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MIXED-LIGAND COMPLEXES OF ZIRCONIUM (IV) AND URANIUM (VI) WITH SALICYLALDEHYDE AND SOME HETEROCYCLIC AZOPYRAZOLONES

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Mixed-ligand complexes of Zr (IV) and U(VI) with salicylaldehyde (SA) and some heterocyclic azopyrazolones (HAP) have been studied spectrophotometrically. All formed chelates have ratio 1:1:1. The stiochiometry and the stability of the binary and mixed chelates have been evaluated. Elemental analysis, molar conductance and IR spectra have been used for identification of the solid mixed complexes.

Key words: Mixed ligands complex, Zr (IV), U(VI), Salicylaldehyde, Heterocyclic azopyrazolones.

Introduction

Azo compounds containing a heterocyclic moiety drew the attention of many workers [1,2]. The importance of heterocyclic pyrazolone dyes in industry [3] as well as their analytical applications [4] prompted us to investigate the mixed ligand complexes of Zr (IV) and U (VI) with salicylaldehyde (SA) and some heterocyclic azopyrazolones. Tentative structures have been proposed for the chelation on the basis of analytical, spectral and conductances data. The heterocyclic azopyrazolones used in the present communication are 3-pyridyl, (PAP), 2-thiazolyl (TAP), 2-benzothiazolyl (BAP) azopyrazolones.

Experimental

Heterocyclic azopyrazolones ligands were prepared by coupling the diazotized 3-aminopyridine, 2-aminothiazol, 2-aminobenzothiazol to 1-phenyl-3-methyl- 2-pyrazoline-5-one, following the standard procedure [5]. They were recrystallized from ethanol solution. The analytical data were within acceptable limits. Salicylaldehyde (SA) is obtained from Sigma and used without further purification.

The solid ternary complexes were prepared by refluxing the alcoholic solution of an equimolar amount of the azo dye, salicylaldehyde and metal ion for about an hour. The mixture was concentrated to half its volume and left to cool. The formed precipitate was filtered, washed with ethanol and dried.

Stock solution ($1x10^{-2}$ M) of the azo compounds (PAP, TAP, BAP) salicylaldehyde (SA) and $UO_2(NO_3)_2.6H_2O$ were prepared by dissolving the accurate wieght of the cyrstallized product in absolute ethanol. $ZrCl_4$ solution was dissolved in 80% ethanol-water mixture due to this salt is partially soluble in absolute alcohol.

The electronic spectra measurements at 25° were obtained on a Shimadzu-240 recording spectrophotometer using 1 cm matched silica cell. The electrolytic conductance measurments were made at 25° in DMF solution, using Kinck conductance bridge and conducting cell of the dipping type. Infrared spectra of the solid complexes were recorded by KBr technique in the range 4000-200 cm^{-1} using Perkin-Elmer 599 B IR spectrophotometer.

Results and Discussion

The analytical data of the synthesized ternary complexes (Table 1) indicate that only 1:1:1 (metal:SA:HAP) stoichoimetry is formed.

The molar conductance values of the solid ternary complexes, in DMF solution, are in the range 113.54 - 250.05 $ohms^{-1}$ cm^2 $mole^{-1}$ indicating the electrolytic nature of such chelates [6].

The absorption spectra of the ligands PAP, TAP and BAP in ethanol comprise 2 bands (Table 2) in the range 250 - 309 and 375 - 385 nm. It was reported that the presence of high intensity band at shorter wavelength is indicative of the presence of the azo - structure, while the presence of a weaker one at much longer wavelength support the hydrazone form [7,8].

On complexation, the shorter wavelegth band shows a red shift due to local $\pi-\pi^r$ nature. Also, a red shift is observed for the hydrazone band which can be ascribed to an easier interamolecular CT interaction in complexed ligands.

Alcoholic solution of salicylaldehyde (SA) shows no measureable absorbance band above λ =430 nm. Solutions containing uranyl ions or zirconium ions and SA in a 1:1 molar ratio were prepared and their spectra were recorded over a wavelength range of 350-750 nm. It has been observed that the formed complexes show a maximum absorbance at λ = 460 for Zr (IV) and λ = 370 nm, λ =420 nm for U(VI). However, the spectra of solutions which contain HAP, SA and Zr(IV) or U(VI) against a blank solution containing the same concentration of the two ligands exhibit new absorption band at λ_{max} corresponding to each mixed ligand formed complex which were listed in Table 2. This band is presumably due to the formation of Zr(IV) or U(VI) - HAP - SA mixed ligand complex (Fig. 1).

The stoichiometry of the different binary and ternary chelates formed from the reaction of salicylaldehyde and the heterocyclic azopyrazolones with the metal ions under investigation was indicated by the appplication of the spectrophotometric molar ratio and continuous variation methods [9,10]. Representative curves are shown in Fig.2, 3.

The essential features of the IR spectra of Zr(IV) or U(VI) ternary complexes (Table 3) with SA and HAP are discussed. Previous work on IR spectra of M-HAP chelates [11,12] is therefore, found invaluable in the assignment of the observed frequencies of the ternary chelates. The strong broad band at 3300-3400 cm^{-1} is assigned to the coordinated water. The band in the 1698-1650 cm^{-1} region for the free ligand (HAP) is shifted to lower frequency in the spectra of the ternary complexes than in binary one. This shift is probably due to the involvement of the C=O linkage in the metal chelate ring. The second chelating site in the ligand is the azo (hydrazone) nitrogen atom, since the assigned band to the $\upsilon_{N=N}$ (N-NH) stretching is shifted on complex formation.

The IR spectra of SA ligand exhibits strong band at 1710 cm^{-1} can be assigned to -CHO. This band is shifted to lower frequency on complexation. This shift is due to the involvement of the C=O linkage of the aldehydic group in the metal chelate. The second chelating site in complexation is the phenolic OH group, since the high intensity band at 1240 cm^{-1} is red shifted. This shift to higher frequencies indicates bonding of SA to metal ion through oxygen of phenolic OH group [13].

The U(VI) binary and ternary complexes show a strong band at ≅ 920 cm^{-1} which assigned to asymetric frequency of O-U-O [14]. The two band at 505-350 cm^{-1} and 390-310 cm^{1} regions can be assigned to υ_{M-N} and υ_{M-O} stretching respectively [15,16]. The observed lowering in the frequencies of the 2 bands for ternary than binary complexes can be attributed to increase in the coordination number on ternary complex formation [17,18]. On the basis of the above data, the

TABLE 1. ELEMENTAL AND PHYSICAL DATA OF COMPLEXES.

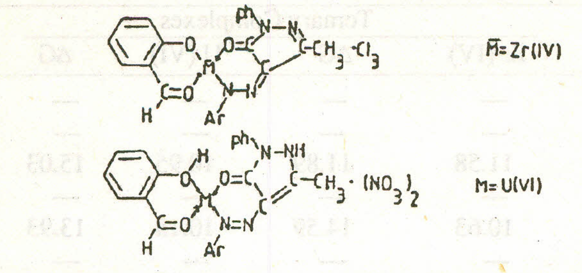
Complexes (colour)	Analysis % : Found / (Calculated) C	 H	 N	Λ s cm^2 mol^{-1}
Chelates of PAP + SA				
Zr $C_{15}H_{12}N_5O.C_7H_5O_2.4H_2O.Cl_2$ (Red)	41.0 (41.5)	3.9 (4.0)	10.9 (11.0)	113.5
$UO_2.C_{15}H_{13}N_5O.C_7H_6O_2.2H_2O(NO_3)_2$(Orange)	31.7 (31.8)	2.9 (2.8)	11.9 (11.8)	214.5
Celates of TAP + SA				
Zr $C_{13}H_{10}N_5OS.C_7H_5O_2.4H_2O.Cl_2$ (Yellow)	37.4 (37.4)	3.5 (3.6)	11.0 (10.9)	143.1
UO_2. $C_{13}H_{11}N_5OS.C_7H_6O_2.2H_2O(NO_3)_2$ (Red)	28.5 (28.6)	2.6 (2.5)	11.8 (11.7)	230.0
Chelates of BAP + SA				
Zr $C_{17}H_{12}N_5OS.C_7H_5O_2.4H_2O.Cl_2$ (Brown)	41.6 (41.7)	3.8 (3.7)	10.2 (10.1)	126.8
$UO_2.C_{17}H_{13}N_5OS.C_7H_6O_2.2H_2O(NO_3)_2$ (Deep red)	32.4 (32.5)	2.5 (2.6)	11.1 (11.1)	250.1

TABLE 2. ELECTRONIC SPECTRAL DATA OF LIGANDS AND THEIR METAL CHELATES IN ETHANOL (λ_{max} nm, ε_{max} x10^{-3} cm^2 mol^{-1}).

	Ligand		Zr(IV)-HAP*		Zr(IV)-SA-HAP		U(VI)-HAP*		U(VI)-SA-HAP	
	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
PAP[a]	250	23.4	340	20.6	–	–	318	6.8	–	–
	380	20.0	535	1.6	530	10.7	522	0.3	520	16.5
TAP[b]	309	4.5	330	7.6	380	22.5	340	19.0	440	28.5
	375sh	1.0	458	2.3	–	–	368	4.3	–	–
BAP[b]	300	4.2	300	7.8	390	7.7	338	5.7	440	10.3
	385sh	1.4	452	1.6	–	–	474	1.8	–	–

*Ref. 11, 12 ; a) Ref. 11, b) Ref. 12

mode of bonding of Zr(IV) and U(VI) with SA and HAP in ternary complexes may be represented by the formula:



Ar= 2-pyridyl (PAP) ; thiazolyl (TAP) ; benzothiazolyl (BAP).

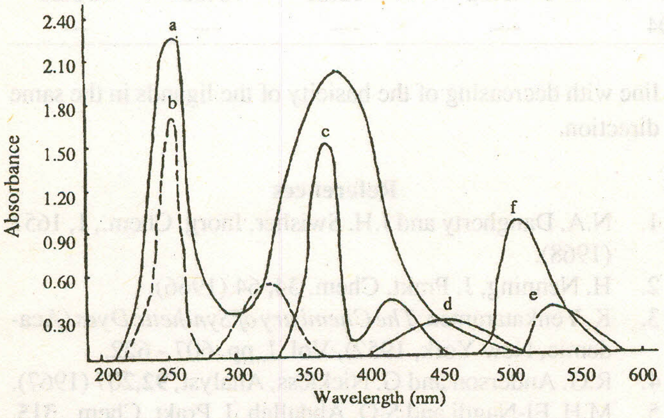


Fig. 1. Absorption spectra of:

(a) PAP, solvent as blank.
(b) SA, solvent as blank.
(c) U(VI)-SA, SA as blank.
(d) Zr (IV)-SA, SA as ligand.
(e) Zr (IV)-SA-PAP, SA+PAP as ligand.
(f) U (VI)-SA-PAP, SA+PAP as ligand.

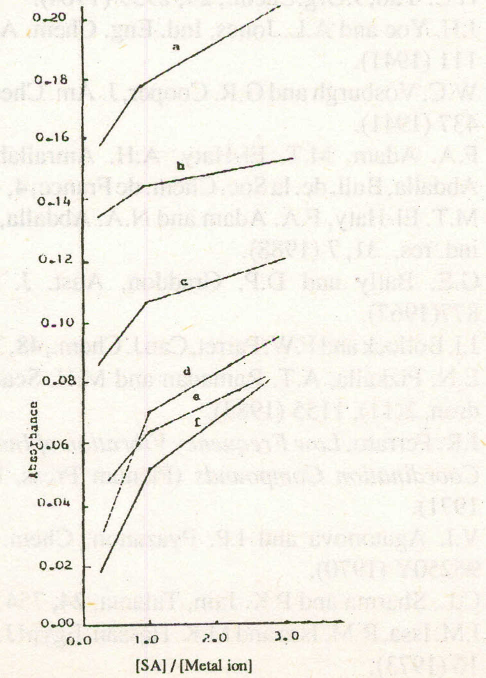


Fig. 2. Molar ratio method of ternary complexes. (Metal ion)=(HAP) = $2x10^{-3}$ M.

(a) U(VI) -SA-TAP λ_{max} =440 nm.
(b) Zr (IV)-SA-TAP λ_{max} =380 nm.
(c) U(VI)-SA-PAP λ_{max} =520 nm.
(d) Zr (IV)-SA-PAPλ_{max} =530 nm.
(e) U (VI)-SA-BAP λ_{max} =440 nm.
(f) Zr (IV)-SA-BAPλ_{max} =390 nm.

The stability constants of the binary complexes were calculated from the spectrophotometric data [19,20]. For the ternary complexes, the stability constants were calculated in a manner similar to that described for the 1:1 metal-ligand complex. The following equations are used:

$$SA + M.HAP \longrightarrow M.SA.HAP$$

If C is the initial concentration of each SA and HAP, A_m the limiting absorbance corresponding to the concentration of M.SA. HAP at full colour development and A corresponds to the concentration of M.SA.HAP existing in euqilibrium, then

TABLE 3. SELECTED IR (cm^{-1}) BANDS OF THE HETEROCYCLIC AZOPYRAZOLONES AND RELATED METAL CHELATES (1:1:1).

	Ligand	Zr(IV)	U(VI)	Assignment	
PAP	–	3350 br	3420 br	OH	Stretching
	–	2720 br	2500 w	NH	"
	1665 s	1652 w	1650 s	C=O	"
	1593 w	1613 m	1610 m	C=N	"
	1570	–	1580 w	N=N	"
	1540 s	1540 vs	1530 br	C=C	"
	1494 s	1490 m	1490 w	N-N	" (pyrazole)
	1405 s	–	1400	N=N	"
	1364 m	1365	–	N-NH	" (pyrazole)
	–	1240 s	1250 s	ϕ-C-O	"
	–	350 w	390 s	M-N	"
	–	320 w	350 s	M-O	"
TAP	–	3380	3360	OH	Stretching
	3150 w	–	–	NH	"
	1682 s	1660 w	1655	C=O	"
	1590	1605 w	1602	C=N	"
	–	–	1575	N=N	Stretching
	1540 s	1538	1532 s	C=C	"
	1490	1485 m	1480	N-N	" (pyrazole)
	1400	–	1405 w	N=N	"
	1364 m	1365 m	–	N-NH	" (pyrazole)
	–	1275 m	1280	ϕ-C-O	"
	–	418	505	M-N	"
	–	350	390	M-O	"
BAP	–	3320 br	3300 br	OH	Streching
	2948 w	–	–	NH	"
	1698	1628	1625	C=O	"
	1590	1610	1600 br	C=N	"
	–	–	1570	N=N	"
	1544 s	1540 s	1530	C=C	"
	1485	1490	1486 m	N-N	" (pyrazole)
	1432	–	1470	N=N	"
	1366	1370	–	N-NH	" (pyrazole)
	–	1270	1260	ϕ-C-O	" (pyrazole)
	–	400 w	420 w	M-N	"
	–	310 w	350 w	M-O	"

br=broad; s=strong; w=weak

TABLE 4. LOGARITHMS OF THE STABILITY CONSTANTS, K_f (1 mol^{-1}) AND FORMATION ENERGY VALUES ΔG (K.cal. mol^{-1}) FOR THE BINARY AND TERNARY COMPLEXES AT 25°.

		Binary Complexes				Ternary Complexes			
		Zr (IV)	ΔG	U (VI)	ΔG	Zr (IV)	ΔG	U (VI)	ΔG
SA	1:1	4.53	6.22	4.2	5.77	—	—	—	—
	1:2	8.51	11.67	8.48	11.36	—	—	—	—
PAP	1:1	6.58	9.39	6.6	9.14	11.58	11.89	10.95	15.03
	1:2	12.58	17.26	11.11	15.34	—	—	—	—
TAP	1:1	5.90	8.10	5.15	7.06	10.63	14.59	10.15	13.93
	1:2	9.90	13.59	9.74	13.37	—	—	—	—
BAP	1:1	5.80	7.10	5.32	7.3	9.92	13.61	9.62	13.20
	1:2	9.11	12.51	9.55	13.04	—	—	—	—

at equilibrium :

$$\mathrm{M.SA.HAP} = C\,(A/A_m)$$
$$[\mathrm{SA}]=[\mathrm{M}]=[\mathrm{HAP}]= C\,(1\text{-}A / A)$$

Then,

$$K_f = [\mathrm{M.SA.HAP}] / [\mathrm{M}][\mathrm{SA}][\mathrm{HAP}]$$
$$= (A / A_m) / (1\text{-}A / A_m)^3\, C^2$$

The obtained data are collected in Table 4 together with ΔG values. The results reveal that the binary complexs which have the stiochiomctry 1:2 are more stable than that which have the stiochiometry 1:1. Moreover, the stability of the ternary complexes are more stable than that of the binary one. This may be due to the increased number of fused chelate ring [21]. The binary and ternary complexes of Zr (IV) are more stable than that of U(VI). The stability of mixed chelates of Zr(IV) and U(VI) follows the order PAP >TAP>BAP which in line with decreasing of the basicity of the ligands in the same direction.

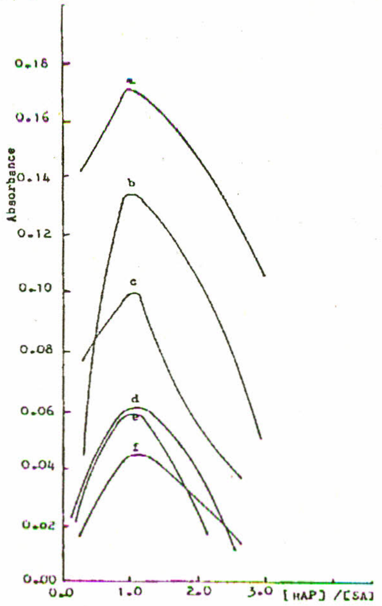


Fig. 3. Continuous variation method of ternary complexes. [Metal ion] =2x10^{-3} M. Total concentration = 6x10^{-3} M.

(a) U(VI) -SA-TAP λ_{max} =440 nm.
(b) Zr (IV)-SA-TAP λ_{max} =380 nm.
(c) U(VI)-SA-PAP λ_{max} =520 nm.
(d) Zr (IV)-SA-PAPλ_{max} =530 nm.
(e) U (VI)-SA-BAP λ_{max} =440 nm.
(f) Zr (IV)-SA-BAPλ_{max} =390 nm.

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