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Preparation, Characterization and Kinetics of Formation of Some Schiff Base Chelates of Sn(II) and UO_2(V1)

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PREPARATION, CHARACTERIZATION AND KINETICS OF FORMATION OF SOME SCHIFF BASE CHELATES OF Sn(II) AND UO_2(VI)

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ABSTRACT

The synthesis, characterization and formation kinetics of Sn(II) and UO_2(VI) complexes of the nitrogen and oxygen donor ligands *m*-chlorophenylsalicylaldimine (Hcps), *m*-nitrophenylsalicylaldimine (Hnps), *m*-methoxyphenylsalicylaldimine (Hmps) and *m*-methylphenylsalicylaldimine (Hmsa) are reported. The structures of the free ligands and their Sn(II) and UO_2(VI) complexes were determined by NMR, elemental analyses, IR and UV-Vis studies and magnetic susceptibility measurements. Under pseudo-first order conditions, having an excess of the Schiff base present, the kinetics of complex formation of Sn(II) and UO_2(VI) with a series of Schiff bases was studied spectrophotometrically using the stopped-flow technique in methanol as solvent. The activation parameters $\Delta H^{\#}$ and $\Delta S^{\#}$ for the formation reactions of the complexes studied in methanol are almost identical which supports the assumption that the reactions have a common mechanism. The reactions are considered to proceed through an associative mechanism.

INTRODUCTION

Generally, Schiff bases are considered as a very important class of organic compounds. Substituted anilines have been widely used as a precursors for the preparation of bidentate Schiff base ligands by simple condensation of their primary amino group with the

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carbonyl group of *ortho*-substituted aromatic carbonyl compounds. Bidentate Schiff bases derived from salicyl- aldehyde and substituted anilines are the simplest ones. Despite this, the kinetics of the formation reactions of Sn(II) and UO_2(VI)-Schiff base complexes have rarely been studied[1,2]. The present study was undertaken in an attempt to better understand the reaction patterns of these reactions.

For this purpose four bidentate Schiff base ligands of N, O type and their Sn(II) and UO_2(VI) complexes have been prepared. Thermodynamic data available for these types of Schiff base complexes generally are scarce, which may be attributed mainly to their insolubility. In this paper we report the kinetics and spectral properties of Schiff base complexes of Sn(II) and UO_2(VI). We have extended a preceding study[3] to examine the kinetic properties of Schiff base complexes and explore the competition between the various functional groups in these ligands.

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EXPERIMENTAL

All the chemicals and solvents used were reagent grade. The Schiff base ligands were obtained as colored crystals in methanol.

Synthesis of Schiff Base Hcps

A quantity of 0.1 mol (17.25 g) *m*-chloroaniline was dissolved in 75 mL methanol and 0.09 mol (10.62 g) of salicylaldehyde was dissolved in 50 mL methanol. The amine solution was added at room temperature dropwise to the aldehyde solution with magnetic stirring. The mixture was refluxed for 30 min with stirring and then left at room temperature for an hour. The color of the solution slowly darkened and some dark orange precipitate formed. The solution was then cooled down to -10 °C. The precipitated product was filtered, recrystallised from hot ethanol-methanol (2:1 ratio) and dried at room temperature at 0.1 mm Hg. The other Schiff bases were prepared in a similar manner. Structures of the ligands are given in Figure 1.

Synthesis of the Complex $UO_2(cps)_2$

To a solution of Hcps (0.05 mol, 11.40 g) in 75 mL methanol was added a methanol solution of hydrated $UO_2(NO_3)_2{\cdot}6H_2O$ (0.02 mol, 10 g) with magnetic stirring. After mixing for 30 min at 40 °C, the mixture was left stirring at room temperature for three hours. The deep orange-brown precipitate was collected, washed with cold ethanol and dried at 25 °C in

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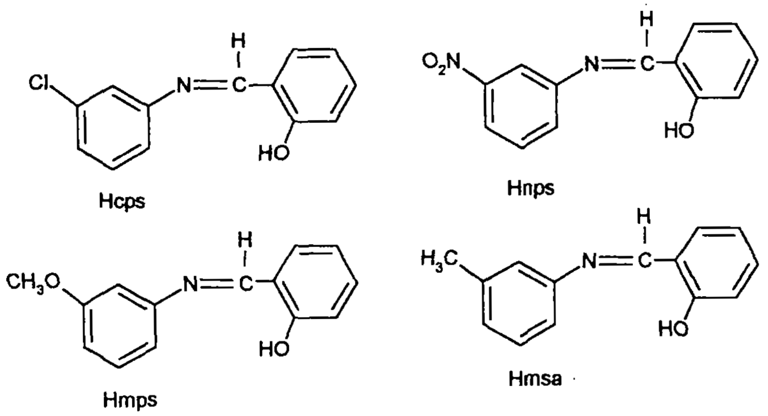

Figure 1. Structures of the Ligands

a vacuum desiccator. The other complexes were prepared in a similar manner. $SnCl_2$ was used for the tin complexes and the kinetic study.

Kinetic Measurements

Kinetic measurements were made by stopped-flow and UV-Vis spectrophotometry in a cell block thermostated to ± 0.1 °C in the temperature range 25-45 °C by means of an external water bath. The complex formation reactions were followed by monitoring λ_{max} of the reactant or product species. Pseudo-first order conditions of excess ligand concentrations were employed. The plots of $\ln(A_\infty - A_t)$ *versus* time were generally linear for three or more half-lives. A_t = absorbance at any time and A_∞ = equilibrium absorbance where no significant absorbance change is observed. A_∞ readings were recorded after 6 half-lives. The reported rate constants were determined from least-squares plots of $\ln(A_\infty - A_t)$ *versus* time. The ionic strength of the solutions was kept constant by the addition of 0.100 M $NaClO_4$. Spectroscopic grade methanol was used for the kinetic runs.

Physical Measurements

Elemental analyses of C, H and N were obtained at the Elemental Analysis Service of the Research Institute of Gebze, Turkey. ^1H NMR spectra of the ligands were recorded on a Bruker-AC 200 L NMR spectrometer using $CDCl_3$ as solvent. Melting points were recorded on a Stuart Scientific melting point apparatus. IR spectra were recorded on a Jasco IR 300E spectrometer on KBr discs. Magnetic susceptibility measurements on powdered samples were carried out with a Gouy balance at 25 °C . Effective magnetic moments were calculated by using the equation $\mu_{eff} = 2.828(\chi_A.T)^{1/2}$ and are given in Table I with the other physical data. UV-Visible spectra were recorded on a Bausch-Lomb Spectronic 2000 spectrophotometer.

RESULTS AND DISCUSSION

Our previous studies[4] of Sn(II) complexes of Schiff bases indicated that coordination occurs through the imine nitrogen of the Schiff base . This conclusion was based on NMR and IR parameters; we were unable to obtain crystals of these complexes suitable for X-ray structure determinations. The suggested structures of the complexes are given in Figure 2. A kinetic study has shown that the formation of the compounds is sensitive to the nature of substituents in aniline. The presence of a methoxy group on aniline facilitates the reaction. The intramolecular hydrogen bond between the fairly acidic phenolic hydrogen and carbonyl oxygen atom in salicylaldehyde catalyses the condensation reaction with substituted anilines so effectively that the corresponding Schiff bases are formed in good yields.

$$SnCl_{2(solv)} + 2\,Hcps \longrightarrow Sn(cps)_2 + 2HCl$$

For the different complexes k_{obs} values are comparable. Based on these observations and from consideration of $\Delta H^{\#}$ and $\Delta S^{\#}$ values which are given in Table II, we propose an associative mechanism, with bond formation by the incoming Schiff bases. The measured negative entropy and small variation between activation enthalpies are consistent with an associative mechanism.

^{1}H NMR Spectra

A sharp singlet appeared at 8.16-9.02 ppm in the spectra of the Schiff bases and was assigned to the imine proton (Table III). The signals occurring at 6.33-8.30 ppm were assigned to the phenyl ring protons. A singlet appearing in the region 10.32-11.04 ppm may be ascribed to the O-H protons, which can form hydrogen bonds with the nitrogen atom of the imine group. The methoxy group displayed a singlet at 3.85 ppm for the three protons in Hmps and at 2.35 ppm for the methyl protons in Hmsa.

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Table I. Physical Data of the Complexes and Ligands

Molecular Formula	Empirical Formula	Molecular Weight (Calc.)	Yield (%)	M.p. (°C)	Analysis, found(calc)			%M	μ_{eff} (B.M.)
					%C	%H	%N		
Hmps	$C_{14}H_{13}NO_2$	227	83	79	(73.99) 73.94	(5.77) 5.96	(6.16) 6.03		
Hcps	$C_{13}H_{10}NOCl$	232	79	110	(67.40) 67.95	(4.35) 4.01	(6.05) 5.92		
Hmsa	$C_{14}H_{13}NO$	211	82	106	(79.59) 79.81	(6.20) 6.43	(6.63) 6.42		
Hnps	$C_{14}H_{10}N_2O_3$	242	85	95	(64.46) 65.11	(4.16) 3.99	(11.56) 11.85		
$UO_2(mps)_2$	$C_{28}H_{24}N_2O_8U$	722	71	160	(46.55) 46.23	(3.35) 3.28	(3.88) 3.78	(32.94) 32.16	0.39
$UO_2(cps)_2$.	$C_{26}H_{18}N_2O_4Cl_2U$	731	70	285	(42.70) 42.36	(2.48) 2.57	(3.83) 3.76	(32.55) 31.98	0.86
$UO_2(msa)_2$.	$C_{28}H_{24}N_2O_4U$	690	81	248	(48.70) 48.93	(3.50) 3.44	(4.06) 4.11	(34.47) 34.12	0.66
$UO_2(nps)_2$.	$C_{26}H_{18}N_4O_8U$	752	76	215	(41.50) 41.77	(2.41) 2.52	(7.45) 7.67	(31.65) 31.07	0.54
$Sn(mps)_2$.	$C_{28}H_{28}N_2O_4Sn$	571	82	161	(58.89) 58.67	(4.24) 4.32	(4.91) 4.76		0.55
$Sn(cps)_2$.	$C_{26}H_{18}N_2O_2Cl_2Sn$	580	77	171	(53.85) 53.60	(3.13) 3.25	(4.83) 4.79		0.57
$Sn(msa)_2$.	$C_{28}H_{24}N_2O_2Sn$	539	88	208	(62.37) 62.03	(4.49) 3.98	(5.20) 5.10		0.47
$Sn(nps)_2$.	$C_{26}H_{22}N_4O_8Sn$	601	73	210	(51.96) 52.27	(3.02) 3.23	(9.32) 9.15		0.33

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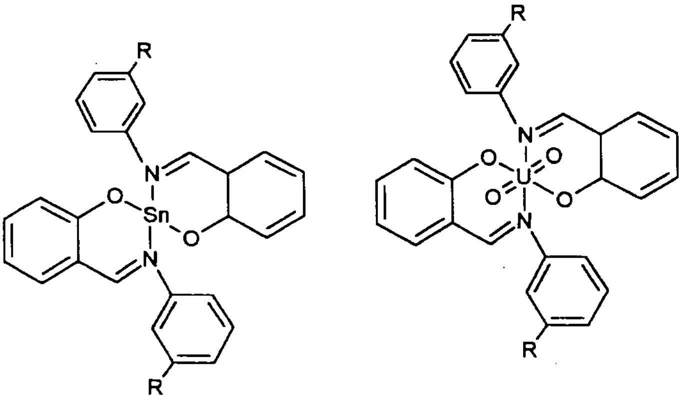

Figure 2. Suggested Structure of the Complexes (R = Cl, NO_2, OCH_3, CH_3)

Table II. Activation Parameters and λ_{max} of the Complexes

Complex	$k_{obs}(s^{-1})x10^3$ 25 °C	$\Delta H^{\#}$(kJ/mol)	$\Delta S^{\#}$(kJ/mol)	$\lambda_{CT(nm)}$ (ε)
$UO_2(msa)_2$	6.41±0.03	24±1	-181±2	356 (980)
$UO_2(mps)_2$	8.45±0.04	27±1	-192±2	365 (810)
$UO_2(cps)_2$	5.88±0.03	23±1	-188±2	350 (830)
$Sn(msa)_2$	8.86±0.02	23±2	-193±3	370 (1580)
$Sn(mps)_2$	9.43±0.03	25±1	-196±3	360 (1110)
$Sn(cps)_2$	6.67±0.04	23±1	-189±1	365 (1240)

Table III. NMR Data of the Schiff Bases

Ligands	δ(N=CH)	δ(N....H-O)	δ(O-CH_3)	δ(CH_3)	δ(Ar-H)
Hcps	8.64 s	10.85 s			7.45-6.45 m
Hnps	9.02 s	11.04 s			8.30-7.25 m
Hmps	8.28 s	10.70 s	3.85 s		7.25-6.40 m
Hmsa	8.16 s	10.32 s		2.35 s	7.20-6.33 m

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Magnetic Properties

All the complexes studied were diamagnetic and are low interest for the investigations of the temperature-dependence of the magnetic susceptibilities.

UV-Vis Spectra

The electronic spectra of the Sn(II) and $UO_2(VI)$ complexes were studied in methanol. The electronic spectrum of the $Sn(msa)_2$ complex is given in Figure 3. The complexes have a very intense color so that low concentrations have been used. In the UV-Vis region, intense bands below 300 nm present in the free ligand and assigned to $\pi \rightarrow \pi^*$ transitions of a substituted benzene ring are also present in the complexes. The band at about 320-350 nm in the Schiff bases due to the $n \rightarrow \pi^*$ transition of non-bonding electrons present on the nitrogen of the imine group undergoes a hypsochromic shift on coordination to Sn(II) and $UO_2(VI)$. The moderately intense bands due to electron transition from the π^* of the ligand to the empty orbital of metal in the range 350-400 nm may be assigned to ligand LMCT[5]. The energy of the LMCT varies with the ability of the electron releasing power of the substituent on the Schiff bases.

Kinetics of Complex Formation

The rate of formation of the Schiff bases with Sn(II) or $UO_2(VI)$ was investigated by the stopped-flow technique, following the formation of the product. Typical first-order behaviour was observed during at least two half-lives, with the ligand always present in excess. The observed rate constants increased linearly with the substituents OCH_3 > CH_3 > Cl. This order may be explained by the effect of electron donating ability of the methoxy group. We were unable to get reliable kinetic data for Hnps that is why those data are not included here. There was a very small absorbance change (at least 0.1 absorbance change is needed for reliable kinetic data) during the kinetic runs of this complex. The mechanism of the formation reaction may be described in terms of an associative SN_2 mechanism. The formation reaction is represented by the following equation for an associated mechanism. In the first step, outer-sphere association has taken place and then inner-sphere association carries the reactions to product.

$$UO_2(MeOH)_x^{2+} + yHL \rightleftharpoons \underset{\text{outer-sphere}}{UO_2(MeOH)_x^{2+}, y(HL)} \rightleftharpoons \underset{\text{inner-sphere}}{UO_2^{2+}(L)_y\,(MeOH)_x\,(H^+)_y} \rightleftharpoons [UO_2(L)_y] + x(MeOH) + yH^+$$

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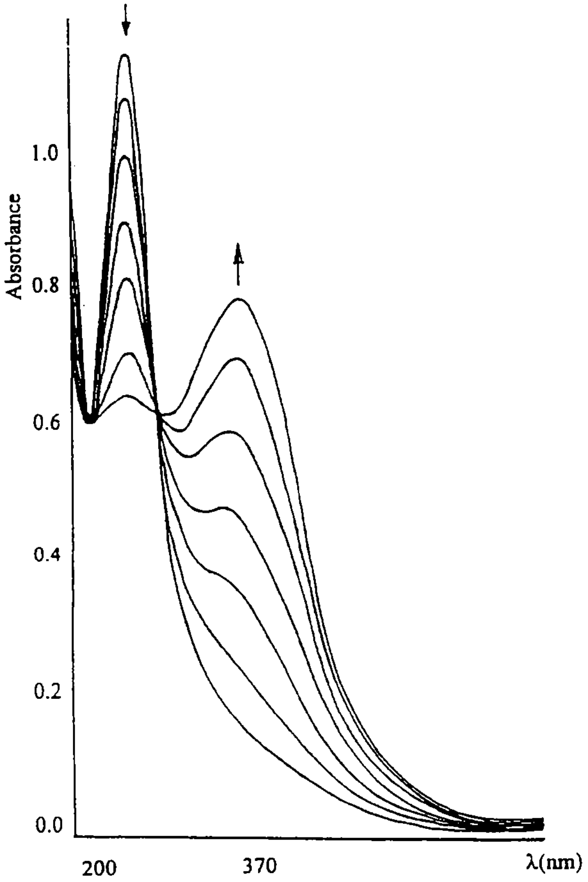

Figure 3. Electronic Spectra of [Sn(msa)$_2$] Measured During the Formation of the Complex in Methanol [SnCl$_2$] : 3.0x10^{-3} and [Hmsa] : 3.0x10^{-3} M

The activation parameters, $\Delta H^{\#}$ and $\Delta S^{\#}$, are consistent with an associative mechanism with negative entropy[6-8]. The activation parameters for the complex formation reactions were calculated from the equation,

$$\ln k/T = \ln k_B/h + \Delta S^{\#}/R - \Delta H^{\#}/RT$$

$\ln k_B/h$ is the frequency factor in the Eyring equation.

Table IV. The Important IR Frequencies (cm^{-1}) of the Ligands and their Complexes (in KBr)

Compound	ν(C=N)	ν(O-H)
Hcps	1635 s	2648 w,br
Hnps	1641 s	2640 w,br
Hmps	1628 s	2650 w,br
Hmsa	1608 s	2644 w,br
$UO_2(mps)_2$	1597 m	
$UO_2(cps)_2$.	1601 m	
$UO_2(msa)_2$.	1598 m	
$UO_2(nps)_2$.	1608 m	
$Sn(mps)_2$.	1604 m	
$Sn(cps)_2$.	1603 m	
$Sn(msa)_2$.	1592 m	
$Sn(nps)_2$.	1595 m	

IR Spectra

Infrared spectra of the Schiff bases show a new band in the region 1600-1640 cm^{-1} which can be attributed to the formation of an imine group. This band is shifted to a lower frequency (1592-1608 cm^{-1}) in the complexes[9], indicating that the C=N group is taking part in coordination. This may be due to a decrease in the bond order of C=N which is further supported by the presence of a new band in far-IR spectra of the complexes which may be assigned to the metal-nitrogen band. The spectrum of Schiff bases should display a ν(O-H) band in the region about 3500 cm^{-1} in the absence of any hydrogen bonding. No absorption band was observed in this region, but instead a broad band of weak intensity was located in the 2650 cm^{-1} region. This band ascribed to the ν(O-H) which is known to shift very significantly to lower frequency as a result of O-H····N intramolecular hydrogen bonding[10]. The disappearance of ν(O-H) in the complexes of Schiff bases indicates deprotonation of O-H group and consequent coordination of the oxygen atom to the metal. The important IR frequencies (in KBr) of the ligands and their complexes with their assignments are given in Table IV.

REFERENCES

1. B. Erk and Y. Baran, Chim. Acta Turcica., 18, 30 (1990); Chem. Abstr., 18, 590795 (1991).
2. B. Erk and N. Gunduz, Inorg. Chim. Acta, 1, 91 (1989).
3. E. M Khairy, M. M Shoukry and M. M Khalil, Trans. Met. Chem., 2, 176 (1996).

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4. Y. Baran and B. Erk, Tr. J. Chem., 4, 312 (1996); Chem. Abstr., 20, 123561 (1997).

5. G. Minu, H. Bhowon, Li Kam Wah and R. Narain, Polyhedron., 18, 341 (1998).

6. H. Toma and E. Malin, Inorg. Chem., 15, 1247 (1973).

7. C. P.Brink and D. Crumbliss, Inorg. Chem., 23, 4708 (1984).

8. B. Erk and Y. Baran, Synth. React. Inorg. Met-Org. Chem., 21, 1321 (1991).

9. M. B. Armando, R. R. Lena, M. E. Refael and D. R. P. Frederico, J. Coord. Chem., 29, 359 (1993).

10. L. J. Bellamy "Advances In Infrared Group Frequencies", Methuen, London, p.275 (1968)

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