

## Synthesis & Characterisation of the Complexes of Lanthanide Tris- (chlorosulphates) with Some Nitrogen & Oxygen Donors

S A A ZAIDI\*, S R A ZAIDI, T A KHAN,  
S A SHAHEER & Z A SIDDIQI

Department of Chemistry, Aligarh Muslim University, Aligarh  
202 001

Received 10 January 1986; revised and accepted 21 March 1986

Complexes of lanthanide tris(chlorosulphates) having the general formulae  $\text{Ln}(\text{SO}_3\text{Cl})_3\text{X}_2$  (where  $\text{Ln} = \text{Dy}^{3+}$ ,  $\text{Ho}^{3+}$  and  $\text{Er}^{3+}$ ;  $\text{X} = \text{pyridine}$ ,  $\text{pyridine N-oxide}$ ,  $\text{acridine}$ ,  $\text{triphenylphosphine oxide}$ ) and  $\text{Ln}(\text{SO}_3\text{Cl})_3\text{X}$  (where  $\text{X} = \text{bipyridine}$ ) have been synthesized and characterized. The IR spectral data and low electrical conductivity values suggest that the  $\text{SO}_3\text{Cl}^-$  groups are covalently bonded to complex cations  $\text{LnX}_2^{3+}$  and  $\text{LnX}^{3+}$ . Electronic spectra and magnetic susceptibility studies of these complexes indicate a coordination number of eight for the metal ions where each chlorosulphate group acts as a bidentate ligand.

In course of our investigations<sup>1-3</sup> on the coordinating properties of chlorosulphate anion, we have synthesised and characterized various transition metal bis(chlorosulphates) and their complexes with several nitrogen containing donor organic bases. We now report here the vibrational and electronic spectra, conductance and magnetic moments of a number of complexes synthesized by the interaction of lanthanide tris(chlorosulphates)<sup>4</sup> with some nitrogen and oxygen containing ligands. Acridine, 2,2'-bipyridine, pyridine N-oxide and triphenylphosphine oxide were commercially available. Pyridine (IDPL), formamide and dimethylformamide (E. Merck) were distilled before use.

### Synthesis of lanthanide tris(chlorosulphates)<sup>4</sup>

Anhydrous metal(III) benzoates were prepared as described earlier<sup>5</sup>. To chlorosulphuric acid (~25 ml) taken in a closed vessel was added the metal(III) benzoate (~5 g) in several fractions. The reaction temperature was adjusted below 40°C. Magnetic stirring of the reaction mixture for about six hours afforded a solid precipitate which was filtered *in vacuo*, repeatedly washed with distilled thionyl chloride and finally dried *in vacuo* at 60-80°C.

### Synthesis of complexes of lanthanide (III) chlorosulphates

Metal tris(chlorosulphates) (~0.05 mol) dissolved in DMF (~25 ml) were mixed with hot ligand solutions

(0.5 mol) in DMF and the resulting mixture was vigorously stirred for about twelve hours. The pyridine complex appeared instantaneously. The reaction mixture on standing for about a week yielded the solid compounds of acridine, bipyridine and pyridine N-oxide. The solid complex of triphenylphosphine oxide separated out in about two weeks. The compounds were filtered *in vacuo*, washed with DMF and dry ether and dried *in vacuo*.

The complexes were analysed for the metal content employing standard procedures<sup>6</sup>. The microanalyses of carbon, hydrogen and nitrogen were performed at the University Science College, Calcutta. Chlorine and sulphur were estimated by reported methods<sup>7</sup>.

Infrared spectra were run on a Perkin Elmer 621 spectrophotometer in nujol, contained in envelope cells on thin polyethylene film sealed from all sides. Magnetic susceptibility measurements were carried out on a vibrating sample magnetometer model 155. Diffuse reflectance spectra were taken on a Carl-Zeiss VSU-2P spectrophotometer. MgO was used as a reflectance standard. The electrical conductivities of  $10^{-2} M$  complex solutions in formamide were measured on a Systronic 302 conductivity bridge thermostated at  $\pm 0.05^\circ\text{C}$ . All manipulations were done in a dry box filled with dry nitrogen.

The elemental analyses of the complexes (Table 1) indicate that these have 1:2 compositions (metal:organic ligand) with the stoichiometry  $\text{LnX}_2(\text{SO}_3\text{Cl})_3$  for  $x = \text{pyridine}$ ,  $\text{acridine}$ ,  $\text{pyridine N-oxide}$ ,  $\text{triphenylphosphine oxide}$ , and have 1:1 compositions (metal:organic ligand) with the stoichiometry  $\text{LnX}(\text{SO}_3\text{Cl})_3$  for  $x = 2,2'$ -bipyridine. Low molar conductance values of the complexes ( $1-2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) indicate that  $\text{SO}_3\text{Cl}^-$  groups are covalently bonded.

The bands observed in the IR spectra of these compounds were assigned assuming a  $C_{3v}$  symmetry of the covalently bonded chlorosulphate group<sup>1-3</sup>. A positive shift in  $\nu_1(A)$  vibrational mode ( $1080-1090 \text{ cm}^{-1}$ ) and the splitting of doubly degenerate  $E$  modes ( $560-590$ ,  $590-620 \text{ cm}^{-1}$  and  $1160-1180$ ,  $1220-1240 \text{ cm}^{-1}$ ) indicate an appreciable interaction between the anion,  $\text{SO}_3\text{Cl}^-$  and the complex cations  $[\text{LnX}_2]^{3+}$  and  $[\text{LnX}]^{3+}$  leading to covalent bonding. The  $\nu_2(A)$  ( $430-450 \text{ cm}^{-1}$ ) and  $\nu_3(A)$  ( $525-540 \text{ cm}^{-1}$ ) vibrations have been observed nearly at the same positions as in the corresponding lanthanum tris(chlorosulphates)<sup>3</sup>. The S-Cl band ( $310-340 \text{ cm}^{-1}$ ) of the  $\text{SO}_3\text{Cl}^-$  group in these complexes is hardly affected as would be expected from the reduced ability of the chlorine atom

Table 1—Analytical Data and Magnetic Moment Data of the Complexes of Ln(III) Chlorosulphates

Compounds	Found (Calc.), %						$\mu_{\text{eff}}$ (B.M.)
	M	S	Cl	C	H	N	
Dy(SO <sub>3</sub> Cl) <sub>3</sub> (Py) <sub>2</sub>	23.98 (24.35)	15.02 (14.41)	15.63 (15.94)	22.19 (21.60)	1.42 (1.50)	4.32 (4.19)	10.39
Dy(SO <sub>3</sub> Cl) <sub>2</sub> (Dipy) <sub>3</sub>	23.91 (24.43)	14.99 (14.46)	16.21 (15.99)	18.93 (18.05)	1.29 (1.36)	4.45 (4.21)	10.41
Dy(SO <sub>3</sub> Cl) <sub>3</sub> (Ac) <sub>2</sub>	17.93 (18.73)	12.01 (11.75)	13.08 (12.26)	36.19 (36.00)	2.03 (2.09)	3.51 (3.22)	10.41
Dy(SO <sub>3</sub> Cl) <sub>3</sub> (PyNo) <sub>2</sub>	23.91 (23.24)	13.91 (13.75)	15.61 (15.21)	21.11 (20.61)	1.51 (1.44)	4.09 (4.00)	10.40
Dy(SO <sub>3</sub> Cl) <sub>3</sub> (TPPO) <sub>2</sub>	14.99 (15.26)	9.32 (9.03)	9.82 (9.99)	41.39 (40.61)	2.91 (2.84)	—	10.42
Ho(SO <sub>3</sub> Cl) <sub>3</sub> (Py) <sub>2</sub>	23.81 (24.63)	14.16 (14.36)	16.12 (16.46)	21.94 (21.52)	1.52 (1.50)	4.24 (4.18)	10.23
Ho(SO <sub>3</sub> Cl) <sub>3</sub> (Bipy)	25.16 (24.70)	14.91 (14.40)	16.25 (15.93)	18.14 (17.99)	1.21 (1.20)	4.23 (4.19)	10.22
Ho(SO <sub>3</sub> Cl) <sub>3</sub> (Ac) <sub>2</sub>	18.16 (18.96)	11.91 (11.05)	12.39 (12.22)	36.15 (35.90)	2.12 (2.08)	3.31 (3.22)	10.22
Ho(SO <sub>3</sub> Cl) <sub>3</sub> (PyNo) <sub>2</sub>	23.15 (23.50)	13.91 (13.70)	15.01 (15.15)	20.91 (20.54)	1.49 (1.43)	4.08 (3.99)	10.21
Ho(SO <sub>3</sub> Cl) <sub>3</sub> (TPPO) <sub>2</sub>	15.90 (15.43)	9.18 (9.00)	10.00 (9.94)	41.10 (40.47)	2.81 (2.83)	—	10.22
Er(SO <sub>3</sub> Cl) <sub>3</sub> (Py) <sub>2</sub>	23.91 (24.39)	14.69 (14.31)	15.11 (15.83)	20.90 (21.44)	1.51 (1.50)	4.26 (4.16)	—
Er(SO <sub>3</sub> Cl) <sub>3</sub> (Bipy) <sub>2</sub>	25.03 (24.96)	13.91 (14.35)	15.43 (15.87)	17.68 (17.92)	1.91 (1.20)	4.31 (4.18)	—
Er(SOCl)(Ac)	19.39 (19.17)	11.61 (11.02)	12.31 (12.19)	35.28 (35.80)	2.06 (2.08)	3.43 (3.21)	—
Er(SO <sub>3</sub> Cl) <sub>3</sub> (PyNo) <sub>2</sub>	23.41 (23.76)	13.91 (13.66)	15.41 (15.11)	20.93 (20.47)	1.45 (1.43)	3.99 (3.97)	—
Er(SO <sub>3</sub> Cl) <sub>3</sub> (TPPO) <sub>2</sub>	15.49 (15.62)	8.91 (8.98)	9.61 (9.93)	40.61 (40.39)	2.79 (2.82)	—	—

to back-donate in contrast to S-F stretching frequency which is strengthened due to mesomeric electron drift towards the cation in transition metal fluorosulphates.

The three characteristic ring vibrational modes (16b at 420-440, 6a at 630-660 and 8a at 1580-1650 cm<sup>-1</sup>) show significant positive shifts on coordination of pyridine and 2,2'-bipyridine to metal ions as reported earlier<sup>9-12</sup>. The doubling of 8a mode may be ascribed either to inter-molecular or intra-molecular interactions of different pyridine or 2,2'-bipyridine molecules in the crystal lattice<sup>12</sup>.

The characteristic  $\nu\text{N}-\text{O}$  and  $\nu\text{P}-\text{O}$  frequencies expected at 1243 and 1195 cm<sup>-1</sup> for free pyridine N-oxide and triphenylphosphine oxide respectively undergo negative shifts (1160-1175 and 1135-1140 cm<sup>-1</sup>) on coordination to the metal ions<sup>13-16</sup>.

The observed positive shift in C=C (1580-1585 cm<sup>-1</sup>) and C=N (1610-1630 cm<sup>-1</sup>) stretching vibrations of acridine molecule in complexes directly indicate the coordination of acridine to the metal ions<sup>17</sup>.

The stereochemistries of these compounds have been suggested on the basis of magnetic moment

values and the bands obtained in the reflectance spectra of these compounds.

The observed magnetic moments for these complexes at room temperature are quite comparable with those of the octa-coordinated complexes indicating that the 4f electrons do not participate in bond formation. This is probably due to very effective shielding of 4f electrons from external forces by overlying 5s<sup>2</sup> and 5p<sup>6</sup> electrons.

#### Electronic spectra

The electronic spectra of all the Dy(III) complexes are nearly similar in solid state and exhibit three nearly sharp bands around 18,335, 19,150 and 21,670 cm<sup>-1</sup> which may be due to the  $^5D_0 \leftarrow ^6H_{15/2}$ ,  $^5D_1 \leftarrow ^6H_{15/2}$  and  $^5D_2 \leftarrow ^6H_{15/2}$  transitions, respectively. The small splittings observed in the absorption bands may be due to the effect of the crystal fields upon the J level of the Dy<sup>3+</sup> ion.

The electronic spectra of the Ho(III) complexes display f-f bands around 15,735, 18,950 and 22,075 cm<sup>-1</sup> which may reasonably be assigned to the transitions  $^5F_3 \leftarrow ^5I_8$ ,  $^5S_2$ ,  $^5F_4 \leftarrow ^5I_8$  and  $^5G_6 \leftarrow ^5I_8$

respectively. A small red shift is observed in these  $f-f$  bands with respect to aquo ion<sup>18</sup>.

Six bands in the visible spectra of the Er(III) complexes have been observed at 25,835, 24,350, 22,550, 20,835, 18,330 and 15,750  $\text{cm}^{-1}$  and have been assigned to the transitions  ${}^4G_{11/2} \leftarrow {}^4I_{15/2}$ ,  ${}^2H_{9/2} \leftarrow {}^4I_{15/2}$ ,  ${}^4F_{5/2} \leftarrow {}^4I_{15/2}$ ,  ${}^4F_{7/2} \leftarrow {}^4I_{15/2}$  and  ${}^4S_{3/2} \leftarrow {}^4I_{15/2}$  and  ${}^4F_{9/2} \leftarrow {}^4I_{15/2}$  respectively.

It is observed that there is not much change in the visible spectra after complexation. The  $f-f$  transitions are least affected by the immediate environment around the metal ion due to the shielding of the  $4f$  orbitals by outerlying  $5s^2$  and  $5p^6$  shells of electrons.

We are thankful to Prof. M.S. Ahmad, Chairman of our Department for providing research facilities. Three of us (SRAZ, TAK and SAS) thank the CSIR, New Delhi, for financial assistance.

### References

- Siddiqi Z A, Aslam M, Ansari N A, Shakir M & Zaidi S A A, *Synth React inorg met-Org Chem*, **11** (1981) 475.
- Siddiqi Z A, Shakir M, Aslam M, Khan T A & Zaidi S A A, *Synth React inorg met-Org Chem*, **4** (1983) 397.
- Siddiqi Z A, Shakir M, Aslam M, Zaidi S R A & Zaidi S A A, *Indian J Chem*, **22A** (1983) 1078.
- Zaidi S A A, Zaidi S R A, Shakir M, Aslam M & Siddiqi Z A, *Polyhedron*, **4** (1985) 365.
- Taylor M D, Carter C P & Wynter C I, *J inorg nucl Chem*, (1968) 1503.
- Welcher Frank J, *The analytical uses of ethylenediamine tetraacetic acid* (D. Van Nostrand Company, Inc. Princeton, New Jersey) 1958, 181.
- Vogel A I, *A text book of quantitative inorganic analysis*, (Longmans, London), 1951, 399, 401.
- Robinson E A & Ciruna J A, *Can J Chem*, **46** (1968) 1715.
- Alleyne C S & Thompson R C, *Can J Chem*, (1974) (3218).
- Gill H S, Nuttal R H, Scarfe D E & Sharp D W A, *J inorg nucl Chem*, **18** (1961) 79.
- Popov A I, Marshall J C, Stute F B & Person W B, *J Am chem Soc*, **83** (1961) 3586.
- Clark R J H & Williams C S, *Inorg Chem*, **4** (1965) 350.
- Quagliano J V, Fujita J, Franz G, Phillips D J, Walmsley J A & Tyree S Y, *J Am chem Soc*, **83** (1961) 3770.
- Dickson F F, Baker E W & Bentley F F, *J inorg nucl Chem*, **31** (1969) 559.
- Goodgame D M L & Cotton F A, *J chem Soc*, 2298 (1961) 3735.
- Sheldon J C, *J Am chem Soc*, **80** (1958) 2117.
- Zaidi S A A, Siddiqi K S & Neelam N S, *Indian J Chem*, **14A** (1976) 309.
- Sinha S P, *J inorg nucl Chem*, **27** (1965) 115.