

TEMPLATE DEPOSITION OF SILVER HALOIDS – MICROSTRUCTURES AND INFLUENCE OF IONIZING RADIATION ON THEM

Marek Buczkowski, Bożena Sartowska, Wojciech Starosta

In recent years in the Institute of Nuclear Chemistry and Technology (INCT), Department of Nuclear Methods of Materials Engineering, investigations concerning template deposition of AgCl microrods into track-etched membranes (TMs) have been carried out [1,2]. Such deposition was made by the chemical reaction in membranes pores ($\text{AgNO}_3 + \text{NaCl}$). TMs with pore diameters 0.2, 0.4 and 0.7 μm used in the experiments were manufactured in the Joint Institute for Nuclear Research (Dubna, Russia). Scanning electron microscope (SEM), DSM 942 (Zeiss, Germany) was used for samples surface morphology as well as membrane fractures observations.

SEM with a Bruker sonde were used for surface X-ray microanalysis of the obtained samples. For such measurements, samples of TMs (0.4 μm and 0.7 μm pore diameter) with AgCl microrods (time of deposition: 5 min and 10 min) were taken.

only in the case of AgBr. For AgI, the obtained structures were in a form of thin, yellow flakes that were weakly connected with the membrane surface. In the case of AgBr light-yellow samples with microrods into pores and micrograins on the surfaces were obtained. Such samples do not change practically their colour at visible, scattering light. One can observe the influence of ionizing radiation on the darkening of samples with AgBr. Experiments of the influence of UV radiation (254 nm and 366 nm) and electron beam radiation were carried out. In the last case a 10 MeV linear accelerator Elektronika 10/10 at the INCT (Centre for Radiation Research and Technology) was used. The following doses were applied: 10, 28, and 3 x 28 kGy. Comparative measurements of optical density of the samples can be carried out using a photographic light meter. A stronger effect of blackening was observed in the case of

Table. Atomic weights and elemental contents relations in case of micrograms deposited on the both sides of template membranes (with AgNO_3 and NaCl solutions, respectively).

No.	Pore size [μm]	Kind of membrane side	Time of synthesis [min]	Atomic weights relation Ag/Cl	Elemental contents relation Ag/Cl
1	0.4	A*	5	3.30	1.08
2	0.4	B**	5	3.13	1.03
3	0.4	A*	10	3.16	1.05
4	0.4	B**	10	3.16	1.04
5	0.7	A*	5	3.25	1.07
6	0.7	B**	5	3.16	1.04
7	0.7	A*	10	3.17	1.04
8	0.7	B**	10	3.13	1.03

* A – measurements on the side with AgNO_3 solution.

** B – measurements on the side with NaCl solution.

Results given in Table concern both sides of membrane samples: “A” and “B” (respectively in AgNO_3 and NaCl solutions). For all cases given in Table, practically there are no differences in atomic weight relation and elemental contents relation for Ag/Cl. Calculated atomic weight relation $m_{\text{Ag}}/m_{\text{Cl}}$ is equal to 3.04 what is similar to the corresponding values from Table. The calculated elemental content relation is practically equal to 1, what means that in the case of microrods in pores and micrograins on membrane surfaces we have stoichiometric compound AgCl.

Nowadays it is observed interest of silver haloids or metallic silver micro- and nanoparticles template deposition [3-5]. In the last year, at the INCT investigations concerning deposition of AgBr and AgI into TMs pores were carried out. In the experiments chemical exchange reactions, respectively ($\text{AgNO}_3 + \text{NaBr}$ and $\text{AgNO}_3 + \text{KI}$) into TMs (pore diameters: 0.2, 1.2 and 2.3 μm) were applied. The experimental setup was similar as in the case with AgCl [1]. Stable deposition took place

samples made with a 0.2 μm pore diameter TM. After exposition to ionizing radiation the samples were treated by photographic procedures (development and fixation). One can observe an intense blackening connected with the formation of metallic silver.

The experiments showed that it was possible to obtain microstructures of some silver haloids (AgCl, AgBr) in TMs as templates. The authors would like to explain why it was not possible to obtain similar structures in the case of AgI. The influence of ionizing radiation in the case of obtaining microstructures connected with their darkening was observed. This needs a detail description and quantitative measurements.

References

- [1]. Buczkowski M., Starosta W., Sartowska B., Kierzek J.: Template deposition of silver chloride microrods into a particle track-etched membrane. In: INCT Annual Report 2007. Institute of Nuclear Chemistry and Technology, Warszawa 2008, pp. 132-133.

- [2]. Buczkowski M., Starosta W., Sartowska B., Kierzek J.: Influence of ionizing radiation on silver chloride micro-rods deposited into particle track-etched membranes. In: INCT Annual Report 2008. Institute of Nuclear Chemistry and Technology, Warszawa 2009, pp. 150-153.
- [3]. Potiyaraj P., Kumlangdudsana P., Dubas S.T.: Mater. Lett., **61**, 11-12, 2464-2468 (2006).
- [4]. Sambhy V., MacBride M., Petersom B.R., Sen A.: J. Am. Chem. Soc., **128**, 9798-9808 (2006).
- [5]. Taurozzi J.S., Tarabara V.V.: Environment. Eng. Sci., **24**, 1, 122-137 (2007).

**CRYSTAL CHEMISTRY OF COORDINATION COMPOUNDS
WITH HETEROCYCLIC CARBOXYLATE LIGANDS.
PARTS LXXIV-LXXVI: THE CRYSTAL AND MOLECULAR STRUCTURES
OF LEAD(II) COMPLEXES WITH PYRIDAZINE-3-CARBOXYLATE,
PYRAZINE-2-CARBOXYLATE
AND 5-METHYLPYRAZINE-2-CARBOXYLATE LIGANDS**

Wojciech Starosta, Andrzej Pawlukoć, Janusz Leciejewicz

Coordination chemistry of Pb(II) complexes with organic ligands has been recently attracting a considerable interest since they exhibit polymeric structures with a variety of molecular patterns and metal ion coordination modes. Apart from a stereo-chemical interest, a number of them has been studied in connection with a search of materials for metal-organic chemical vapour deposition of lead-containing films and as potential synthetic precursors. Since the structures of Pb(II) carboxylate complexes containing pyridazine and pyrazine rings have not been up to now reported, X-ray crystallographic studies of Pb(II) complexes with pyridazine-3-carboxylate, pyrazine-2-carboxylate and 5-methylpyrazine-2-carboxylate ligands have been undertaken.

In the structure of *catena*-Poly[lead(II)-bis(μ_2 -pyridazine-3-carboxylato- κ^3 N²,O:O)], each Pb(II) ion is coordinated by two symmetry independent ligand molecules *via* their N,O bonding moieties; their O atoms act as bidentate and bridge adjacent metal ions to form molecular ribbons which extend in the *a* direction in the unit cell. The second

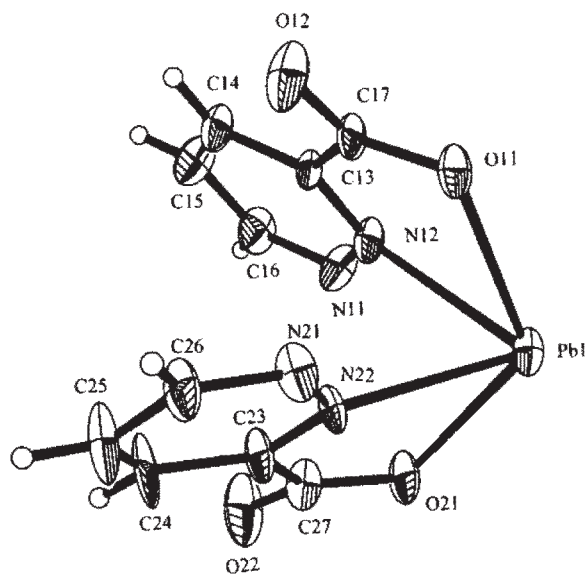


Fig.1. A molecular unit of *catena*-Poly[lead(II)-bis(μ_2 -pyridazine-3-carboxylato- κ^3 N²,O:O)] with atom numbers. Non-hydrogen atoms are shown at 50% probability level.

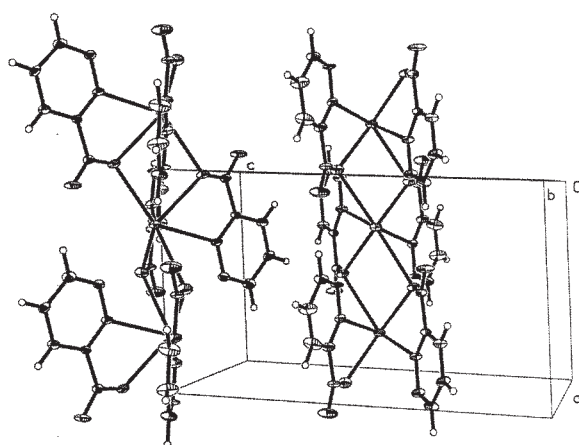


Fig.2. The alignment of molecular ribbons in a unit cell of *catena*-Poly[lead(II)-bis(μ_2 -pyridazine-3-carboxylato- κ^3 N²,O:O)].

O atom of each carboxylate group does not participate in coordination. Figure 1 shows a structural unit with atom labels, Fig.2 – the alignment of a ribbon in the unit cell. The coordination environment of a Pb(II) ion consists of O11, N12, O21, N22 and two bridging carboxylate O11⁽ⁱ⁾ and O21⁽ⁱⁱ⁾ atoms. They form a strongly distorted polyhedron with eight triangular faces. Pb(II) ion is situated inside, closely to the (O11⁽ⁱ⁾/O21⁽ⁱⁱ⁾/O21) face. Bond distances and bond angles fall in the range commonly observed in Pb(II) complexes with carboxylate ligands. The observed distinct empty space in the coordination environment may be attributed to the action of the lone electron pair 6s² of the Pb(II) ion. Both pyridazine rings are planar: r.m.s. are 0.0037(2) Å and 0.0120(2) Å for ligand 1 and ligand 2, respectively. The dihedral angle between the rings is 45.2(1)°. Carboxylate planes make dihedral angles with the respective rings of 9.7(1)° (C13/O11/O12) and of 8.8(2)° (C23/O21/22). Bond distances and bond angles within both ligand molecules are in fair agreement with those reported for pyridazine-3-carboxylic acid chloride and other metal complexes with this ligand. The ribbons are held together by weak interactions between ring carbon atoms and carboxylate O atoms belonging to adjacent ribbons *via* hydrogen atoms attached