

## CHELATING BEHAVIOUR OF SOME AZO COMPOUNDS DERIVED FROM HETEROAROMATIC AMINES AND PYRAZOLIN-5-ONES

M. T. El-Haty, F. A. Adam and N.A. Abdalla

*Chemistry Department, Faculty of Science, Aswan, Egypt*

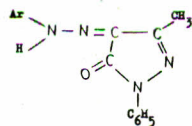
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The complexes of 3-pyridyl-5-hydroxy (HAP), thiazolyl (TAP) and benzthiazolyl (BAP) azo of 5-pyrazolones with some heavy metal ions have been prepared and investigated. The formation of 1:1 and 1:2 species were inferred from electronic spectra, conductivity measurements and pH-titrations. The probable structure of each compound and its metal chelates are examined based on X-ray, IR, NMR spectra. It is concluded that the (HAP) compound acts as tridentate, while (TAP) and (BAP) act as bidentate ligands. The bonding sites are the oxygen of C=O group and the nitrogen of aryl azo, all ligands and the complexes are existed in the azo-hydrazones structure.

*Key words:* Heterocyclic azopyrazolones chelates, Complexes, Derivatives.

### INTRODUCTION

The chelating behaviour of pyrazolin-5-ones has been extensively studied as complexing reagents [1-3]. These compounds can be coupled with aromatic diazonium salts to give hydrazo compound, which are more sensitive toward complexation. The structure of these complexes was interesting due to their tautomeric behaviour [4,5]. Little information has been reported in the chelating behaviour of azo compounds derived from heterocyclic amines and pyrazolone derivatives. It is of considerable interest to study the structural configurations of the compounds, 1-phenyl-3-methyl-4-(5-hydroxy-2-pyridylazo)-5-pyrazolone (HAP) 1-phenyl-3-methyl-4-(2-thiazolylazo)-5-pyrazolone (TAP) and 1-phenyl-3-methyl-4-(2-benzothiazolylazo)-5-pyrazolone (BAP) with the heavy metal ions Zr(IV), La(III), Y(III), and  $UO_2^{2+}$ . The structure of the complexing reagents are:



Ar = 3-pyridyl-5-hydroxy (HAP); = thiazolyl (TAP); = benzthiazolyl (BAP)

### EXPERIMENTAL

The materials used were of reagent grade. The complexes were prepared according to the recommended method [6]. The corresponding diazonium compound of heterocyclic amine was coupled to 1-phenyl-3-methyl-5-pyrazolone in aqueous-ethanol mixture solution, buffered

with sodium acetate. The crude compounds were crystallized from dioxane.

The metal chelates were generally prepared by dropwise addition of a cooled concentrated ethanolic solution of each azo-compound in slight excess over the stoichiometric 1:1 ratio to an ethanolic metal solution. The mixture was heated under reflux for ~ 1 hr with stirring. Then the mixture was concentrated to half volume and cooled. Solid complexes which precipitated were filtered, washed with ethanol and dried over  $P_2O_5$  in vacuo. The microanalytical, colour, m.p. and molar conductivity data are given in Table 1.

Conductance measurements were carried out in ethanol solution at 30° on a WPA, C.M 25 conductivity-meter, using an immersion cell. Ultra violet and visible spectra were measured with a Shimadzu-240 recording spectrophotometer, using 1 cm silica cell. X-ray diffraction patterns of single crystals of solid complexes were carried out using computer controlled X-ray Diano diffractometer with nickel filtered and copper radiation. The interplaner spacing and relative intensities values are calculated using Bragg's equation [7]. Infrared spectra of the solid compounds and their metal chelates were obtained on a Perkin-Elmer 599B IR spectrophotometer using KBr pellets of the samples. Nuclear magnetic resonance spectra ( $^1H$  nmr) were determined on a EM. 390-90 MHZ spectrometer. Chemical shifts values are reported in parts per million ( $\delta$ ) downfield from internal TMS.

### RESULTS AND DISCUSSION

(a) *Electronic spectra.* The absorption spectra of HAP, TAP and BAP compounds in ethanol comprise two bands

Table 1. Elemental analysis, colour, decomposition temperature and molar conductance ( $\Lambda_M$ ) of the azopyrazolones chelates.

Formula	% Calc. (Found)			Colour	Decomp.	
	C	H	N		Temp. °C	$\Lambda_M$
<i>Chelates of HAP ligand</i>						
[C <sub>15</sub> H <sub>13</sub> N <sub>5</sub> O <sub>2</sub> ZrCl <sub>3</sub> ·3H <sub>2</sub> O] Cl	30.9 (30.8)	3.3 (3.3)	12.0 (11.8)	Yellow	165	65.4
[(C <sub>15</sub> H <sub>13</sub> N <sub>5</sub> O <sub>2</sub> ) <sub>2</sub> ZrCl <sub>2</sub> ·H <sub>2</sub> O] Cl <sub>2</sub>	42.8 (42.7)	3.4 (3.2)	16.6 (16.8)	Orange	188	121.7
[C <sub>15</sub> H <sub>13</sub> N <sub>5</sub> O <sub>2</sub> LaNO <sub>3</sub> ·4H <sub>2</sub> O] (NO <sub>3</sub> ) <sub>2</sub>	26.0 (26.2)	3.1 (3.0)	16.2 (16.5)	Yellow	172	139.4
[(C <sub>15</sub> H <sub>13</sub> N <sub>5</sub> O <sub>2</sub> ) <sub>2</sub> LaNO <sub>3</sub> ·4H <sub>2</sub> O] (NO <sub>3</sub> ) <sub>2</sub>	36.5 (36.7)	3.5 (3.6)	18.4 (18.4)	Orange	180	171.9
[C <sub>15</sub> H <sub>12</sub> N <sub>5</sub> O <sub>2</sub> Y·H <sub>2</sub> O] Cl <sub>2</sub>	38.2 (38.0)	3.0 (2.8)	14.8 (14.7)	Yellow	176	166.0
C <sub>15</sub> H <sub>11</sub> N <sub>5</sub> O <sub>2</sub> UO <sub>2</sub> ·H <sub>2</sub> O	31.0 (31.1)	2.3 (2.5)	12.0 (12.2)	Red	266	21.3
[(C <sub>15</sub> H <sub>13</sub> N <sub>5</sub> O <sub>2</sub> ) <sub>2</sub> UO <sub>2</sub> ·4H <sub>2</sub> O] (NO <sub>3</sub> ) <sub>2</sub>	34.1 (34.0)	3.2 (3.0)	15.9 (16.0)	Brown	270	19.4
<i>Chelates of TAP ligand</i>						
[C <sub>13</sub> H <sub>11</sub> N <sub>5</sub> SOZrCl <sub>3</sub> ·H <sub>2</sub> O] Cl	29.1 (28.9)	2.4 (2.5)	13.0 (13.3)	Yellow	240	80.2
[(C <sub>13</sub> H <sub>11</sub> N <sub>5</sub> SO) <sub>2</sub> ZrCl <sub>2</sub> ·H <sub>2</sub> O] Cl <sub>2</sub>	38.0 (37.7)	2.9 (2.8)	17.0 (16.9)	Yellow-orange	198	117.8
[C <sub>13</sub> H <sub>11</sub> N <sub>5</sub> SOLaNO <sub>3</sub> ·4H <sub>2</sub> O] (NO <sub>3</sub> ) <sub>2</sub>	22.9 (23.0)	2.8 (3.1)	16.4 (16.5)	Yellow	182	126.4
[(C <sub>13</sub> H <sub>11</sub> N <sub>5</sub> SO) <sub>2</sub> LaNO <sub>3</sub> ·4H <sub>2</sub> O] (NO <sub>3</sub> ) <sub>2</sub>	32.3 (32.5)	3.1 (3.3)	18.8 (18.6)	Yellow	179	134.9
[C <sub>13</sub> H <sub>11</sub> N <sub>5</sub> SOYCl·4H <sub>2</sub> O] Cl <sub>2</sub>	28.3 (28.4)	3.5 (3.6)	12.7 (12.5)	Yellow	177	119.8
[(C <sub>13</sub> H <sub>11</sub> N <sub>5</sub> SO) <sub>2</sub> YCl·2H <sub>2</sub> O] Cl <sub>2</sub>	38.9 (39.0)	3.3 (3.5)	17.5 (17.7)	Yellow-orange	163	168.4
[C <sub>13</sub> H <sub>11</sub> N <sub>5</sub> SOUO <sub>2</sub> ] NO <sub>3</sub>	25.3 (25.3)	1.6 (1.8)	13.6 (13.5)	Brown	250	52.0
(C <sub>13</sub> H <sub>11</sub> N <sub>5</sub> SO) <sub>2</sub> UO <sub>2</sub>	37.2 (37.0)	2.4 (2.5)	16.7 (16.6)	Deep-brown	249	18.7
<i>Chelates of BAP ligand</i>						
[C <sub>17</sub> H <sub>12</sub> N <sub>5</sub> SOZrCl <sub>2</sub> ·H <sub>2</sub> O] Cl	37.1 (37.0)	2.6 (2.6)	12.7 (13.0)	Yellow	228	72.6
[(C <sub>17</sub> H <sub>11</sub> N <sub>5</sub> SO) <sub>2</sub> Zr·5H <sub>2</sub> O] Cl <sub>2</sub>	44.3 (44.5)	3.7 (3.9)	15.2 (15.1)	Orange	235	150.0
[C <sub>17</sub> H <sub>13</sub> N <sub>5</sub> SOLaNO <sub>3</sub> ·4H <sub>2</sub> O] (NO <sub>3</sub> ) <sub>2</sub>	27.9 (28.1)	2.9 (3.0)	15.3 (15.5)	Orange	246	124.8

(Continued.....)

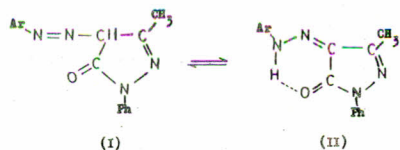
(Table 1, continued)

$[(C_{17}H_{13}N_5SO)_2 LaNO_3 \cdot 5H_2O] (NO_3)_2$	37.6 (38.0)	3.3 (3.2)	16.8 (17.0)	Yellow- orange	252	155.3
$[C_{17}H_{13}N_5SOYCl \cdot 5H_2O] Cl_2$	32.9 (32.8)	3.7 (3.8)	11.3 (11.1)	Orange	163	118.6
$[C_{17}H_{12}N_5SOUO_2 \cdot H_2O] NO_3$	29.8 (29.6)	2.1 (2.3)	12.3 (12.1)	Deep- yellow	258	57.0
$[(C_{17}H_{12}N_5SO)_2 UO_2 \cdot 4H_2O]$	40.4 (40.4)	3.2 (3.0)	13.9 (13.8)	Orange	268	18.5

Table 2. Electronic spectral data of the ligands and their metal chelates in ethanol ( $\lambda_{max}$ , (nm),  $\epsilon_{max}$ ,  $\times 10^{-3}$  ( $cm^2 mol^{-1}$ )).

	Ligand		Zr(IV)		La(III)		Y(III)		UO <sub>2</sub> <sup>2+</sup>	
	$\lambda_{max}$ .	$\epsilon_{max}$ .	$\lambda_{max}$ .	$\epsilon_{max}$ .	$\lambda_{max}$ .	$\epsilon_{max}$ .	$\lambda_{max}$ .	$\epsilon_{max}$ .	$\lambda_{max}$ .	$\epsilon_{max}$ .
HAP:	310	5.1	330	4.6	325	7.0	326	6.0	338	13.0
	380 sh	1.2	—	—	506	2.5	465	1.4	460	3.2
TAP:	309	4.5	330	7.6	314	19.4	316	21.2	340	19.0
	375 sh	1.0	458	2.3	476	6.6	470	3.6	368 sh	4.3
BAP:	300	4.2	300	7.8	315	8.4	318	9.0	338	5.7
	385 sh	1.4	452	1.6	492	2.0	480	1.4	474	1.8

(Table 2) at around 310 and 380 nm. It has been reported that the presence of high intensity bands at shorter wavelength is indicative of the azo-structure, while the presence of a weaker one at much longer wave-length supports the hydrazone form [8,9]. On this basis, the compounds HAP, TAP and BAP have the azo-hydrazone tautomeric equilibrium of the form I, II:



On complexation, the shorter wavelength band (310 nm) show a red shift due to its local II-II\* nature. The hydrazone band (380 nm) displays high red shifts, which can be ascribed to an easier intramolecular CT interaction in complexed ligands. The analytical data of the solid complexes (Table 1) confirm the presence of the above tautomeric structure in the complexed ligands.

The results of the molar conductance of the solid complexes in DMF solutions, indicates that with few exceptions, all complexes behave as 1:2 electrolytes (118.6-171.9 mhos  $cm^2 mol^{-1}$ ). While 1:1 Zr(IV) and UO<sub>2</sub> com-

plexes with TAP and BAP behave as 1:1 electrolytes (52.0-80.2 mhos  $cm^2 mol^{-1}$ ). The low values of the molar conductance of 1:2 UO<sub>2</sub> complexes of the three ligands and 1:1 UO<sub>2</sub>: HAP complex (18.5-21.3 mhos  $cm^2 mol^{-1}$ ) suggests they are non electrolytes [10].

(b) *Stoichiometry*. The composition of the formed complexes in ethanolic solution has been established spectrophotometrically by applying the molar ratio and modified Job's methods [11,12]. The blank used was of the same concentration of azo-compound as in the complex solution. The measured solution was left ~ 3 hrs before reading to attain equilibrium. Measurements were taken at  $\lambda_{max}$  of the formed complexes. The results are represented graphically Fig. 1 and 2. The curves are generally indicate the possible existence of 1:1 and 1:2 ( $M^{n+}:L$ ) complex types except in the case of Y(III): HAP, where 1:1 ratio complex is formed.

The pH-metric titration curves obtained for the metal ions with each ligand in ethanolic medium, show distinct inflections at 1:1 and 1:2 mole of metal ion per moles of ligand. This confirms the stepwise formation  $ML$  and  $ML_2$  species. However, the sharp decrease in the pH values of all UO<sub>2</sub> complexes, Y(III)-HAP and Zr(IV)-BAP complexes suggests the possible liberation of protons from the ligands

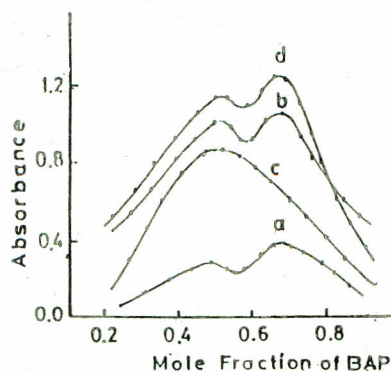


Fig. 1. Continuous variation method for BAP ligand - metal ion chelates.

- a - Zr(IV),  $\lambda = 452$  nm,  $[\text{Zr(IV)} + \text{BAP}] = 1.0 \times 10^{-3}$  M  
 b - La(III),  $\lambda = 490$  nm,  $[\text{La(III)} + \text{BAP}] = 1.5 \times 10^{-3}$  M  
 c - Y(III),  $\lambda = 480$  nm,  $[\text{Y(III)} + \text{BAP}] = 1.5 \times 10^{-3}$  M  
 d -  $\text{UO}_2^{2+}$ ,  $\lambda = 475$  nm,  $[\text{UO}_2^{2+} + \text{BAP}] = 1.8 \times 10^{-3}$  M

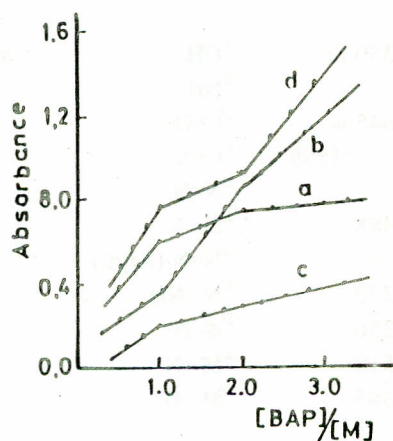


Fig. 2. Molar ratio method for BAP ligand - Metal ion chelates

- a - Zr(IV),  $\lambda = 450$  nm,  $[1 \times 10^{-3}$  M]  
 b - La(III),  $\lambda = 492$  nm,  $[6 \times 10^{-4}$  M]  
 c - Y(III),  $\lambda = 480$  nm,  $[4 \times 10^{-4}$  M]  
 d -  $\text{UO}_2^{2+}$ ,  $\lambda = 475$  nm,  $[6 \times 10^{-4}$  M]

during complexation which decreases the pH of the solution.

The above results are also confirmed by conductometric titration of 50 ml ( $1 \times 10^{-3}$  M) of each metal ion by  $1 \times 10^{-2}$  M ligand. The sharp increase of the titration curves of Y(III)-HA, Zr(IV)-BAP and  $\text{UO}_2$  complexes confirmed the liberation of hydrogen ions during complexation. These results are in accordance with the formulae suggested on the basis of analysis and molar conductances of the solid complexes (Table 1 and Fig. 3).

(c) *X-ray, IR and  $^1\text{H}$  NMR spectra.* The X-ray diffraction of the azopyrazolone compounds and their metal ions complexes carried out to give us some information on the crystal lattice properties of these complexes. The values

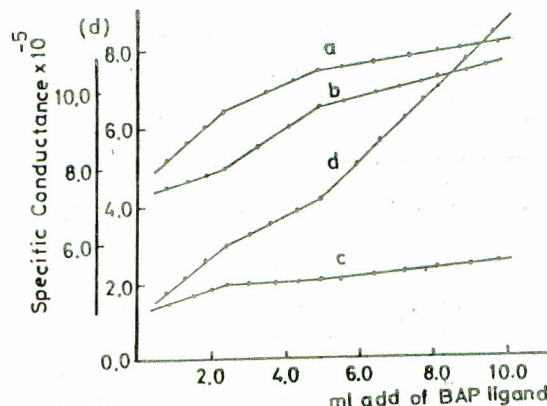


Fig. 3. Conductometric titration of 25 ml ( $1 \times 10^{-3}$  M) of: a-Zr(IV); b - La(III); c - Y(III); d -  $\text{UO}_2^{2+}$  with ( $1 \times 10^{-2}$  M) BAP ligand.

of the interplaner spacing (d) and relative intensity ( $I/I_0$ ) at various angle ( $\theta$ ) of the complexes show a large similarity indicate that the complexes under investigation have the same structure and chemical composition. The small change in (d) and ( $I/I_0$ ) values can be attributed to the change in the number of the coordinated water molecules around the central metal ions [13]. A small shifts in some ( $\theta$ ) values accompanied by enlargement of the line profile of the diffracted beam in some x-ray diffraction patterns of complexes, this can be explained on the principle that a strain occurred in the crystal lattice due to the different ionic radii of the metal ions forming the complex compounds [14].

Table 3 includes the important bands observed in the IR spectra of the studied ligands and their metal chelates. The coordinated water molecules is indicated by the broad band appearing at  $3380\text{-}3120$   $\text{cm}^{-1}$  and confirmed by the presence of a new band around  $980$   $\text{cm}^{-1}$  [15]. The medium band observed in the spectra of the free azopyrazolone compounds at  $1700\text{-}1682$   $\text{cm}^{-1}$  region suggested to the keto-form structure of the ligands. On complexation this  $\nu\text{C}=\text{O}$  band is shifted to lower energy side, this indicate that the carbonyl group is involved in the complex formation. The two bands located at  $\sim 1590$  and  $\sim 1560$   $\text{cm}^{-1}$  can be assigned to  $\nu\text{C}=\text{N}$  (ring) and  $\nu\text{N}=\text{N}$  groups stretching respectively [16,17]. The former band is not sensitive with complexation indicate that the ring heteropyrazolone nitrogen atom is not taking part in coordination. However, the changing of  $\nu\text{N}=\text{N}$  band confirming the involvement of the azo group in complexation. The  $\text{UO}_2$  complexes show a strong band at  $\sim 920$   $\text{cm}^{-1}$  which assigned to asymmetric frequency of O-U-O [18]. Moreover, the two newly developed bands appeared at  $510\text{-}410$   $\text{cm}^{-1}$  and  $365\text{-}310$   $\text{cm}^{-1}$

Table 3. Selected IR bands of the heteroazopyrazolones ligands and related metal chelates (1:1) ratio.

Ligand	Chelates				Assignment		
	Zr(IV)	La(III)	Y(III)	UO <sub>2</sub> <sup>+</sup>			
HAP :	3450 br	3370 br	3380 br	3360 br	3380 br	$\nu$ OH	stretching
	—	2365 w	2350 w	2313 w	—	$\nu$ NH	"
	1700 s	1630 m	1620 s	1650	1638 w	$\nu$ C=O	"
	1590 m	1590 s	—	1590 m	1600	$\nu$ C=N	"
	—	—	1560 w	1555 w	—	$\nu$ N=N	"
	1494	1490 s	1490 m	1490 s	1505	$\nu$ N—N (pyraz.)	"
	1405	—	—	1410 w	—	$\nu$ N=N (Aryl.)	"
	1372 m	1380 s	1375	1370 s	1378 m	$\nu$ N—NH	"
	1268	1270 w	—	1300	1268	$\nu$ $\phi$ —N	"
	—	418	414	430 s	445	$\nu$ M—N	"
	—	380	360 s	350 m	355	$\nu$ M—O	"
TAP	—	3280 br	3310 br	3294 br	3350 br	$\nu$ OH	stretching
	3150 w	—	—	—	—	$\nu$ NH	"
	1682 s	1674 w	1680	1668	1645 w	$\nu$ C=O	"
	1590	1615, 1588	1615, 1580	1615, 1590	—, 1598	$\nu$ C=N	"
	—	—	—	—	—	$\nu$ N=N	"
	1490	1490	1495	1486	1488	$\nu$ N—N	"
	1400	1424	1454	1420	—	$\nu$ N=N (Aryl.)	"
	1364 m	1362 m	1368 w	1360 m	1372	$\nu$ N—NH	"
	1225 m	1218 m	1225	1215	1250	$\nu$ $\phi$ —N	"
	—	440	440	440	510	$\nu$ M—N	"
	—	365	355	350	345	$\nu$ M—O	"
BAP :	—	3220	3280	3300	3200	$\nu$ OH	stretching
	2948 w	—	—	—	—	$\nu$ NH	"
	1698 m	1640 m	1632	1635	1654 w	$\nu$ C=O	"
	1590	1590	1594	1598 w	1598 w	$\nu$ C=N	"
	—	1558	1560 w	1554	—	$\nu$ N=N	"
	1485	1488	1484	1490	1485	$\nu$ N—N	"
	1432	—	1450	1449	—	$\nu$ N=N (Aryl.)	"
	1366 w	—	1365	1368	1370	$\nu$ N—NH	"
	1250	1244	1246	1250	1258	$\nu$ $\phi$ —N	"
	—	432 m	436	460 m	488	$\nu$ M—N	"
	—	365	310 w	325	344 s	$\nu$ M—O	"

s = strong; br = broad ; m = medium ; w = weak.

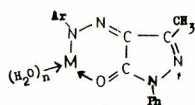
regions can be assigned to  $\nu$ M—N and  $\nu$ M—O stretching respectively [19,20].

The proton NMR spectral data of the complexes exhibits proton signals ( $\delta$ ) (ppm) from 3.9 to 3.4 indicating to the coordinated water molecules [21]. The lower integration of the methine proton (C<sub>4</sub>H) of the azopyra-

zone compounds appeared at  $\delta = 6.4$  ppm relative to the methyl signal at  $\delta = 1.2$  ppm (1:6) supports the presence of the tautomeric structure of the ligands. The methyl signals in the spectra of the complexes showed upfield shifts relative to that of free compounds, this is attributed to the deshielding of methyl protons as a result of complex-

ation. The broad NH signal observed at  $\delta = 12.8$  ppm (5) for the organic compounds disappeared by chelation with the metal ions.

On the basis of the above analysis and discussion, the linkage between the azopyrazolone compounds and the metal ions under investigation can be represent as follows:



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