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Dioxouranium(VI) Complexes with Sulphur Donor Schiff Bases Derived from Salicylaldehyde, Substituted Salicylaldehydes & 3-Aminothiophenol

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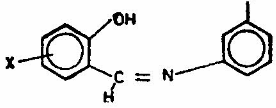
New dioxouranium(VI) complexes of schiff bases derived from 3-aminothiophenol and salicylaldehyde, 5-bromosalicylaldehyde, 3-methoxysalicylaldehyde, 4-methoxysalicylaldehyde, 5-methoxysalicylaldehyde or 2-hydroxy-1-naphthaldehyde have been synthesized and characterized on the basis of analytical, conductance, molecular weight, magnetic susceptibility, IR and electronic spectral data. The complexes are of the types $[UO_2L.CH_3OH]_2$, $UO_2(LH)_2$, $UO_2(LH_2)_2(NO_3)_2$ and $UO_2(LH)(NO_3)(AA)$ (where LH_2 =schiff base, AA=2,2′-bipyridine or *o*-phenanthroline). The absolute coordination number of uranium is six, seven, nine and twelve in $UO_2(LH)_2$, $[UO_2L.CH_3OH]_2$, $UO_2(LH)(NO_3)(AA)$ and $UO_2(LH_2)_2(NO_3)_2$ respectively. The complexes are non-electrolytes and diamagnetic.

In recent years, considerable interest has been evoked by the complexes of first and second transition series metal ions with sulphur donor schiff bases having NS or ONS donor atoms[1]. But there appears to be no report on sulphur donor schiff base complexes with actinide elements, though actinide complexes with sulphur containing ligands are known[2]. We report here the synthesis and characterisation of new dioxouranium(VI) complexes of the schiff bases (I) derived from 3-aminothiophenol and salicylaldehyde or substituted salicylaldehydes. Only the copper(II) and oxovanadium(IV) complexes of the schiff bases(I) have been reported so far[3].



I. X=H, 5-BROMO, 5-METHOXY, 3-METHOXY, 4-METHOXY AND 5,6-BENZO

Salicylaldehyde(sal) was a Sarabhai M. reagent while 5-bromosalicylaldehyde (5-bromosal), 4-methoxysalicylaldehyde (4-methoxysal), 5-methoxysalicylaldehyde (5-methoxysal), 3-aminothiophenol (3-amtp), 2, 2′-bipyridine (bipy) and *o*-phenanthroline (ophen) were Aldrich reagents. 3-Methoxysalicylaldehyde (3-methoxysal) and 2-hydroxy-1-naphthaldehyde (hydroxynaph) were Fluka AG products. Dioxouanium(VI) acetate dihydrate and dioxouranium(VI) nitrate hexahydrate were Hopkins and Williams, and BDH reagents respectively. Sodium methoxide was supplied by SD's Lab-Chem. Industry.

Uranium and nitrogen analyses were done as described previously[4]. Conductance, molecular weight, magnetic susceptibility and IR measurements were also done as reported earlier[4]. Quantitative determination of ligand was carried out by bromometric titration technique. Electronic spectra were recorded on a Unicam SP-1600 spectrophotometer having an attached reflectance arrangement. The magnetic susceptibility measurements were done by the Gouy method using $Hg[Co(NCS)_4]$ as the standard.

General method of syntheses of schiff bases — An ethanolic solution of 3-aminothiophenol (0.63 g, 0.005 mol in 10 ml) was added to an ethanolic solution of appropriate aldehyde (0.005 mol in 30 ml). The mixture was stirred magnetically for 30 min. The separated compound was suction filtered, washed with ethanol and dried *in vacuo* at room temperature, yield = 90%.

Syntheses of dioxouranium (VI) complexes : Complexes of the type $[UO_2L.CH_3OH]_2$ — A methanolic solution of the appropriate aldehyde (0.001 mol in 15 ml) was added to a methanolic solution of 3-aminothiophenol (0.13 g, 0.001 mol in 10 ml). The mixture was refluxed on a water-bath for 30 min when a clear yellow solution was obtained. It was added to a methanolic solution of dioxouranium(VI) acetate dihydrate (0.43 g, 0.001 mol in 20 ml) and the contents refluxed on a water-bath for 2 hr. A methanolic solution of sodium methoxide (0.11 g, 0.002 mol in 15 ml) was added and the mixture further refluxed for 1 hr. The separated compound was filtered, washed with methanol and dried *in vacuo*, yield = 70%.

Complexes of the type $UO_2(LH)_2$ — A methanolic solution of the appropriate aldehyde (0.002 mol in 20 ml) was added to a methanolic solution of 3-aminothiophenol (0.25 g, 0.002 mol in 15 ml). The mixture was refluxed on a water-bath for 30 min. The freshly prepared methanolic solution of dioxouranium(VI) acetate dihydrate (0.43 g, 0.001 mol in 20 ml) was added to this solution. The mixture was refluxed on a water-bath for 4 hr. The partial evaporation of the solvent under a fan produced the compound which was filtered, washed with methanol and recrystallized from methanol. The compound was dried *in vacuo*, yield = 60%.

Complexes of the type $UO_2(LH_2)_2(NO_3)_2$ — A methanolic solution of the appropriate aldehyde (0.002 mol in 20 ml) was added to a methanolic solution of 3-aminothiophenol (0.25 g, 0.002 mol in 15 ml). The mixture was refluxed on a water-bath for 30 min. A freshly prepared methanolic solution of dioxouranium(VI) nitrate hexahydrate

TABLE 1 — ANALYTICAL, MOLECULAR WEIGHT AND INFRARED SPECTRAL DATA OF DIOXOURANIUM(VI) COMPLEXES OF SCHIFF BASES

Compound/ Stoichiometry	Found (Calc.)					IR Bands (cm^{-1})					
						ligand (complex)					
	U%	N%	S%	Ligand %	Molec. wt	ν(C=N)	ν(C-O)	ν(C-S)	ν(C-O) (CH$_3$OH)	ν_{as} (OUO)	ν_s (OUO)
[UO$_2$(sal-3-amtp).CH$_3$OH]$_2$	44.63	2.90	5.83	42.96	1043	1645	1500	775	975	920	805
$U_2C_{28}H_{26}N_2O_3S_2$	(44.69)	(2.65)	(6.05)	(42.91)	(1058)	(1625)	(1510)	(840)			
[UO$_2$(5-bromosal-3-amtp). CH$_3$OH]$_2$	38.83	2.39	5.08	50.63	1236	1640	1510	775	970	910	795
U_2-$C_{28}H_{24}N_2O_8S_2Br_2$	(39.14)	(2.30)	(5.26)	(50.33)	(1216)	(1615)	(1540)	(830)			
[UO$_2$(3-methoxysal-3-amtp). CH$_3$OH]$_2$	42.32	2.78	5.48	45.93	1028	1640	1500	—	975	905	790
$U_2C_{30}H_{30}N_2O_{10}S_2$	(42.58)	(2.50)	(5.72)	(45.97)	(1118)	(1605)	(1530)	(845)			
[UO$_2$(4-methoxysal-3-amtp). CH$_3$OH]$_2$	42.40	2.38	5.40	46.00	1105	1620	1510	785	975	910	795
$U_2C_{30}H_{30}N_2O_{10}S_2$	(42.58)	(2.50)	(5.72)	(45.97)	(1118)	(1605)	(1525)	(850)			
[UO$_2$(5-methoxysal-3-amtp). CH$_3$OH]$_2$	42.71	2.59	5.61	45.95	1134	1620	1510	785	960	915	—
$U_2C_{30}H_{30}N_2O_{10}S_2$	(42.58)	(2.50)	(5.72)	(45.97)	(1118)	(1600)	(1535)	(850)			
UO$_2$(sal-3-amtp)$_2$	32.50	3.61	8.61	62.65	715	1645	1500	775		890	a
$UC_{26}H_{20}N_2O_4S_2$	(32.78)	(3.86)	(8.32)	(62.81)	(726)	(1625)	(1515)	(770)			
UO$_2$(3-methoxysal-3-amtp)$_2$	30.09	3.80	8.25	65.43	802	1640	1500	—		885	a
$UC_{28}H_{24}N_2O_6S_2$	(30.28)	(3.56)	(8.14)	(65.65)	(786)	(1600)	(1515)	(780)			
UO$_2$(4-methoxysal-3-amtp)$_2$	30.53	3.27	8.35	65.56	763	1620	1510	785		890	a
$UC_{28}H_{24}N_2O_6S_2$	(30.28)	(3.56)	(8.14)	(65.65)	(786)	(1605)	(1520)	(785)			
UO$_2$(5-methoxysal-3-amtp)$_2$	30.49	3.35	7.93	65.20	778	1620	1510	785		890	a
$UC_{28}H_{24}N_2O_6S_2$	(30.28)	(3.56)	(8.14)	(65.65)	(786)	(1600)	(1520)	(780)			
UO$_2$(hydroxynaph-3-amtp)$_2$	28.62	3.18	7.40	67.62	843	1645	1520	790		890	a
$UC_{34}H_{24}N_2O_4S_2$	(28.81)	(3.39)	(7.75)	(67.31)	(826)	(1630)	(1530)	(790)			
UO$_2$(sal-3-amtp)$_2$(NO$_3$)$_2$	27.78	6.40	7.38	53.40	867	1645	1500	775		940	840
$UC_{26}H_{22}N_4O_{10}S_2$	(27.93)	(6.57)	(7.51)	(53.76)	(852)	(1630)	(1535)	(855)			
UO$_2$(hydroxynaph-3-amtp)$_2$ (NO$_3$)$_2$	24.72	6.10	6.95	58.49	941	1645	1520	790		935	835
$UC_{34}H_{26}N_4O_{10}S_2$	(25.00)	(5.88)	(6.72)	(58.61)	(952)	(1625)	(1530)	(850)			
UO$_2$(sal-3-amtp)(NO$_3$(bipy)	33.06	7.50	4.21	53.97	703	1645	1500	775		910	810
$UC_{23}H_{18}N_4O_6S$	(33.24)	(7.82)	(4.47)	(53.63)	(716)	(1620)	(1540)	(830)			
UO$_2$(sal-3-amtp)(NO$_3$)(ophen)	33.47	7.21	4.68	54.85	753	1645	1500	775		905	805
	(32.16)	(7.57)	(4.33)	(55.14)	(740)	(1615)	(1540)	(830)			

(a) Band masked by the absorption of schiff base.

(0.51 g, 0.001 mol in 10 ml) was added and the mixture was refluxed on a water-bath for 2 hr. The partial evaporation of the solvent under a fan gave the desired compound. This was filtered, washed with methanol and recrystallized from methanol. The compounds were dried *in vacuo*, yield = 40%.

Complexes of the type $UO_2(LH)(NO_3)(AA)$ — A methanolic solution of salicylaldehyde (0.13g, 0.001 mol in 10 ml) was added to a methanolic solution of 3-aminothiophenol (0.13g, 0.001 mol in 10 ml). The mixture was refluxed on a water-bath for 30 min. A freshly prepared methanolic solution of dioxouranium(VI) nitrate hexahydrate (0.51 g, 0.001 mol in 10 ml) was added and the mixture was further refluxed on a water-bath for 1 hr. A methanolic solution of 2, 2′-bipyridine (0.16 g, 0.001 mol in 5 ml) or *o*-phenanthroline monohydrate (0.20 g, 0.001 mol in 10 ml) was added to this solution. The mixture was refluxed on a water-bath for 1 hr. The separated brown precipitate was filtered, washed with methanol and dried *in vacuo*, yield = 60%.

The freshly prepared methanolic solution of dioxouranium(VI) acetate dihydrate or dioxouranium (VI) nitrate hexahydrate reacts with the schiff base-(I) in 1:2 molar ratio and the complexes of the types $UO_2(LH)_2$ and $UO_2(LH_2)_2(NO_3)_3$ are formed, respectively. On the other hand, the equimolar amounts of dioxouranium(VI) acetate dihydrate and the schiff base(I) react in presence of sodium methoxide and produce the complexes of the type $[UO_2L.CH_3OH]_2$. The reaction of equimolar amounts of dioxouranium(VI) nitrate hexahydrate and the schiff base (I, X=H) in presence of 2,2′-bipyridine or *o*-phenanthroline(AA) gives the complex $UO_2(LH)(NO_3)$-(AA). The analytical results (Table 1) support these formulations. The complexes $[UO_2L.CH_3OH]_2$ do not lose weight on heating at 120°C for a few hours indicating that methanol is not lost at this temperature and is coordinated to uranium. The complexes are non-electrolytes in DMSO (Λ_m = 1.09-8.2 ohm^{-1} cm^2 mole^{-1}). The molecular weight measurements indicate the monomeric nature of the $UO_2(LH)_2$,$UO_2(LH_2)_2(NO_3)_2$ and $UO_2(LH)(NO_3)$-(AA) and the dimeric nature of $[UO_2L.CH_3OH]_2$ complexes. The complexes are diamagnetic as expected for the $5f^0$ system (μ_{eff} = 0-0.3 B.M.).

The schiff bases exhibit a medium intense IR band around 3100 cm^{-1} assignable to ν(OH) mode of the hydrogen-bonded phenolic OH group[5]. The complexes $UO_2(LH)_2$ and $UO_2(LH)(NO_3)(AA)$ do not show this band indicating the deprotonation and consequent coordination of phenolic OH group. The presence of a broad band around 3400 cm^{-1}

in the spectra of $[UO_2L.CH_3OH]_2$ and $UO_2(LH_2)(NO_3)_2$ is due to the ν(OH) of co ordinated methanol in the former and ν(OH) of coordinated schiff base in the latter complexes. The schiff bases(I) exhibit a broad band of medium intensity around 2500 cm^{-1} assignable to ν(S-H)[6,7]. In the $[UO_2L.CH_3OH]_2$ complex this band disappears indicating the deprotonation of the thiol group and consequent coordination of sulphur atom to uranium[8,9]. ν(C=N) mode of the schiff bases(I) occurs[3] at 1620-1645 cm^{-1}. In the dioxouranium(VI) complexes this band shifts to lower energy by 15-40 cm^{-1} indicating coordination of the nitrogen atom ofthe azomethine moiety to uranium[10]. The schiff bases exhibit ν(C-O) (phenolic) at 1500-1520 cm^{-1}. On complex formation this band shifts to higher energy by 5-35 cm^{-1} indicating the coordination of phenolic oxygen atom to uranium[3]. Methanol exhibits ν(C-O) (alcoholic)[11] at 1034 cm^{-1} and the complexes $[UO_2L.CH_3OH]_2$ exhibit this band at 960-975 cm^{-1}; the negative shift is indicative of oxygen coordination of methanol to uranium[12]. The schiff bases exhibit ν(C-S) at 775-790 cm^{-1}. In the complexes $[UO_2L.CH_3OH]_2$, $UO_2(LH_2)_2(NO_3)_2$ and $UO_2(LH)(NO_3)$(AA)this band shifts to higher energy by 45-80 cm^{-1} indicating the coordination of sulphur atom to uranium[7,8]. The ν(C-S) mode does not shift appreciably in the $UO_2(LH)_2$ complexes in comparison with the free ligand band indicating the non-participation of SH group in coordination. The complexes exhibit the ν_{as} (O=U=O) mode at 885-940 cm^{-1}, the usual range reported for the majority of dioxouranium(VI) complexes[13,14]. The plot of ν_s vs ν_{as} is linear and the data satisfy the equations: (i) $\nu_s = -115+1.0\ \nu_{as}$ for $[UO_2L.CH_3OH]_2$ and (ii) $\nu_s=-100+1.0\ \nu_{as}$ for $UO_2(LH)_2$, $UO_2(LH_2)_2(NO_3)_2$ and $UO_2(LH)(NO_3)$(AA). The greater negative value of the intercept in 1:1 complexes may be due to greater covalent nature of the 1 : 1 complexes. The force constant (f_{U-O}) for U=O bond has been calculated by the method of McGlynn *et al.*[14] and the values (6.51-7.34 mdynes/Å) agree well with those for similar dioxouranium(IV) complexes[10,15]. The U-O bond length (R) has been calculated using the equation[16], $R = 1.08\ f^{-1/3} + 1.17$ and the present values (1.73-1.75) are in the expected range (1.60-1.92 Å)[17].

The complexes, UO_2(sal-3-amtp)$_2(NO_3)_2$, UO_2(hydroxynaph-3-amtp)$_2$ $(NO_3)_2$, UO_2 (sal-3-amtp)(NO_3) (bipy) and UO_2 (sal-3-amtp)(NO_3)(ophen) do not exhibit any strong band around 1380 cm^{-1} but show two bands at 1505-1515 and 1280-1295 cm^{-1} characteristic of ν_1(NO) and $\nu_4(NO_{2(as)})$ modes respectively of the nitrate group in C_{2v} symmetry[18,19] indicating that the nitrate group in the complexes is not free but is coordinated[20]. Electrical conductance data also support this view. The bidentate nature of nitrate group is revealed by the presence of bands[20,21] at 1030-1040 cm^{-1} (ν_2), 765-800 cm^{-1} (ν_6), 730-750 cm^{-1} (ν_3) and 675-680 cm^{-1} (ν_5). The combination bands ($\nu_2 + \nu_3$) and ($\nu_2 + \nu_5$) appear at 1765-1790 and 1725-1740 cm^{-1} respectively. For bidentate coordination of nitrate group[22,24], the energy separations between the bands ($\nu_2+\nu_3$), ($\nu_2+\nu_5$); ($\nu_1+\nu_2$), ($\nu_2+\nu_4$); (ν_1-ν_4); ($\nu_3-\nu_6$) are of the order ~41 -53, ~190-245, ~185-235 and ~38-71 cm^{-1} respectively; these energy separations lie ~16-21, ~115-135, ~105-115, and ~13-20 cm^{-1} in monodentate nitrate complexes[22-24]. We have observed the energy separations of these bands to occur in the range 40-55, 220-260, 215-220 and 65-75 cm^{-1} respectively indicating the bidentate coordination of nitrate group.

The electronic spectra of $[UO_2$ (sal-3-amtp)-$CH_3OH]_2$, UO_2(sal-3-amtp)$_2$, UO_2(sal-3-amtp)$_2$-$(NO_3)_2$ and UO_2(sal-3-amtp) (NO_3)(bipy) exhibit a new band around 20000 cm^{-1} which is assigned to the $^1E_g^+ \longrightarrow {}^3\pi_u$ transition, typical of OUO moiety[25]. The analytical and IR data and valence requirement of the metal ion indicate the neutral tridentate (ONS donor), monobasic bidentate (ON donor), monobasic tridentate (ONS donor) and dibasic tridentate (ONS donor) nature of the schiff bases in the complexes $UO_2(LH_2)_2(NO_3)_2$, $UO_2(LH)_2$, $UO_2(LH)(NO_3)$(AA), and $[UO_2L.CH_3OH]_2$ respectively. The absolute coordination number of uranium appears to be six, seven, nine and twelve in the complexes $UO_2(LH)_2$, $[UO_2L.CH_3OH]_2$, $UO_2(LH)(NO_3)$(AA) and $UO_2(LH_2)_2(NO_3)_2$ respectively.

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Studies on Chelates Derived from Salicylic Acid-Urea-Formaldehyde Copolymer

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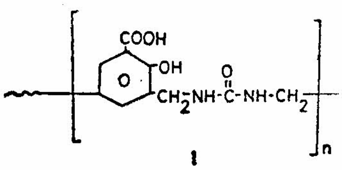
Chelates of Cu(II), Ni(II), Co(II), Fe(III), Mn(II), oxovanadium(IV), Zn(II), and dioxouranium(VI) with salicylic acid-urea-formaldehyde copolymer (SUF) have been prepared and characterized on the basis of their elemental analyses, magnetic susceptibility measurements, infrared and electronic spectral studies. Except for the oxovanadium(IV) chelate, all the other chelates are assigned distorted octahedral configuration. Most probably, oxovanadium(IV) chelate may have a square-pyramidal structure.

METAL chelates of salicylic acid-formaldehyde polymer are reported to be useful in photographic development[1] and for pressure-sensitive copy paper[2]. We have earlier prepared and characterized salicylic acid-urea-formaldehyde (SUF) copolymer[3]. The probable average repeating unit of the copolymer has been assigned as (I).



I

We report here the preparation and characterization of Cu(II), Ni(II), Co(II), Fe(III), Mn(II), oxovanadium(IV), Zn(II) and dioxouranium(VI) chelates with SUF.

All the chemicals used were either Sarabhai Merck reagents or other reagents of C.P. grade.

The ligand SUF was prepared by heating the stoichiometric proportion of the concerned monomer in the presence of dil.HCl as a catalyst at 100°C for 5 hr[3].

Preparation of chelates— Copper(II) nitrate (1.81 g, 0.0075 mol) was dissolved in DMF-water mixture (100 ml). The ligand (3.33 g, 0.015 mol) was dissolved in DMF (100 ml). Both the solutions were filtered through a G_2 sintered funnel and the metal ion solution was added dropwise to the polymer solution with constant stirring. A saturated aq. solution of sodium acetate was added to the above mixture when an yellowish-green product precipitated out (pH = 6.0). The product was digested for sometime on a water-bath, filtered and washed successively with DMF, hot water and acetone. The air dried chelate was powdered and allowed to dry in an oven at 60°C for 2 hr; yield, 3.2 g. Other chelates were prepared employing the same procedure. For Ni(II), Co(II), Fe(III), Zn(II) and dioxouranium(VI) chelates, metal nitrates were used while chloride and sulphate salts were used for Mn(II) and oxovanadium(IV) chelates repsectively. Elemental analyses of these chelates are presented in Table1.

All the chelates under study were found to be insoluble in common organic solvents except the oxovanadim(IV) chelate which was slightly soluble in DMF and pyridine. Decomposition points of these chelates and ligand lie around 200°C and 210°C respectively indicating the chelates to be less stable than the polymeric ligand. The metal ion content in each chelate was estimated by titrating against standard EDTA and by the gravimetric (oxide) method, after decomposing the parent chelate. C, H and N were determined by microanalytical methods. The metal analyses indicated 1 : 2 (metal : ligand) stoichiometry for divalent metal ion complexes and 1 : 3 stoichometry for Fe(III) complex.

Reflectance spectra of the chelates were recorded on a Beckman DU spectrophotometer using MgO as the reference. Magnetic measurements were made on a Gouy balance.

The diffuse electronic spectrum of Cu(II) chelate shows a weak broad band, poorly resolved into two bands; one at 13070 cm^{-1} and the other at 11770 cm^{-1}. The bands may be assigned to $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2A_{1g}$ transitions respectively. An intense band at 24390 cm^{-1} may be of charge-transfer origin[4]. These band positions suggest a distorted octahedral structure for the chelate[5]. The electronic spectrum of Ni(II) chelate shows three bands [9250, 14155 and 25310 cm^{-1}; assignable to $^3A_{2g} \rightarrow {}^3T_{2g}$; $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions respectively] as normally expected for octahedral Ni(II) chelates[6]. The reflectance spectrum of Co(II) chelate is less resolved and dissimilar in band envelope from both octahedral and tetrahedral Co(II) chelates[7]. However, an approximately octahedral structure can be predicted from the positions of the observed bands. It shows a very broad and weak band (ν_1) at 8300 cm^{-1} and a medium band at 19420 cm^{-1} which may be assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions respectively. The reflectance spectrum of Fe(III) chelate exhibits three bands in the regions, 14290—17850, 21980 and 28170 cm^{-1}