SYNTHESIS OF BIS(CITRATO)GERMANATE AND STANNATE WITH TRIS(PHENANTHROLINE)NICKEL(II) CATION

Olha Pirozhok, Elena Martsinko, Inna Seifullina, Elena Chebanenko

Odessa I.I. Mechnikov National University

Abstract. The new complexes $[Ni(phen)_3][Ge(HCit)_2]\cdot 2H_2O$ (1), $[Ni(phen)_3][Sn(HCit)_2]\cdot 3H_2O$ (2) (where phen is 1,10-phenanthroline, H_4Cit is citric acid) were synthesized. The purpose of this work was to characterize the new methods of synthesis. The identity, composition, and thermal stability of the complexes were established by elemental analysis, thermogravimetry, and IR spectroscopy. Improved methods of synthesis, as well as crystals for the continuation of research work.

Keywords. Citric acid, 1,10-phenanthroline, nickel(II) complexes, tin(IV), structure, germanium(IV).

Introduction. Obtaining and determining of the structure of coordination compounds formed with biometals and hydroxycarbonic acids are of great interest nowadays because of the creation of new medicines on their basis. Citric acid is the direct participant of a cycle of three carbonic acids (the Krebs cycle) and is present in blood plasma [1]; germanium lactate-citrate possesses radioprotective properties [2].

In the past few years, authors have shown that germanium(IV) and tin(IV) in water solution are able to form cation–anion coordination compounds with bis(citrate)germanate $[Ge(HCit)_2]^{2-}$ or bis(citrate)stannate $[Sn(HCit)_2]^{2-}$ anions and octahedral $[M(H_2O)_6]^{2+}$ cations (M= Mg, Mn, Fe, Co, Ni, Cu, Zn) [3,4]. Such a type of coordination compounds show santihypoxic, cerebroprotective and antiviral properties [5]. Subsequently, new complexes with similar bis(citrate)germanate anions and cations $[M(phen)_3]^{2+}$ (phen - 1,10-phenantroline, M = Fe(II), Co(II)) and $[CuCl(phen)_2]^{+}$ have been synthesized and described by the authors [6]. A group of

British and Portuguese scientists also have synthesized a number of complex compounds which contain tris(oxalato-O,O')germanate anion $[Ge(C_2O_4)_3]^{2-}$ and transition-metal cationic complexes $[M(phen)_3][Ge(C_2O_4)_3]xH_2O$ (where M^{2+} = Cu^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}). Synthesis of new analogical bis(citrato)stannates is also of great. These complexes can not be prepared from SnO_2 because it is poorly soluble in water and acids.

Experimental. Germanium(IV) oxide (GeO_2, 99.99%), Tin(IV) chloride ($SnCl_4$, 98%), citric acid ($H_4Cit·H_2O$, 99%), 1,10-phenanthroline (phen, 99%), nickel(II) salts $NiCl_2·6H_2O$ (99%) and $Ni(CH_3COO)_2·4H_2O$ (98%) were used as initial reagents for the synthesis of new complexes.

$[Ni(phen)_3][Ge(HCit)_2]·2H_2O$ (1). A suspension of germanium(IV) oxide (0.0523 g, 0.5 mmol) and citric acid (0.21 g, 1 mmol) in 100 mL of hot distilled water was stirred to dissolve reagents completely and slowly evaporated at 50°C to a 20 mL volume. After cooling the solution to the room temperature, 20 mL of a 95% ethanol solution containing 1,10-phenanthroline (0.27 g, 1.5 mmol) and $NiCl_2·6H_2O$ (0.119 g, 0.5 mmol) were added. In 3 days, a pink-colored crystalline solid precipitated. Single crystals suitable for X-ray diffraction were collected from the reaction medium.

Elemental composition, based on single-crystal data for $C_{48}H_{38}GeN_6NiO_{16}$ (1086.14), analytically calculated in %: C 53.03, H 3.50, Ge 6.68, N 7.73, Ni 5.43; found for the as-synthesized bulk material (in %): C 52.78, H 3.29, Ge 6.57, N 7.63, Ni 5.38. The thermal destruction of **1** (weight losses, *Δm*): 80-140°C, endothermic peak 100°C (-3.3%); 290-360°C, endothermic peak 350°C (-24.7%); 420-580°C, exothermic peak 530°C (-54.0%). Selected IR data for **1** (in cm^{-1}): 3396 *ν*(OH), 1722 *ν*(C=O), 1626 $\nu_{as}(COO^-)$, 1588, 1518 $\nu(C–C_{Ar})$, 1393 $\nu_s(COO^-)$, 1349 *ν*(C–N), 1086 *ν*(C–O), 1151, 905, 855 *δ*(CH), 641 *ν*(Ge–O).

$[Ni(phen)_3][Sn(HCit)_2]·3H_2O$ (2). It was prepared by dissolving citric acid (0.01 mol, 4.2 g) in water (20 mL), then this solution was brought to boiling, $SnCl_4$ (0.005 mol, 0.625 mL) was added, heated for 10 min and cooled. After addition of tin tetrachloride to the acid solution, pH was brought to 1 by adding ammonium hydroxide. This was done because of complexation does not take place in highly

acidic medium, while further increase in the pH results in hydrolysis. In the second step, solution of $Ni(CH_3COO)_2 \cdot 4H_2O$ in water (5 mL) was added, the mixture was stirred and complex $[Ni(H_2O)_6][Sn(HCit)_2] \cdot 4H_2O$ [3,4,5] was crystallized at the room temperature. The blue precipitate was filtered off on a Schott glass filter, washed with cold water, and dried at room temperature (20°C).In the third step, a suspension of $[Ni(H_2O)_6][Sn(HCit)_2] \cdot 4H_2O$ (0.0523 g, 0.5 mmol) and 1,10-phenanthroline (0.27 g, 1.5 mmol) was stirred in 20 mL of warm distilled water. The next day, a red crystalline solid precipitated, from which single crystals were collected mechanically and analyzed by X-Ray crystallography.Elemental composition, based on single-crystal data for $C_{48}H_{40}N_6NiO_{17}Sn$ (1150.25), analytically calculated in %: C 50.12, H 3.39, N 7.31, Ni 5.13, Sn 10.35; found for the as-synthesized bulk material (in %): C 50.00, H 3.11, N 7.58, Ni 5.10, Sn 10.24. The thermal destruction of **2** (weight losses, *Δm*): 80-160°C, endothermic peak 150°C (-4.7%); 270-320°C, endothermic peak 280°C (-15.7%); 320-360°C, endothermic peak 330°C (-7.7%); 360-680°C, exothermic peak 570°C (-50.2%). Selected IR data for **2** (in cm^{-1}): 3417 *ν*(OH), 1723 ν(C=O), 1625 $\nu_{as}(COO^-)$, 1589, 1518 $\nu(C–C_{Ar})$, 1427 $\nu_s(COO^-)$, 1341 *ν*(C–N), 1077 *ν*(C–O), 1144, 940, 869 *δ*(CH), 537 *ν*(Sn–O).

Conclusions. The complexes of germanium(IV) and nickel(II) with citric acid and 1,10-phenanthroline were synthesized. The method of synthesis of tris(phenanthroline)nickel(II) bis(citrate)stannate using complex $[Ni(H_2O)_6][Sn(HCit)_2] \cdot 4H_2O$ as a starting compound was proposed for the first time.

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[$Ge(HCit)_2$] $\cdot 4H_2O$ (M = Mg, Mn, Co, Cu, Zn) and [$M(H_2O)_6$][$Sn(HCit)_2$] $\cdot 4H_2O$ (M = Mg, Co, Ni). *Russian Journal of Inorganic Chemistry.*

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