

## Metal complexes of Schiff's bases derived from 3-(arylozo)-2,4-pentanediones with 2-aminophenol and 2-aminothiophenol

K. KRISHNANKUTTY<sup>1\*</sup>, P. SAYUDEV<sup>2</sup> and MUHAMMED BASHEER UMMATHUR<sup>3</sup>

<sup>1</sup>Department of Chemistry, University of Calicut, Kerala–673635, <sup>2</sup>Department of Chemistry, NSS College, Manjeri, Kerala–676122 and <sup>3</sup>Department of Chemistry, Unity Women's College, Manjeri, Kerala–676122, India

(Received 8 February 2007)

**Abstract:** Phenylazo- and thiazolylazo-2,4-pentanediones on reaction with 2-aminophenol and 2-aminothiophenol yielded a new series of polydentate Schiff's base ligands. The structure and tautomeric nature of these compounds and their metal complexes were established on the basis of their IR, <sup>1</sup>H-NMR and mass spectral data. The spectral and analytical data revealed the condensation of both carbonyl groups of 3-(2-thiazolylazo)-2,4-pentanedione with 2-aminophenol to form an N<sub>2</sub>O<sub>2</sub> tetradentate ligand. Details on the formation of its [ML] complexes with Ni(II), Cu(II) and Zn(II) and the nature of their bonding are discussed based on analytical, IR, <sup>1</sup>H-NMR and mass spectral data.

**Keywords:** 3-(arylozo)-2,4-pentanediones, Schiff's bases, metal complexes, IR spectra, <sup>1</sup>H-NMR spectra, mass spectra.

### INTRODUCTION

Design and synthesis of polydentate Schiff's bases and their metal complexes having novel structural features and unusual physico-chemical properties have considerable importance in biological processes and constitute an active area of research in modern coordination chemistry.<sup>1</sup> In this context Schiff's bases of 1,3-diketones have been extensively studied.<sup>2</sup> However little attention has been paid to Schiff's bases derived from arylazo derivatives of 1,3-diketones in which two nitrogen donor sites are additionally present. Besides having wide application as yellow dyes and pigments,<sup>3</sup> arylazo-1,3-diketones have been widely used as intermediates in the preparation of a large number of biologically important heterocyclic compounds and as precursors of potential anti-diabetic drugs.<sup>4</sup> As part of our investigation on arylazo derivatives of 1,3-diketones,<sup>5,6</sup> the synthesis and characterization of four Schiff's bases from phenylazo- and thiazolylazo- derivatives of acetylacetone and aromatic amines are reported. Typical metal complexes of these ligand systems were also studied.

\* Corresponding author. E-mail: mbummathur@rediffmail.com  
doi: 10.2298/JSC0711075K

## EXPERIMENTAL

*Methods and instruments*

Carbon, hydrogen and nitrogen percentages were determined by micro analyses (Heraeus Elemental analyzer) and the metal contents by AAS (Perkin Elmer 2380). The electronic spectra of the compounds were recorded in methanol solution ( $10^{-4}$  M) on a 1601 Shimadzu UV-Vis spectrophotometer; the IR spectra (KBr discs) on a 8101 Shimadzu FTIR spectrophotometer; the  $^1\text{H-NMR}$  spectra ( $\text{CDCl}_3$  or  $\text{DMSO-}d_6$ ) on a Varian 300 NMR spectrometer; the ESR spectra (X-band) at 77 K using a Varian E 112 ESR 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 at  $28 \pm 1$  °C using a solution of about  $10^{-3}$  M concentration. The magnetic susceptibilities were determined at room temperature on a Guoy-type magnetic balance.

*Synthesis of Schiff's bases derived from 3-(phenylazo)acetylacetone*

The phenylazo derivative of acetylacetone was prepared as previously reported.<sup>5</sup> Condensation of the compound with 2-aminophenol and 2-aminothiophenol yielded the Schiff's bases  $\text{H}_2\text{pap}$  and  $\text{H}_2\text{pat}$ , respectively. The synthetic details are given below.

*Synthesis of  $\text{H}_2\text{pap}$* 

An ethanolic solution of 2-aminophenol (1.09 g, 0.01 mol, 20 ml) was added to an ethanolic solution of 3-(phenylazo)acetylacetone (2.04 g, 0.01 mol, 20 ml). The mixture was refluxed on a boiling water bath for  $\approx 5$  h and kept over night. The solution was then poured into hot water ( $\approx 70$  °C) under vigorous stirring. The precipitated compound was filtered, washed with hot water and recrystallized twice from hot methanol to obtain the chromatographically (tlc) pure compound.

*Synthesis of  $\text{H}_2\text{pat}$* 

An ethanolic solution of 2-aminothiophenol (1.25 g, 0.01 mol, 20 ml) was added to an ethanolic solution of 3-(phenylazo)acetylacetone (2.04 g, 0.01 mol, 20 ml). The mixture was refluxed on a boiling water bath for  $\approx 4$  h and then the volume was reduced. After cooling to room temperature, the precipitated compound was filtered, washed with an excess water and recrystallized from hot methanol to obtain the chromatographically (tlc) pure compound.

*Synthesis of Schiff's bases derived from 3-(2-thiazolylazo)acetylacetone*

Thiazolylazo derivative of acetylacetone was prepared as reported.<sup>7</sup> Condensation of the compound with 2-aminophenol and 2-aminothiophenol yielded the Schiff's bases  $\text{H}_2\text{tap}$  and  $\text{H}_2\text{tat}$ . Synthetic details are given below.

*Synthesis of  $\text{H}_2\text{tap}$* 

An ethanolic solution of 2-aminophenol (1.09 g, 0.01 mol, 20 ml) was added to an ethanolic solution of 3-(2-thiazolylazo)acetylacetone (2.11 g, 0.01 mol, 20 ml) and refluxed on a boiling water bath for  $\approx 8$  h. The volume was reduced and the mixture poured onto crushed ice under vigorous stirring. The formed precipitate was filtered and recrystallized twice from hot methanol to obtain the chromatographically (tlc) pure compound.

*Synthesis of  $\text{H}_2\text{tat}$* 

To an ethanolic solution of 3-(2-thiazolylazo)acetylacetone (2.11 g, 0.01 mol, 20 ml) was added dropwise an ethanolic solution of 2-aminothiophenol (1.25 g, 0.01 mol, 20 ml). The solution was stirred for  $\approx 9$  h in a closed flask, whereby the temperature was maintained between 50 and 55 °C. The formed crystalline product was filtered and recrystallized from hot methanol to obtain the chromatographically (tlc) pure compound.

*Synthesis of metal complexes of  $\text{H}_2\text{pap}$ ,  $\text{H}_2\text{pat}$ ,  $\text{H}_2\text{tap}$  and  $\text{H}_2\text{tat}$* 

A concentrated aqueous solution of metal(II) acetate (0.001 mol, 15 ml) was added to an ethanolic solution of the ligand (0.001 mol, 20 ml) and the mixture was refluxed for  $\approx 4$  h on a boiling

water bath. The solution was kept overnight. The precipitated complex was filtered, washed with water, then with methanol, recrystallized from hot ethanol and dried under vacuum.

## RESULTS AND DISCUSSION

The analytical, IR,  $^1\text{H-NMR}$  and mass spectral data (Tables I and II) of the reaction products of 3-(aryloxy)acetylacetone with the aromatic amines suggest that the condensation occurred in a 1:1 ratio, except for 3-(2-thiazolylazo)acetylacetone with 2-aminophenol where a 1:2 condensation product was formed. The analytical data (Table III), together with the non-electrolytic nature in DMF (specific conductance  $< 10 \Omega^{-1}\text{cm}^{-1}$ ;  $10^{-3}$  M solution) suggest 1:1 metal ligand stoichiometry of the complexes. The Ni(II) and Zn(II) chelates are diamagnetic while the Cu(II) complexes showed a normal paramagnetic moment. The IR,  $^1\text{H-NMR}$  and mass spectral data of the Schiff's bases,  $\text{H}_2\text{pap}$ ,  $\text{H}_2\text{pat}$  and  $\text{H}_2\text{tat}$ , are in conformity with Fig. 1 and their complexes with Fig. 2. The analytical (Table V) and spectral data of  $\text{H}_2\text{tap}$  are in agreement with Fig. 3 and of its complexes with Fig. 4. These data of the compounds are discussed separately.

TABLE I. Analytical, IR and  $^1\text{H-NMR}$  spectral data of  $\text{H}_2\text{pap}$ ,  $\text{H}_2\text{pat}$  and  $\text{H}_2\text{tat}$ 

Compound	M.p. °C	Yield %	Found (Calcd.), %			$\nu / \text{cm}^{-1}$			$\delta / \text{ppm}$		
			C	H	N	C=O	C=N	C=C	NH	OH/SH	$\text{CH}_3$
$\text{H}_2\text{pap}$ $\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2$	72	76	69.00 (69.15)	5.64 (5.76)	14.20 (14.24)	1678	1624, 1618	1591, 1588, 1584, 1580	14.45 (1H)	10.80 (1H)	2.32 (3H), 2.58 (3H)
$\text{H}_2\text{pat}$ $\text{C}_{17}\text{H}_{17}\text{N}_3\text{SO}$	62	70	65.42 (65.60)	5.44 (5.47)	13.43 (13.50)	1672	1622, 1612	1592, 1586, 1582	14.20 (1H)	6.20 (1H)	2.36 (3H), 2.68 (3H)
$\text{H}_2\text{tat}$ $\text{C}_{13}\text{H}_{14}\text{N}_4\text{S}_2\text{O}$	130	74	50.84 (50.98)	4.52 (4.58)	18.33 (18.30)	1670	1630, 1618, 1612	1596, 1590, 1586, 1580	13.25 (1H)	5.85 (1H)	2.38 (3H), 2.72 (3H)

TABLE II. Mass spectral data of  $\text{H}_2\text{pap}$ ,  $\text{H}_2\text{pat}$ ,  $\text{H}_2\text{tat}$  and their Cu(II) complexes

Compound	$m/z$
$\text{H}_2\text{pap}$	295, 252, 218, 203, 202, 175, 160, 125, 93, 92, 77
$\text{H}_2\text{pat}$	311, 268, 248, 234, 219, 202, 191, 176, 125, 109, 92, 77
$\text{H}_2\text{tat}$	306, 263, 229, 222, 215, 207, 197, 186, 154, 109, 99, 91, 84, 77
$[\text{Cu}(\text{pap})(\text{H}_2\text{O})]$	376, 374, 333, 331, 299, 297, 282, 280, 252, 218, 202, 160, 92, 77
$[\text{Cu}(\text{pat})(\text{H}_2\text{O})]$	392, 390, 349, 347, 377, 375, 315, 313, 299, 268, 248, 219, 191, 176, 109, 92, 77
$[\text{Cu}(\text{tat})(\text{H}_2\text{O})]$	387, 385, 344, 342, 308, 303, 301, 294, 276, 260, 258, 229, 222, 207, 154, 109, 91, 84

*Characterization of  $\text{H}_2\text{pap}$ ,  $\text{H}_2\text{pat}$ ,  $\text{H}_2\text{tat}$  and their metal complexes*

*Infrared spectra.* The IR spectra of  $\text{H}_2\text{pap}$ ,  $\text{H}_2\text{pat}$  and  $\text{H}_2\text{tat}$  show strong bands at  $\approx 1670 \text{ cm}^{-1}$  and  $\approx 1625 \text{ cm}^{-1}$  due to  $\nu(\text{C=O})$  and  $\nu(\text{C=N})$  vibrations, respecti-

vely.<sup>8</sup> The thiazole C=N of H<sub>2</sub>tat is observed at 1612 cm<sup>-1</sup>. The  $\nu(\text{C}=\text{C})$  vibrations of the aromatic rings are observed as several medium intensity bands in the 1580–1600 cm<sup>-1</sup> region (Table I).<sup>9</sup> The broad band observed in the 2500–3500 cm<sup>-1</sup> region is due to the intramolecularly hydrogen-bonded N–H proton. A slightly broadened medium intensity band which appeared at  $\approx 2425$  cm<sup>-1</sup> in the spectra of H<sub>2</sub>pat and H<sub>2</sub>tat can be assigned to  $\nu(\text{S}-\text{H})$ .

TABLE III. Physical and analytical data of the metal complexes of H<sub>2</sub>pap, H<sub>2</sub>pat and H<sub>2</sub>tat

Complex	Yield %	M.p. °C	Found (Calcd.), %			
			C	H	N	M
[Ni(pap)(H <sub>2</sub> O)], C <sub>17</sub> H <sub>17</sub> N <sub>3</sub> NiO <sub>3</sub>	70	298	55.34 (55.18)	4.76 (4.60)	11.58 (11.36)	15.96 (15.88)
[Ni(pat)(H <sub>2</sub> O)], C <sub>17</sub> H <sub>17</sub> N <sub>3</sub> NiSO <sub>2</sub>	65	286	53.00 (52.90)	4.40 (4.41)	10.72 (10.89)	15.36 (15.22)
[Ni(tat)(H <sub>2</sub> O)], C <sub>13</sub> H <sub>14</sub> N <sub>4</sub> NiS <sub>2</sub> O <sub>2</sub>	72	293	44.00 (40.98)	3.71 (3.68)	14.80 (14.71)	15.58 (15.42)
[Cu(pap)(H <sub>2</sub> O)], C <sub>17</sub> H <sub>17</sub> CuN <sub>3</sub> O <sub>3</sub>	76	296	54.56 (54.47)	4.66 (4.54)	11.37 (11.21)	16.80 (16.96)
[Cu(pat)(H <sub>2</sub> O)], C <sub>17</sub> H <sub>17</sub> CuN <sub>3</sub> SO <sub>2</sub>	74	288	52.12 (52.24)	4.30 (4.35)	10.60 (10.75)	16.32 (16.27)
[Cu(tat)(H <sub>2</sub> O)], C <sub>13</sub> H <sub>14</sub> CuN <sub>4</sub> S <sub>2</sub> O <sub>2</sub>	68	284	40.45 (40.46)	3.70 (3.63)	14.42 (14.53)	16.50 (16.48)
[Zn(pap)(H <sub>2</sub> O)], C <sub>17</sub> H <sub>17</sub> N <sub>3</sub> O <sub>3</sub> Zn	72	244	54.30 (54.20)	4.66 (4.52)	11.28 (11.16)	17.59 (17.37)
[Zn(pat)(H <sub>2</sub> O)], C <sub>17</sub> H <sub>17</sub> N <sub>3</sub> SO <sub>2</sub> Zn	74	258	52.01 (51.99)	4.22 (4.33)	10.81 (10.70)	16.44 (16.66)
[Zn(tat)(H <sub>2</sub> O)], C <sub>13</sub> H <sub>14</sub> N <sub>4</sub> S <sub>2</sub> O <sub>2</sub> Zn	76	220	40.44 (40.27)	3.72 (3.61)	14.44 (14.46)	16.95 (16.88)

The acetyl carbonyl band of the ligand at  $\approx 1670$  cm<sup>-1</sup> remained almost unaffected in the spectra of all the complexes, indicating its non-involvement in the bonding with the metal ion. The bands at  $\approx 1625$  cm<sup>-1</sup>, due to  $\nu(\text{C}=\text{N})$ , shifted to a lower wave number and appeared as a new broad band at  $\approx 1600$  cm<sup>-1</sup> in the spectra of all the complexes.<sup>10</sup> The thiazole  $\nu(\text{C}=\text{N})$  of H<sub>2</sub>tat was only marginally affected, indicating the non-involvement of the thiazole nitrogen in the coordination. That the intramolecularly hydrogen-bonded O–H/S–H and N–H protons are replaced by the metal ion is confirmed by the disappearance of the broad free ligand band in the region 2500–3500 cm<sup>-1</sup>. Instead, several medium intensity bands assignable to various aliphatic and aromatic  $\nu(\text{C}-\text{H})$  vibrations appeared in this region. The spectra of all the complexes show additional medium intensity bands in the 420–450 cm<sup>-1</sup> and 520–550 cm<sup>-1</sup> regions, presumably due to  $\nu(\text{M}-\text{O})$  and  $\nu(\text{M}-\text{N})$  vibrations.<sup>11</sup> That the complexes contain coordinated water molecule is clearly indicated by the presence of a band at 3500 cm<sup>-1</sup> in the spectra. Thus, the observed IR spectra strongly suggest that the phenolic O–H/thiol sulphur, the imi-

no nitrogen and the hydrazone nitrogen are involved in coordination with the metal ion. Important bands which appeared in the spectra of the complexes are given in Table IV.

TABLE IV. IR spectral data ( $\text{cm}^{-1}$ ) of the metal complexes of H<sub>2</sub>pap, H<sub>2</sub>pat and H<sub>2</sub>tat

Complex	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
[Ni(pap)(H <sub>2</sub> O)]	1672	1601	1592, 1585	428, 437	532, 540
[Ni(pat)(H <sub>2</sub> O)]	1670	1602	1595, 1590	428, 438	522, 540
[Ni(tat)(H <sub>2</sub> O)]	1669	1604, 1610	1592, 1588	422, 442	532, 542
[Cu(pap)(H <sub>2</sub> O)]	1675	1603	1592, 1582	422, 440	530, 542
[Cu(pat)(H <sub>2</sub> O)]	1668	1598	1594, 1590	420, 438	528, 536
[Cu(tat)(H <sub>2</sub> O)]	1668	1601, 1612	1597, 1591	418, 430	528, 546
[Zn(pap)(H <sub>2</sub> O)]	1676	1604	1595, 1590	420, 432	522, 535
[Zn(pat)(H <sub>2</sub> O)]	1670	1597	1590, 1585	422, 432	530, 540
[Zn(tat)(H <sub>2</sub> O)]	1668	1600, 1611	1587, 1582	430, 446	520, 542

<sup>1</sup>H-NMR spectra. The <sup>1</sup>H-NMR spectra of H<sub>2</sub>pap, H<sub>2</sub>pat and H<sub>2</sub>tat show a low field one proton singlet at  $\delta = 14$  ppm due to the intramolecularly hydrogen-bonded hydrazone N–H proton.<sup>6,12</sup> The O–H and S–H proton signals are observed at  $\delta = 10.8$  ppm and  $\delta \approx 6$  ppm, respectively (Table I). The methyl proton signals are observed as two singlets at  $\delta \approx 2.3$  (3H) and 2.6 (3H) ppm. The absence of any signal due to the methine proton supports the hydrazone form of the compound. The aryl protons appeared in the  $\delta$  range 6.8–7.8 ppm as a complex multiplet. In the <sup>1</sup>H-NMR spectra of the diamagnetic Ni(II) and Zn(II) complexes, the low field signals due to the N–H and O–H/S–H protons disappeared, indicating that these protons are replaced by the metal ion.<sup>5</sup> The methyl and aryl proton signals are slightly low field shifted and the integrated intensities of these signals agree well with the formulation of the complexes.

Mass spectra. The mass spectra of the compounds show an intense molecular ion peak. Peaks due to the elimination of CH<sub>3</sub>CO, ArNH, C<sub>6</sub>H<sub>5</sub>O/C<sub>6</sub>H<sub>5</sub>S, C<sub>6</sub>H<sub>5</sub>/thiazole, etc., from the molecular ion are present in the spectra.<sup>5,13</sup> The FAB mass spectra of the Cu(II) complexes showed molecular ion peaks corresponding to [CuL(H<sub>2</sub>O)] stoichiometry. Peaks due to the elimination of CH<sub>3</sub>CO, ArNH, C<sub>6</sub>H<sub>5</sub>O/C<sub>6</sub>H<sub>5</sub>S, etc., from P<sup>+</sup> also appeared in the spectra. The spectra of all the chelates contain a number of fragments containing copper in the natural 3:1 abundance of <sup>63</sup>Cu and <sup>65</sup>Cu isotopes (Table II).

Electronic spectra. The UV spectra of the compounds show two broad bands with maxima at  $\approx 380$  nm and  $\approx 250$  nm due to the various  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions. In the complexes, these absorption maxima shifted appreciably to lower wave numbers. The Cu(II) complexes showed a broad visible band,  $\lambda_{\text{max}}$  at  $\approx 15,000$   $\text{cm}^{-1}$ . This, together with the measured  $\mu_{\text{eff}}$  values ( $\approx 1.72 \mu_{\text{B}}$ ) suggests square-planar geometry.<sup>14</sup> The observed diamagnetism and broad medium-intensity

band at  $\approx 17,600 \text{ cm}^{-1}$  in the spectra of the Ni(II) chelates suggest their square-planar geometry.

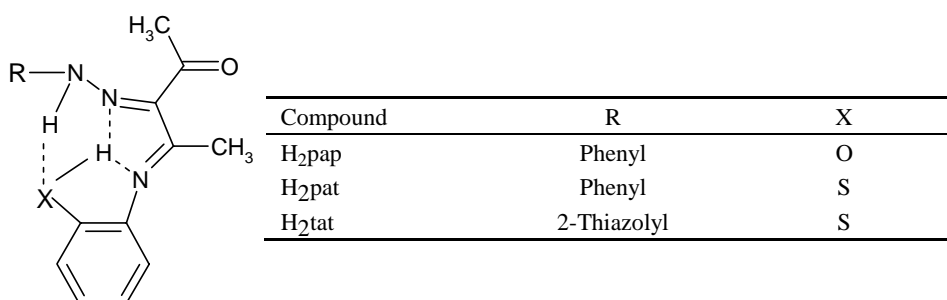


Fig. 1. Structure of H<sub>2</sub>pap, H<sub>2</sub>pat and H<sub>2</sub>tat.

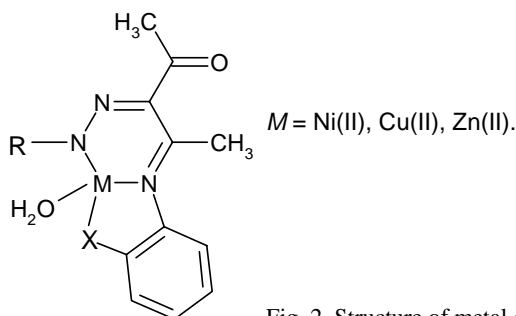


Fig. 2. Structure of metal complexes of H<sub>2</sub>pap, H<sub>2</sub>pat and H<sub>2</sub>tat.

#### Characterization of H<sub>2</sub>tap and its metal complexes

**Infrared spectra.** That both the carbonyl groups of 3-(2-thiazolylazo)acetylacetone are involved in the Schiff's base condensation with 2-aminophenol is clearly indicated in the IR spectrum of H<sub>2</sub>tap. Thus, the spectrum of the compound in the region  $1600\text{--}1800 \text{ cm}^{-1}$  showed no band assignable to a free acetyl carbonyl. However, the spectrum displayed three medium intensity bands at  $1605 \text{ cm}^{-1}$ ,  $1615 \text{ cm}^{-1}$  and  $1625 \text{ cm}^{-1}$ , assignable, respectively, to the stretching of the hydrazone C=N, CH<sub>3</sub>-C=N and the thiazole ring C=N. The broad band observed in the  $2500\text{--}3800 \text{ cm}^{-1}$  region suggest the involvement of the OH function in strong hydrogen bonding with the C=N group. In the IR spectra of all the complexes, the  $\nu(\text{C}=\text{N})$  bands are shifted appreciably to low wave numbers, indicating the involvement of these groups in bonding with the metal ion. The thiazole  $\nu(\text{C}=\text{N})$  is only marginally affected, indicating the non-involvement of the thiazole nitrogen in coordination. The bending mode of the hydrazone N-H remained almost unaffected in the spectra of complexes, indicating its non-involvement in complexation. The broad free ligand band in the region  $2500\text{--}3800 \text{ cm}^{-1}$  almost vanished in the spectra of complexes and instead several weak and medium intensity bands appeared in this region, assignable to  $\nu(\text{N-H})$  and various  $\nu(\text{C-H})$  vi-

brations. That the imino nitrogens and the phenolic oxygens are involved in complexation with the metal ion is clearly evident from the appearance of new medium intensity bands at  $\approx 425 \text{ cm}^{-1}$  and  $\approx 530 \text{ cm}^{-1}$ , assignable to  $\nu(\text{M-O})$  and  $\nu(\text{M-N})$  in the spectra.<sup>11</sup> Important bands that appeared in the spectra are given in Table V.

<sup>1</sup>H-NMR spectra. The <sup>1</sup>H-NMR spectrum of the compound displayed a slightly broadened, two proton signal at  $\delta = 12.18$  ppm and a one proton signal at  $\delta = 13.5$  ppm, due to intramolecularly hydrogen bonded phenolic groups and the hydrazone N-H proton, respectively.<sup>5,6</sup> The spectrum of the compound also displayed two three proton signals at  $\delta = 2.35$  ppm and  $\delta = 2.58$  ppm due to two methyl groups. The aryl proton signals are observed in the  $\delta 6.68$ – $7.90$  region. In the <sup>1</sup>H-NMR spectra of the diamagnetic Ni(II) and Zn(II) complexes, the signals due to the phenolic proton of the free ligand disappeared, while the hydrazone proton signal remained almost unaltered, indicating that only the phenolic hydrogens are replaced by metal ion and the hydrazone N-H proton remained as such.

Table V. Analytical, IR and <sup>1</sup>H-NMR spectral data of H<sub>2</sub>tap and its metal complexes

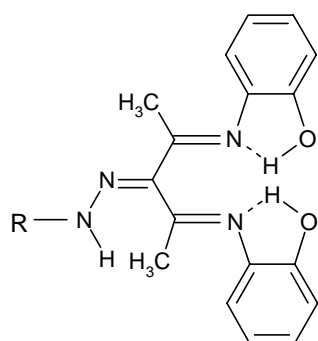
Compound	M.p. Yield		Found (Calcd.), %				$\nu / \text{cm}^{-1}$			$\delta / \text{ppm}$		
	°C	%	C	H	N	M	C=N	M-O	M-N	NH	OH	CH <sub>3</sub>
H <sub>2</sub> tap	125	60	58.74	5.08	18.68	–	1625,	–	–	13.50	12.18	2.35
C <sub>18</sub> H <sub>19</sub> N <sub>5</sub> SO <sub>2</sub>			(58.54)	(5.15)	(18.97)		1615,			(1H)	(2H)	(3H),
							1605					2.58
												(3H)
[Ni(tap)]	298	76	50.94	3.92	16.23	13.94	1622	432,	550,	13.46	–	2.33
C <sub>18</sub> H <sub>17</sub> N <sub>5</sub> NiSO <sub>2</sub>			(50.74)	(3.99)	(16.44)	(13.79)	1602	420	538	(1H)		(3H),
							1560					2.56
												(3H)
[Cu(tap)]	290	72	50.20	3.85	16.18	14.82	1620	422,	555,	–	–	–
C <sub>18</sub> H <sub>17</sub> CuN <sub>5</sub> SO <sub>2</sub>			(50.17)	(3.95)	(16.26)	(14.76)	1600	415	540			
							1565					
[Zn(tap)]	224	68	50.00	3.83	16.14	15.00	1622	428,	545,	13.48	–	2.34
C <sub>18</sub> H <sub>17</sub> N <sub>5</sub> SO <sub>2</sub> Zn			(49.96)	(3.93)	(16.19)	(15.12)	1600	418	530	(1H)		(3H),
							1570					2.59
												(3H)

*Mass spectra.* The formation of the compound is well confirmed from the presence of an intense P<sup>+</sup> peak at  $m/z$  369 in its mass spectrum. Fragments corresponding to the elimination of C<sub>3</sub>H<sub>2</sub>NS, C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>, C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>S and C<sub>6</sub>H<sub>5</sub>O from the parent ion were present in the spectrum (Table VI). The mass spectrum of the Cu(II) complex clearly shows the presence of a molecular ion peak. Other important peaks appearing in the spectrum are due to the elimination of thiazole, tz-NH, etc., from the molecular ion (Table VI).

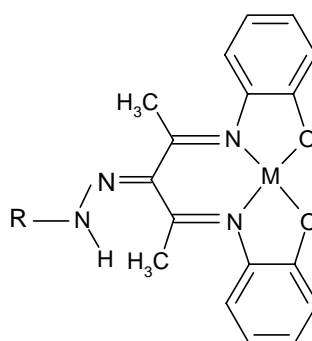
TABLE VI. Mass spectral data of H<sub>2</sub>tap and its Cu(II) complex

Compound	$m/z$
H <sub>2</sub> tap	369, 302, 285, 276, 270, 256, 113, 99, 93, 84, 77
[Cu(tap)]	432, 430, 348, 346, 366, 364, 339, 337, 331, 319, 317, 303, 285, 256, 113, 93, 84

*Electronic spectra.* The UV spectrum of the compound show two broad bands with maxima at 370 nm and 245 nm due to  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions. In the complexes these absorption maxima shifted appreciably to lower wave numbers. The Cu(II) complex showed a broad visible band,  $\lambda_{\max}$  at  $15,000 \text{ cm}^{-1}$ . This, together with the measured  $\mu_{\text{eff}}$  value ( $1.74 \mu_B$ ) suggests square-planar geometry.<sup>14</sup> The observed diamagnetism and broad medium-intensity band at  $17,500 \text{ cm}^{-1}$  in the spectrum of the Ni(II) chelate suggest its square-planar geometry.



R = 2-Thiazolyl

Fig. 3. Structure of  $\text{H}_2\text{tap}$ .

M = Ni(II), Cu(II), Zn(II)

Fig. 4. Structure of the metal complexes of  $\text{H}_2\text{tap}$ .

*ESR Spectra.* The ESR spectra of the Cu(II) complexes were recorded at 77 K in DMF solution. The spectra gave four well-resolved peaks due to the hyperfine interaction of copper (Table VII), indicating considerable covalent character<sup>15</sup> for the metal–ligand bonds. The observed  $A$  values indicate that the odd electron density is less on [Cu(tap)] compared to the other three chelates. Hence the delocalization of the metal d-electrons is greater in [Cu(tap)] compared to the other three complexes.

TABLE VII. ESR parameters of the Cu(II) complexes in DMF at 77 K

Complex	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel} \times 10^{-4} / \text{cm}^{-1}$	$A_{\perp} \times 10^{-4} / \text{cm}^{-1}$
[Cu(pap)( $\text{H}_2\text{O}$ )]	2.172	2.052	210	25
[Cu(pat)( $\text{H}_2\text{O}$ )]	2.171	2.075	202	26
[Cu(tat)( $\text{H}_2\text{O}$ )]	2.182	2.068	198	28
[Cu(tap)]	2.160	2.065	183	38

#### CONCLUSIONS

Four new polydentate Schiff base ligands have been prepared by the condensation of 3-(phenylazo)- and 3-(2-thiazolylazo)-2,4-pentanediones with 2-aminophenol and 2-aminothiophenol. Analytical, IR,  $^1\text{H-NMR}$  and mass spectral data revealed a 1:2 product ( $\text{H}_2\text{tap}$ ) with 3-(2-thiazolylazo)-2,4-pentanedione and 2-aminothiophenol in which both carbonyl groups of the dione are involved in the Schiff base formation. In all other cases, 1:1 condensation products ( $\text{H}_2\text{pap}$ ,  $\text{H}_2\text{pat}$  and  $\text{H}_2\text{tat}$ ) are formed. The analytical, physical and spectral data of the [ML] com-



plexes of Ni(II), Cu(II) and Zn(II) showed dibasic tetradentate N<sub>2</sub>O<sub>2</sub> coordination involving the azomethine nitrogens and the phenolic oxygens of H<sub>2</sub>tap. All the other ligands functioned as dibasic tridentates where the imine and hydrazone nitrogens and the O–H/S–H groups are coordinated in their 1:1 metal chelates.

## ИЗВОД

## МЕТАЛНИ КОМПЛЕКСИ ШИФОВИХ БАЗА ДОБИЈЕНИ У РЕАКЦИЈИ 3-(АРИЛАЗО)-2,4-ПЕНТАНДИОНА СА 2-АМИНОФЕНОЛОМ И 2-АМИНОТИОФЕНОЛОМ

К. KRISHNANKUTTY<sup>1</sup>, П. SAYUDEV<sup>2</sup> и МУHAMMED BASHEER UMMATHUR<sup>3</sup>

<sup>1</sup>Department of Chemistry, University of Calicut, Kerala–673635, <sup>2</sup>Department of Chemistry, NSS College, Manjeri, Kerala–676122 и <sup>3</sup>Department of Chemistry, Unity Women's College, Manjeri, Kerala–676122, India

Фенилазо- и тиазолилазо-2,4-пентандиони у реакцији са 2-аминофенолом и 2-аминотиофенолом дају нову серију полидентатних лиганда који су Шифове базе. Структура и таутомерна природа ових једињења и њихових комплекса установљена је на основу њихових IR, <sup>1</sup>H-NMR и масених спектра. Спектрални и аналитички подаци указују на то да се N<sub>2</sub>O<sub>2</sub> тетрадентатни лиганди формирају кондензацијом обе карбонилне групе 3-(2-тиазолилазо)-2,4-пентандиона са 2-аминофенолом. Детаљи око формирања [ML] комплекса ових лиганда са Ni(II), Cu(II) and Zn(II), као и природа везе, дискутовани су на основу аналитичких, IR, <sup>1</sup>H-NMR и масених спектралних података.

(Примљено 8. фебруара 2007)

## REFERENCES

1. a) K. Sharma, A. Srivastava, S. Srivastava, *J. Serb. Chem. Soc.* **71** (2006) 917; b) V. E. Kuzmin, A. G. Artemenko, R. N. Lozytska, A. S. Fedtchouk, V. P. Lozitsky, E. N. Muratov, A. K. Mescheriakov, *SAR QSAR Environ. Res.* **16** (2005) 219; c) D. Kumar, A. Syamal, A. K. Singh, *Indian J. Chem.* **42A** (2003) 280
2. a) P. D. Benny, J. L. Green, H. P. Engelbrecht, C. L. Barnes, S. S. Jurisson, *Inorg. Chem.* **44** (2005) 2381; b) T. D. Thangadurai, K. Natarajan, *Synth. React. Inorg. Met.-Org. Chem.* **31** (2001) 549
3. K. Venkataraman, *Chemistry of Synthetic Dyes*, Vol. 5, Academic Press, New York, 1977
4. a) H. J. Garg, C. Prakash, *J. Pharm. Sci.* **60** (1971) 323; b) H. J. Garg, C. Prakash, *J. Org. Chem.* **35** (1970) 1056
5. a) K. Krishnankutty, J. Michael, *J. Coord. Chem.* **22** (1991) 327; b) K. Krishnankutty, J. Michael, *J. Coord. Chem.* **24** (1993) 259; c) K. Krishnankutty, J. Michael, *J. Coord. Chem.* **70** (1993) 238
6. a) K. Krishnankutty, P. Ummer, *J. Indian Chem. Soc.* **65** (1988) 213; b) K. Krishnankutty, P. Ummer, *J. Indian Chem. Soc.* **66** (1989) 194; c) N. Thankarajan, K. Krishnankutty, *Indian J. Chem.* **23A** (1984) 401
7. K. Krishnankutty, D. K. Babu, *J. Indian Chem. Soc.* **73** (1996) 379
8. P. Gilli, V. Bertolasi, V. Ferretti, G. Gilli, *J. Am. Chem. Soc.* **122** (2000) 1405
9. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Chapman and Hall, London, 1980
10. P. Viswanathamurthi, A. Geetha, R. Karvembu, K. Natarajan, *Indian J. Chem.* **44A1** (2005) 90
11. K. Nakamoto, *Infrared Spectra and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1997
12. D. C. Nonhebel, A. Mitchell, *Tetrahedron* **35** (1979) 2013

13. H. Budzikiewicz, C. Djerassi, D. H. Williams, *Mass Spectrometry of Organic Compounds*, Holden Day, San Francisco, 1967
14. K. C. Joshi, V. N. Pathak, *Coord. Chem. Rev.* **22** (1977) 37
15. a) H. R. Gersmann, G. D. Swalen, *J. Chem. Phys.* **36** (1962) 3221; b) A. H. Maki, B. R. Mc Garvey, *J. Chem. Phys.* **29** (1958) 31.