

SYNTHESIS AND SPECTRAL STUDIES OF MIXED LIGAND COMPLEXES OF SOME AZOPYRAZOLONES

NADIA A. ABDAILA

Chemistry Department, Faculty of Science, Aswan, Egypt

(Received July 3, 1995; revised January 28, 1997)

Mixed complexes of Zr (IV) and UO_2 (II) with the ligands 4 (3-pyridylazo) 1-phenyl-3-methyl-2 pyrazolin-5-one (PMP); 4- (2-thiazolyazo) 1-phenyl-3-methyl-2-pyrazolin-5-one (PMT); methyl- (2-benzothiazolyazo)-1-phenyl (-3-methyl-2-pyrazolin-5-one (PMB) and salicylaldehyde (SA) 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 octahedral for the complexes were discussed in the light of electronic spectra of the solid complexes.

Key words: Mixed complexes, Analysis, Azopyrazolones.

Introduction

Considerable attention has been directed towards the methyl pyrazolones and their azo analogues due to their biological activity [1-3]. Mixed metal complexes of these compounds are also of great importance, and have been used in dying industry [4]. Scanning of the literature [5-8] indicated that no work was published on the azo compounds derived from heterocyclic amines and 2-pyrazolin-5-one mixed ligand complexes, the present investigation describes the synthesis, structure and relative stabilities of Zr (IV) and UO_2 (II) chelates with azopyrazolone-5-ones such as PMP, PMT, PMB and salicylaldehyde mixed ligand.

Experimental

Preparation of ligands. The azopyrazolone was obtained according to the metal described before [9]. An appropriate amine was dissolved in dil. HCl and then, diazotized with $NaNO_3$ solution below $5^\circ C$. Diszonium solution was added slowly with mechanical stirring to a solution of the pyrazolin-5-one in 50% (V/V) ethanol buffered with sodium acetate. The colour product was separated, collected and recrystallized from ethanol.

Preparation of metal solution. The ethanol was used for the preparation of all solution $UO_2(NO_3)_2 \cdot 6H_2O$ solution 1×10^{-2} mol dm^{-3} Zr Cl_4 solution 1×10^{-2} mol dm^{-2} prepared using (A.R) in mixture of 80% EtOH- 20% H_2O .

Preparation of ternary complex. The mixed ligand complexes prepared by a general method [10], the parent complex M^{n+} -pyrazolone was dissolved in ethanolic solution of the same mol salicylaldehyde with stirring and the resulting mixture was kept over-night, the solution obtained after filtration was allowed to concentrate at room temperature for 24 hrs. The coloured microcrystalline compound separated, was collected and dried.

Working procedure for spectral measurement. In the ternary complex system studied the three components has been simplified to a two component system M^{n+} and salicylaldehyde azopyrazolone. For the spectrophotometric continuous variation method, a set of solutions having the total molar concentration constant 6×10^{-3} mol dm^{-3} of M^{n+} -SA-azopyrazolone or total molar concentration 6×10^{-2} mol dm^{-3} of $UO_2(II)$ /SA/PMP complexes, a blank containing the same concentration of SA and azopyrazolone as in the test solution was made.

Apparatus. The UV and visible absorption measurements were determined on Shimadzu UV-240 UV-visible Recording Spectrophotometer. Infrared spectra of subject ligands and mixed ligand chelates in the (4000-2000 cm^{-1} region) were recorded on Perkin-Elmer 599B Infrared Recording Spectrophotometer. Molar conductance of mixed ligand complexes in DMF solution was carried out using a PYE conductance bridge at $25^\circ C$ and conducting cell of the dipping type. The elemental analysis (C,H) were carried out by the Microanalytical center-Cairo University.

Results and Discussion

Absorption spectra. The electronic absorption spectra of the free subject azo compounds, SA and their 1: 1: 1 metal chelates solution are recorded (Fig.1). The spectra of azopyrazolones or salicylaldehyde three absorption bands 200-350 nm range. However, the solution containing M^{n+} -SA-azopyrazolone spectrum of the 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. Accordingly, the longer wavelength band observed in the spectra of all chelates formed is ascribed to an intramolecular C. T. transition within the es-

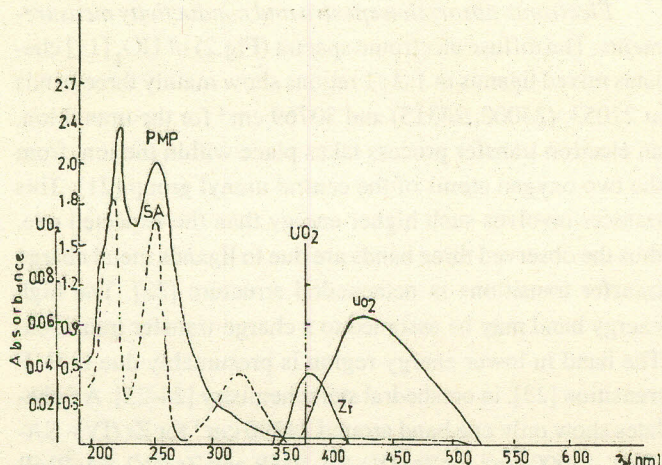


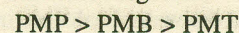
Fig. 1. Mixed Ligand of Zr^{4+} , UO_2^{2+} with PMP and SA.

established six member chelate ring. The observed red shift of the free ligand band on chelation, can presumably be due to easier intramolecular charge transfer taking place within the chelated molecules relative to that in the free ligand [11]. This results from the high acceptor character of the coordinating positively charged metal ion. Job's method of continuous variation [12] was applied to establish the composition of the ternary complexes under investigation. A blank containing the same concentration of azopyrazolone and salicylaldehyde as in the test solution was made. This is made in order to cancel the effect of the absorption band of the unreacted salicylaldehyde and azopyrazolone ligands. The spectra are characterized by one absorption band located at 530 nm for Zr (IV)/SA/PMP; 520 nm for UO_2 (11)/SA/PMP; 385 nm for Zr (IV)/SA/PMT; 380 nm for Zr (IV)/SA/PMB, 40 nm for UO_2 /SA/PMB (depending on the nature of the azopyrazolone used) suggesting the possible formation of only one type of complexes. The measured absorbance values at the selected wavelength was plotted against the mole

fraction of SA/azo + SA. The relation obtained is characterized by a maximum at a point corresponds to a mole fraction equal to 0.5. This suggests that the stoichiometric ratio of the ternary complex formed is 1: 1: 1. The apparent stability constants (K_f) of the complexes formed in solution are determined utilizing the following equation in the case of the type (1: 1: 1).

$$BI = \frac{A/A_m}{(1-A/A_m)^2 C}$$

Where A_m is 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 concentration of the metal ion $2 \times 10^{-3} \text{ mol dm}^{-3}$. The analytical data for carbon and hydrogen collected in Table 1, and the results BI shown 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 decrease in the following order



Infrared spectra of the mixed ligands. On comparing the characteristic frequencies of the free ligands with those of their metal chelates one can observe the following facts;

(i) Their spectra of the free ligands azopyrazolone exhibit no absorption band due to the stretching vibration of free or hydrogen bonded OH-group. This suggests the keto-azo structure of ligand. The azo form supported by the strong $\nu C=O$ stretching band observed at $1700-1665 \text{ cm}^{-1}$ [13-14]. The blue frequency shift of the strong $\nu C=O$ band to $1600-1656 \text{ cm}^{-1}$ on chelation is probably due to the involvement of the $C=O$ group of the ligand in the metal chelate ring formation. This can be explained on the principle that coordination of the oxygen carbonyl group to the metal ion reduces the electron density in the $C=O$ linkage.

TABLE 1. ELEMENTAL ANALYSIS, COLOR, MELTING POINT, MOLAR CONDUCTANCE (M) OHMS-1 CM² MOLE⁻¹ AND ELECTRONIC (CM⁻¹) OF MIXED LIGAND CHELATES.

Mixed ligand	%calc. (found)		Color	Melting point	Electronic transition	Structural configuration
	C	H				
$[Zr(SA)Cl_2 PMP]Cl_2$	41.6 (37.8)	2.8 (3.0)	113.54	Red	240 400	C-T transition
$[UO_2 SA PMP (NO_3)_2]$	33.14 (37.7)	2.38 (2.8)	14.5	orang	238 475 380 26315	octahedral
$Zr SA Cl_2 PMT]Cl_2$	37.5 (31.8)	2.7 (3.5)	143.2	Yellow	251 410	24390 C-T transition
$[Zr SA Cl_2 PMB]Cl_2$	41.74 (41.8)	2.75 (3.3)	126.79	Brown	235 400	25000 C-t transition
$[UO_2 (SA) PMP (H_2O) (NO_3)] NO_3$	33.06 (32.0)	2.41 (3.0)	50.05	Deap red	200 405 325 30769	24691 Octahedral

TABLE 2. FORMATION CONSTANT AND FREE ENERGY CHANGES (G IN K CAL/MOLE AT 25°C OF Zr (IV) AND UO₂ (11) (1: 1: 1) TERNARY COMPLEXES.

Complex	B1	G*
Zr-SA-PMP	4.38x10 ⁴	6.39
UO ₂ -SA-PMP	1.75x10 ⁴	7.22
Zr-SA-PMT	1.24x10 ³	4.26
Zr-SA-PMB	3.96x10 ⁴	6.33
UO ₂ -SA-PMB	7.51x10 ⁴	6.71

(ii) The strong and 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. The appearance of this band in chelates suggests that the molecule of the ligands are involved in chelate formation.

(iii) In the i.r spectrum of UO₂ (11)-SA-PMB the strong broad band located in the region 3600-3680 cm⁻¹, suggests the presence of water molecules in chelate. Since it was known that the free water molecules absorb at 3095cm⁻¹ [15], once can suggest that the water molecule in the prepared chelate should exist as coordinated water [16].

(iv) 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 NH stretching vibration [17].

On the basis of the suggested formulas of the solid chelates deduced from the microanalytical results, the absence of NH band in the spectra of UO₂ (11)-SA-PMB is presumably due to its obscurity under the strong broad band of the coordinated water molecules. The UO₂ (11) chelate show a strong band at 920 cm⁻¹ which is assigned to asymmetric stretching frequency of O-U-O [18].

(v) The two new developed bands appearant at 448-500 cm⁻¹ and 310-390 cm⁻¹ region is tentatively assigned to ν M-N and ν M-O stretching vibrations respectively [19-20].



Where x = Cl, NO₃ and y = H₂O

TABLE 3. IMPORTANT VIBRATIONAL FREQUENCIES (cm) OF PMP, PMT OR PMB AND SALYSALDHYDE AND ITS Zr (IV) AND UO₂ (11) CHELATES (1:1:1) RATIO.

Complex	ν OH	ν NH	ν C=O	ν C=N	ν N-N	ν -PYR.N	ν O-N	ν C-CH ₃	ν C-H	Chelating	ν M-N	ν M-O
Zr-SA PMP	3450	2500	1656m	1540s	1490m	1240br	-	908s	765s	670	450	350w
UO ₂ -SA-PMP	3455	2100W	1650s	1530br	1490w	1250s	-	920m	767vs	672vs	460	390s
Zr-SA-PMT	3450	2140	1660w	1550	1495m	1240m	1200w	930	670s	670s	448	350m
Zr-SA-PMB	3453	2200	1610br	1550s	1490	-	1270m	908m	690vs	690vs	460	350m
UO ₂ -SA-PMB	3400-3080 br		1600 br	1570w	1486m	-	1260m	925s	690m	690m	500	310m

Electronic absorption spectra and conductivity measurements. The diffuse electronic spectra (Fig.2) of UO₂ [11] chelates mixed ligands in 1: 1: 1 ratios show mainly three bands at 21053, (25000, 26315) and 30769 cm⁻¹ for the uranyl ion, an electron transfer process takes place within the ion, from the two oxygen atoms of the central uranyl group [21]. This transfer involves such higher energy than the expected one, thus the observed three bands are due to ligands metal charge transfer transitions in octahedral structure [22]. 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 [23], in octahedral stereochemistry [24-25]. All chelates show only one band around 24390 cm⁻¹ for Zr (IV)- SA-PMT, 25000 cm⁻¹ for Zr (IV)-SA-PMB and Zr (IV)-SA-PMB which is in good agreement with the values for octahedral structure [26-27]. The band around 24691 cm⁻¹ for Zr (IV) complexes assigned to the charge transfer is in a coordinated with the (n-1)d⁰ ns⁰ electronic configuration [28]. Conductivity measurements in DMF solutions (10⁻³ mol dm⁻³) were commensurate with values characteristic for 1:2 electrolytes 113-143 s mol⁻¹ cm², the 1: 1 mononuclear chelate of UO₂ (11-SA-PMP (50. 05 mol⁻¹ cm²). These results supports the suggested formula I and II of the solid chelates on the bases of elemental analysis.

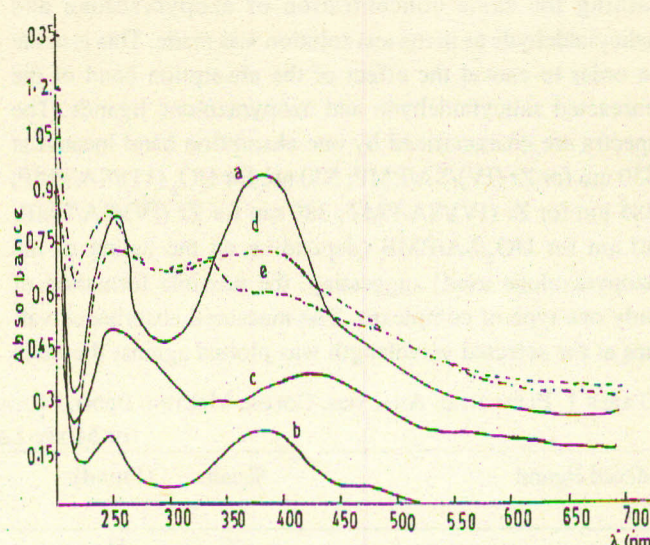


Fig. 2. U. V. Visible spectrograms of the mixed ligands in Nujol Mull (a)-Zr⁴⁺-SA-PMP,(b)-UO₂⁺SA-PMP (c)-Zr⁴⁺-SA-PMT (d) UO₂⁺-S-PMB.

References

1. W. Schell, K. I. Sihundehntti, K. Loverenz and W. Mennicke, Ger. Offen. 2, 840, 651 (cl. co. 9B 45 116) 27 Mar Appl. 19 sep (1980).
2. R. G. Anderson and G. Nickless, *Analyst*, **92**, 297 (1967).
3. V. M. Savostina, F. I. Lobanov and R. G. Opasova, *Koord. Khim.*, **2**, 1614 (1976).
4. P. R. Shukla, C. Sureshi, S. Chandreshwari and N. Gopal, *Indian J. Chem.*, **23 (A)**, 445, (1984).
5. K. M. Purohit and D. V. Rao Ramana, *Indian J. Chem., sect. A*, **22A (6)**, 520 (1983).
6. Hoang Nham and Le Bathwan (Khao Hoa, Truong Dat Hoe Tong Hop Hanoi, Hanio, vitenam) *Top Chi Hoc Hoc (22 (1))*, 18-20 (vietnames) (1984).
7. Nityananda Saha and Asok K. Adak, *J. Indian Chem. Soc.* **62 (2)**, 96 (1985).
8. M. Sayeed and Ahmed Nassor, *J. Inorg. Nucl. Chem.*, **43 (12)**, 3197(1981).
9. M. H. El-Nagdi and S. O Abdallah, *J. Prakt. Chem.*, **315**, 1009 (1973).
10. K. K. Idriss, M. M. Seleim, M. S. Abu-Bakr and M. S. Saleh, *Analyst* **107**, 12-16 (1988).
11. M. T. El-Haty, F. A. Adam and Nadia A. Abdalla; *J. Chem. Chem Soc.* **31**, 46 (1984).
12. *Jop. Compt. Rend (Paris)* **180**, 928 (1925).
13. F. A. Snavly, W. S. Trahanovsky, and F. H. suydam, *J. Org. Chem.*, **27**, 994 (1962).
14. W. Pelz, W. Puschel. H. Schellenberger and K. Loffler, *Angew. Chem.*, **72**, 967 (1960).
15. L. J. Teriot, G. Carlisle and H. J. Hu *Inorg. Nucl. Chem.*, **31**, 33033 (1969).
16. V. J. T. Raju, V. Banhaor, V. Atre and M. C. Ganokor, *J. Indian Chem. Soc.*, **59**, 190 (1982).
17. C. W. Reimann. A. V. Sentoro and A. D. Mighell. *Acta Crystallogr.*, **13**, 521 (1970).
18. J. I. Bullock and F. W. Patrel *Can. J. Chem.*, **84**, 3095 (1970).
19. F. M. Rizkalla. A. T. Ramadan and M. H. Scada, *Polyhedron*, **2**, 1155 (1983).
20. J. R. Ferraro "*Low Frequency Vibrations of Inorganic and Coordination Compounds*". (Plenum press. New York 1971), pp.93.
21. U. Casellato, D. Fregons S. Sitran, S Tamburini and P. A. Vigato, *Inorg Chim. Acta*, **110**, 161 (1985).
22. G. C. Pappalarbo and A. Seminara, *J. Inorg. Nucl. Chem.*, **38**, 1993 (1976).
23. C. P. Prabhakaran and C. C Patel, *J. Inorg. Nucl. Chem.*, **34**, 3485 (1972).
24. A. K. Rana, and J. R. Shah, *Ind. J. Chem.*, **20A**, 14(1981).
25. A. K. Rana and J. R. Shah *Ind. J. Chem.*, **20A**, 615 (1981).
26. E. C. Okafor *polyhedron*, **2**, 309 (1983).
27. T. M. Dunn. R. S. Nyholm and S. Yamada. *J. Chem. Soc* 1564 (1962).
28. P. B. Doraini, H. H. Patterson and P. C. Jordan *J. C. Phys.*, **49**, 3845 (1968).