SYNTHESIS AND CHARACTERIZATION OF COMPLEXES OF MCI $_4$ WITH PYRAZINE (M = Si, Sn)

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Group 14 element tetrahalides are Lewis acids and can form donor-acceptor complexes with nitrogen-containing ligands [1, 2]. It is known that tin tetrachloride forms with pyrazine (pyz) the complex of 1:2 composition $SnCl_4$ · 2pyz [2]. However, pyz can behave not only as monodentate ligand, but also as bifunctional one [3]. Therefore, in the present work we report syntheses and characterization of complexes of MX_4 (M = Si, Sn) with pyz in the initial ratio MX_4 :pyz = 1:1 (M = Si, Sn).

Due to moisture and air sensitivity of group 14 element tetrahalides and the reaction products, syntheses and preparation of samples for physical measurements were carried out in wholeglass apparatus under vacuum or under an argon atmosphere in a glovebox Inertlab 2GB. Initial MCI₄-to-pyz ratio was 1.08:1 and 1:1.06 for SiCI₄ and SnCI₄, respectively. MCI₄ was sublimed to pyz and the reagent mixture was kept at room temperature for 9 days (SiCI₄) and 7 days (SnCI₄). Then the excess of MCI₄ was removed by sublimation into special compartment and sealed off. For SiCI₄ additional syntheses were performed in the glove box using a solvent (dichloromethane and toluene). Single crystals suitable for X-ray structure analysis (XRA) were grown from solutions at -28°C.

Products were characterized by mass spectrometry, IR spectroscopy, XRA and Powder X-Ray Diffraction analyses (PXRD). The results of XRA showed that only pyz and [pyzH]Cl were isolated from toluene and CH_2Cl_2 solutions, respectively. Thus, complex of $SiCl_4$ with pyz does not crystallize from the solution. However, IR spectrum for sample synthesized under vacuum showed that pyz was coordinated to $SiCl_4$. The complex $SnCl_4$ ·2pyz was characterized by PXRD resulting in a powder pattern that matches that of known $SnCl_4$ ·2pyz complex. Observation of ions $SiCl_3C_4H_4N_2^+$ (0,3%) and $SnCl_3C_4H_3N_2^+$ (0,7%) in mass spectra indicates existence of the compounds containing Si-N and Sn-N bonds in the gas phase.

To conclude, we have synthesized two complexes MCl_4 with pyz (M = Si, Sn). According to obtained results, the solid complex $SiCl_4$ with pyz is formed in synthesis under vacuum. From the synthesis in a ratio $SnCl_4$:pyz = 1:1 already known complex $SnCl_4$:2pyz is formed. Both complexes dissociate into free fragments upon heating.

References

- [1] Davydova E.I., Sevastianova T.V., Suvorov A.V., Timoshkin A.Y. Coord. Chem. Rev. 2010, 254, 2031-2077
- [2] Grigsby W.A., Morien T.S., Raston C.L., Skelton B.W., White A.H. Aust. I. Chem. 2004, 57, 507-508
- [3] Sevastianova T.V., Bodensteiner M., Lisovenko A.S., Davydova E.I., Scheer M., Susliakova T.V., Krasnova I.S., Timoshkin A.Y. *Dalt. Trans.* **2013**, *42*, 11589-11599

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