone nitrogen and the intramolecularly hydrogen bonded carbonyl oxygen were involved in the complexation from the appearance of two additional medium intensity bands at ≈ 420 and $\approx 550\text{ cm}^{-1}$, assignable to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ vibrations,²⁰ in the spectra of the complexes. Important bands found in the spectra are given in Table II.

¹H-NMR Spectra. The ¹H-NMR spectrum of Hnan is characterized by the presence of two low field signals corresponding to one proton at δ 15.85 and 11.78 ppm due to intramolecularly hydrogen bonded hydrazone and anilide NH protons.^{21,22} The integrated intensities of all the signals are in accordance with the compound presentation in Fig. 3. In the ¹H-NMR spectra of the diamagnetic Ni(II) and Zn(II) complexes, the low field signal due to the chelated hydrazone proton disappeared while the anilide proton remained unchanged, indicating the replacement of the hydrazone proton with a metal ion during coordination, whereas the anilide NH was excluded from the coordination.²³ The position of the methyl proton signals indicates that the acetyl carbonyl does not participate in coordination. The integrated intensities of all other protons are in agreement with the presentation in Fig. 4 (Table III).

Mass spectra. The structure of the compound shown in Fig. 3 is clearly supported by the presence of an intense molecular ion peak at m/z 331 in the mass spectrum. Since the peak due to the elimination of ArN_2 ,^{24,25} a characteristic feature of the azo tautomer, was not observed in the mass spectrum; thus the existence of the compound in the hydrazone form was assumed. The other important peaks found were due to the elimination of CH_3CO , $\text{C}_6\text{H}_5\text{NHCO}$, etc. from the molecular ion or subsequent fragments. The FAB mass spectrum of the Cu(II) complex showed the molecular ion peak of appreciable intensity corresponding to $[\text{CuL}_2]$ stoichiometry. Peaks corresponding to the elimination of CH_3CO , $\text{C}_6\text{H}_5\text{NHCO}$, dicarbonyl moieties, etc. from the molecular ion are also present in the spectrum. The spectrum of the chelate had a number of fragments containing copper in the 3:1 natural abundance of ⁶³Cu and ⁶⁵Cu isotopes (Table IV).

Electronic spectra. The UV spectrum of Hnan showed two absorption maxima at 370 and 260 nm due to the various $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions. In the complexes, these maxima were shifted to appreciably lower wave numbers. The Cu(II) complex showed a broad visible band, with a maximum at 14850 cm^{-1} .

This, together with the μ_{eff} value (1.77 μ_{B}), suggests a square-planar geometry. The observed diamagnetism and broad medium-intensity band at 17,650 cm^{-1} in the spectrum of the Ni(II) chelate suggested square-planar geometry. In addition, the spectrum of the chelate in pyridine solution (10^{-3} mol/dm³) showed three bands, corresponding to a configurational change to octahedral due to the association of pyridine.²⁶ The three well-separated absorption maxima at 8230, 13570 and 24360 cm^{-1} corresponded to the transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}$; ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{F})$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{P})$, respectively.

CONCLUSIONS

A new series of bidentate ligands were prepared by the coupling of diazotized 1-aminonaphthalene with acetylacetone, methylacetoacetate and acetoacetanilide (HL). The analytical, IR, ¹H-NMR and mass spectral data revealed a 1:1 product in which one of the carbonyl group of the dicarbonyl compound was involved in intramolecular hydrogen bonding with the hydrazone hydrogen. The analytical, physical and spectral data of their [ML₂] complexes with Cu(II), Ni(II) and Zn(II) showed monobasic bidentate N,O coordination involving one of the hydrazone nitrogen atoms and the carbonyl oxygen. In the metal complexes of the naphthylazo derivatives of acetylacetone and methylacetoacetate, the acetyl carbonyl was involved in the coordination, whereas in the chelates of the naphthylazo derivative of acetoacetanilide, the anilide carbonyl was bonded with the metal ion.

ИЗВОД

1-НАФТИЛАЗО ДЕРИВАТИ НЕКИХ 1,3-ДИКАРБОНИЛНИХ ЈЕДИЊЕЊА И ЊИХОВИ Cu(II), Ni(II) И Zn(II) КОМПЛЕКСИ

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Купловањем диазотованог 1-аминонафталена са 1,3-дикарбонилним једињењима (ацетилацетоном, метилацетоацетатом и ацетоацетанилидом) добијена је нова серија бидентатних лиганата (HL). Аналитички, IR, ¹H-NMR и масени спектрални подаци указују да једињења постоје у интрамолекуларски водонично-везаном кето-хидразонском облику. Ови потенцијално монобазни бидентатни лиганди са Ni(II), Cu(II) и Zn(II) граде [ML₂] тип комплекса. IR, ¹H-NMR и масени спектрални подаци комплекса су у складу са заменом хелатног хидразонског протона металним јоном, при чему настаје стабилан шесточлани хелатни прстен који укључује хидразонски азот и водонично везан карбонилни кисеоник. Хелати Ni(II) и Zn(II) су дијамагнетични, док су Cu(II) комплекси парамагнетични. У металним комплексима нафтилазо деривата ацетилацетона и метилацетоацетата, ацетил карбонил је укључен у координацију, док је у хелатима нафтилазо деривата ацетоацетанилида анилидни карбонил везан за метални јон.

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