Synthesis and Spectral Studies of Mixed Ligand Complexes of some Azopyrazolones

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Mixed complexes of Zr^{4+} and UO_2^{2+} (with PMP, PMT, PMB as primary ligands and salicylaldehyde as secondary ligand) have been synthesised. Elemental analysis, IR, molar conductance and electronic spectral data indicate the stoichiometric ratio of 1:1:1 complexes. The stereochemistry of octahedra for the complexes were discussed in the light of electronic spectra of the solid complexes.

Considerable attention has been directed towards the methyl pyrazolones and their azo analogues because of their biological activity [1-3]. Mixed metal complexes of these compounds are also of great imporatance and have been used in dying industry [4]. The present investigation describes the synthesis, structure and relative stabilities of Zr^{4+} and UO_2^{2+} chelates with azopyrazol-5-ones such as 4-(3-pyridylazo)-1-phenyl-3-methyl-2-pyrazolin-5-one **(PMP)**; 4-(2-thiazolylazo)-1-phenyl-3-methyl-2-pyrazolin-5-one **(PMT)**; methyl-(2-benzothiazolylazo)-1-phenyl -3-methyl-2-pyrazolin-5-one **(PMB)** as primary ligands and salicylaldehyde **(SA)** as secondary ligand.

EXPERIMENTAL

Ethanol and DMF were of the reagent grade. The azopyrazolone was prepared by the reported method [5] as followes: An appropriate amine was dissolved in dilute HCl, diazotized with $NaNO_2$ solution below 5°C, diazonium solution was added slowly with mechanical stirring to solution of the pyrazolin-5-one in 50% (V/V) ethanol buffered with sodium acetate. The coloured product was separated, collected and recrystallized from ethanol.

Stock solutions ($1x10^{-2}$ mol.dm^{-3} of $UO_2(NO_3)_2.6H_2O$ or $ZrCl_4$ were prepared using A.R. grade salts in of 80 % aqueous ethanol.

The mixed ligand complexes were prepared from binary complexes by a general method [6]. The parent complex M^{+n}-pyrazolone was dissolved in ethanolic solution of salicylaldhyde of the same concentration with stirring and the resulting mixture was kept over-night; the solution obtained after filtration was allowed to concentrate at room temperature for 24 hours. A coloured microcystalline compound separated; it was collected and dried. Different ternary complex solutions were prepared in reagent grade ethanol for spectral measurement.

The UV and visible absorption measurements were determined on shimadzu UV - 240 UV - visible recording spectrophotometer. Infrared spectra of the ligands and mixed ligand chelates were taken in the range 4000 - 200 cm^{-1} on Perkin - Elmer 599 B Infrared Recording spectrophotometer. Molar conductance of

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mixed ligand complexes in DMF solution was carried out at 20°C using a PYE conductance bridge and a dipping type conductance cell. The (C,H,N) elemental analysis were carried out by the microanalytical center -Cairo University.

RESULTS AND DISCUSSION

Absorption spectra

The electronic absorption spectra of the free azo ligands, SA and their 1:1:1 metal chelates solution are recorded (typical graph in Fig. 1). Blank was ethanolic solution of the same concentration of azopyrazolone and salicylaldhyde as in the test solution. This ensures cancelling of the effect of the absorption band of the unreacted ligands. The spectra of azopyrazolones or salicylaldhyde exhibit an absorption band at about 200-350 nm range. However the spectrum of the solution containing M^{+n}-SA-azopyrazolone reaction mixture against a blank solution containing the same concentration of the two ligands shows an apparent new band in the region 350-530 nm. This band is presumably due to the formation of mixed ligand complex with metal. The observed red shift of the free ligand band on chelation can presumably be due to easier

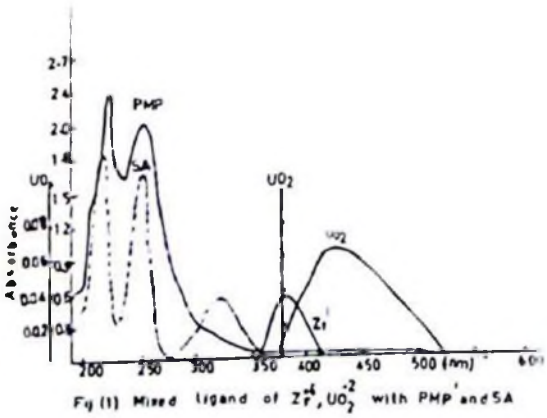


Fig (1) Mixed ligand of Zr^{4+}, UO_2^{+2} with PMP and SA

intramolecular charge transfer taking place within the six memberd ring formed in chelated molecules [7]. This results from the high acceptor character of the co-ordinating positively charged metal ion. The spectra are characterized by one absorption band located at 530 nm for Zr^{4+} - SA - PMP; 520 nm for UO_2^{2+} - SA - PMP; 385 nm for Zr^{4+} - SA - PMT; 380 nm for Zr^{4+} - SA - PMB and 440nm for UO_2^{2+} - SA - PMB (Peak depends on the nature of the azopyrazolone used) suggesting the formation of only one type of complex. Job's method of continuous variation [8] was applied to establish the composition of the ternary complexes under investigation. For the spectrophometric continuous variation method, a set of solutions having a constant total molar concentration of $6x10^{-3}$ mol.dm^{-3} of M^{+n} - SA - azopyrazolone or total molar concentration $6x10^{-2}$ mol. dm^{-3} of UO_2^{2+} - SA - PMP complexes were prepared. The blank contained SA and azopyrazolone of the same concentration as in the test solution. The measured absorbance values at the selected wavelength was plotted aginst the mole fraction of SA/ (Azo + SA). The relation obtained is characterized by a maximum at a point corresponding to a mole fraction equal to 0.5. This suggests that the stoichiometric ratio of the ternary complex formed is 1:1:1. The apparant stability constants (K_f) of the complexes formed in solution are determined utilizing the following equation

$$\beta_1 = \frac{A/A_m}{[1 - A/A_m]^2 C}$$

where A_m, the limiting absorbance, corresponds to the concentration of ML at full colour development, A corresponds to the concentration of the complex molecules existing in equilibrium and C is the initial

Table 1

Elemental Amalysis, properties of the Isolated Complexes

Calculated composition in brackets Melting point in °C; Molar Conductance L_M in ohms $^{-1}cm^2mole^{-1}$

Complex Species	Ele. Comp. C	H	Λ_M	Properties colour	m.pt	λ_{max} nm	Assignment
$[Zr(SA)(Cl)_2PMP]Cl_2$	37.8(41.6)	3.0(2.8)	113.54	red	240	400	C-T Transition
$[UO_2(SA)PMP](NO_3)_2$	37.5(33.14)	2.8(2.38)	214.5	orange	238	475 380	Octahedral
$[Zr(SA)Cl_1PMT]$	31.8(37.5)	3.5(2.7)	43.2	yellow	251	410	C-T Transition
$[Zr(SA)Cl_2PMP]Cl_2$	41.8(41.74)	3.3(2.75)	126.79	brown	235	400	C-T Transition
$[UO_2(SA)PMB(H_2O)](NO_3)_2$	32.0(33.06)	3.0(2.41)	250.05	deep red	200	405 325	Octahedral

concentration of the metal ion.

The analytical data for carbon and hydrogen are collected in Table 1. Calculated values are included in parenthesis for comparison. The values of β_1 in Table 2, indicate that the complexes under study have 1:1:1 stoichiometry. The formation constant values of the (1:1:1) mixed ligand complexes decrease in the following order PMP > PMB > PMT.

The Infrared Spectra of the Mixed Ligand Complexes

The important bands in the IR spectrum of the complexes are listed in Table 3.

On comparing the characteristic frequencies of the free ligands with those of their metal chelates, one can observe the following facts:

Table 2

Formation Constants (β_1) Free energy Changes (ΔG in k.cal/mole) of 1:1:1 complexes

T = 25°

Complex	β_1	ΔG
Zr - SA -PMP	4.38×10^4	6.39
UO_2 - SA - PMP	1.75×10^5	7.22
Zr - SA - PMT	1.24×10^3	4.26
Zr - SA - PMB	3.96×10^4	6.33
UO_2 - SA - PMB	7.51×10^4	6.71

$\beta \pm (1.5 - 2.1)$ %; $\Delta G \pm (0.09 - 0.12)$ %

1. The i.r spectra of the free azopyrazolone ligands exhibit no absorption band due to the streching vibration of free or hydrogen bonded OH - group. This suggests the keto - azo structure of ligand. The azo form is supported by

Table 3

Important Vibrational Frequencies (cm^{-1}) of Different 1:1:1 Chelates

Vibrational mode	Zr-SA-PMP	UO_2-SA-PMP	Zr-SA-PMT	Zr-SA-PMB	UO_2-SA-PMB
ν_{O-H}	-	-	-	-	3400-3080 br
ν_{N-H}	2500	2100 w	2140	2200	-
$\nu_{C=O}$	1656 m	1650 s	1660 w	1610 br	1600 br
$\nu_{C=N}$	1540 s	1530 br	1550	1550 s	1570 w
ν_{N-N}	1490 m	1490 w	1495 m	1490	1486 m
ν_{Ph-N}	1240 br	1250 s	1240 m	-	-
ν_{O-N}	-	-	1200 w	1270 m	1260 m
ν_{C-Me}	908 s	920 m	930	908 m	925 s
ν_{C-H}	765 s	767	760	750 s	758
chelate ring	670	672 vs	670 s	690 vs	690 m
ν_{M-N}	450	460	448	460	500
ν_{M-O}	350 w	390 s	350 m	350 m	310 m

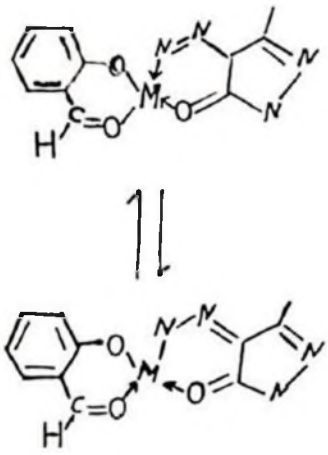
the strong $\nu_{C=O}$ stretching band observed at 1700 - 1665 cm^{-1} [9,10]. The blue frequency shift of the strong $\nu_{C=O}$ band to 1600 - 1656 cm^{-1} on chelation is probably due to the involvement of the C=O group of the ligand in the metal chelate ring formtion. Co-ordination of the carbonyl oxygen with the metal ion reduces the electron density in the C=O linkage.

2. The strong band located at 3450 cm^{-1} in the i.r spectrum of the free salicylaldehyde can be assigned to the stretching vibration of the free OH group attached to the phenyl moiety of the ligand. Its disappearance on chelation suggests its involvement in chelate formation. An upward shift of the phenolic C-O streching vibration by ~ 30 cm^{-1} suggests bonding of phenolic oxygen to the metal ion.

3. In the IR spectrum of UO_2^{2+} - SA - PMB, the strong broad band located in the region 3600-3680 cm^{-1}, suggests the presence of water molecules in the chelate. Since it was known that, the free water molecules absorb at 3095 cm^{-1} [11], one can suggest that the water molecule should be existing as co-ordinated water [12] in the chelate.

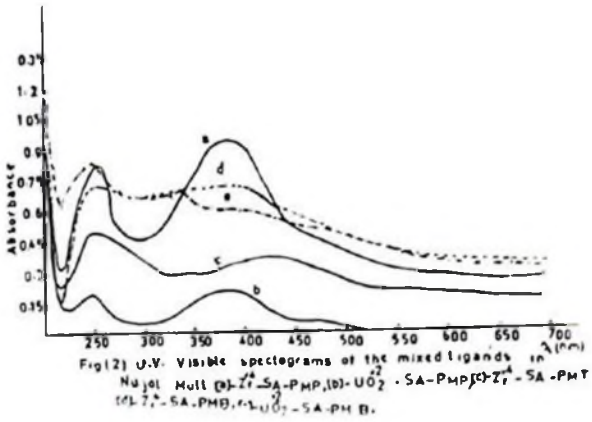
4. A very weak band is observed in the range of 2100 - 2500 cm^{-1} in all free pyrazolone ligands and their chelate. These bands are assigned to the pyrazolone N-H stretching vibration [13]. NH band does not show itself in the spectra of UO_2^{2+} - SA - PMB presumably because of its obscurity under the strong broad band of the coordinated water molecules. The UO_2^{2+} chelates show a strong band at 920 cm^{-1} which is assigned to asymetric frequency of O-U-O stretching [14].

5. The two new developed bands appearant at 448-500 cm^{-1} and 310 - 390 cm^{-1} regions are tentatively assigned to ν_{M-N} and ν_{M-O} stretching vibrations respectively [15].



Electronic Absorption Spectra and Conductivity Measurements

The diffuse electronic spectra (Fig.2) of UO_2^{2+} mixed ligand chelates in 1:1:1 ratios show mainly three bands at 475, (400, 385) and 325 nm. For the uranyl ion, an electron transfer process takes place within the ion, from the two oxygen atoms of the central uranyl group [16]. This transfer involves much higher energy than the expected one. Thus the observed three bands are due to ligands - Metal charge transfer transitions in octahedral structure [17]. The high energy band may be assigned to a charge - transfer transition. The band in lower energy region is presumably due to F-F transition [18] in octahedral stereochemistry [19,20]. All chelates show only one band around 410 nm for Zr - SA - PMT, 400 nm for Zr - SA - PMB and Zr - SA - PMB which are in a good agreement with the values for octahedral structure [21].



Fig(2) U.V. Visible spectograms of the mixed ligands in Nujol Mull (a)-Zr^{4+}-SA-PMP, (b)-UO_2^{2+}-SA-PMP, (c)-Zr^{4+}-SA-PMT (d)-Zr^{4+}-SA-PMB, (e)-UO_2^{2+}-SA-PMB.

The band around 405 nm for Zr^{4+} complexes is assigned to the charge transfer which is in accord with that (n-1) d^o ns^o electronic configuration [22].

Conductivity measuremnts in DMF solutions (113-250 $smol^{-1}$ cm^2 for 10^{-3} $mol.dm^{-3}$ solution) were as expected for 1:2 electrolytes, the 1:1 mononuclear chelate of Zr - SA - PMT (43.12s.mol^{-1}.cm^2).

These results support the suggested formula of the solid chelates on the bases of elemental analysis (Table 1).

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