

range 1370-1400 in these compounds might be due to chelation of alcoholic group. Instead of single band at 1097, as reported for tartaric acid, split bands around 1116-1145 and 1050-1080 are observed which means that one of the two secondary alcoholic groups is coordinated. The positions of all these bands compare well with those of  $\text{NaCuT(OH)}^1$  with an additional band of medium intensity present in the range 925-950. This may be attributed to the presence of bridging OH group<sup>9</sup>.

However, room temperature  $\mu_{\text{eff}}$  values of the complexes (Table 1) reflect the magnetic moments of the individual metal ions constituting the complex and absence of any interaction.

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## Anil Complexes of Uranyl Acetate

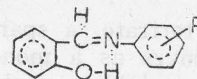
SUSHIL K. MISRA\* & FARIDA S. SIDDIQUI  
Chemistry Department, Lucknow University  
Lucknow 226007

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accepted 16 November 1978

Anil complexes of uranium(VI) of the type  $\text{UO}_2(\text{CH}_3\text{COO})(\text{SB})$  (where SB represents the anions of the Schiff bases derived from salicylaldehyde and arylamines) have been synthesized in almost quantitative yields by the reaction of uranyl acetate with the Schiff base (HSB) in 1:1 molar ratio. Conductance, electron and IR spectral studies have been carried out to characterize the complexes. The complexes are assigned octahedral structures in which acetate group acts as a bidentate ligand.

SEVERAL Schiff base complexes of dioxouranium(VI) have been reported<sup>1-4</sup>. However, uranyl complexes of Schiff bases derived from salicylaldehyde and substituted anilines have not been reported. Synthesis and physicochemical studies of some new complexes of uranyl acetate with ligands of type (I) have been described in this note.

Uranyl acetate, amines and salicylaldehyde (all BDH reagents) as well as the solvents (BDH and E. Merck reagents) were used without further purification.



Where R = o-, m-, p- $\text{CH}_3$ ;  
o-, m-, p- $\text{OCH}_3$   
m-, p- $\text{NO}_2$   
p-Cl  
(I)

The ligands were prepared by condensing salicylaldehyde with different aromatic amines. In a typical experiment, equimolar ethanolic solutions of salicylaldehyde and the aromatic amine were refluxed for an hour. On cooling a crystalline product separated which was filtered and recrystallized from the same solvent.

The complexes were prepared by the direct interaction of uranyl acetate (1 mmole) and the base (1 mmole) using methanol as the solvent and refluxing for 1-2 hr. The product was dried and filtered *in vacuo*.

Carbon, hydrogen and nitrogen in the complexes were determined by semimicro methods and uranium was estimated as oxinate (Table 1).

Using the bidentate Schiff bases HSB, complexes of the type  $\text{UO}_2(\text{CH}_3\text{COO})(\text{SB})$  were obtained. These complexes are soluble in common organic solvents and are stable in the solid and solution states. Molecular weights were measured by the cryoscopic method and the results show that the complexes are monomers. The complexes are non-electrolytes in absolute methanol indicating coordinated nature of the acetate group. In DMF also the complexes behave as non-electrolytes indicating that the acetate ion is not replaced even by the strongly coordinating DMF molecule<sup>5</sup>.

The molar magnetic susceptibilities ( $X_m$ ) of the complexes determined (Gouy method) at room temperature ( $30 \pm 1^\circ$ ) show them to be diamagnetic.

The hydrogen-bonded  $\nu$  O—H vibration present at  $2800 \text{ cm}^{-1}$  in the ligands is not observed in the

TABLE 1 — ANALYTICAL DATA AND MELTING POINTS OF THE COMPLEXES

Complex	Found (Calc.), %				
	C	H	N	U	m.p.
$\text{UO}_2(\text{CH}_3\text{CO}_2)$	35.68	2.70	2.62	44.00	195
( $\text{C}_{14}\text{H}_{12}\text{ON}-o$ )	(35.62)	(2.78)	(2.59)	(44.15)	
$\text{UO}_2(\text{CH}_3\text{CO}_2)$	35.70	2.82	2.64	44.32	192 (d)
( $\text{C}_{14}\text{H}_{12}\text{ON}-m$ )	(35.62)	(2.78)	(2.59)	(44.15)	
$\text{UO}_2(\text{CH}_3\text{CO}_2)$	35.55	2.69	2.50	44.22	210
( $\text{C}_{14}\text{H}_{12}\text{ON}-p$ )	(35.62)	(2.78)	(2.59)	(44.15)	
$\text{UO}_2(\text{CH}_3\text{CO}_2)$	34.65	2.80	2.59	42.94	168 (d)
( $\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}-o$ )	(34.59)	(2.70)	(2.52)	(42.88)	
$\text{UO}_2(\text{CH}_3\text{CO}_2)$	34.48	2.75	2.60	42.80	196 (d)
( $\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}-m$ )	(34.59)	(2.70)	(2.52)	(42.88)	
$\text{UO}_2(\text{CH}_3\text{CO}_2)$	34.62	2.64	2.55	42.82	160
( $\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}-p$ )	(34.59)	(2.70)	(2.52)	(42.88)	
$\text{UO}_2(\text{CH}_3\text{CO}_2)$	31.58	2.04	5.00	41.77	168 (d)
( $\text{C}_{13}\text{H}_9\text{O}_3\text{N}-m$ )	(31.63)	(2.10)	(4.92)	(41.82)	
$\text{UO}_2(\text{CH}_3\text{CO}_2)$	31.70	2.01	4.86	41.80	150
( $\text{C}_{13}\text{H}_9\text{O}_3\text{N}-p$ )	(31.63)	(2.10)	(4.92)	(41.82)	
$\text{UO}_2(\text{CH}_3\text{CO}_2)$	32.08	2.19	2.43	42.62	135 (d)
( $\text{C}_{13}\text{H}_9\text{OCl}-p$ )	(32.14)	(2.14)	(2.50)	(42.50)	

complexes. The disappearance of this band clearly indicates the loss of the phenolic proton on coordination.

In accordance with the published data<sup>6,7</sup> the sharp, strong band in the region 1620-1635  $\text{cm}^{-1}$  in the spectra of the Schiff bases may be assigned to  $\nu$  C=N vibrations. In the metal chelates lowering of the C=N stretch has been reported by several workers<sup>8-10</sup>. Certain cases have been reported where no appreciable change in the  $\nu$  C=N was noted<sup>11,12</sup>. Another change observed in the  $\nu$  C=N mode on complexation is the splitting of the band into two strong peaks at 1640 and 1600  $\text{cm}^{-1}$  in the U(V) derivatives<sup>13</sup>. In the present case the spectra of the metal chelates show a strong band around 1640  $\text{cm}^{-1}$  i.e. shifting of the  $\nu$  C=N mode to higher frequency side. This assignment is in agreement with that of Patel *et al.*<sup>14</sup>. A band of medium intensity observed around 1265  $\text{cm}^{-1}$  in the present ligands is ascribed to the C—O vibration of the H-bonded ring system of the ligand. In the spectra of the complexes this band is shifted to the region 1240-1255  $\text{cm}^{-1}$ . This is supported by a similar assignment made earlier<sup>15</sup> where the shift is explained as being due to the possible weakening of the C—O linkage on coordination of metal to oxygen.

The uranyl ion exhibits<sup>16,17</sup> three vibrational modes. In the spectra of the complexes a band appears in the region 885-900  $\text{cm}^{-1}$  which is assignable to the  $\nu_3$  (asymmetric stretching) vibration. A rather weak band around 850-860  $\text{cm}^{-1}$  may be attributed to the symmetric stretch,  $\nu_1$ , which is formally IR-forbidden but can become IR-active due to slight bending or crystalline perturbation<sup>18,19</sup>. In the far IR region, only one band is observed around 250  $\text{cm}^{-1}$ . The presence of an intense band at 570  $\text{cm}^{-1}$  is probably due to the  $\nu$  U—N mode. A band in the region 450-480  $\text{cm}^{-1}$  may be attributed to the  $\nu$  U—O mode<sup>20,21</sup>. This confirms the idea of the *o*-hydroxy oxygen being involved in bond formation.

Useful information on the coordination of the potentially bidentate anions, like acetate, can be had from the IR data. In the acetate ion if the coordination occurs symmetrically both the symmetric and asymmetric stretching bands will be shifted to lower frequencies as compared to the free ion which is known to absorb at 1425 and 1582  $\text{cm}^{-1}$ . In the present case,  $\nu_1$  is observed at 1356  $\text{cm}^{-1}$  and  $\nu_3$  at 1550  $\text{cm}^{-1}$ . Thus, in the present complexes the acetate ion is bidentate.

On the basis of the above discussion an octahedral geometry is proposed for the complexes, in which the linear uranyl group is surrounded by one nitrogen and three oxygen atoms.

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### Complexes of Sn(IV), Ge(IV), Si(IV), Ti(IV) & Zr(IV) Halides with Piperazine 1,4-Dicarbodithioate

S. A. A. ZAIDI\*, T. A. KHAN & N. S. NEELAM

Department of Chemistry, Aligarh Muslim University  
Aligarh 202001

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accepted 5 October 1978

Complexes of group (IV) metal tetrahalides with piperazine 1,4-dicarbodithioate (Pzdtc) of the type  $\text{SnX}_2$  (Pzdtc) [ $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ],  $\text{MCl}_2$  (Pzdtc)<sub>2</sub> [ $\text{M} = \text{Ge}, \text{Si}, \text{Ti}$ ] and  $\text{Zr}_2\text{Cl}_6$  (Pzdtc) have been synthesized and characterized. IR studies reveal that Pzdtc acts as a quadridentate ligand in Sn(IV) and Zr(IV) complexes and as a bidentate ligand in Ge(IV), Si(IV) and Ti(IV) complexes leaving a  $\text{CS}_2$  group uncoordinated to which a proton is attached. A hexacoordinated polymeric structure involving ligand bridging is proposed for the tin(IV) complexes. An octahedral *trans*-configuration is suggested for Sn(IV), Ge(IV), Si(IV) and Ti(IV) complexes.

THE transition metal complexes<sup>1-4</sup> of dithiocarbamates (carbodithioates) have been studied extensively. However, very few studies on group (IV) metal complexes<sup>5-8</sup> have been carried out. Most of the studies on complexing properties of bis-dithiocarbamates are concerned with piperazine derivatives<sup>2,9,10</sup> containing two  $\text{CS}_2$  groups at two ends of the heterocyclic ring which form polymeric chelates insoluble in water and numerous organic solvents. It was, therefore, of interest to synthesize and characterize the complexes of tetrahalides of