

PREPARATION AND CHARACTERIZATION OF Ti(BH₄)₃(THF)₃ and V(BH₄)₂(TMEDA)₂ COMPLEXES

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ABSTRACT : We have recently synthesized Ti(BH₄)₃(THF)₃ and V(BH₄)₂(TMEDA)₂ complexes. The reaction of TiCl₃(THF)₃ with NaBH₄ in dry THF gave flat blue crystals, Ti(BH₄)₃(THF)₃. The reaction of VCl₃ with NaBH₄ in presence of N, N, N', N' - tetramethylethylenediamine, TMEDA, produced violet crystals, V(BH₄)₂(TMEDA)₂. Vibrational and magnetic properties of Ti(BH₄)₃(THF)₃ and V(BH₄)₂(TMEDA)₂ have been studied.

KEY WORDS : Ti(BH₄)₃(THF)₃, V(BH₄)₂(TMEDA)₂, Preparation, Vibrational Spectra.

INTRODUCTION :

The tetrahydroborate anion, BH₄⁻, provides a large variety of covalent complexes with transition metal, lanthanide and actinide ions [1-4]. Coordination of BH₄⁻ to the metal ions occurs through bridging hydrogen atoms and can be unidentate [in Cu^I(η¹-BH₄)(PMePh₂)₃], bidentate [in V(η²-BH₄)₃(PMe₃)₂], and tridentate [in Zr^{IV}(η³-BH₄)₄] [4-7]. Few unidentate and tridentate complexes are known, but bidentate complexes are most common. Many metal hydroborate complexes have been struc-

turally characterized, although infrared and Raman spectroscopy are useful criterion. For example, the different modes of bonding of tetrahydroborates give rise to distinct and characteristic patterns of vibrational frequencies [2,8,9]. More tetrahydroborate complexes exist for Ti(III) than for V(III) or V(II). Preparation and characterization of V(η²-BH₄)₃(PMe₃)₂ and V(η¹-BH₄)₂(dmpe)₂ are reported recently [4]. The structure of (η⁵-C₅H₅)₂Ti(η²-BH₄) has been determined via single-crystal X-ray

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diffraction study [10]. The preparation of $(\eta^5\text{-C}_5\text{H}_5)_2\text{V}(\text{BH}_4)$ was quite similar to that of the corresponding titanium compound, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\eta^2\text{-BH}_4)$. The vibrational spectrum of $(\eta^5\text{-C}_5\text{H}_5)_2\text{V}(\text{BH}_4)$ indicated a very strong and covalent metal-ligand interaction in the bidentate geometry [11]. In $\text{Ti}(\eta^3\text{-BH}_4)_3$, three tridentate BH_4 groups generating a structure with C_{3h} symmetry with a planar TiB_3 skeleton [9]. In $\text{Ti}(\text{BH}_4)_3(\text{PMe}_3)_2$, one of the three BH_4^- group is bidentate whereas the other two BH_4^- groups possess unusual geometries involving interaction of the titanium center with one B-H bond in a "Side-on" manner [3].

In this article preparation and characterization of $\text{Ti}(\text{BH}_4)_3(\text{THF})_3$ and $\text{V}(\text{BH}_4)_2(\text{TMEDA})_2$ are reported.

EXPERIMENTAL :

Owing to the air sensitivity of the complexes, all operations were carried out under a dry box oxygen-free nitrogen atmosphere, 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, ICP, and an atomic absorption, 2830, *Perkin-Elmer*. Infrared spectra were recorded on a *Perkin-Elmer 393* spectrophotometer from Nujol mulls prepared in a dry-box. Samples for magnetic susceptibility measurements were sealed in calibrated tube inside a dry-box. Measurements were carried out at room temperature using a Gouy balance (Johnson-Mathey). Magnetic moments were calculated by following standard methods [12], and corrections for underlying diamagnetism were applied to the data [13].

Preparation

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

50g (32.41×10^{-2} mol) violet and very sensitive TiCl_3 was transferred into 2L three necked flask and 600mL THF was added. The suspension was refluxed under a dry nitrogen atmosphere for 48 hours. The blue suspension was filtered and washed with three 50mL

portions of THF. The blue solid was dried and stored under nitrogen in sealed ampoules (yield $\approx 80\%$).

IR (Nujol mull, KBr, cm^{-1}):

[Nujol: 3000- 2860 (vs), 1455 (s), 1375 (s), 1345 (w, sh)].

$\text{TiCl}_3(\text{THF})_3$: 1245 (m), 1205 (m), 1170 (m), 1035 (s), 1005 (s), 960 (m), 935 (s), 845(s), 775 (m), 720(w), 685 (s), 575 (w), 420 (s), 350 (m).

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

To a stirred 200 mL THF solution of $\text{TiCl}_3(\text{THF})_3$ (4.00g , 10.79×10^{-3} mol) an excess of sodium tetrahydroborate was added. The suspension was stirred for two 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 up to dryness. The residue was dissolved in ether. The clear solution was slowly cooled to -40°C . Bright flat blue crystals were separated out. The compound was filtered, dried and stored under nitrogen in sealed ampoules (yield $\approx 40\%$). Anal. Calcd (found) for $\text{C}_{12}\text{H}_{36}\text{O}_3\text{B}_3\text{Ti}$: C, 46.69 (46.59); H, 11.75 (11.81); O, 15.55 (15.61); B, 10.51 (10.43); Ti, 15.51 (15.58). IR(Nujol mull, KBr, cm^{-1}):

[Nujol: 3000- 2855 (vs), 1460(s), 1375(s), 1345 (w,sh)].

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

(BH_4 , tetrahydroborate group): 2455- 2405 (s, doublet), 2130 (s), 2045 (sh), 1115 (s).

(THF group): 1245 (m), 1200 (m), 1170 (m), 1035 (s), 1005 (s), 960 (m), 925 (s), 840 (s), 775 (m), 720(w), 680(s), 575(w), 420(s), 355(m).

Magnetic measurement: $\mu_{\text{eff}} = 1.7$ B.M.

3) Preparation of $\text{V}(\text{BH}_4)_2(\text{TMEDA})_2$

To a stirred 200 mL THF solution of VCl_3 (4.00g , 25.43×10^{-3} mol) were added N,N,N',N' -tetramethyl ethylenediamine, TMEDA(in excess, 9.5 mL, 63.5×10^{-3} mol) and an excess of sodium tetrahydroborate. After filtration and concentration, the clear blue solution was slowly cooled to -10°C . Bright violet crystals were separated out. The compound was filtered, dried

and stored under nitrogen in sealed ampoules (yield $\approx 50\%$). Anal. Calcd (found) for $C_{12}H_{40}N_4B_2V$: C, 46.04 (46.15); H, 12.88 (12.82); N, 17.90 (17.83); B, 6.91 (6.83); V, 16.27 (16.36). IR(Nujol mull, KBr, cm^{-1}):

[Nujol: 3000- 2850 (vs), 1460 (s), 1380 (s), 1345 (w, sh)].

$V(BH_4)_2(TMEDA)_2$

(BH_4 , tetrahydroborate group): 2360- 2410 (s, doublet), 2190 (sh), 2140(s), 1125(s).

(TMEDA group): 1400(w), 1295(w), 1285 (m), 1240 (m), 1190(w), 1165(m), 1095(vs), 1070(m), 1040(m), 1025(vs), 1005(m), 955 (vs), 930 (vw), 800(vs), 780 (m), 590 (vw), 500 (m), 480(w), 460(w), 375(w).

Magnetic measurement: $\mu_{eff} = 3.7$ B.M.

RESULTS AND DISCUSSION ;

BH_4^- ion (belongs to T_d symmetry) has four normal modes (A_1 , E , and $2T_2$), with the T_2 IR active. The local symmetry at the tetrahydroborate ion is reduced to C_{3v} , if it serves as unidentate and tridentate ligands, and it is reduced to C_{2v} , as a bidentate ligand. it is usually possible to ascertain the number of bridges in tetrahydroborate in a new compound, simply by consideration of infrared and Raman spectra. MBH_4 unit (a singly bridged group) has two terminal bond stretching modes ($a_1 + e$) and one for the bridge (a_1), at 2300-2450 and ≈ 2000 cm^{-1} and at lower frequency shows a strong band, (possibly with weaker one at slightly higher frequency) at 1000- 1150 cm^{-1} ($a_1 + e$) which could be assigned to BH_3 deformation. MBH_4 unit (a doubly- bridged group) has four stretching modes, two belonging to the terminal bonds ($a_1 + b_1$) (typically between 2400 and 2600 cm^{-1}), two for the bridges ($a_1 + b_2$) (1950 to 2150 cm^{-1}), a strong broad band at 1300-1500 cm^{-1} (a_1) and another strong band at 1100-1200 cm^{-1} (b_2) which could be assigned to bridge stretching* and BH_2 deformation respectively. MBH_4 unit (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 and at lower frequency shows one strong band at 1150- 1250 (e) which could be assigned to bridge deformation [2, 8, 9].

$Ti(BH_4)_3(THF)_3$ shows strong doublet at 2405- 2455 cm^{-1} , strong band at 2130 cm^{-1} (with shoulder at 2045 cm^{-1}), and strong band at 1115 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 [2, 8, 9].

Magnetic measurement of $Ti(BH_4)_3(THF)_3$ complex shows the complex is paramagnetic ($\mu_{eff} = 1.7$ B.M.) which is near to the spin- only value for one unpaired electron.

$V(BH_4)_2(TMEDA)_2$ shows strong doublet at 2360- 2410 cm^{-1} , strong band at 2140 cm^{-1} (with shoulder at 2190 cm^{-1}), and strong band at 1125 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 [2, 8, 9].

Magnetic measurement indicates that $V(BH_4)_2(TMEDA)_2$ complex possesses magnetic moment characteristic of monomeric d^3 species. Thus, the magnetic moment of 3.7 B.M. is near to the spin- only value for three unpaired electrons.

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