LETTERS TO THE EDITOR

Dedicated to the 90th Anniversary of Academician M.G. Voronkov

New Intracomplex Compounds of Pentacoordinate Germanium. Hypogermatranes, Ge-Substituted (N→Ge) 2-Oxa-5-aza-1-germacyclopentanes

M. G. Voronkov, G. S. Samokhin, D. V. Vrazhnov, and T. A. Kochina

Grebenshchikov Institute of Silicate Chemistry of Russian Academy of Sciences, nab. Admirala Makarova 2, St. Petersburg, 199034 Russia e-mail: voronkov@isc.nw.ru

Received June 3, 2011

DOI: 10.1134/S1070363212010288

The chemistry of intracomplex compounds of pentacoordinate germanium, germatranes $XGe(OCH_2CH_2)_3N$, containing the transannular coordination bond $N\rightarrow Ge$, has begun in 1968 and continues to actively develop [1–4]. In the present century, a great attention was attracted by their bicyclic analogs, quasigermatranes $X_2Ge(OCH_2CH_2)_2NH$ [5, 6].

In continuation of the investigations in this field, monocyclic hypogermatranes (N \rightarrow Ge) X_3 Ge(OCH₂·CH₂)NH₂, 2-oxa-5-aza-1-germacyclopentanes, also containing an intramolecular coordination bond N \rightarrow Ge, were first synthesized. They can be classified as dragonoids [7].

The first representative of these compounds, 1,1,1-trihydroxy-2-oxa-5-aza-1-germacyclopentane ↓ (HO)₃Ge(OCH₂CH₂)NH₂ (I) was synthesized by the reaction of germanium dioxide with 2-hydroxy-ethylamine in aqueous-alcoholic medium at 80°C in

the absence of catalyst.

$$GeO_{2} + H_{2}N \xrightarrow{C} OH + H_{2}O \xrightarrow{H_{2}N} CH_{2} (1)$$

$$HO \longrightarrow HO \longrightarrow HO$$

$$OH$$

Reaction (1) is accomplished by complete dissolution of GeO₂, which requires no less than 1 h.

The precipitate formed after removal of the solvent was filtered off and dried by heating in a vacuum. The yield of hypogermatranetriol was 93%. The product is a stable colorless powder with the temperature of decomposition ~300°C and the elemental analysis given below.

$C_2H_9GeNO_4$	C	Н	Ge	N
Found, %	13.57	5.02	7.31	42.51
Calculated, %	13.08	4.94	7.62	39.52

Using the reaction we had earlier found between the germatranol and ammonium salts [8], the 1,1,1-substituted hypogermatranes were synthesized.

X = F (II, decomp. 300°C), Cl (III, decomp. 270°C), Br (IV, decomp. 280°C), I (V, decomp. 230°C), NO₃ (VI, subl. 240°C), ClO₄ (VII, decomp. 280°C), SCN (VIII, decomp. 290°C).

Compounds having anions CO_3^{2-} (IX) or SO_4^{2-} (X) and two germatrane cycles have been prepared similarly.

$$\longrightarrow$$
 [H₂N(CH₂CH₂O)Ge]₂(Y)₃ + 6 NH₃ + 6 H₂O (3)

 $Y = CO_3$ (IX, mp 300°C), SO_4 (X, mp 270°C).

Reactions (2) and (3) were carried out in boiling ethanol till the evolution of ammonia ceased. The composition and the structure of the obtained 1,1,1-trisubstituted hypogermatranes was confirmed by the data of elemental analysis, IR, ¹H and ¹³C NMR spectroscopy. They all are colorless powders decomposed upon heating to 300°C.

REFERENCES

- 1. Voronkov, M.G., Zelchan, G.I., Mironov, V.F., Bleidelis, Ya.Ya., and Kemme, A.A., *Khim. Geterotsikl. Soedin.*, 1968, no. 2, p. 227.
- 2. Gar, T.K. and Mironov, V.F., *Metalorg. Khim.*, 1988, no. 1, p. 260.
- 3. Karlov, S.S. and Zaitseva, G.S., *Chem. Heterocycl. Comp.*, 2001, vol. 37, no. 11, p. 1325.
- 4. Voronkov, M.G., Kochina, T.A., Vrazhnov, V.V., Samokhin, G.S., Albanov, A.I., Aksamentova, T.N., Klyba, L.V., and Chipanina, N.N., *Russ. J. Gen. Chem.*, 2008, vol. 78, no. 12, p. 2339.
- 5. Selina, A.A., Karlov, S.S., and Zaitseva, G.S., *Chem. Heterocycl. Comp.*, 2006, vol. 42, no. 12, p. 1518.
- Cea-Olivares, R., Garcia-Montalvo, V., and Moya-Cabrera, M.M., Coord. Chem. Rev., 2005, vol. 249, p. 859.
- 7. Voronkov, M.G., Russ. Chem. Bull. Int. Ed., 1991, vol. 40, no. 12, p. 2319.
- 8. Voronkov, M.G., Ovchinnikova, Z.A., and Baryshok, V.P., *Metalorg. Khim.*, 1991, no. 4, p. 1194.