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Synthesis and Characterization of Iron(III) and Uranyl(II) Complexes of Some Salicyloylhydrazones

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Iron(III) and uranyl(II) complexes of salicyloyl hydrazones derived from 2,6-diphenylpiperidin-4-one (DPSH) and 3-methyl-2,6-diphenylpiperidin-4-one (MDPSH) were prepared and characterized by elemental analysis, conductance, magnetic, cyclic voltammetric and spectral studies. UO_2(II) complexes derived from DPSH and MDPSH have 1:1 and 2:1 metal to ligand stoichiometries, respectively. The metal ligand ratio was found to be 1:3 in Fe(III)-DPSH complex and 1:2 in Fe(III)-MDPSH complex. Based on the relevant data probable structure of the complexes were proposed.

Key Words: Salicyloylhydrazone complexes, Iron(III), Uranyl(II).

INTRODUCTION

The study of hydrazones and their complexes are growing due to their wide range of applications in biological processes such as in treatment of tumour, tuberculosis, leprosy and mental disorder[1,2]. They also find application in the field of analytical chemistry as extraction reagents for spectroscopic determination[3-5]. Literature survey shows many reports on aroylhydrazones complexes derived from aliphatic, aromatic and heteroaromatic carbonyl compounds. However studies on aroyl hydrazones derived from saturated heterocyclic carbonyl compounds are less. In continuation of our work on metal complexes of aroyl hydrazones, herein, the synthesis and characterization of aroyl hydrazones (**Scheme-I**) and their UO_2(II) and Fe(III) complexes are reported.

EXPERIMENTAL

The ligands 2,6-diphenylpiperidin-4-one salicyloyl hydrazone (DPSH) and 3-methyl-2,6-diphenylpiperidin-4-one (MDPSH) were prepared as reported in literature by reacting salicyloyl hydrazide with corresponding heterocyclic ketones and characterized by spectral studies[6].

Preparation of DPSH complexes: Ligand DPSH (1.93 g, 5 mmol) and the metal salt (ferric chloride hexahydrate. 1.35 g and uranyl acetate dihydrate 2.12 g, 5 mmol each) were mixed in 75 mL ethanol and refluxed for *ca.* 8 h. The resulting solution was allowed to stand overnight. A solid product obtained was filtered,

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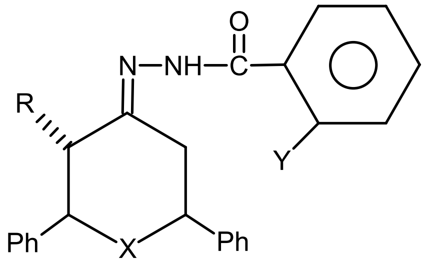
washed thoroughly with hot benzene and then with hot water and then dried over calcium chloride in a desiccator.



X	Y	R	Compound
NH	OH	H	DPSH
NH	OH	CH_3	MDPSH

Scheme-I

Preparation of $FeCl_3$ MDPSH complex: To a solution of MDPSH (2.0 g, 5 mmol) in 20 mL DMF, methanolic solution of ferric chloride hexahydrate 1.35 g, 5 mmol) was added and refluxed for 5 h. The complexes separated out were filtered, washed well with hot benzene, then with hot water and dried over calcium chloride in a desiccator.

Preparation of $UO_2(OAc)_2$ MDPSH complex: To a hot well stirred solution of uranyl acetate dihydrate (1.7 g in methanol, 4 mmol) dry finely powdered ligand MDPSH (1.6 g, 4 mmol) was added slowly. After the addition of ligand was over, stirring was continued for another 15 min. The mixture was heated under reflux for 8 h and then allowed to cool at room temperature and kept overnight. Precipitated complex was filtered, washed with methanol and then with hot water and dried over calcium chloride in a desiccator.

Analyses: Elemental analysis were carried out in HCE1108 elemental analyzer at Central Drug Research Institute (CDRI), Lucknow.The metal contents were estimated after decomposition with concentrated H_2SO_4 as reported[7]. The infrared spectra of the ligands and metal complexes in the region 4000-400 cm^{-1} were recorded on NA 360 FT-IR spectrometer using potassium bromide discs. Electronic spectra of the ligands and their complexes were recorded on HITACHI MODEL UV-2001 double beam spectrophotometer. The spectra were recorded in DMF solvent in the range 200-800 nm. Conductivities in DMF [10^{-3} M] were measured using electrolytic resistance bridge. The magnetic susceptibility measurements were made at room temperature using EG and G Model 155 vibrating sample magnetometer at RSIC, IIT, Chennai. Cyclic voltammetric studies were carried out using a model ECDA-001, basic electrochemistry system. A three electrode configuration comprising glassy carbon working electrode, platinum wire counter electrode and Ag/AgCl reference electrode at room temperature in deareated DMF using tetra butylammonium perchlorate as supporting electrolyte.

RESULTS AND DISCUSSION

All the complexes are non-hygroscopic in nature, stable in air and are insoluble in water, ethanol, methanol, chloroform and dichloromethane, but soluble in coordinating solvents like dimethyl formamide and dimethyl sulphoxide. The physical and analytical data of the complexes are displayed in Table-1. The analytical data show that UO_2(II) complexes derived from DPSH and MDPSH have 1:1 and 2:1 metal to ligand stoichiometries, respectively. The metal ligand ratio was found tobe 1:3 in Fe(III)-DPSH complex and 1:2 in Fe(III)-MDPSH complex. The ligand DPSH behaves as neutral/uninegative bidentate ligand during coordination. In MDPSH complexes, the ligand MDPSH acts as mononegative/neutral bidentate/tetradentate ligand. Conductivity studies were performed for all the complexes in DMF. The observed molar conductance values are in the range 6-15 ohm^{-1} cm^2 mol^{-1} and the values show non-ionic nature of all the complexes. The molar conductance data also support the formulae proposed for all the complexes based on analytical data obtained. The magnetic moment values were calculated for Fe(III) complexes from the susceptibility measurements after correcting for diamagnetic contributions. These values correspond to the presence of only one unpaired electron suggesting strong field nature of the ligands in complexes. The electronic spectra of the complexes were recorded in DMF in the region 200-800 nm and the relevant spectral data are tabulated in Table-2. The absorptions below 350 nm in all the complexes are attributed to the transitions within the ligand molecules. The Fe(III)-MDPSH complex exhibits bands at 370 and 440 nm and these are assigned to charge transfer transition[8] and *d-d* transition respectively[9,10]. The IR spectra of the complexes were recorded as KBr disc in the region 4000-400 cm^{-1} and the data are furnished in Table-3 In all the complexes, broad bands of medium intensity centered around 3450-3000 cm^{-1} are attributed to ν(N-H) and ν(O-H) present in the complexes[11]. The bands due to ν(C=O) around 1600 cm^{-1} exhibit a shift to lower frequencies in complexes compared to the ligands. Moreover, the bands due to ν(C=N) are also shifted to lower frequencies in complexes. This indicates that both carbonyl oxygen and azomethine nitrogen are involved in coordination in these complexes[12,13]. In UO_2(II) complexes, the presence

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF Fe(III) AND UO_2(II) COMPLEXES

Compd.	m.f.	F.Wt. (colour)	Yield (%)	Dp (ºC)	Micro analysis data (%): Found (Calcd.)			
					C	H	N	M
Fe(III)- DPSH	[Fe(LH)L_2OH] $C_{72}H_{68}N_9O_7Fe$	1227.34 (Brown)	50	192	71.00 (70.45)	5.08 (5.59)	9.51 (10.27)	4.48 (4.55)
UO_2(II)- DPSH	[UO_2L(OAc)(H_2O)]·3H_2O $C_{26}H_{33}N_3O_{10}U$	785.50 (Orange)	50	> 300	39.15 (39.72)	3.22 (4.20)	4.98 (5.35)	29.24 (30.30)
Fe(III)- MDPSH	[Fe$(LH)_2Cl_2$]CH_3OH $C_{51}H_{54}N_6O_5Cl_3Fe$	992.30 (Brown)	60	220	61.41 (61.61)	4.78 (5.44)	9.27 (8.46)	6.50 (5.62)
UO_2(II)- MDPSH	[$(UO_2)_2$L$(OAc)_2$(H_2O)OH] $C_{29}H_{33}N_3O_{12}U$	1091.69 (Orange)	60	> 300	32.02 (31.88)	3.04 (3.02)	3.62 (3.85)	42.71 (43.60)

Values within parentheses are calculated values; L = anionic ligand, LH = neutral ligand.

TABLE-2
ELECTRONIC SPECTRAL, CONDUCTIVITY AND MAGNETIC MOMENT DATA OF Fe(III) AND UO_2(II) COMPLEXES

Complex	λ_{max} (nm)	Λ_m (Ω^{-1} cm^2 mol^{-1})	μ_{eff} (BM)
Fe(III)-DPSH	310	15.80	1.56
UO_2(II)-DPSH	305, 375	9.58	–
Fe(III)-MDPSH	300, 370, 440	6.59	1.78
UO_2(II)-MDPSH	305, 415	12.14	–

TABLE-3
IR DATA (cm^{-1}) OF Fe(III) AND UO_2(II) COMPLEXES

DPSH	A	B	MDPSH	C	D	Assignment
3727	3726		3757		3789, 3701	ν(OH)
3250 3059	3241 3028	3400 3214	3409 3296	3450 3253	3190	ν(NH) amide + ν(OH)
3030		3060	3026	3060		ν(NH) ring
1632	1628	1606	1608	1599	1605	ν(C=O)
		1573			1571	ν_{as}(OCO)
1604	1560	1530	1557	1530(w)	1527	ν(C=N)
1306	1309		1363	1374		Bending vibration of phenolic OH group
	1375			1314		δ(OH)
		1317			1319	ν_{as}(OCO)
1233	1235	1249	1237	1251	1249	Amide III band
1151	1154	1153	1155	1157	1152	ν(C-O) phenolic
1032	1031	1033	1049	1035	1029	ν(N-N)
		907(s)			903(s)	$\nu_{asy}(UO_2)$
	856			857		Fe-OH bending mode
	534	585 510		585 505	585 506	ν(M-O)
	403	405		444	409	ν(M-N)

A = $[Fe(LH)(L_2)OH]$; B = $[UO_2L(OAc)H_2O]\cdot 3H_2O$; C = $[Fe(LH)_2Cl_3]CH_3OH$;
D = $[(UO_2)_2L(OAc)_2(H_2O)OH]$

of acetate anion is confirmed by the observation of new bands around 1570 and 1320 cm^{-1} and these bands are due to ν_{as}(OCO) and ν_{sym}(OCO) modes, respectively[13,14]. The mode of coordination of acetate group (unidentate or bidentate) can be determined by finding out the difference (Δ) between two ν(OCO) bands[15]. If the difference, Δ is much larger than free acetate ion (144 cm^{-1}) then it coordinates through unidentate fashion and if it is much smaller, bidentate behaviour is expected. In the present study large difference between the two ν(OCO) bands (252 cm^{-1}) was noted and it confirms unidentate coordinating behaviour of acetate ion in these complexes[14]. The new intense bands appeared at 907 cm^{-1} in UO_2(II)-DPSH complex and 903 cm^{-1} in UO_2(II)-MDPSH complex are attributed to the asymmetric stretching vibration of the UO_2 group present in the complexes[16]. Deprotonation of the phenolic hydroxyl group of the ligands DPSH and MDPSH in UO_2(II) complexes is evidenced from the absence of bands due to δ_{OH} in the region 1300 cm^{-1}. In Fe(III)-DPSH complex, the new peak observed at 1375 cm^{-1} is attributed to the bending mode of hydroxyl ligand present in the complex. The presence of solvent CH_3OH[8] is evidenced from the observation of δ_{OH} mode at 1314 cm^{-1} in Fe(III)-MDPSH complex. The neutral bidentate behaviour of both the ligands in Fe(III)-MDPSH complex and one of the ligands in Fe(III)-DPSH complex is confirmed from the absence of appreciable change in the bending vibration of phenolic OH group δ_{OH} in these complexes. The bands in the region 600-400 cm^{-1} are due to ν(M-O) and ν(M-N) modes[12,13]. The electrochemical behaviour of all the complexes and the ligand MDPSH have been investigated through cyclic voltammetric studies and the results are tabulated in Table-4. The ligand MDPSH however exhibits a different electrochemical behaviour compared to DPSH in solution[17]. Absence of cathodic peak indicates that the reduction of carbonyl group does not occur in the working potential range. Probably the ligand MDPSH may exists predominantly in the enolic form in solution as shown below and the enolic form contributes more to the electrochemical behaviour than the keto form.

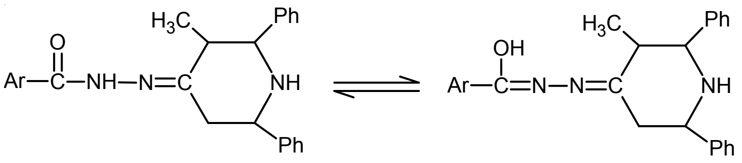
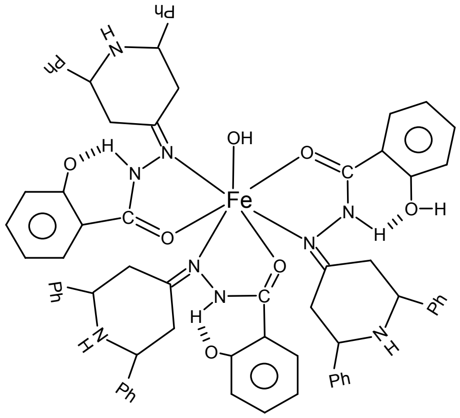


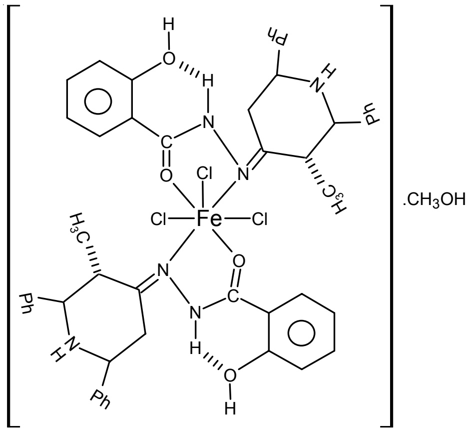
TABLE-4
CYCLIC VOLTAMMETRIC DATA OF Fe(III) AND UO_2(II) COMPLEXES

Compound	Electrochemical reduction		Electrochemical oxidation		
	E_{pc} (V)	E_{pa} (V)	E_{pa} (V)	E_{pc} (V)	ΔE_p (V)
DPSH	- 1.05	–	+ 0.92	–	–
Fe(III)-DPSH		–	+ 1.71	–	–
UO_2(II)-DPSH	- 0.23	–	+ 1.73	–	–
MDPSH	–	–	+ 1.20 + 1.79	–	–
Fe(III)-MDPSH	- 1.37	–	+ 0.33 + 1.46 + 1.76	+ 0.46	–
UO_2(II)-MDPSH	- 0.19	–	+ 1.28 + 1.55	–	–

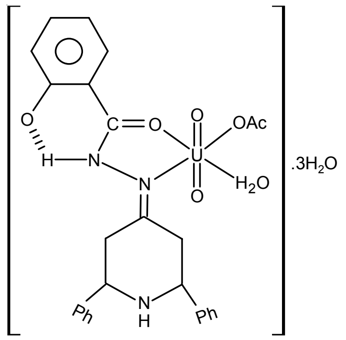
The presence of two anodic peaks during electrochemical oxidation of the ligand MDPSH also supports that the ligand MDPSH mainly exists in the enolic form than in the keto form. The anodic potentials at +1.20 V and +1.79 V for the ligand MDPSH correspond to the oxidation of enolic OH/amide NH and phenolic OH group, respectively. Comparison of peak potentials of the ligand with complexes reveals that the reduction processes are metal centered. Absence of peaks in the reverse scan indicates that the reduction processes are irreversible in nature. The cathodic peak at -0.23 V in UO_2(II)-DPSH complex and -0.19 V in UO_2(II)-MDPSH complex are probably due to the reduction[18] of $UO_2^{2+} \rightarrow UO_2$. The reduction process $Fe^{3+} \rightarrow Fe^{2+}$ is responsible for the peak at -1.37 V in Fe(III)-MDPSH complex[19,20]. Comparison of anodic peak potentials of the ligand MDPSH and its complexes reveals that oxidation processes are mainly ligand centered oxidation and moreover the irreversible nature of the oxidation process is evident from the absence of peaks in the reverse scan. In the case of Fe(III)-MDPSH complex, a small hump is observed at + 0.33 V which probably corresponds to the oxidation of methanol associated in the complex. The cathodic peak at 0.46 V is probably due to absorption peak. In DPSH complexes there is a vast difference in the oxidation potentials compared to the free ligand DPSH. The high anodic potentials around + 1.7 V probably corresponds to the oxidation of phenolic OH which is intramolecularly hydrogen bonded with amide NH in the complexes. Based on experimental evidences, the probable structures of the complexes are predicted to be



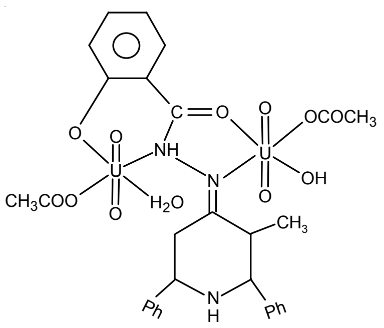
Fe(III)-DPSH



Fe(III)-MDPSH



UO_2(II)-DPSH



UO_2(II)-MDPSH

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