A New Germanium Complex Containing Chelating Pyridinecarboxylate Ligands: *cis*-Dihydroxybis(pyridine-2-carboxylato-$\kappa N^1,\kappa O^2$)germanium Hydrate (1:2) (*cis*-$[Ge(pyca)_2(OH)_2] \cdot 2\,H_2O$)

by **Michael A. Shestopalov***[a]), **Olga A. Efremova**[a]), **Anton I. Smolentsev**[a]), **Yuri V. Mironov**[a]),
Vladimir E. Fedorov[a]), and **Yong-Won Song**[b])

[a]) Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences,
Novosibirsk, 630090, Russia (e-mail: shtopy@gmail.com)
[b]) Department of Nano-Optics, Korea Polytechnic University, 2121 Jeongwang-Dong Siheung City
Gyeonggi-Do, 429-793, Korea (e-mail: ywsong@kpu.ac.kr)

A new germanium complex, *cis*-$[Ge(pyca)_2(OH)_2] \cdot 2\,H_2O$ (**1**; pyca = pyridine-2-carboxylato), was synthesized by the reaction of $[Ge(acac)_2Cl_2]$ (acac = acetylacetonato = pentane-2,4-dionato) with potassium pyridine-2-carboxylate (Kpyca) in H_2O/THF. According to the single-crystal X-ray diffraction analysis, each Ge-atom of **1** is coordinated by two pyca ligands and two OH^- groups (*Fig. 1*). These molecules are bonded to each other *via* a system of H-bonds resulting in a sheet-like structure (*Fig. 2*). The complex is decomposed during heating with stepwise mass loss and formation of GeO_2 as final product (*Fig. 3*).

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1. Introduction. – Germanium is a well-known semiconductor widely used in micro- and optoelectronics [1]. Over the past few years, there has been rapidly increasing interest in the preparation of germanium films and nanocrystals [2]. Different germanium compounds, especially volatile complexes with organic ligands, are very attractive as potential precursors for obtaining the films by MO CVD (metal-organic chemical vapor deposition) processes. Recently a novel approach was suggested for thin-film preparation with a coating technique by using a soluble organogermanium compound as precursor [3]. In spite of the fact that the organometallic chemistry of germanium is widely developed, there are no suitable precursors commercially available for this purpose. Therefore, the search of new coordination complexes with organic ligands is a rather actual task. In this work, we report the synthesis and characterization of a new germanium complex, *cis*-$[Ge(pyca)_2(OH)_2] \cdot 2\,H_2O$ (**1**), in which the organic ligand pyca (= pyridine-2-carboxylato) contains two types of donor atoms, O and N.

2. Experimental Part. – 2.1. *General.* All reagents were used as purchased. $[Ge(acac)_2Cl_2]$ (acac = acetylacetonato = pentane-2,4-dionato) was synthesized from $GeCl_4$ and acetylacetone according to the technique described in [4]. Kpyca was obtained from pyridine-2-carboxylic acid by the neutralization reaction with KOH and purified by recrystallization from H_2O. Thermogravimetric analysis was carried out under He with the derivatograph *MOM* (Hungary) equipped with a computer device. X-Ray powder-diffraction data were collected with a *DRON-3M* diffractometer. FT-IR: *Scimitar-FTS-2000* spectrometer; $\tilde{\nu}$ in cm^{-1}. ESI-MS: *Finnigan Thermo Quest TSQ7000* spectrometer; in *m/z*. Elemental analysis: *Vario EL* of *Elementar Analysensysteme GmbH.*

2.2. cis-*Dihydroxybis(pyridine-2-carboxylato-κ*N*¹,κ*O*²)germanium Hydrate (1:2)* (*cis*-[Ge(pyca)$_2$(OH)$_2$]·2 H_2O; **1**). To a soln. of [Ge(acac)$_2$Cl$_2$] (100 mg) in THF (40 ml), a soln. of Kpyca (94 mg) in H_2O (20 ml) was added. The obtained mixture was heated with stirring until the volume was reduced to *ca.* 10 ml and then left in the open glass vessel. Within 3 d, crystals appeared. The solid was filtered off and washed with Et_2O (5 ml) and acetone (5 ml): 0.104 g (92%) of **1**. IR (KBr): 3450*s*, 3228*s*, 3065*w*, 2924*w*, 2700*w*, 2459*w*, 2029*w*, 1897*w*, 1686*s*, 1613*s*, 1572*s*, 1478*s*, 1451*s*, 1435*w*, 1348*s*, 1290*s*, 1267*s*, 1240*s*, 1171*s*, 1158*s*, 1101*s*, 1057*s*, 1034*s*, 984*w*, 915*w*, 865*s*, 822*s*, 769*s*, 717*s*, 692*s*, 664*s*, 627*s*, 553*w*, 475*s*, 454*s*, 419*w*. ESI-MS: 353.13 ([Ge(pyca)$_2$(OH)$_2$]$^+$).

2.3. *X-Ray-Structure Analysis of* cis-*[Ge(pyca)$_2$(OH)$_2$]·2 H_2O* (**1**). The structure of **1** was solved by X-ray diffraction analysis. Single-crystal X-ray diffraction data were collected with graphite-monochromatized MoK_α radiation (λ 0.71073 Å) at 150 K with a *Bruker-Nonius-X8Apex* diffractometer equipped with a *4K-CCD* area detector. The φ-scan technique was employed to measure intensities. Decomposition of the crystal did not occur during the data collection. Data reduction and multi-scan absorption were carried out with SADABS [5]. The structure was solved by direct methods by means of difference *Fourier* syntheses and refined anisotropically for all non-H-atoms by full-matrix least-squares techniques on F^2 by means of the SHELX-97 software package [6]. The H-atoms of the organic ligands and OH^- groups were assigned geometrically in idealized positions and refined as riding. The H-atoms of the H_2O molecules were not located. Crystallographic data as well as details of data collection and refinement are given in the *Table*[1]).

Table. *Crystallographic Data of [Ge(pyca)$_2$(OH)$_2$]·2 H_2O* (**1**) *and Single-Crystal X-Ray Diffraction Analysis*

Solvent for crystallization	H_2O/THF	Z	4
Empirical formula	$C_{12}H_{14}GeN_2O_8$	D_x [g cm^{-3}]	1.747
M_r	386.84	μ [mm^{-1}]	2.129
Crystal size [mm]	0.20 × 0.08 × 0.04	T_{min}; T_{max}	0.675; 0.920
Crystal system	monoclinic	Number of collected reflections	12465
Space group	$P2_1/c$	Unique reflections	4234
Unit cell parameters:		R_{int}	0.0370
a [Å]	7.8181(3)	Number of refined parameters	210
b [Å]	24.3636(10)	$R_1(F)$ ($F_o^2 > 2\sigma(F_o^2)$)	0.0248
c [Å]	7.7547(2)	R_w (F^2) (all data)	0.0690
β [°]	95.335(1)	S (goodness-of-fit)	1.081
V [Å^3]	1470.69(9)	ρ_{min}; ρ_{max}	– 0.356; 0.526

3. Results and Discussion. – 3.1. *Synthesis and Crystal Structure of [Ge(pyca)$_2$(OH)$_2$]·2 H_2O* (**1**)[1]).The complex *cis*-[Ge(pyca)$_2$(OH)$_2$]·2 H_2O (**1**) was obtained starting from [Ge(acac)$_2$Cl$_2$] by reaction with Kpyca in H_2O/THF under heating and stirring. That led to the simultaneous acac$^-$ and Cl$^-$ ligands metathesis giving colorless transparent plate crystals of **1**. Compound **1** is soluble in H_2O and can be recrystallized from it.

According to the single-crystal X-ray analysis, compound **1** has a molecular structure in which the central atom Ge is coordinated by two pyca ligands through the N-atom of the pyridine ring and the O-atom of the carboxylato group as well as by two OH^- groups (*Fig. 1*). Thus, the Ge-atoms have a distorted octahedral coordination environment, formed by two N-atoms and four O-atoms, in which the OH^- groups and

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[1]) CCDC-637680 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request.cif.

O-atoms of the carboxylato groups are *cis*-oriented to each other, while the N-atoms are in *trans*-positions. The interatomic distances have the following values (Å): Ge–N 2.018 – 2.019, Ge–O 1.933 – 1.935, and Ge–O(OH) 1.790 – 1.802.

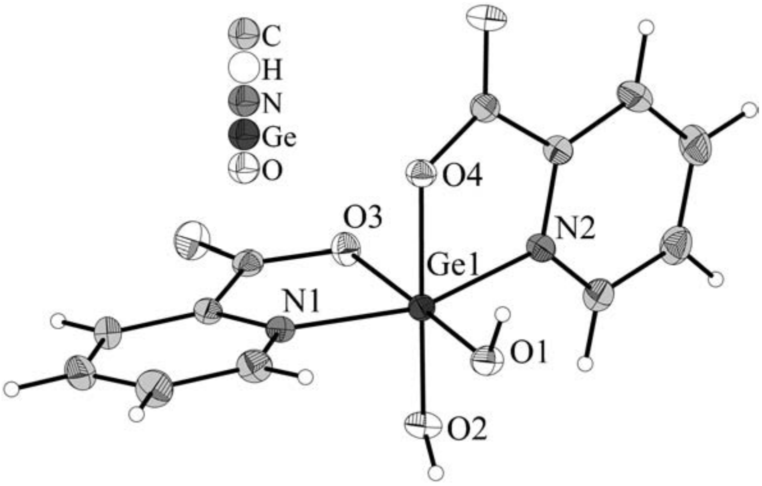

Fig. 1. *X-Ray structure of the molecule* cis-*[Ge(pyca)$_2$(OH)$_2$]* (**1**). The thermal ellipsoids are at the 50% probability level. Arbitrary atom numbering.

The unit cell contains four molecules which are bound to each other through H-bonds involving OH^- and the uncoordinated O-atoms of the COO^- groups as well as solvate H_2O molecules forming a sheet-like structure in the *ac* plane. The O ··· O distances are in the range of 2.677 – 2.836 Å with an average of 2.77(6) Å. The only interaction between the sheets is stacking of the π-systems of the pyridine moieties with the average distance of 3.85 Å, forming piles (*Fig. 2*).

In the literature, only a single example of a Ge-complex with pyridinecarboxylato ligands, namely [GeEt$_2$(pyca-κN,κO)(pyca-κO)] · 0.5 C_6H_6, is known [7]. The structure of that complex shows two types of coordination of the pyca ligands, *i.e.*, coordination through the pyridine N-atom and caboxylato O-atom, and coordination only through the carboxylato O-atom. The Ge–O and Ge–N distances are close to corresponding distances of our complex **1**. It is also interesting to note that there are only two examples of metal complexes containing both pyca and OH^- ligands, namely [(Cr(pyca)$_2$)$_2$(μ-OH)$_2$] [8] and [(Sc(pyca)$_2$(H$_2$O)$_2$(μ-OH)$_2$] [9]. In the case of [(Cr(pyca)$_2$)$_2$(μ-OH)$_2$], the Cr-atoms has the same coordination environment as that of **1**, but the OH groups are bridging the two Cr^{3+} cations.

3.2. *Thermogravimetric Analysis.* Thermogravimetric analysis of **1** under He showed a stepwise mass loss (overall *ca.* 64%; *Fig. 3*). In the range 30 – 105°, this is attributed to the removal of H_2O guest molecules (10%). The next stage (180 – 210°) can be due to the decomposition of the molecule with loss of H_2O molecules from the two OH^- groups (6%). A mass loss of *ca.* 48% was then observed in the range 250 – 385°, which can be attributed to the decomposition of the pyridine-2-carboxylato groups. The final product presented fine particles (*ca.* 20 Å in diameter) of germanium dioxide as a main phase with a small impurity of C-atoms formed during the

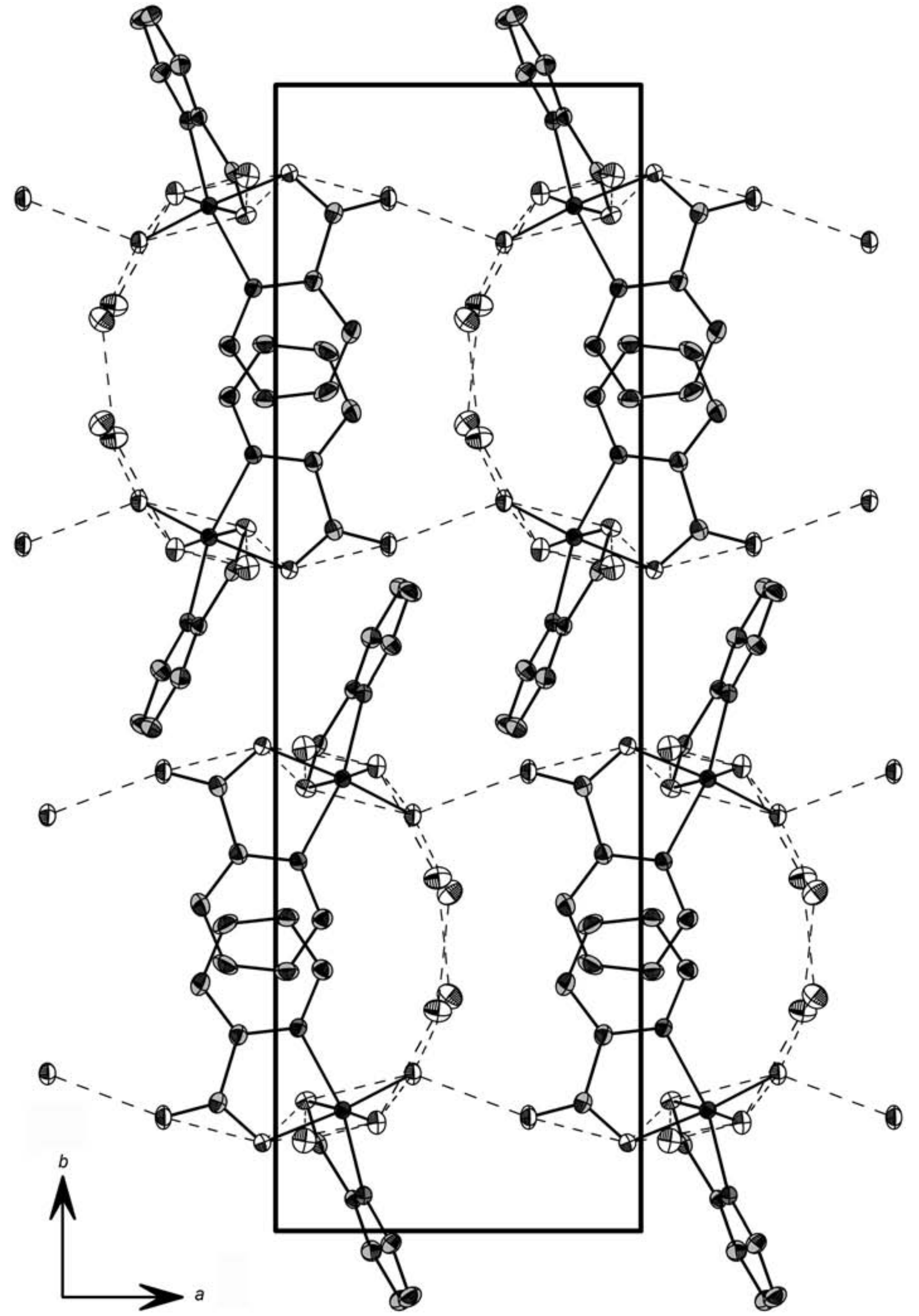

Fig. 2. *The packing of H-bonded sheets in the structure of* cis-*[Ge(pyca)$_2$(OH)$_2$] · 2 H$_2$O* (**1**). H-Bonds are depicted by thin dashed lines. The H-atoms of the pyridine-2-carboxylato ligands are omitted for clarity.

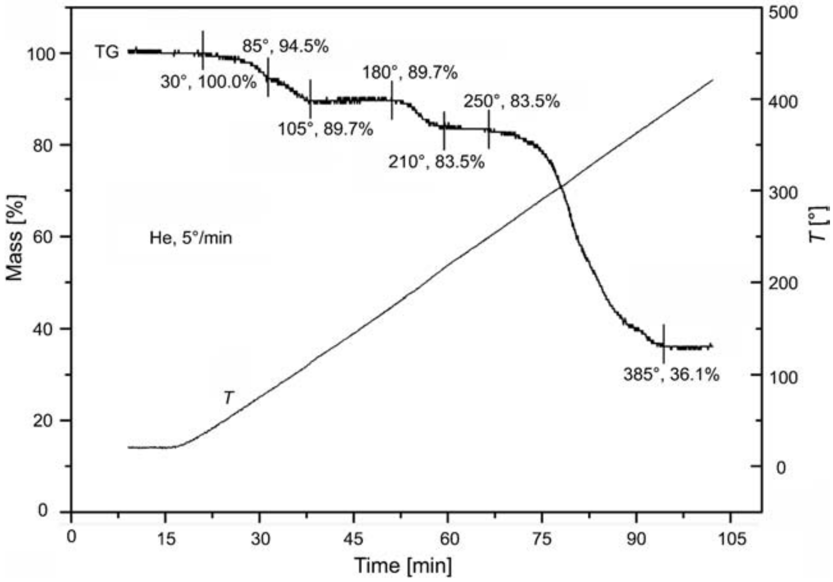

Fig. 3. *Thermogravimetric curve obtained upon heating of* cis-*[Ge(pyca)$_2$(OH)$_2$]·2 H$_2$O* (**1**)

decomposition of the organic ligand. This result is not surprising because it is common knowledge that Ge has a high affinity for oxygen. For example, thermal decomposition of compounds like $Ge(OEt)_4$ or $[Ge(acac)_2Cl_2]$ in which Ge-atoms are coordinated by O-donor ligands (*via* O-atoms) also results in the formation of germanium oxide, GeO_2 [10].

It is interesting to note that the use of a ligand such as pyridine-2-carboxylato gives a possibility to substitute acetylacetonato groups that, as is well known, possess high coordination ability. To prevent the formation of germanium oxide in the final decomposition product, it is necessary to replace O-donor ligands by N-donor ones. For example, the compound 2,5-bis(*tert*-butyl)-2,5-diaza-1-germacyclopentane (=1,3-bis(1,1-dimethylethyl)-1,3,2-diazagermolidin-2-ylidene) synthesized recently [11] is a proper example, in which the Ge-atom is bound to N-atoms. Thermal decomposition of this precursor results in a pure amorphous germanium film [12]. Undoubtedly, the further study of Ge coordination with other N-donor ligands will lead to the synthesis of new complexes containing Ge–N bonds.

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