

PREPARATION AND CHARACTERIZATION OF $\text{SmCl}_3(\text{THF})_3$ AND $\text{Sm}(\text{BH}_4)_3(\text{THF})_3$ COMPLEXES

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ABSTRACT : The synthesis of $\text{SmCl}_3(\text{THF})_3$ from $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ is described. The reaction of $\text{SmCl}_3(\text{THF})_3$ with NaBH_4 in dry THF gave white microcrystalline tris (tetrahydroborato) tris (tetrahydrofuran)samarium (III), $\text{Sm}(\text{BH}_4)_3(\text{THF})_3$. The vibrational and magnetic properties of $\text{Sm}(\text{BH}_4)_3(\text{THF})_3$ have been studied.

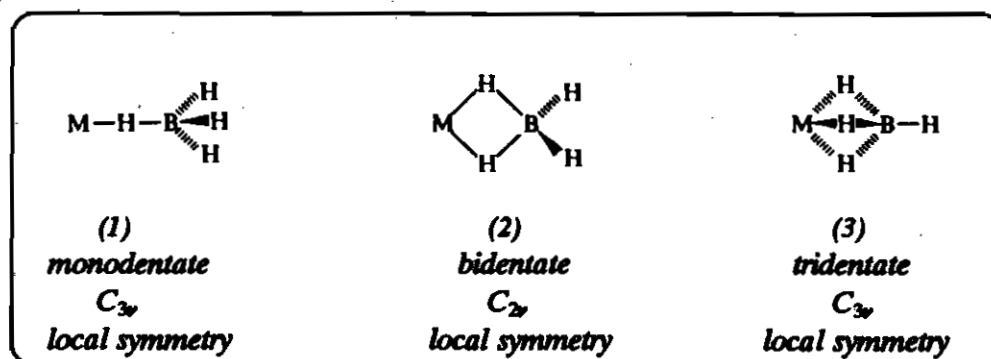
KEY WORDS : $\text{SmCl}_3(\text{THF})_3$, $\text{Sm}(\text{BH}_4)_3(\text{THF})_3$, Preparation, Vibrational spectra.

INTRODUCTION :

The tetrahydroborate anion, BH_4^- , forms alkali metal tetrahydroborates (also known as borohydrides) and a large variety of covalent complexes with transition metal, lanthanide and actinide ions [1-4]. The tetrahydroborate ligand

has three potential modes of coordination to a metal ion and classified as mono-, bi-, or tridentate ligand [structures (1), (2), and (3)].

Few monodentate and tridentate complexes are known, but bidentate complexes are most



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common [5-8]. The different modes of bonding of tetrahydroborates give rise to distinct and characteristic patterns of vibrational frequencies [1, 9, 10].

In this article preparation and characterization of $\text{SmCl}_3(\text{THF})_3$ and $\text{Sm}(\text{BH}_4)_3(\text{THF})_3$ from $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ are reported.

EXPERIMENTAL :

Owing to the air and moisture sensitivity of the complexes, all operations were carried out under an oxygen-free dry nitrogen atmosphere in a dry box using standard *Schlenk* techniques. Solvents were dried and distilled by standard methods before using. Elemental analyses were performed with an *Elemental Analyzer CHN-O-RAPID*, Heraeus. Infrared spectra were recorded on a *Perkin-Elmer 393* spectrophotometer from Nujol mulls prepared in a dry box.

Preparation :

1) Preparation of $\text{SmCl}_3(\text{THF})_3$

50g (13.7×10^{-2} mol) $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ was transferred into a 2L three necked flask and 800mL thionyl chloride (SOCl_2) was added. The suspension was refluxed under a dry nitrogen atmosphere until the evolution of HCl and SO_2 had ceased, and the thionyl chloride was distilled off. The residue was washed with three 50 mL portions of THF and dried in vacuum. The product obtained was free from water (IR spectrum), but contained some residual SOCl_2 which could easily be removed in the THF complexation reaction.

The white solid, $\text{SmCl}_3(\text{SOCl}_2)_x$, was transferred into a 2L three necked flask and 800mL THF was added. The suspension was refluxed under a dry nitrogen atmosphere for two days. The white suspension was filtered and the solid was dried in vacuum and extracted with 800mL THF. The white microcrystalline compound was filtered and the solid was dried and stored under nitrogen in a sealed ampoules (yield $\approx 80\%$).

Analytical data, confirms the formula $\text{SmCl}_3(\text{THF})_3$ (H_2O and SOCl_2 were shown to be absent).

IR (Nujol mull, KBr, cm^{-1}): [Nujol: 3000- 2860 (vs), 1455 (s), 1375 (s), 1345 (w, sh)].

$\text{SmCl}_3(\text{THF})_3$: 1295 (w), 1248 (w), 1180 (w), 1010 (vs), 915 (s), 860 (vs), 720 (m), 662 (m).

2) Preparation of $\text{Sm}(\text{BH}_4)_3(\text{THF})_3$

To a stirred 200 mL THF solution of $\text{SmCl}_3(\text{THF})_3$ (4.00g, 8.46×10^{-3} mol) was added excess of sodium tetrahydroborate. The suspension was stirred for four days. After filtration the solution was taken to dryness and residue was dissolved in toluene, the precipitated sodium chloride being removed before the solution was again taken to dryness. Again the residue was dissolved in THF. After addition of hexane by syringe as a layer, white microcrystalline compound was crystallized during a few days at room temperature. The white microcrystalline compound was filtered and the solid was dried and stored under nitrogen in a sealed ampoules (yield $\approx 65\%$). Analytical data, confirms the formula $\text{Sm}(\text{BH}_4)_3(\text{THF})_3$.

IR (Nujol mull, KBr, cm^{-1}): [Nujol : 3000- 2850 (vs), 1455 (s), 1375 (s), 1345 (w, sh)].

$\text{Sm}(\text{BH}_4)_3(\text{THF})_3$:

(BH_4 , tetrahydroborate group) : 2460 (s), 2440 - 2400 (s, doublet), 2140 (s), 2200- 2260 (s, doublet), 1160 (s), 1090 (s).

(THF group) : 1295 (w), 1248 (w), 1180 (w), 1010 (vs), 915 (s), 860 (vs), 720 (m), 662(m).

Magnetic measurement : $\mu_{\text{eff}} = 1.53$ B.M.

RESULTS AND DISCUSSION :

The different modes of bonding of tetrahydroborates give rise to distinct and characteristic patterns of vibrational frequencies. BH_4 group belongs to T_d symmetry, therefore, deformation of BH_4 group is also characteristic, and it is possible to ascertain the number of bridges in tetrahydroborate in a new compound, simply by consideration of infrared and Raman spectra. Structure (1) (a singly bridged group) has two stretches of terminal bonds ($a_1 + e$) and one of the bridge (a_1), at 2300- 2450 and ≈ 2000 cm^{-1} , respectively. Structure (2) (a doubly- bridged group) has four stretching modes, two of the ter-

terminal bonds (a_1+b_1) (typically between 2400 and 2600 cm^{-1}) and two of the bridges (a_1+b_2) (1950 to 2150 cm^{-1}). Structure (3) (a triply bridged group) has one terminal (a_1) and two bridge stretching modes ($a_1 + e$), at 2450-2600 and 2100-2200 cm^{-1} , respectively [9,10]. At lower frequencies, structure (1) shows a strong band, possibly with a weaker one at slightly higher frequency at 1000-1150 cm^{-1} ($a_1 + e$) which could be assigned to BH_3 deformation; structure (2) shows a strong broad band at 1300-1500 cm^{-1} (a_1) and a strong band at 1100-1200 cm^{-1} (b_2) which could be assigned to bridge stretching and BH_2 deformation, respectively; structure (3) shows one strong band at 1150-1250 (e) which could be assigned to bridge deformation [9,10].

$\text{Sm}(\text{BH}_4)_3(\text{THF})_3$ shows one strong band at 2460 cm^{-1} , a strong doublet at 2200-2260 cm^{-1} and a strong band at 1160 cm^{-1} , which is characteristic of tridentate BH_4 group. In addition, a strong doublet at 2400-2440 cm^{-1} , a strong band at 2140 cm^{-1} and another strong band at 1090 cm^{-1} (bridge stretching at 1300- 1500 cm^{-1} which is not seen very easily, could be hidden under Nujol band) which is characteristic of bidentate BH_4 group.

Infrared spectra of $\text{Sm}(\text{BH}_4)_3(\text{THF})_3$ and $\text{Y}(\text{BH}_4)_3(\text{THF})_3$ are very similar. The molecular structure of $\text{Y}(\text{BH}_4)_3(\text{THF})_3$ has been determined by a single X-ray diffraction method. In this complex, one of three tetrahydroborate groups is bidentate and the other two are tridentate, therefore, because of strong similarity between the infrared spectra of these two tetrahydroborate complexes, we can conclude $\text{Sm}(\text{BH}_4)_3(\text{THF})_3$ has a similar structure to $\text{Y}(\text{BH}_4)_3(\text{THF})_3$ complex.

Magnetic measurement of $\text{Sm}(\text{BH}_4)_3(\text{THF})_3$

complex shows the complex is paramagnetic ($\mu_{\text{eff}} = 1.53$ B.M.) which is reasonable for $\text{Sm}^{3+}(4f^5)$ electronic configuration) at room temperature.

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REFERENCES :

- [1] Marks, T. J., and Kolb, J. R., *Chem. Rev.*, **77**, 263 (1977).
- [2] Jensen, J. A., and Girolami, G. S., *J. Am. Chem. Soc.*, **110**, 4450 (1988).
- [3] Dapporto, P., Midollini, S., Orlandini, A., and Sacconi, L., *Inorg. Chem.*, **15**, 2768 (1976).
- [4] Jensen, J. A., Wilson, S. R., and Girolami, G. S., *J. Am. Chem. Soc.*, **110**, 4977 (1988).
- [5] Takusagawa, F., Fumagalli, A., Koetzle, T. F., Shore, S. G., Schmitkors, T., Fratini, A. V., Morse, K. W., Chiau-Yu Wei, and Bau, R., *J. Am. Chem. Soc.*, **103**, 5165 (1981).
- [6] Melmed, K. M., Coucouvanis, D., and Lippard, S. J., *Inorg. Chem.*, **12**, 232 (1973).
- [7] Bird, P. H., and Churchill, M. R., *Chem. Commun.*, 403 (1967).
- [8] Segal, B. G., and Lippard, S. J., *Inorg. Chem.*, **17**, 844 (1978).
- [9] Marks, T. J., Kennelly, W. J., Kolb, J. R., and Shimp, L. A., *Inorg. Chem.*, **11**, 2540 (1972).
- [10] Dain, C. J., Downs, A. J., Goode, M. J., Evans, D. G., Nicholls, K. T., Rankin, D. W. H., and Robertson, H.E., *J. Chem. Soc., Dalton Trans.*, 967 (1991).