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Synthesis & Characterization of Eu(III), Tm(III) & Yb(III) Chlorosulphates & Their Complexes with 2-Aminothiazole & 5-Aminoindazole

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Solvolytic reaction of Eu(III) benzoate or of Tm(III) and Yb(III) carbonates with chlorosulphuric acid yields the corresponding metal tris(chlorosulphate). The infrared spectra of the chlorosulphates indicate a bidentate coordination of the SO_3Cl^- group. An octahedral geometry has been suggested for these chlorosulphates. The metal tris(chlorosulphates) react with 2-aminothiazole and 5-aminoindazole in DMF solution to give the metal complexes which have been characterized by elemental analyses and detailed IR data.

The transition metal complexes of 2-aminothiazole and 5-aminoindazole have been extensively studied[1-5]. Presently we have prepared chlorosulphates of Eu(III), Tm(III) and Yb(III) by solvolytic reactions of the corresponding benzoate [for Eu(III)] or carbonate [Tm(III) and Yb(III)] and complexes of these chlorosulphates with the above two ligands. The characterization of the chlorosulphates and the complexes is based on IR data, molar conductance, magnetic moment etc.

Oxides of Eu(III), Tm(III) or Yb(III) were used as received. Thalium(III) and Yb(III) carbonates were prepared by adding slowly sodium carbonate to a solution of the corresponding oxide in nitric acid when metal carbonates precipitated out. These were filtered, washed with water followed by methanol and dried for 6 hr at 110°C. Eu(III) benzoate was synthesized in the manner described earlier[6].

Dimethylformamide was distilled after drying over KOH for 2-3 days.

Metal tris(chlorosulphates [M(SO_3Cl)]; M= Eu(III) Tm(III) and Yb(III)]

Anhydrous Eu(III) benzoate or carbonate of Tm(III) or Yb(III) (2 g) was added in portions to chlorosulphuric acid (~ 20 ml) under ice cooling. A vigorous reaction took place and the temperature of reaction mixture was maintained below 40°C. After the reaction was over, the solution was stirred for about 6 hr, the solid obtained was filtered *in vacuo*, washed with chlorosulphuric acid followed by thionyl chloride and dried *in vacuo* at 80°C to a constant weight.

Synthesis of bis(2-aminothiazole) M(III) chlorosulphate (M = Eu, Tm and Yb)

A 0.05 *M* solution of metal tris(chlorosulphate) in dimethylformamide was added in excess (~ 0.5 mol) to a solution of 2-aminothiazole in the same solvent and stirred for 24 hr, not allowing the temperature to rise > 80°C. A solid compound which appeared on cooling was filtered *in vacuo*, washed with dimethylformamide and finally dried *in vacuo*.

Synthesis of (5-aminoindazole) M(III) chlorosulphates (M = Eu, Tm and Yb)

Anhydrous metal tris(chlorosulphate) (~ 0.05 mol) was dissolved in portions in hot dimethylformamide and to this was added a hot solution of 5-aminoindazole (~ 0.5 mol) in dimethylformamide. The reaction mixture was refluxed for 40 hr and stirred at 80°C for about two weeks. The solid complexes thus obtained were filtered *in vacuo*, washed with DMF and dried *in vacuo* to a constant weight.

Infrared spectra of the compounds were recorded on a Perkin Elmer 621 spectrophotometer. Magnetic susceptibilities were measured on a vibrating sample magnetometer 155. The emission spectrum of the europium compound was obtained by the reported method[7].

The results of elemental analyses (Table 1) on rare earth metal tris(chlorosulphates) are in good agreement with the proposed composition as $M(SO_3Cl)_3$ (M = Eu, Tm and Yb).

The IR spectra of these chlorosulphates in nujol exhibit bands in the region 1070-1090 cm^{-1} assignable to ν_sSO_3 (ν_1) modes, which appear at higher wavenumber ($\Delta\eta = 40\ cm^{-1}$) as compared to that of the free SO_3Cl^- in $CsSO_3Cl$ (see ref. 8). This may be ascribed to the strong cation-anion covalent interaction and lower symmetry causing ν_sSO_3 modes to appear at higher wavenumber. Further, the doubly degenerate modes, viz. asymmetric deformation (ν_5) and $\nu_{as}SO_3(\nu_4)$ appear as doublets of medium intensity at 640 ± 10, 680 ± 10 and 1240 ± 10, 117° ± 10 cm^{-1}, respectively. This observation further substantiates the presence of some covalency in these lanthanide tris(chlorosulphates). This may be due to the tendency of $p\pi$-$d\pi$ bonding between sul-

Table 1—Analytical Data and Magnetic Moments of Chlorosulphates of Eu, Tm and Yb and Their Complexes with 2-Aminothiazole(2-AThz) and 5-Aminoindazole(5-AInz)

Compounds	Found (Calc), %						μ eff. B.M.
	M	S	Cl	C	H	N	
Eu(SO$_3$Cl)$_3$*	38.41	20.51	20.61	—	—	—	3.36
	(38.48)	(19.29)	(21.33)				
Eu(SO$_3$Cl)$_3$(2-AThz)$_2$	20.61	23.64	16.16	10.63	1.03	8.61	3.40
	(21.74)	(22.99)	(15.22)	(10.31)	(1.15)	(8.02)	
Eu(SO$_3$Cl)$_3$(5-AInz)	23.19	15.94	17.91	13.69	1.12	5.00	3.50
	(24.05)	(15.22)	(16.83)	(13.31)	(1.11)	(5.02)	
Tm(SO$_3$Cl)$_3$	30.99	18.16	20.19	—	—	—	7.2
	(32.77)	(18.66)	(20.63)				
Tm(SO$_3$Cl)$_3$(2-AThz)$_2$	22.91	22.19	13.91	10.19	1.12	7.61	7.6
	(23.60)	(22.39)	(14.83)	(10.07)	(1.13)	(7.82)	
Tm(SO$_3$Cl)$_3$(5-AInz)	26.10	14.31	16.51	12.2	1.08	7.61	7.6
	(26.04)	(14.83)	(16.39)	(12.96)	(1.08)	(7.81)	
Yb(SO$_3$Cl)$_3$	32.15	18.69	20.99	—	—	—	4.4
	(33.30)	(18.51)	(20.47)				
Yb(SO$_3$Cl)$_3$(2-AThz)$_2$	23.61	21.29	14.96	10.01	1.12	7.61	4.6
	(24.04)	(22.27)	(14.77)	(10.01)	(1.13)	(7.78)	
Yb(SO$_3$Cl)$_3$(5-AInz)	25.19	14.23	16.96	12.35	1.07	6.61	4.5
	(26.53)	(14.73)	(16.20)	(12.88)	(1.08)	(6.43)	

*Determined by complexometric titration with EDTA (see reference 16).
†Estimated gravimetrically (reference 17).

phur and chlorine similar to that suggested for lanthanide fluorosulphates[9], although there would be some reduction in the ability of the chlorine atom to back-donate in contrast to fluorine. The expected absorption band in the region of 250-300 cm^{-1} due to S-Cl wag (ν_6) vibration is either too weak to be observed or is more likely obscured by polyethylene absorption. The positions of $\nu_{as}SO_3(\nu_sSO_3)$ in the chlorosulphates [Eu(SO$_3$Cl)$_3$: 1240, 1170(1070); Tm(SO$_3$Cl)$_2$: 1250, 1180(1080); Yb(SO$_3$Cl)$_3$: 1245, 1160(1070) cm^{-1}] are in good agreement with those reported[10] for the bidentate chlorosulphate groups. The μ_{eff} values of 3.36, 7.2 and 4.4 B.M. for Eu(SO$_3$Cl)$_3$, Tm(SO$_3$Cl)$_3$ and Yb(SO$_3$Cl)$_3$, respectively are comparable with those reported for hexacoordinated lanthanides. An octahedral geometry for these chlorosulphates similar to the chlorosulphates of other rare earth metals[11] can, therefore, be suggested.

The molar conductivities of 10^{-3} molar solutions of these chlorosulphates in DMF lie in the range 50-55 Ohm^{-1}cm^{2}mol^{-1} which are quite below that expected for a 1:1 electrolyte. The low conductance values support the IR findings that the SO$_3$Cl$^-$ moiety is covalently bonded to the cations.

Complexes of metal chlorosulphate with 2-aminothiazole and 5-aminoindazole

The complexes of 2-aminothiazole have the composition M(SO$_3$Cl)$_3$(C$_3$H$_4$N$_2$S)$_2$ while those of 5-aminoindazole have the composition M(SO$_3$Cl)$_3$.C$_7$H$_7$N$_2$.

The IR spectra of these complexes suggest that the chlorosulphate group is covalently bonded with the complex cations [M(C$_3$H$_4$N$_2$S)$_2$]$^{3+}$ and [M(C$_7$H$_7$N$_2$)$_2$]$^{3+}$ as indicated by a positive shift in ν_sSO$_3$ modes (ν_1) of chlorosulphates in the region of 1070 to 1090 cm^{-1} in the complexes. The observed splitting of doubly degenerate ν_{as} SO$_3$ and asymmetric SO$_3$ deformation modes further lends support to the above observation. The S-Cl stretching (ν_2) and symmetric SO$_3$ deformation (ν_3) modes have been observed at 450 ± 5 and 580 ± 10 cm^{-1}, respectively, as in the corresponding metal tris(chlorosulphates).

The νN-N mode in 2-aminothiazole appears as a doublet at 3460 and 3360 cm^{-1}. In the complexes with Eu(III), Tm(III) and Yb(III) chlorosulphates the νN-H modes appear at 3350, 3255; 3355, 3260; and 3390, 3300 cm^{-1} respectively. The νC-N modes in 2-aminothiazole appear at 1350 cm^{-1} as a medium intensity band. In the complexes of Eu, Tm and Yb chlorosulphates the νC-N modes appear at 1400, 1410 and 1390 cm^{-1} respectively. This observation indicates coordination of the ligand through amino nitrogen. The νC = S and νC = N modes of the free ligand are not much affected, indicating that ring sulphur and nitrogen atoms do not take part in bonding[1]. In case of 5-aminoindazole complexes the νN-H of the free ligand appearing at

3350 cm^{-1} undergoes shift to lower wavenumbers and appear at 3320, 3320, 3300 cm^{-1} in Eu, Tm and Yb chlorosulphate complexes respectively, in agreement with the coordination of the pyrrolic nitrogen (– NH) atom[4,5]. The ηC = N of 5-aminoindazole appearing at 1517 cm^{-1} undergoes only a little change upon complex formation. This observation is consistent with the pyridyl nitrogen coordination[5,12,13]. The bands observed in the 350-400 cm^{-1} region are attributed to νM-N modes in these complexes.

The magnetic moments of the complexes at room temperature are close to the theoretical values for the respective tripositive ions[14]. The small difference between observed and theoretical values indicates either minor or no involvement of the 4 f orbitals in bonding.

The luminescence spectrum of the Eu^{3+} complexes exhibit sharp emissions in the region 21.14-18.45 kK. The more intense band observed in the region of 18.61-18.45 kK is assigned to the transition $^7F_2 \leftarrow {}^5D_0$. Comparatively weak bands between 21.45 and 21.14 kK have been assigned to $^7F_1 \leftarrow {}^5D_0$ transition[15]. On the basis of the above studies a coordination number of eight may tentatively be assigned to these complexes.

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