

## Synthesis and characterization of the complexes of La(III), Ce(III), Pr(III) and Tb(III) chlorosulphates with some donor bases

S Aftab A Zaidi\*, S Rehan A Zaidi, M Akhtar Zahoor & Tabrez A Khan

Department of Chemistry, Aligarh Muslim University, Aligarh 202 002

Received 23 March 1989; revised and accepted 8 June 1989

Several complexes of La(III), Pr(III) and Tb(III) chlorosulphates with triphenylphosphine (TPP), triphenylphosphine oxide (TPPO), triphenylarsine (TPA) and triphenylarsine oxide (TPAO) and of Ce(II) chlorosulphate with TPA and TPAO have been isolated and characterized by magnetic moment, infrared and reflectance spectral studies.

The interest in the chemistry of the compounds containing coordinated  $\text{SO}_3\text{Cl}^-$  anion has increased rapidly in recent years. We have earlier synthesized various lanthanon chlorosulphates and their complexes<sup>1,2</sup>. The present note describes the preparation and characterization of some new complexes of La(III), Pr(III) and Tb(III) trischlorosulphates with TPP, TPPO, TPA and TPAO and that of Ce trischlorosulphate with TPA and TPAO only. The preparation of  $\text{Ce}(\text{SO}_3\text{Cl})_3$  by a different method and its adducts with 2,2'-bipyridyl, triphenylphosphine and triphenylphosphine oxide are reported in the literature<sup>3</sup>.

### Experimental

Chlorosulphuric acid (Riedel), triphenylphosphine, triphenylphosphine oxide, triphenylarsine and triphenylarsine oxide (all BDH) were used as received.

#### Preparation of the complexes

La(III), Ce(III), Pr(III) and Tb(III) chlorosulphates were synthesized as reported earlier<sup>1</sup>. Their complexes were obtained by reacting a 0.05 M solution (~50ml) of the lanthanon trischlorosulphates in dimethylformamide with excess of the ligand solution in the same solvent. The reaction mixture, on stirring at 80°C for about 24 hr in a closed vessel, yielded the solid product on cooling. The compounds were filtered *in vacuo*, washed and dried *in vacuo* to a constant weight. The physical measurements and analysis were done as reported<sup>1,2</sup>.

### Results and discussion

The results of chemical analyses (Table 1) are in agreement with the proposed formulation of the complexes as  $\text{Ln}(\text{SO}_3\text{Cl})_3\text{L}_2$  (Ln=La, Pr and Tb; L=TPP, TPPO, TPA or TPAO; Ce, L=TPA or TPAO).

The infrared spectra of the lanthanon trischlorosulphate complexes display bands in the region 1070-1090  $\text{cm}^{-1}$  assignable to the  $\nu_1(A)$  mode of  $\text{SO}_3$  moiety. These bands are about 40-50  $\text{cm}^{-1}$  higher with respect to that in free  $(\text{SO}_3\text{Cl}^-)$  indicating<sup>4</sup> an increased covalent interaction between the  $\text{SO}_3\text{Cl}^-$  group and the complex cation  $[\text{ML}_2]^{3+}$  and lowering of symmetry in comparison with alkali metal or silver salts. The two degenerate *E* modes are split into two vibrations which further substantiate the presence of the covalency in the metal-ligand bond. The expected absorption in the range 300-250  $\text{cm}^{-1}$  due to S-Cl(wag),  $\nu_6(E)$ , is either too weak to be observed or is, more likely, obscured by polyethylene absorption. The  $\nu\text{S}-\text{Cl}$  mode of  $\text{SO}_3\text{Cl}^-$  group is not significantly altered. The positions of the  $\text{SO}_3$  vibrations [ $\nu_5\text{SO}_3$  ( $\nu_{as}\text{SO}_3$ ):La, 1075 (1240, 1180); Ce, 1080 (1250, 1170); Pr, 1090 (1245, 1175); Tb, 1080 (1240, 1170)  $\text{cm}^{-1}$ ] are consistent with the bidentate coordination of the  $\text{SO}_3\text{Cl}$  group in these complexes.

In the spectra of TPP complexes, a new band in the region 280-260  $\text{cm}^{-1}$  is observed which can be assigned to  $\nu\text{M}-\text{P}$  and provides a direct evidence of the coordination of TPP to the metal ions<sup>5</sup>. A weak absorption band at 2370-2360  $\text{cm}^{-1}$  in TPP complexes is due to  $\nu\text{P}-\text{H}$  absorption. The  $\nu\text{P}-\text{C}$  band occurring at 1089  $\text{cm}^{-1}$  in the ligand is shifted to higher frequency on complexation. Coordination of the TPP is further supported by the presence of a band in the 725-710  $\text{cm}^{-1}$  region, as expected for coordinated phosphines. A characteristic pattern of three bands in the range 540-490  $\text{cm}^{-1}$  suggests the presence of coordinated TPP and TPA. In TPAO complexes, the coordination through the oxygen results in the lowering of  $\nu\text{P}=\text{O}$  (1140-1120  $\text{cm}^{-1}$ ) and an increase in  $\nu\text{P}-\text{C}$  (1480-1460  $\text{cm}^{-1}$ ). Uncomplexed TPPO exhibits  $\nu\text{P}=\text{O}$  and  $\nu\text{P}-\text{C}$  at 1192 and 1440  $\text{cm}^{-1}$ , respectively. The  $\nu\text{As}-\text{O}$  (observed at 879  $\text{cm}^{-1}$  in free  $\text{Ph}_3\text{AsO}$ ) is lowered by 20.30  $\text{cm}^{-1}$  on coordination through the oxygen atom<sup>8</sup>.

The magnetic moments of the complexes of Ce(III), Pr(III) and Tb(III) chlorosulphates lie in the ranges 2.85-2.70, 3.8-3.9 and 9.6-9.9 B.M., re-

NOTES

Table 1—Characterisation data of the complexes

Compounds	Colour (yield, %)	Found (Cal.) %					
		M	S	Cl	C	H	P/As
La(SO <sub>3</sub> Cl) <sub>3</sub> ·2TPP	Colourless (70)	13.61 (13.75)	9.96 (9.50)	10.66 (10.54)	42.39 (42.77)	3.09 (2.97)	6.46 (6.13)
La(SO <sub>3</sub> Cl) <sub>3</sub> ·2TPPO	Colourless (75)	13.67 (13.33)	9.49 (9.21)	10.41 (10.22)	41.95 (41.46)	2.80 (2.88)	5.63 (5.94)
La(SO <sub>3</sub> Cl) <sub>3</sub> ·2TPA	Colourless (71)	12.97 (12.65)	8.91 (8.74)	9.99 (9.70)	39.03 (39.35)	2.34 (2.73)	14.89 (13.66)
La(SO <sub>3</sub> Cl) <sub>3</sub> ·2TPAO	Colourless (74)	12.36 (12.29)	8.81 (8.49)	9.93 (9.40)	38.67 (38.23)	2.96 (2.65)	14.46 (13.28)
Ce(SO <sub>3</sub> Cl) <sub>3</sub> ·2TPA	Colourless (71)	12.26 (12.74)	8.94 (8.73)	9.46 (9.69)	39.64 (39.30)	2.43 (2.73)	14.66 (13.65)
Ce(SO <sub>3</sub> Cl) <sub>3</sub> ·2TPAO	Colourless (75)	12.86 (12.38)	8.13 (8.45)	9.92 (9.41)	38.46 (38.19)	2.96 (2.65)	14.46 (13.26)
Pr(SO <sub>3</sub> Cl) <sub>3</sub> ·2TPP	Colourless (71)	13.93 (13.92)	9.01 (9.49)	10.52 (10.52)	41.61 (42.71)	2.59 (2.96)	5.83 (6.12)
Pr(SO <sub>3</sub> Cl) <sub>3</sub> ·2TPPO	Light green (69)	13.63 (13.51)	9.51 (9.19)	10.62 (10.20)	41.75 (41.48)	2.55 (2.87)	5.65 (5.93)
Pr(SO <sub>3</sub> Cl) <sub>3</sub> ·2TPA	Light green (65)	12.63 (12.81)	8.91 (8.73)	9.42 (9.68)	39.59 (39.27)	2.49 (2.73)	14.81 (13.64)
Pr(SO <sub>3</sub> Cl) <sub>3</sub> ·2TPAO	Light green (68)	12.71 (12.44)	8.14 (8.48)	9.69 (9.40)	38.51 (38.16)	2.69 (2.65)	13.42 (13.25)
Tb(SO <sub>3</sub> Cl) <sub>3</sub> ·2TPP	Colourless (64)	15.61 (15.43)	9.12 (9.32)	10.49 (10.34)	42.21 (41.96)	3.01 (2.91)	5.92 (6.01)
Tb(SO <sub>3</sub> Cl) <sub>3</sub> ·2TPPO	Colourless (74)	14.51 (14.96)	9.21 (9.04)	10.41 (10.03)	40.99 (40.68)	3.04 (2.82)	5.91 (5.83)
Tb(SO <sub>3</sub> Cl) <sub>3</sub> ·2TPA	Colourless (71)	14.41 (14.22)	8.83 (8.59)	9.81 (9.53)	38.21 (38.64)	2.79 (2.68)	14.00 (13.42)
Tb(SO <sub>3</sub> Cl) <sub>3</sub> ·2TPAO	Colourless (72)	13.61 (13.82)	8.49 (8.35)	9.01 (9.26)	37.61 (37.57)	2.71 (2.61)	14.11 (13.04)

spectively, in agreement with theoretical values<sup>9</sup>. La(III) chlorosulphate complexes are diamagnetic as expected.

The reflectance spectra of the Pr(III) complexes recorded in the solid state show bands in the regions 22302-22321; 21170-21276; 20202-20221; and 16277-16478 cm<sup>-1</sup> corresponding to the transitions from the ground state level <sup>3</sup>H<sub>4</sub> to the energy levels <sup>3</sup>P<sub>2</sub>, <sup>3</sup>P<sub>1</sub>, <sup>3</sup>P<sub>0</sub> and <sup>1</sup>D<sub>2</sub>, respectively. The spectral bands show a shift towards lower energy with respect to aquo ion (nephelauxetic effect). The nephelauxetic parameters ( $\bar{\beta}$ )<sup>10</sup>, the Henry and Choppin bonding parameters ( $b^{1/2}$ )<sup>11</sup> and Sinha's covalency parameter ( $\delta$ )<sup>12</sup> for Pr(SO<sub>3</sub>Cl)<sub>3</sub>·2TPP are 0.9830, 0.0922 and 1.7294; for Pr(SO<sub>3</sub>Cl)<sub>3</sub>·2TPPO 0.9813, 0.0967 and 1.9056; for Pr(SO<sub>3</sub>Cl)<sub>3</sub>·2TPA 0.9810, 0.0975 and 1.9860; and for Pr(SO<sub>3</sub>Cl)<sub>3</sub>·2TPAO 0.9790, 0.1025 and 2.1450, respectively. The value of  $\bar{\beta}$  is

less than unity and the  $b^{1/2}$  and  $\delta$  values are positive indicating the covalency in the metal-ligand bonding. The magnitudes of  $b^{1/2}$  and  $\delta$  show an increase with the increase in the molecular weight of the ligand. In Tb(III) complexes, a low intensity band between 20200 and 20100 cm<sup>-1</sup> has been assigned<sup>13</sup> to the transition <sup>7</sup>F<sub>6</sub> → <sup>5</sup>D<sub>4</sub>. The complexes of lanthanum and cerium do not show any recognisable band assignable to  $f-f$  transitions.

We thank Prof S M Osman for his interest. One of us (SRAZ) is thankful to the CSIR, New Delhi for financial support.

References

- Zaidi S A A, Zaidi S R A, Shakir M, Aslam M & Siddiqi Z A, *Polyhedron*, 4 (1985) 365.
- Zaidi S A A, Zaidi S R A & Khan T A, *Synth react inorg met-org Chem*, 17 (1987) 901.
- Singh S, Maninder & Verma R D, *Indian J Chem*, 23 (1984) 1038.
- Robinson E A & Ciruna J A, *Can J Chem*, 46 (1968) 1715.

- 5 Selbin J, Ahmad N & Pribble M J, *J inorg nucl Chem*, 32 (1970).
- 6 Vson R *et al.*, *J organometal Chem*, 256 (1983) 331.
- 7 Clark J P, Longford V M & Wilkins C J, *J chem Soc*, (1967) 792; Cotton F A. Goodgame D W L & Soderberg R H, *Inorg Chem*, 2 (1963) 1162.
- 8 Philips D J & Tyree S Y, *J Am chem Soc*, 83 (1961) 1806.
- 9 Van Vleck J H & Frank N, *Phys Rev*, 34 (1929) 1494.
- 10 Jorgensen C K, *Prog inorg Chem*, 4 (1962) 73.
- 11 Henrie D E & Choppin G R, *J chem Phys*, 49 (1968) 477.
- 12 Sinha S P, *Spectrochim Acta*, 22 (1966) 57.
- 13 West D X & Frouk C A, *J inorg nucl Chem*, 41 (1979) 49.