

NOTE**Praseodymium(III) and Samarium(III) Complexes with *p*-(Methoxy or Chloro) Phenylglyoxal N,N-dimethyl thiosemicarbazones**

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Praseodymium(III) and samarium(III) complexes with *p*-methoxy phenylglyoxal N,N-dimethyl thiosemicarbazone and *p*-chloro phenyl glyoxal N,N-dimethyl thiosemicarbazone of composition $[ML_2(CH_3COO)_2]CH_3COO$ where HL = respective thiosemicarbazone ligand have been prepared and characterized by electrical conductance, magnetic susceptibility measurements, UV, ESR and IR studies.

Key Words: UV and IR and magnetic susceptibility measurements, *p*-Substituted phenylglyoxal N,N-dimethyl thiosemicarbazone.

Ligands containing sulphur¹ as donor atom are powerful chelating agents due to high charge on lanthanide ion which could only be stabilized by highly electronegative atoms of the ligands. Thiosemicarbazide and thiosemicarbazones have physiological activity against viruses, protozoa small pox tuberculosis and certain kinds of tumour²⁻⁴. Hence, lanthanide-thiosemicarbazone complex have been prepared and characterized considering its probable wide applications.

Praseodymium chloride and samarium chlorides (Indian Rare Earth's Udyogmandal, 99.99 % purity) was used as such. Rest of the chemicals used were of analR grade. *p*-Methoxy phenyl glyoxal and *p*-chlorophenyl glyoxal were prepared by standard method⁵.

The ligands PMPGT (C₁₂H₁₅O₂N₃S) and PCPGT (C₁₁H₁₂ON₃SCl) were synthesized by refluxing *p*-methoxy-phenylglyoxal and *p*-chloro phenylglyoxal with N,N-dimethyl thiosemicarbazide⁶. (1:1 ratio) in absolute alcohol for 4 h and recrystallizing the product from ethanol.

Preparation of complexes: To an alcoholic solution of PrCl₃ or SmCl₃ (2.5 mmol) an alcoholic solution of sodium acetate trihydrate (1.02 g, 7.5 mmol) was added. Sodium chloride was precipitated. It was filtered off. Now to this filtrate an ethanolic solution of ligand (5 mmol) was added. This mixture was refluxed for 3 h on water bath. The excess solvent was removed by distillation and the remaining solution was left for overnight. The solid complex separated out. It was washed with ethanol and dried in air.

The percentage of Pr and Sm-metal was estimated by heating to oxide, then dissolved in 50 % HCl and the resulting solution was titrated with EDTA using xylenol as indicator. Elemental analysis was done by standard method. The magnetic moment was measured at room temperature using Gouy's balance. Electronic spectra were recorded on a Toshniwal spectronic-20D spectrophotometer and IR spectra on a perkin-Elmer577 spectrophotometer. These values were compared well with the results found by Mishra *et al.*⁷.

The analytical data of the complexes indicate 1:2 stoichiometry between metal and ligand (Table-1).

TABLE-1

Compound (colour)	m.p. (°C) / (μ_{eff}) BM	Elemental analysis: Found (Calcd.) %			
		C	N	S	M
C ₁₂ H ₁₅ N ₃ O ₂ S (Brown)	170 (-)	54.30 (54.33)	15.60 (15.84)	11.85 (12.07)	-
C ₁₁ H ₁₂ N ₃ O ₃ Cl (Brown)	~160 (-)	48.34 (78.97)	15.50 (15.58)	11.72 (11.87)	-
[Pr(C ₁₂ H ₁₅ N ₃ O ₂ S) ₂ (CH ₃ COO) ₂](CH ₃ COO) (Deep gray)	>190 (3.48)	41.88 (42.45)	9.65 (9.90)	7.40 (7.54)	16.58 (16.62)
[Pr(C ₁₁ H ₁₂ N ₃ O ₃ Cl) ₂ (CH ₃ COO) ₂](CH ₃ COO) (Brown)	>195 (3.40)	38.98 (39.20)	9.72 (9.80)	7.38 (7.46)	16.41 (16.45)
[Sm(C ₁₂ H ₁₅ NO ₂₃ S) ₂ (CH ₃ COO) ₂](CH ₃ COO) (Gray)	>200 (1.52)	41.91 (42.00)	9.71 (9.80)	7.36 (7.46)	17.41 (17.50)
[Sm(C ₁₁ H ₁₂ N ₃ O ₃ Cl) ₂ (CH ₃ COO) ₂](CH ₃ COO) (Brown)	>205 (1.58)	38.68 (38.79)	9.62 (9.69)	7.33 (7.39)	17.28 (17.32)

These are coloured solid complexes, having high melting points and are soluble in acetone, dioxane and in DMF. The observed magnetic moments are in good agreement with the theoretical values calculated for the Van Vleck formula⁸. Both the complexes are paramagnetic in nature (Table-1).

The electronic spectral data of complexes (Table-2) exhibited red shifts, with respect to aquo ion. This is a consequence of complex formation found in many lanthanide complexes⁹.

The values of nephelauxetic ratio (β), bonding parameter ($b^{1/2}$) and convalency angular overlap parameter η have been calculated¹⁰. Complexes show β less than unity while the $b^{1/2}$ values are positive. These correspond covalent nature of the metal ligand bond¹⁰. In the IR spectra of the ligands, the $\nu(\text{C}=\text{S})$ bond appears at 860 cm^{-1} , respectively. In metal complexes, this value shifts by 10-40 cm^{-1} showing the coordination through sulphur atoms. Two or three IR bands in the region (3340-3110 cm^{-1}) assignable to $\nu(\text{NH}_2)$ and $\nu(\text{NH})$ vibrations are found.

TABLE-2
ELECTRONIC SPECTRA DATA OF THE Pr(III) AND Sm(III)
COMPLEXES OF PMPGT AND PCPGT

Ion	λ_{\max} (cm ⁻¹)	Assignment	β	$b^{1/2}$	η
Pr(III)	16807 (16670)	³ H ₄ → ¹ D ₂	0.9916 (0.9836)	0.0648 (0.0906)	0.0042 (0.0032)
	20619 (20410)	³ H ₄ → ³ P ₀			
	22466 (22220)	³ H ₄ → ³ P ₂			
Sm(III)	211505 (21280)	⁶ H _{5/2} → ⁴ G _{5/2}	0.9991 (0.9884)	0.0212 (0.0762)	0.0045 (0.0058)
	23868 (24094)	⁶ H _{5/2} → ⁴ I _{5/2}			
	25320 (25360)	⁶ H _{5/2} → ⁶ P _{3/2}			

The thioamide band I [$\nu(\text{CN}) + \delta(\text{NH})$] in the region 1525-1485 cm⁻¹. Thioamide band II near 1340-1310 cm⁻¹. Thioamide band III at 1280-1230 cm⁻¹ were observed in free ligands. The shift of $\nu(\text{C}=\text{N})$ mode of the free ligand at 1618 and 1580 cm⁻¹ in PMPGT and PCPGT, respectively to the lower wave-numbers by 20-40 cm⁻¹ in the complexes indicates involvement of azomethine nitrogen in co-ordination. The bands at 1680 and 1675 cm⁻¹ (C=O) in these free ligands do not show appreciable shift in the complexes. So glyoxalic >C=O group in ligands is not involved in coordination. The new bands in the spectra of the complexes at 480-510 and at 420-380 cm⁻¹ indicate the presence of (M-N) and (M-S) bond¹¹. Bands at 1520-1450 and 1420-1380 cm⁻¹ due to $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO}^-)$ modes of acetate group indicate the presence of acetate group in coordination sphere of these complexes.

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