

## ATOMIC-ELECTRONIC STRUCTURE OF M(SALEN) COMPLEXES: STUDY USING SYNCHROTRON RADIATION\*

*P.M. KORUSENKO, A.V. VERESHCHAGIN, O.V. LEVIN, D.V. SIVKOV, O.V. PETROVA AND A.S. VINOGRADOV*

*St. Petersburg State University, Saint Petersburg, Russia*

Functional polymeric materials obtained by the electrochemical polymerization of transition metal complexes with salen-type ligands [M(Salen)] (M=Ni, Co, Cu) (Fig. 1) are actively studied due to the prospects of their application as new energy storage electrodes [1]. Despite a significant amount of research on the atomic and electronic structure as well as properties of electroconductive redox poly-[M(Salen)] polymers, there is no single point of view on the mechanism of polymerization of monomer molecules. There are two main models: (i) monomers are connected to each other through a carbon-carbon bond (Fig. 1b); (ii) individual fragments are bound to each other by donor-acceptor and intermolecular interactions (Fig. 1c). The difference in approaches to describing the nature of the electrochemical activity of polymers also lies in the fact that two types are considered as positions for redox reactions - metal cations or ligand atoms [2]. At the same time, the mechanism of redox reactions in these complexes is also not fully understood. Thus, for the purposeful development of methods for the synthesis of these polymers and their successful practical application, detailed knowledge of the chemical (charge) state of metal atoms in monomers and their changes in poly-[M(Salen)] polymers in various (oxidized or reduced) states, and also of the role of 3d electrons of the metal atom in the formation of the electronic structure of these complexes are required. This information can be obtained using modern methods of X-ray spectroscopy (X-ray Photoelectron Spectroscopy – XPS and Near Edge X-ray Absorption Fine Structure – NEXAFS) with synchrotron radiation (SR). Unfortunately, X-ray spectral studies of M(Salen) complexes are currently extremely limited, which makes this study relevant.

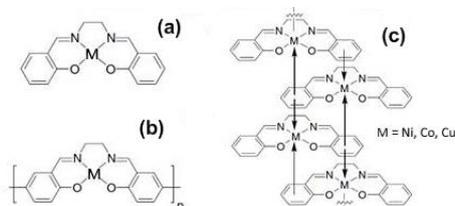


Fig.1. The polymerization scheme of the monomer [M(Salen)] (a) due to the linkage of the phenyl rings of the ligands of neighboring complexes (b); due to the linkage of the metal cation of one monomeric complex to the phenyl ring of another (c).

In this work, using the equipment of RGLB (BESSY II, Berlin: Germany) and K6.5.(KISI-Kurchatov, Moscow: Russia) SR beamlines, we studied the local atomic and electronic structure of [M(Salen)] complexes by NEXAFS and XPS. The M(Salen) monomers powders were synthesized according to the known method [3]. Layers of monomeric complexes for XPS and NEXAFS were obtained *in-situ* under vacuum conditions by thermal evaporation of the [M(Salen)] powders and their deposition onto Pt plates. Poly-[M(Salen)] samples were prepared *ex-situ* by electrochemical polymerization from a monomer solution in an electrolyte in the form of polymer layers on pure Pt plates.

As a result of the studies carried out, information was obtained on the distribution of electron density and the charge (chemical) state of M (Ni, Co, Cu) and ligand (O, N, and C) atoms, as well as on their changes upon replacement of the M3d atom for poly-[M(Salen)] in comparison with monomers [M(Salen)]. In addition, data was obtained on the chemical state of electrolyte ion atoms absorbed by the poly-[M(Salen)] films. The obtained information made it possible to determine the mechanism of polymerization of monomers [M(Salen)].

### REFERENCES

- [1] T.A. Skotheim, R.L. Elsenbaumer, J. R. Reynolds, Handbook of Conducting Polymers, 2nd Ed. New York: Marcel Dekker, 1998.
- [2] O. V. Levin, M. P. Karushev, et al., "Charge transfer processes on electrodes modified by polymer films of metal complexes with Schiff bases", *Electrochim. Acta*, vol. 109, pp. 153–161, 2013.
- [3] R. H. Holm, G. W. Everett and A. Chakravorty, "Metal Complexes of Schiff Bases and B-Ketoamines", *Prog. Inorg. Chem.*, vol. 7, pp. 83–214, 2007.

\* The work was supported by Russian Science Foundation (grant No. 21-72-10029).