

COORDINATION COMPOUNDS

Interaction of Zirconium, Yttrium, and Zinc Tetrahydroborate Complexes $\text{NaM}^n(\text{BH}_4)_{n+1}(\text{DME})_m$ ($\text{M} = \text{Zr}, \text{Y}, \text{Zn}$) with Triethylcarbinol: Crystal and Molecular Structure of $\text{B}[\text{OC}(\text{C}_2\text{H}_5)_3]_3$

V. D. Makhaev*, A. S. Antsyshkina**, L. A. Petrova*, and G. G. Sadikov**

* Institute of Problems of Chemical Physics, Russian Academy of Sciences,
Chernogolovka, Moscow oblast, 142432 Russia

** Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,
Leninskii pr. 31, Moscow, 119991 Russia

Received November 27, 2003

Abstract—The reactions of zirconium, yttrium, and zinc tetrahydroborate complexes $\text{NaM}^n(\text{BH}_4)_{n+1}(\text{DME})_m$ ($\text{M} = \text{Zr}, \text{Y}, \text{Zn}$; $\text{DME} = 1,2\text{-diethoxyethane}$) with triethylcarbinol in tetrahydrofuran were studied. The products of the transformation of the BH_4 groups in these reactions were isolated and identified. The reaction of triethylcarbinol with the yttrium and zirconium complexes yields bis(3-ethyl-3-pentoxy)borane $\text{BH}[\text{OC}(\text{C}_2\text{H}_5)_3]_2$, whereas the reaction with the zinc complex yields tris(3-ethyl-3-pentyl) borate $\text{B}[\text{OC}(\text{C}_2\text{H}_5)_3]_3$. The physicochemical properties of the compounds obtained were studied. The crystal and molecular structure of $\text{B}[\text{OC}(\text{C}_2\text{H}_5)_3]_3$ was determined. Crystals of $\text{B}[\text{OC}(\text{C}_2\text{H}_5)_3]_3$ are trigonal: $a = 12.562(2)$ Å, $c = 9.048(2)$ Å, $Z = 2$, space group $P\bar{3}$. The B atom is located at the crystallographic axis 3, the BO_3 fragment is planar ($\text{B}-\text{O} = 1.362(2)$ Å). The C_2H_5 groups experience considerable thermal vibrations.

Reactions of metal tetrahydroborates with tertiary alcohols have been poorly studied. As is known, NaBH_4 does not react with tertiary alcohols; it reacts only in the presence of acetic acid to form the corresponding dialkoxyboranes [1]. Previously [2], it was shown that zirconium and hafnium tetrahydroborates react with *tert*-butyl alcohol to produce tris(*tert*-butyl) borate and the complexes $\text{M}(\text{OBu}^t)_4 \cdot \text{BH}(\text{OBu}^t)_2$ ($\text{M} = \text{Zr}, \text{Hf}$), whereas the reaction with triethylcarbinol yields dialkoxyborane $\text{BH}[\text{OC}(\text{C}_2\text{H}_5)_3]_2$ and alkoxide complexes of these metals. To explore in more detail the effect of the structure of tetrahydroborate complexes and the nature of the complex-forming metal on the reaction course and the composition of the reaction products, we studied the reactions of the anionic zirconium, yttrium, and zinc tetrahydroborate complexes— $\text{NaZr}(\text{BH}_4)_5 \cdot 3\text{DME}$ (**1**), $\text{NaY}(\text{BH}_4)_4 \cdot 4\text{DME}$ (**2**), and $\text{NaZn}(\text{BH}_4)_3 \cdot 3\text{DME}$ (**3**) ($\text{DME} = 1,2\text{-dimethoxyethane}$), respectively—with triethylcarbinol ($\text{C}_2\text{H}_5)_3\text{COH}$ (3-ethyl-3-pentanol) in tetrahydrofuran (THF). The products of the transformation of BH_4 groups in these reactions were isolated and identified.

EXPERIMENTAL

All the operations with transition-metal tetrahydroborates and dialkoxyborane were carried out in an

inert atmosphere. The solvents and the alcohol were dried and physicochemical studies were performed as described elsewhere [2]. ^{11}B and $^{11}\text{B}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker WP-200SY spectrometer (working frequency, 64.2 MHz; benzene as a solvent; $\text{BF}_3 \cdot \text{OEt}_2$ as the external reference).

The anionic tetrahydroborate complexes **1–3** were synthesized by reacting NaBH_4 with a corresponding metal chloride in dimethoxyethane [3–5].

Reactions of complexes **1–3** with triethylcarbinol were carried out in a round-bottom flask with a dropping funnel and a reflux condenser, which was equipped with a cell for collection of the hydrogen evolved in the course of the reactions. An excess of the alcohol in 10 ml of THF was added dropwise at room temperature to a weighed portion of a tetrahydroborate complex in 50 ml of the same solvent stirred with a magnetic stirrer. This was accompanied by gas evolution without noticeable self-heating. Stirring was continued for 1 h, whereupon it was stopped and the reaction mixture was allowed to stand for the reaction to be completed. The course of the reaction was monitored by observing the decrease in the intensity of the BH_4 absorption bands of the initial complexes in the IR spectra. After the completion of the reaction, the resulting precipitate was filtered off. The products were separated by fractionating the filtrate in vacuum.

Reaction of triethylcarbinol with the zirconium tetrahydroborate complex $\text{NaZr}(\text{BH}_4)_5 \cdot 3\text{DME}$ (1).

A portion of 6.5 ml (46 mmol) of the alcohol in 10 ml of THF was added dropwise to a solution of 1.2 g (2.6 mmol) of **1** in 50 ml of THF. The reaction was accompanied by vigorous gas evolution without noticeable self-heating of the reaction mixture. Within 5 days, a transparent solution with a small amount of a fine precipitate was formed. The precipitate was separated by filtration (identified as NaBH_4 by X-ray diffraction and IR spectroscopy; yield, 0.065 g (66%)). The filtrate was distilled in a vacuum (0.1 mmHg) at room temperature to remove the solvent and at 50°C to remove the unreacted alcohol excess. The residue was pumped out in a vacuum at 100–115°C, and a volatile product was collected in a trap cooled with liquid nitrogen. On defrosting the trap, bis(3-ethyl-3-pentoxo)borane $\text{BH}[\text{OC}(\text{C}_2\text{H}_5)_3]_2$ was obtained as a colorless liquid readily hydrolyzable in air. The yield was 1.65 g (65% in terms of $\text{Zr}(\text{BH}_4)_4$). The IR spectrum of the product corresponds to the literature data [2].

For $\text{C}_{14}\text{H}_{31}\text{BO}_2$ anal. calcd. (%): B, 4.46; H_{hydr} , 0.42. Found (%): B, 4.43; H_{hydr} , 0.40.

Reaction of triethylcarbinol with the yttrium tetrahydroborate complex $\text{NaY}(\text{BH}_4)_4 \cdot 4\text{DME}$ (2). A portion of 5 ml (35 mmol) of the alcohol in 10 ml of THF was added dropwise to a solution of 0.8 g (1.5 mmol) of **2** in 50 ml THF. The reaction was accompanied by gas evolution without noticeable self-heating. After 5 days, the reaction mixture was filtered. The precipitate was separated by filtration (identified as NaBH_4 by IR spectroscopy; yield, 0.04 g (70%)). The product $\text{BH}[\text{OC}(\text{C}_2\text{H}_5)_3]_2$ was isolated from the filtrate as described above. The yield was 0.75 g (69% in terms of $\text{Y}(\text{BH}_4)_3$).

Reaction of triethylcarbinol with the zinc tetrahydroborate complex $\text{NaZn}(\text{BH}_4)_3 \cdot 3\text{DME}$ (3). A portion of 5.1 ml (36.4 mmol) of the alcohol in 10 ml of THF was added dropwise to a solution of 1.05 g (2.6 mmol) of **3** in THF. After 12 days, the IR spectrum of the reaction mixture lacked the absorption bands at 2080, 2400, and 2460 cm^{-1} corresponding to the vibrations of the BH_4 groups bound to zinc. The reaction mixture was filtered. The filtrate was distilled in a vacuum at room temperature to remove the solvent and at 50°C to remove the alcohol excess. The white solid residue was placed in a setup for sublimation and heated in vacuum at 100–120°C. Colorless transparent crystals of $\text{B}[\text{OC}(\text{C}_2\text{H}_5)_3]_3$ were sublimed. The yield was 1.3 g (70% in terms of $\text{Zn}(\text{BH}_4)_2$), mp 74–75°C.

For $\text{C}_{21}\text{H}_{45}\text{BO}_3$ anal. calcd. (%): C, 70.77; H, 12.73; B, 3.03. Found (%): C, 70.60; H, 12.86; B, 3.06.

IR spectrum, cm^{-1} : 463 m, 580 m, 657 s, 682 s, 725 m, 760 w, 794 s, 921 s, 942 s, 1034 w, 1074 w, 1152 s, 1300 s, 1315 s, 1349 s, 1365 s, 1390 m, 1398 m, 1456 s, 2879 s, 2943 s, 2969 s.

Table 1. Fractional atomic coordinates and thermal parameters $U_{\text{eq}}/U_{\text{iso}}$ for $\text{B}[\text{OC}(\text{C}_2\text{H}_5)_3]_3$

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{eq}}/U_{\text{iso}}$ |
|-------|-----------|-----------|------------|--------------------------------|
| B(1) | 0.6667(0) | 0.3333(0) | 0.2504(7) | 0.055(2) |
| O(1) | 0.5440(2) | 0.2507(2) | 0.2500(2) | 0.058(1) |
| C(1) | 0.4426(3) | 0.2756(3) | 0.2495(6) | 0.064(1) |
| C(2) | 0.4483(5) | 0.3467(5) | 0.1115(7) | 0.091(2) |
| C(3) | 0.4487(8) | 0.2897(9) | −0.0346(9) | 0.135(2) |
| C(4) | 0.4482(4) | 0.3466(5) | 0.3873(7) | 0.087(2) |
| C(5) | 0.4513(8) | 0.2922(7) | 0.5352(9) | 0.136(2) |
| C(6) | 0.3308(3) | 0.1454(4) | 0.2503(9) | 0.098(2) |
| C(7) | 0.2061(4) | 0.1441(5) | 0.247(2) | 0.178(4) |
| H(21) | 0.519(3) | 0.427(3) | 0.123(3) | 0.07(1) |
| H(22) | 0.377(3) | 0.361(3) | 0.116(4) | 0.10(1) |
| H(31) | 0.518(4) | 0.269(3) | −0.036(4) | 0.15(2) |
| H(32) | 0.472(5) | 0.339(4) | −0.117(5) | 0.17(3) |
| H(33) | 0.365(5) | 0.202(5) | −0.033(5) | 0.19(3) |
| H(41) | 0.378(3) | 0.362(3) | 0.383(3) | 0.09(1) |
| H(42) | 0.521(3) | 0.426(3) | 0.376(3) | 0.07(1) |
| H(51) | 0.522(4) | 0.274(4) | 0.538(5) | 0.16(2) |
| H(52) | 0.375(3) | 0.215(3) | 0.538(4) | 0.13(2) |
| H(53) | 0.465(5) | 0.340(5) | 0.628(7) | 0.22(3) |
| H(61) | 0.336(3) | 0.101(3) | 0.158(4) | 0.10(2) |
| H(62) | 0.343(4) | 0.113(4) | 0.344(5) | 0.13(2) |
| H(71) | 0.144(4) | 0.068(3) | 0.256(4) | 0.15(2) |
| H(72) | 0.192(8) | 0.153(8) | 0.149(9) | 0.37(7) |
| H(73) | 0.202(6) | 0.170(6) | 0.343(7) | 0.26(5) |

X-ray diffraction pattern, *d*, Å (I_{rel} , %): 6.899 (69), 5.409 (19), 5.125 (7), 4.638 (10), 4.096 (100), 3.618 (9), 3.008 (16), 2.897 (9), 2.053 (8), 2.038 (6) (reflections with $I_{\text{rel}} > 5\%$ are listed).

Crystals for X-ray crystallography were obtained by sublimation in vacuum (0.1 mmHg) at 100–120°C.

X-ray crystallography of $\text{B}[\text{OC}(\text{C}_2\text{H}_5)_3]_3$. Crystals of prismatic habit are trigonal: *a* = 12.562(2) Å, *c* = 9.048(2) Å, *Z* = 2, space group $P\bar{3}$. Experimental intensity data were collected from a sample sealed in a capillary on an Enraf-Nonius CAD4 diffractometer ($\lambda\text{MoK}\alpha$, graphite monochromator, $\theta/2\theta$ scan mode, $\theta_{\text{max}} = 54^\circ$). The intensities of 4098 reflections were measured. The crystal and molecular structure of $\text{B}[\text{OC}(\text{C}_2\text{H}_5)_3]_3$ was solved by direct methods and refined by a least-squares procedure in the anisotropic-isotropic (for hydrogen) approximation using the SHELXL93 program package [6]. Some hydrogen atoms were located from difference Fourier syntheses.

Table 2. Bond lengths (*d*) and bond angles (ω) for B[OC(C₂H₅)₃]₃

| Bond | <i>d</i> , Å | Bond | <i>d</i> , Å |
|----------------|----------------|----------------|----------------|
| B(1)–O(1) | 1.361(2) | O(1)–C(1) | 1.456(5) |
| C(1)–C(2) | 1.516(8) | C(1)–C(4) | 1.514(8) |
| C(1)–C(6) | 1.533(5) | C(2)–C(3) | 1.50(1) |
| C(4)–C(5) | 1.51(1) | C(6)–C(7) | 1.559(8) |
| C(2)–H(21) | 0.96(3) | C(2)–H(22) | 1.00(4) |
| C(3)–H(31) | 1.03(5) | C(3)–H(32) | 0.92(5) |
| C(3)–H(33) | 1.08(6) | C(4)–H(41) | 0.99(4) |
| C(4)–H(42) | 0.97(3) | C(5)–H(51) | 1.03(6) |
| C(5)–H(52) | 0.96(4) | C(5)–H(53) | 0.99(6) |
| C(6)–H(61) | 1.02(4) | C(6)–H(62) | 0.99(5) |
| C(7)–H(71) | 0.88(4) | C(7)–H(72) | 0.92(9) |
| C(7)–H(73) | 0.94(6) | | |
| Angle | ω , deg | Angle | ω , deg |
| B(1)O(1)C(1) | 128.0(3) | O(1)C(1)C(2) | 109.9(4) |
| O(1)C(1)C(4) | 109.6(4) | O(1)C(1)C(6) | 101.8(4) |
| C(2)C(1)C(4) | 110.9(4) | C(2)C(1)C(6) | 112.4(4) |
| C(4)C(1)C(6) | 111.9(4) | C(1)C(2)C(3) | 116.9(6) |
| C(1)C(4)C(5) | 117.8(5) | C(1)C(6)C(7) | 113.0(6) |
| C(1)C(2)H(21) | 106(2) | C(1)C(2)H(22) | 107(2) |
| C(3)C(2)H(21) | 112(2) | C(3)C(2)H(22) | 110(2) |
| H(21)C(2)H(22) | 104(3) | C(2)C(3)H(31) | 110(3) |
| C(2)C(3)H(32) | 118(3) | C(2)C(3)H(33) | 104(3) |
| H(31)C(3)H(32) | 98(4) | H(31)C(3)H(33) | 105(4) |
| H(32)C(3)H(33) | 121(5) | C(1)C(4)H(42) | 105(2) |
| C(1)C(4)H(41) | 107(2) | C(5)C(4)H(42) | 110(2) |
| C(5)C(4)H(41) | 111(2) | C(4)C(5)H(51) | 110(3) |
| H(41)C(4)H(42) | 106(3) | C(4)C(5)H(53) | 121(4) |
| C(4)C(5)H(52) | 104(3) | H(51)C(5)H(53) | 102(4) |
| H(51)C(5)H(52) | 108(4) | H(52)C(5)H(53) | 111(4) |
| C(1)C(6)H(61) | 108(2) | C(1)C(6)H(62) | 102(3) |
| C(7)C(6)H(61) | 109(2) | C(7)C(6)H(62) | 112(3) |
| H(61)C(6)H(62) | 114(4) | C(6)C(7)H(71) | 110(3) |
| C(6)C(7)H(72) | 105(6) | C(6)C(7)H(73) | 102(5) |
| H(71)C(7)H(72) | 96(7) | H(71)C(7)H(73) | 97(5) |
| H(72)C(7)H(73) | 144(8) | | |

The non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were refined isotropically. The final refinement parameters were $R_1 = 0.0559$, $wR_2 = 0.0694$, and GOOF = 1.446 for 464 reflections

with $F_o \geq 4\sigma(F_o)$. The values obtained for all 1297 unique reflections were $R_1 = 0.2103$, $wR_2 = 0.095$, and GOOF = 1.069. The number of refined parameters was 136. The residual electron densities were $\Delta\rho_{\max} = 0.122 \text{ e/Å}^3$ and $\Delta\rho_{\min} = -0.110 \text{ e/Å}^3$.

Atomic coordinates are presented in Table 1 and bond lengths and bond angles, in Table 2.

RESULTS AND DISCUSSION

Comparison of the results of this work with those obtained previously in [2] for the reaction of triethylcarbinol with zirconium tetrahydroborate $\text{Zr}(\text{BH}_4)_4$ shows that the anionic complex $\text{NaZr}(\text{BH}_4)_5(\text{DME})_3$ is considerably less reactive: its reaction is completed within a week, whereas the reaction with $\text{Zr}(\text{BH}_4)_4$ is completed in 24 h. The formation of sodium tetrahydroborate indicates that, under the action of the alcohol, the anionic complex is decomposed to NaBH_4 , which is precipitated, and zirconium tetrahydroborate, which enters into a further reaction. As in the reaction with $\text{Zr}(\text{BH}_4)_4$, the major product of transformation of the tetrahydroborate groups of $\text{NaZr}(\text{BH}_4)_5(\text{DME})_3$ is dialkoxyborane $[\text{BH}[\text{OC}(\text{C}_2\text{H}_5)_3]_2]$, the product of the incomplete substitution of alkoxy groups for the hydride hydrogen atoms. The anionic yttrium complex $\text{NaY}(\text{BH}_4)_4(\text{DME})_4$ reacts with triethylcarbinol in the same manner to produce NaBH_4 and dialkoxyborane $\text{BH}[\text{OC}(\text{C}_2\text{H}_5)_3]_2$. Dialkoxyborane $\text{BH}[\text{OC}(\text{C}_2\text{H}_5)_3]_2$ is a colorless transparent liquid, which is distilled in a vacuum (0.1 mmHg) at 100–115°C, stable on storage in an inert atmosphere, and readily hydrolyzable in air. Due to the large volume of the alkoxyl radicals, this compound can be a candidate for a selective hydroboring reagent.

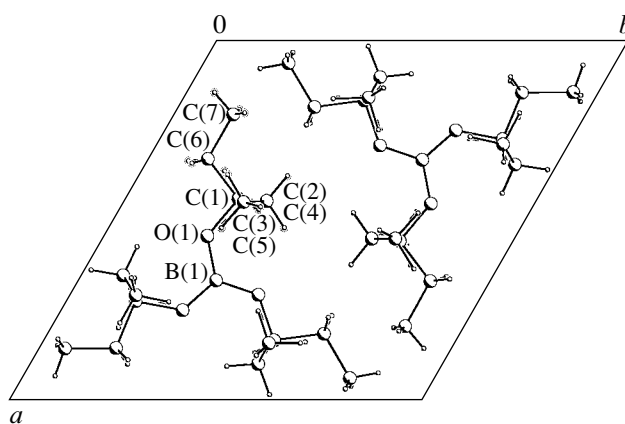
The ^{11}B NMR spectrum of $\text{BH}[\text{OC}(\text{C}_2\text{H}_5)_3]_2$ shows a broad singlet with a half-width of 480 Hz and a chemical shift of 24.7 ppm downfield from $\text{BF}_3 \cdot \text{OEt}_2$. Upon broad-band decoupling $^{11}\text{B}\{^1\text{H}\}$, the line width decreases to 330 Hz. Gaussian multiplication [7] leads to the splitting of the ^{11}B NMR signal into a doublet with the spin coupling constant $J(^{11}\text{B}-^1\text{H}) = 147 \text{ Hz}$, which is not observed in the common spectrum due to the considerable natural line width. The chemical shift and SCC in the ^{11}B NMR spectrum of $\text{BH}[\text{OC}(\text{C}_2\text{H}_5)_3]_2$ are close to the corresponding values for $\text{BH}[\text{OC}(\text{CH}_3)_3]_2$ ($\delta = 25.8 \text{ ppm}$, $J_{\text{BH}} = 166 \text{ Hz}$) [8]. As was previously shown, sterically unhindered dialkoxyboranes with small alkyl radicals give rise to the ^{11}B NMR signal at $27 \pm 0.2 \text{ ppm}$, whereas for $\text{BH}[\text{OC}(\text{CH}_3)_3]_2$ this signal is shifted upfield by 2 ppm. Our findings show that a further increase in the volume of the alkoxyl radicals leads to a further upfield shift of the corresponding signal. The reaction of triethylcarbinol with zinc complex **3** is considerably slower than those with the zirconium and yttrium complexes

and results in a new compound, tris(3-ethyl-3-pentyl) borate $B[OC(C_2H_5)_3]_3$, which has not hitherto been described. This compound is a colorless crystalline solid with a melting point of 74–75°C, which is stable in air and readily sublimable on heating in vacuum. The ^{11}B NMR spectrum of this compound shows a signal at 16.4 ppm. As distinct from most known trialkylborates, which are readily hydrolyzable, $B[OC(C_2H_5)_3]_3$ is hydrolytically stable and can be steam distilled without decomposition. The high hydrolytic stability of $B[OC(C_2H_5)_3]_3$ is evidently due to the presence of the bulky hydrophobic triethylcarbinol substituents, which hinder the access of water to the boron atom. An increase in the hydrolytic stability of trialkyl borate with an increase in the volume of the substituents at the boron atom was previously stated in [9].

Thus, the composition of the products of transformation of the BH_4 groups of the zirconium, yttrium, and zinc tetrahydroborate complexes in the course of their reaction with triethylcarbinol significantly depends on the nature of the complex-forming metal. The difference in the composition of the reaction products indicates that the zinc atom is involved in the alcoholysis of B–H bonds: the lower steric overcrowding of the nascent zinc alkoxide, as compared to zirconium and yttrium alkoxides, is favorable for the reaction of the intermediate dialkoxyborane (as a free molecule or as a ligand in the coordination sphere of the zinc complex) with the central atom.

The unusual hydrolytic stability of $B[OC(C_2H_5)_3]_3$ and its crystalline state made it possible to determine its structure by X-ray crystallography. The B atom is at the crystallographic threefold axis. The BO_3 moiety is flat (the B–O distances are 1.362(2) Å). The symmetry of the molecule is $3/m$ (S_6). In the $B[OC(C_2H_5)_3]_3$ molecule, the O–C, C–C, and C–H distances are 1.47(5), 1.50–1.56, and 0.85–1.11 Å, respectively. The molecules experience significant thermal vibrations.

The $B[OC(C_2H_5)_3]_3$ molecules in the crystal (figure) form the two-layer hexagonal close packing perpendicular to the threefold axis. Shortened contacts of molecules in the crystal are not observed. Due to a relatively flattened molecular shape, the hcp appears to be somewhat contracted along the c axis and the molecular num-



Molecular packing in the crystal of $B[OC(C_2H_5)_3]_3$.

ber is 8 (6 + 2); the distances between the centers of molecules (boron atoms) are 8.55 Å ($\times 6$) and 9.05 Å ($\times 2$).

To the best of our knowledge, the molecular and crystal structure of $B[OC(C_2H_5)_3]_3$ is the first example of X-ray crystallographic analysis of trialkylborate $B(OR)_3$.

REFERENCES

1. B. M. Mikhailov, *Chemistry of Boranes* (Nauka, Moscow, 1967) [in Russian].
2. L. A. Petrova, A. P. Borisov, and V. D. Makhaev, *Koord. Khim.* **18** (5), 492 (1992).
3. V. D. Makhaev, A. P. Borisov, G. N. Boiko, and B. P. Tarasov, *Izv. Acad. Nauk SSSR, Ser. Khim.*, No. 6, 1207 (1990).
4. V. D. Makhaev, A. P. Borisov, and E. B. Lobkovskii, *Zh. Neorg. Khim.* **29** (5), 1160 (1984).
5. A. P. Borisov, L. A. Petrova, and V. D. Makhaev, *Zh. Neorg. Khim.* **38** (6), 965 (1993).
6. G.M. Sheldrick, SHELXL93. Program for Crystal Structure Refinement, Univ. of Göttingen, Germany, 1993.
7. A. E. Derome, *Modern NMR Technique for Chemistry Research* (Pergamon, New York, 1987; Mir, Moscow, 1992).
8. D. J. Pasto, V. Balasubramanian, and P. W. Woitkowski, *Inorg. Chem.* **8** (3), 594 (1969).
9. H. Steinberg and D. L. Hunter, *Ind. Eng. Chem.* **49** (2), 174 (1957).