Synthesis and characterization of yttrium and lanthanide perchlorate complexes of 4-salicylideneamino-3-mercapto-6-methyl-1,2,4-triazin (4H)-5-one

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A few complexes of La (III), Ce (III), Pr (III), Nd (III), Sm (III), Eu (III), Gd (III), Tb (III), Dy (III) and Y (III) perchlorates with 4-salicylideneamino-3-mercapto-6-methyl-1,2,4-triazine (4H)-5-one (SMMT) have been isolated and characterised by analytical, magnetic, molar conductance, thermal and infrared spectral studies and it is found that the ligand molecule coordinate to the metal ions through the carbonyl oxygen, phenolic oxygen and the azomethine nitrogen atoms. The complexes formed are neutral in nature which suggests that the perchlorate ion is bonded to the metal ion undoubtedly. The complexes are formulated as $[\text{Ln} \text{(SMMT)ClO}_4]$ with a coordination number of seven for the lanthanide ions (where $\text{Ln} = \text{La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Y}$). All these complexes are thermally stable up to about 120°C.

Lanthanide Schiff base complexes find varied applications in agriculture and medicine. Such complexes like 2-hydroxyphenyl-4-diaminomethylaminophenyl-2-thienyl-s-benzoyldithiocarbazate derived from s-bensoyldithiocarbazate and aldehyde provide high percentage of inhibition value and demonstrated greater efficiency than free ligands as pesticides in the present note we have undertaken synthesis and spectral studies of La (III), Ce (III), Pr (III), Nd (III), Sm (III), Eu (III), Gd (III), Tb (III), Dy (III) and Y (III) perchlorates with Schiff base derived from salicylaldehyde.

Experimental

The chemicals used were of AR grade or chemically pure. The ligand was synthesised by dissolving thiocarbohydrazide (25 g) in water (170 ml) and heated to boiling. Pyruvic acid (14 g) was then added with vigorous stirring. Light yellow crystals of 4-amino-3-mercapto-6-methyl-1, 2, 4-triazine (4H)-5-one obtained were recrystallised from hot water. This ligand (15.8 g) was then refluxed for 3 h with 13 ml of salicylaldehyde in 250 ml absolute ethanol containing three drops of conc. HCl. On cooling, the solid separated which was filtered and recrystallised from ethanol. Yield 72%. M.p. 230-232°C.

Synthesis of complexes

The perchlorates of La, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Y were prepared by taking the respective oxides (Indian Rare earth Ltd, Alwa) and cerium nitrate (Aldrich USA) in 60% perchloric acid and recrystallising the salt by evaporating the solution on a steam bath. A hot solution of the ligand, SMMT (4 mmol) in 20 ml of ethanol was added to a boiling solution of lanthanide perchlorate (2 mmol) in 10 ml ethanol and the resulting solution was refluxed for 2 h. The solid separated out was filtered and washed with ethanol and ether. The complexes were dried in vacuo over $\text{P}_2\text{O}_5$. The complexes thus obtained are: La (Light brown; 71%), Ce (Light yellow; 63%), Dy (Reddish brown; 69%), Pr (Yellow; 72%), Eu (Light yellow; 68%), Nd (Bright yellow; 74%), Sm (Yellow; 73%), Gd (Lemon yellow; 74%), Tb (Light cream; 74%) and Y (Reddish brown). The complexes are sparingly soluble in DMF and stable up to 120°C.

The perchlorate and the metal ion content in the complexes were determined by standard methods. Carbon, hydrogen and nitrogen were analysed on microscale at the RSIC of Punjab University. The magnetic susceptibilities of all the complexes were determined with a Gouy balance at room temperature. The thermogravimetric analysis of the complexes were carried out on Mettler TA 4000 thermal analyser by heating the complexes in air at the rate of 20°C/min upto 700°C at the Dept. of Chemical Engineering, KREC Surathkal. The molar conductivities of the synthesised complexes in 1x$10^{-3}$ mol/dm$^3$ DMF solution were measured using Elico digital conductivity meter. The absorption spectra of the ligand and complexes were recorded on Chimtote-2500 UV-vis spectrometer in DMF, in the range 900-
Results and discussion

From the analytical data, all the perchlorate complexes may be formulated as [Ln(SMMT)$_2$ClO$_4$] (where Ln= La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Y) (Table 1). All these complexes are non-hygroscopic solids with varying colours. Conclusive evidences for all the above type of complexes and its geometry has been elucidated by the spectral data.

The magnetic susceptibility studies shows that room temperature magnetic moments of the complexes are in good agreement with the theoretical values calculated by Van Vleck formula. Thus, La and Y complexes are diamagnetic and all other complexes are paramagnetic in nature; Ce (2.57 BM), Pr (3.47 BM), Nd (3.60 BM), Sm (1.88 BM), Gd (8.10 BM), Tb (9.78 BM) and Dy (10.58 BM). However, it is found that the experimental values of all the complexes including those of Sm and Eu agree with the theoretical values calculated from Van Vleck formula.

Thermogravimetric analysis of these complexes show a weight loss in the temperature range 120-250°C which indicates the loss of organic component or starting of the decomposition of the complexes. The decomposition is complete at about 700°C, yielding the respective rare earth oxide as the final product. The molar conductance values of complexes in DMF were in the range of 12.5-16.5 ohm$^{-1}$ cm$^2$ mol$^{-1}$. This result reveals that they are non-electrolytes. Hence, the complexes may be formulated as [Ln(SMMT)$_2$ClO$_4$].

The electronic spectrum of the ligand in the solid state show the n→π* transition at 382 nm and two π→π* transitions at 255 and 260 nm. In the spectra of the complexes, the n→π* bands are absent and the π→π* bands appear at 242-244 nm. The electronic spectra of the complexes have the same three bands in the UV region as in the case of the ligand. However, all these bands are slightly blue shifted in the spectra of the perchlorate complexes. No absorption band due to f/f transition of the lanthanide ions could be located in the visible region in the spectra of all these complexes. This is probably due to the fact that f/f bands are very weak and are obscured by the intense charge-transfer bands that appear in the spectral region.

The IR spectral studies shows that v (C=O) of the ligand at 1660 cm$^{-1}$ is lowered in the complexes indicating that oxygen of C=O is involved in bonding. The stretching frequency v (C-S) (thioamide band IV) of the ligand is found at 850 cm$^{-1}$ is not shifted in all its complexes. This supports the non-participation of
S atom in bonding. The ligand molecule basically contains thioamide group (N=\(\text{C-SH}\) or H-N-\(\text{C-S}\)) besides phenyl and azomethine groups. The presence of thioamide moiety is confirmed by the IR spectrum of SMMT. The thioamide bands did not shift in the complexes which shows that N or S of this group are not involved in bonding. The band at 1610 cm\(^{-1}\) of the spectrum of SMMT may be assigned to azomethine group and it is shifted towards lower wavenumber 11.12 \(^{13,14}\) in the spectra of the complexes. This indicates the bonding through nitrogen atom of the azomethine group. The infrared spectra of the ligand SMMT have the bands in the region 3100-3000 and 2900 cm\(^{-1}\). These bands may be assigned to \(\nu (\text{N-H})\) and \(\nu (\text{C-H})\) respectively. There is no change observed in the spectra of the complexes which rules out the possibility of bonding through N or S end of the thioamide group. In the spectrum of SMMT, a band at 1290-1320 cm\(^{-1}\) is observed which may be assigned to \(\nu (\text{C-O})^{13,14}\). In the spectra of the complexes, this band is shifted to higher wavenumber indicating the coordination through oxygen of the phenolic group.

Apart from the vibrational modes, most of which are common in the spectra of the ligand and the complexes, there are four additional band in the spectra of the perchlorate complexes of SMMT at 1150, 1080, 660 and 170 cm\(^{-1}\). The first three bands are assigned to the stretching vibrations of the perchlorate ions as \(\nu_1\), \(\nu_4\) and \(\nu_3\) respectively \(^{15}\). The bands at 1150 and 1080 cm\(^{-1}\) are split bands and corresponds to \(\nu_1\) and \(\nu_4\) modes of the unidentately coordinated perchlorate ions. This kind of splitting indicates that the perchlorate ion is coordinated unidentately. The lanthanide perchlorate complexes are formulated as \([\text{Ln(SMMT)\text{ClO}_4}]^{n}\). With a coordination number of seven for the lanthanide ions (where \(\text{Ln} = \text{La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Y}\) (Structure I).

References