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The experimental and theoretical study on the influence of alkali metals on the electronic charge distribution in five-membered aromatic acids (2-thiophenecarboxylic, 2-furanecarboxylic and 2-pyrrolecarboxylic acids)

G. Świderski [a,*], M. Kalinowska [a], S. Wojtulewski [b], W. Lewandowski [a]

[a] Division of Chemistry, Bialystok University of Technology, Zamenhofa 29, 15-435 Bialystok, Poland
[b] Institute of Chemistry, University of Bialystok, Hurtowa 1, 15-399 Bialystok, Poland

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ABSTRACT

In the work the effect of alkali metal cations on the electronic system of heterocyclic five-membered heterocyclic acids that possess S, N and O atoms was studied (2-thiophenecarboxylic, 2-furanecarboxylic and 2-pyrrolecarboxylic acids). The experimental (IR, Raman, NMR) and theoretical (in B3LYP/6-311++G** and MP2/6-311++G** levels) methods were applied in this study. The studies showed that formation of alkali metal salts of the aromatic and heteroaromatic six-membered acids caused perturbation of the aromatic system of ligand. The strength of the perturbation of the electronic charge distribution in the aromatic ring and carboxylate anion of salts depended on the kind of alkali metal cations and changed along with the series of Li → Na → K → Rb → Cs compounds. Alkali metal cations perturbed the structure of heterocyclic acids depending on the kind of heteroatom in the ring. Ionic potential and ionization energy were the main parameters of metal cation which decided on the electronic charge distribution in salt molecules.

1. Introduction

The pyrrole, furan and thiophene derivatives with great biological significance have application as e.g. pharmaceuticals [1–3]. The chemicals with heterocyclic five-membered ring are widely distributed in nature [4–7]. Pyrrole ring and their derivatives form macrocyclic rings (porphyrins) that consist of four pyrrole subunits. Heme, chlorofil, vitamin B_{12} are those of the best-known porphyrins which contain a metal cation in the center of the heterocyclic ring. The structure of pyrrole ring derivatives and the kind of coordinated metal determine the biological properties of these systems [8]. Furan derivatives possess a broad spectrum of biological activity. The products of condensation of the formyl group of 5-nitrofurfural with an amino (hydrazino) group (presents in e.g. nitrofurantoin, furazolidone, nifurimide) are commonly used antibacterial drugs active toward Gram-positive and Gram-negative microorganisms [9]. Organosilicon derivatives of furan had antibacterial and fungicidal properties in a concentration of 1% [10]. The complexes of furanthiocarboxyhydrazides with transition metals possessed antibacterial activity [11]. The studies revealed that the complexes with Cu(II), Zn(II), and Ni(II) were more active toward Gram-positive bacteria than furan-2-thiocarboxyhydrazides and other complexes, whereas the complex with Ag(I) was the most active with respect to Gram-negative bacteria. The N–C=S group occurred crucial in these compounds that possess high antimicrobial activity. Furaldazin and its Pt(II), Pd(II), W(V,0) and Mo(V) complexes showed moderate antimicrobial activity [12]. The antiviral activity of furan derivatives was widely described (e.g. furyl ketone derivatives active toward retrovirus infections, including the HSV-1 virus) [12]. Some nitro derivatives of furan showed fungicidal properties. The presence and the kind of substituents in the 2 position of the furan ring influence on the selectivity of the fungicidal activity of the compounds to a great degree. The cytostatic and antitumorigenic activity of uracil derivatives of 3-(5-nitro-2-furyl)acrylic acid is well known [12]. Thiophene derivatives showed antibacterial (e.g. benzo thieno[3,2-*e*]triazolo, thienopyrimidines, s-triazine incorporated thiophene derivatives) [13], antiinflammatory (e.g. thieno[2,3-*d*]pyrimidin-4(3*H*)-ones, thiophene based thiazine, benzo-thiophene derivatives) [13–14], cytotoxic activities (e.g. analogs of triazolo[4,3-*a*]pyrimidin-6-sulfonamide with an incorporated thiazolidinone moiety,

* Corresponding author. Tel.: +48 085 746 97 96; fax: +48 085 746 97 82.
E-mail address: swider30@gmail.com (G. Świderski).

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thieno[2,3-*d*]pyrimidine derivatives) [15] and are used as pesticides [13]. Metal complexes of thiophene and furan are still screened for their biological Gunduzalp et al. synthetized Zn(II) and Cu(II) carboxamide complexes with thiophene and furan derivatives which possessed a broad spectrum of activity toward *Staphylococcus aureus*, *Escherichia coli*, *Bacillus megaterium*, *Bacillus cereus*, *Salmonella enteritidis* and *Bacillus subtilis*, but lower than the parent ligands [16]. It was explained by the decrease of the electron density on donor atoms by coordination through thiophene and furan rings. Series of Ti(III), Mn(III), V(III), Fe(III), Co(III), Ru(III), Ru(II), Vo(IV) and Cu(II) complexes have been synthesized from the Schiff base ligand derived from 2-furancarboxaldehyde and O-phenylenediamine [17]. Some of the obtained complexes showed higher antimicrobial activity than ligands against *E. coli*, *Pseudomonas aeruginosa* and *Streptococcus pyogenes*.

The carboxylic derivatives of furan, thiophene and pyrrole possess important biological properties. 2-Furanecarboxylic acid is one of the product of the anaerobic degradation of ascorbic acid [18] and in the next step it can undergo decarboxylation to furan which is toxic compound [19]. 2-Pyrrolocarboxylic acid is an oxidation product of hydroxy-L-proline – isomer of D-amino acid oxidase in mammals. It is excreted from the human body in the urine [20]. A number of derivatives of 2-pyrrole, 2-thiophene and 2-furanecarboxylic acids are used as pharmaceuticals. For example, an ester of 2-furanecarboxylic acid (mometasone furoate) is used in the treatment of allergic rhinitis and inflammatory skin diseases [1]. Articaine [(*RS*)-methyl 4-methyl-3-(2-propylaminopropanoylamino)thiophene-2-carboxylate] has been used in dentistry for local anesthesia [2]. Sodium salt of 2-thiophenecarboxylic acid is an active substance of drug Soufrane used in the form of an aerosol for the treatment of local inflammation of the nasal mucosa [21]. The derivative of strontium ranelate is used in the treatment of osteoporosis [22].

Heterocyclic five-membered acids can coordinate metal cations in different ways (Fig. 1). The presence of heteroatom in ortho position to carboxylate group enables formation of chelating bonding through the heteroatom (N, S or O).

There are only several structures of metal complexes with 2-furanecarboxylic acid (2FCA) where the coordination through the oxygen atom from the ring takes place, i.e. complexes with Ba [23], Ca [24], and Sr [25] (tridentate bridging and chelating) and Pb (Fig. 2A) [26] (monodentate and chelating). The most common type of bonding in metal complexes of 2FCA are: (i) bidentate chelating through carboxylate group (e.g. complexes with Er, Gd, [27]; (ii) bidentate bridging (e.g. complexes with Tb [28], Mg [29] (Fig. 2B); (iii) monodentate (e.g. complexes with Cu, [30], Zn [31]); (iv) tridentate bridging and chelating (e.g. Tb [32] Nd [33] compounds).

In case of 2-thiophenecarboxylates, four general types of coordination may be distinguished, i.e.: (i) bidentate chelating (e.g. Eu [34], Sn [35], complexes); (ii) bidentate bridging (e.g. Cu [36], Mo [37] (Fig. 3A) (iii) monodetate (e.g. complexes with Cu [38],

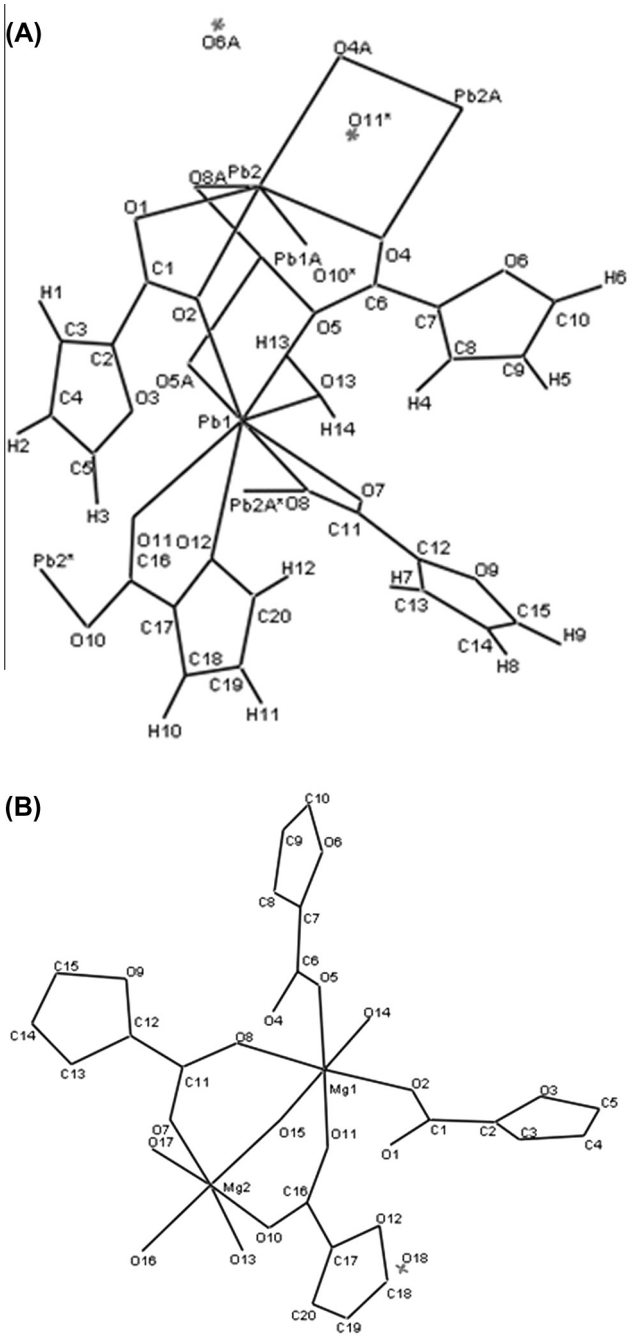

Fig. 2. The exemplary structures of metal complexes of 2-furanecarboxylic acid: (A) catena-((μ4-furan-2-carboxylato-O,O,O′,O′,O″)-bis(μ2-furan-2-carboxylato-O,O,O′)-(μ2-furan-2-carboxylato-O,O,O′,O″)-aqua-di-lead(ii)) [26]; (B) (2-aqua)-bis(μ2-2-furancarboxylato-O,O′)-bis(2-furancarboxylato-O)-tetra-aqua-di-magnesium monohydrate [29].

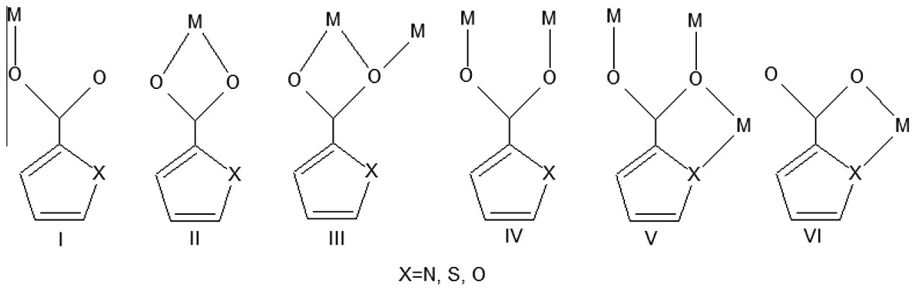

Fig. 1. Type of metal coordination by heterocyclic five-membered acids (I – monodentate, II – bidentate chelating, III – tridentate chelating and bridging, IV – bidentate bridging, V – tridentate bridging and chelating, VI – monodentate and chelating).