

## Synthesis & Vibrational Spectra of Dioxouranium(VI), Th(IV), Zr(IV) & Oxozirconium(IV) Chlorosulphates & Their Complexes with Some Organic Donors

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Solvolytic of uranyl, thorium, zirconium and zirconyl acetates in chlorosulphuric acid results in the formation of the compounds of compositions  $\text{UO}_2(\text{SO}_3\text{Cl})_2$ ,  $\text{Th}(\text{SO}_3\text{Cl})_4$ ,  $\text{Zr}(\text{SO}_3\text{Cl})_4$  and  $\text{ZrO}(\text{SO}_3\text{Cl})_2$ , respectively. The presence of strong metal-chlorosulphate covalent interaction has been inferred from the IR data of the compounds. Th(IV) and Zr(IV) chlorosulphates seem to be eight-coordinated while dioxouranium(VI) and oxozirconium(IV) chlorosulphates are six- and five-coordinated, respectively. Their complexation with pyridine, pyridine N-oxide, acridine, and 1,10-phenanthroline has also been studied.

Earlier reports<sup>1-4</sup> from our laboratory described the synthesis and characterization of various transition metal and lanthanon chlorosulphates and their complexes with several organic donors. We report here, the preparation and characterization of  $\text{UO}_2(\text{SO}_3\text{Cl})_2$ ,  $\text{Th}(\text{SO}_3\text{Cl})_4$ ,  $\text{Zr}(\text{SO}_3\text{Cl})_4$  and  $\text{ZrO}(\text{SO}_3\text{Cl})_2$  and their adducts with some organic donors. Out of these,  $\text{UO}_2(\text{SO}_3\text{Cl})_2$  and  $\text{Th}(\text{SO}_3\text{Cl})_4$  have been prepared earlier<sup>5</sup> by a slightly different method along with their adducts with 2,2'-bipyridyl, triphenylphosphine and triphenylphosphine oxide only.

All the reagents used were of AR grade. Chlorosulphuric acid (Riedel), metal nitrates and the ligands (all BDH reagents) were used as such. Solvents were distilled before use.

The anhydrous acetates were prepared by refluxing the metal nitrates a mixture of acetic anhydride and acetic acid (60:40, v/v) taken in excess. The reaction was highly exothermic in nature and had to be carefully monitored initially.

### Preparation of the metal chlorosulphates

Anhydrous metal acetates (0.05 mol) were taken in a reaction vessel and an excess of chlorosulphuric acid was slowly added. When the reaction subsided, the contents were magnetically stirred for about three hours. The precipitated compounds were filtered *in vacuo*, washed several times with neat chlorosulphuric acid and thionyl chloride and finally dried *in vacuo*

to a constant weight. The solids thus isolated were found to be hygroscopic in nature.

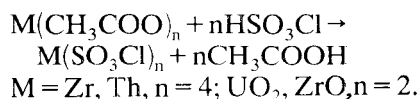
### Preparation of the complexes

Metal chlorosulphates (0.05 mol) in benzene were mixed with the hot ligand solution (0.5 mol) in dimethylformamide and the resulting mixture was stirred for about 4-5 days. The compounds thus formed were filtered *in vacuo*, washed with benzene, dimethylformamide and dry ether and finally dried *in vacuo*.

The estimations of C, H and N were done microanalytically. Chlorine and sulphur were estimated as reported<sup>1,3</sup>. Metals were estimated by known methods.

Infrared spectra were run on a Perkin Elmer 621 spectrophotometer as reported earlier<sup>3</sup>. The electrical conductivities were measured on a Systronic 302 conductivity bridge thermostated at  $\pm 0.05^\circ\text{C}$ . Experiments were performed in a glove box flushed with dry  $\text{N}_2$ .

Uranyl, thorium, zirconium and zirconyl chlorosulphates have been synthesized by carrying out the solvolytic reactions of the corresponding anhydrous metal acetates with chlorosulphuric acid according to the following reaction:



The analytical data listed in Table 1 are consistent with the proposed formulations. The infrared spectra of these chlorosulphates display the nine fundamental modes of vibration characteristic of a bonded chlorosulphate group<sup>1,2</sup>. The position of the sym.  $\text{SO}_3$  stretching vibration  $\nu_1(A)$  ( $1070-1080\text{ cm}^{-1}$ ) and the magnitude of the splitting of the *E* modes of vibration (as a consequence of the symmetry lowering) in these chlorosulphates indicate the existence of a substantial covalent interaction between the metal and  $(\text{SO}_3\text{Cl})^-$  group. The values of  $\nu_s\text{SO}_3$  bands are in good agreement with those reported for the bridging bidentate  $\text{SO}_3\text{Cl}$  groups. The splitting of the  $\nu_6(E)$  mode is not observed, but a relatively weak band has been found in the region  $290-320\text{ cm}^{-1}$ . The resemblance of the IR spectra of these chlorosulphates with those of the corresponding fluorosulphates<sup>6</sup>, where bridging bidentate nature of the fluorosulphates group has been proposed, provides a good evidence for the bidentate coordination of the chlorosulphate group.

The characteristic  $\nu_{\text{U}=\text{O}}$  and  $\nu_{\text{Zr}=\text{O}}$  bands<sup>7</sup> are observed in  $\text{UO}_2(\text{SO}_3\text{Cl})_2$  and  $\text{ZrO}(\text{SO}_3\text{Cl})_2$  at  $\sim 960$

Table 1—Analytical Data of the Complexes

Compound	Found (Calc.), %					
	C	H	N	M	S	Cl
UO <sub>2</sub> (SO <sub>3</sub> Cl) <sub>2</sub>	—	—	—	46.59 (47.41)	11.91 (12.75)	15.01 (14.35)
UO <sub>2</sub> (Py) <sub>2</sub> (SO <sub>3</sub> Cl) <sub>2</sub>	19.31 (18.22)	1.40 (1.53)	4.39 (5.25)	37.01 (36.11)	9.56 (9.37)	10.66 (10.76)
UO <sub>2</sub> (PyNO) <sub>2</sub> (SO <sub>3</sub> Cl) <sub>2</sub>	16.01 (16.70)	1.39 (1.40)	3.95 (3.89)	33.04 (33.09)	8.88 (8.92)	9.95 (9.86)
UO <sub>2</sub> (Acr) <sub>2</sub> (SO <sub>3</sub> Cl) <sub>2</sub>	35.93 (36.33)	2.12 (2.11)	3.33 (3.26)	26.84 (27.69)	7.62 (7.46)	8.31 (8.25)
UO <sub>2</sub> (Phen)(SO <sub>3</sub> Cl) <sub>2</sub>	43.76 (44.66)	2.41 (2.59)	4.01 (4.00)	33.35 (34.04)	9.31 (9.17)	10.24 (10.14)
Th(SO <sub>3</sub> Cl) <sub>4</sub>	—	—	—	32.71 (33.33)	17.93 (18.39)	19.24 (20.69)
Th(Py) <sub>2</sub> (SO <sub>3</sub> Cl) <sub>4</sub>	15.61 (14.09)	1.17 (1.18)	3.28 (3.29)	26.98 (27.22)	15.15 (15.05)	16.95 (16.64)
Th(PyNO) <sub>2</sub> (SO <sub>3</sub> Cl) <sub>4</sub>	13.31 (13.17)	1.10 (1.10)	3.11 (3.07)	26.13 (25.43)	15.01 (14.06)	15.92 (15.54)
Th(Acr) <sub>2</sub> (SO <sub>3</sub> Cl) <sub>4</sub>	30.11 (29.67)	1.73 (1.72)	2.67 (2.66)	21.89 (22.65)	12.31 (12.19)	12.94 (13.47)
Th(Phen)(SO <sub>3</sub> Cl) <sub>4</sub>	16.14 (16.15)	1.13 (1.13)	3.21 (3.14)	26.61 (26.00)	14.31 (14.37)	16.01 (15.89)
Zr(SO <sub>3</sub> Cl) <sub>4</sub>	—	—	—	17.09 (16.39)	22.91 (23.06)	24.69 (25.95)
Zr(Py) <sub>2</sub> (SO <sub>3</sub> Cl) <sub>4</sub>	16.61 (16.83)	1.43 (1.42)	3.79 (3.94)	13.19 (12.82)	18.91 (18.63)	19.99 (19.93)
Zr(PyNO) <sub>2</sub> (SO <sub>3</sub> Cl) <sub>4</sub>	14.95 (15.49)	1.28 (1.30)	3.66 (3.61)	11.79 (11.76)	16.91 (16.54)	18.22 (18.29)
Zr(Phen)(SO <sub>3</sub> Cl) <sub>4</sub>	7.61 (7.99)	1.21 (1.34)	3.49 (3.73)	12.33 (12.14)	23.19 (23.18)	25.67 (25.63)
ZrO(SO <sub>3</sub> Cl) <sub>2</sub>	—	—	—	26.89 (26.84)	18.68 (18.88)	21.86 (21.24)
ZrO(Py) <sub>2</sub> (SO <sub>3</sub> Cl) <sub>2</sub>	24.61 (24.19)	2.04 (2.03)	5.66 (5.64)	18.91 (18.37)	13.41 (12.92)	15.01 (14.28)
ZrO(PyNO) <sub>2</sub> (SO <sub>3</sub> Cl) <sub>2</sub>	21.66 (21.58)	1.82 (1.81)	5.04 (5.03)	16.71 (16.39)	11.55 (11.52)	12.19 (12.74)
ZrO(Acr) <sub>2</sub> (SO <sub>3</sub> Cl) <sub>2</sub>	45.95 (44.82)	2.65 (2.60)	4.07 (4.02)	12.94 (13.09)	9.21 (9.20)	10.01 (10.18)
ZrO(Phen)(SO <sub>3</sub> Cl) <sub>2</sub>	22.33 (22.39)	1.86 (1.88)	5.22 (5.22)	17.19 (17.00)	11.09 (11.95)	12.92 (12.22)

Py, PyNO, Acr and Phen represent pyridine, pyridine N-Oxide, acridine and phenanthroline, respectively.

cm<sup>-1</sup>. A band of medium intensity at 240 cm<sup>-1</sup> in UO<sub>2</sub>(SO<sub>3</sub>Cl)<sub>2</sub> may be assigned as O-U-O bending mode. The ν<sub>1</sub> mode of the uranyl group is IR-forbidden in the free linear ion and the absence of a band assignable to this mode at ~ 850 cm<sup>-1</sup> indicates that the linearity of the O-U-O group is maintained. The low molar conductance values of these chlorosulphates (26-28 cm<sup>2</sup>mol<sup>-1</sup>ohm<sup>-1</sup>) are consistent with their non-electrolytic nature and further support the covalent linkage of the SO<sub>3</sub>Cl<sup>-</sup> group to the cation or oxy-cation.

If all the three (SO<sub>3</sub>Cl)<sup>-</sup> groups coordinate in a bidentate manner then the metal atom will be eight-coordinated in Zr(SO<sub>3</sub>Cl)<sub>4</sub> and Th(SO<sub>3</sub>Cl)<sub>4</sub>. Although many hexacoordinated complexes are known, relatively few octa-coordinated zirconium(IV) complexes are reported<sup>8</sup>. The complexes UO<sub>2</sub>(SO<sub>3</sub>Cl)<sub>2</sub> and ZrO(SO<sub>3</sub>Cl)<sub>2</sub> may be considered to involve six-coordinated uranium and five-coordinated zirconium with four oxygen atoms as donors from two bidentate chlorosulphate groups.

The analytical data in Table 1 are consistent with 1:2 (metal:ligand) stoichiometry for all the complexes except the phenanthroline complexes where the metal:ligand ratio has been found to be 1:1.

The observed upward shifts (~ 30 cm<sup>-1</sup>) in the absorption bands found at 1595 (pyridine ring deformation), 620 (in-plane ring deform) and 430 cm<sup>-1</sup> (out-of-plane ring deform.) in the pyridine complexes are consistent with the involvement of pyridine nitrogen atom in coordination to the metal ions<sup>9</sup>. The splitting

of the pyridine bands presumably arises from the intermolecular or intramolecular interactions between different pyridine molecules in the crystal lattice<sup>10</sup>.

The characteristic  $\nu_{N-O}$  vibrations in the pyridine-N-Oxide complexes show significant shifts to lower wave numbers ( $\sim 25 \text{ cm}^{-1}$ ) indicating complexation which may be attributed to coordination of the oxygen atom of the base causing decrease in  $\pi$ -character of the N—O bond<sup>11</sup>. The bands observed in 350-400  $\text{cm}^{-1}$  region are assigned to  $\nu_{M-O}$  frequency<sup>12</sup>.

The  $\nu_{C=C}$  and  $\nu_{C=N}$  vibrations occurring at 1515 and 1555  $\text{cm}^{-1}$ , respectively, in the free acridine appear in the complexes at a higher frequency around 1540-1550 and 1573-1580  $\text{cm}^{-1}$ , respectively, indicating coordination through the nitrogen atom of the acridine molecule<sup>13,14</sup>. The bands observed at 415-550  $\text{cm}^{-1}$  are assigned to  $\nu_{M-N}$  mode. The characteristic bands (1505 and 1650  $\text{cm}^{-1}$ ) of the free phenanthroline undergo appreciable shifts to 1520-1530 and 1630-1645  $\text{cm}^{-1}$ , respectively, on complexation<sup>15</sup>.

The positions of  $\nu_{S-O_3}$  frequencies in these complexes (1080-1085  $\text{cm}^{-1}$ ) indicate the bidentate nature of the chlorosulphate group. The  $\nu_{U=O}$  and  $\nu_{Zr=O}$  bands appear at lower wave numbers (910-920  $\text{cm}^{-1}$ ) which may be ascribed to the change in U=O and Zr=O bond order in view of the increased electron density around the metal.

The diamagnetic nature of the zirconium complexes and absence of any *d-d* transition confirm the quadrivalent state of the metal ion.

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