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**POTASSIUM COMPLEXATION WITH IODINE  
AND CERTAIN ORGANIC LIGANDS, STRUCTURE  
AND PROPERTIES OF GENERATED COMPOUNDS**

**Abstract.** Potassium cations are coordinated predominantly by oxygen atoms of carbonyl, hydroxyl, and ether groups. Complexes with cyclodextrins and crown ethers can serve as an example. The halogens are equally interesting, and iodine in particular. Triiodide  $[K]^+[I_3]^-$  is the well-known and simple complex between potassium and iodine. The uniqueness of iodine lies in the ability to form long, almost infinite polyiodide chains (I ... I-I). Their electronic structure allows us to consider them as molecular conductors and semiconductors of electric current. The thermoelectric voltage potential is higher for the cyclodextrin-triiodide compound than that of for semiconductors. Potassium iodide in combination with organic molecules forms a new class - semi-organic substances. The presence of a chiral organic molecule determines their optical activity. The inclusion of potassium iodide enhances the nonlinear optical properties of crystal structures.

**Keywords:** Potassium iodide, triiodide, polyiodide, coordination compound, ligand.

Cations of alkali metals of sodium and potassium are expanded in all living organisms being components of nonspecific buffer systems. These cations fulfill the function of cofactors in enzymes, provide electrical potential of cells and transport of substances. Sodium and potassium cations are more often coordinated by oxygen atoms, which are part of the carbonyl, ether and hydroxyl groups of different ligands [1]. Of considerable interest are compounds in which metals can also be coordinated by other electronegative elements, for example iodine. Due to the large ionic radius and the removal of the electron shells from the nucleus, the iodine anion is easily polarized and is able to form one-dimensional, two-dimensional and three-dimensional polyiodides [2]. Thus, as a result of the interaction of potassium iodide and iodine, the simple complex  $KI_3$  ( $I_2+KI \rightarrow [K]^+[I_3]^-$ ) is formed. This complex is the basis of many pharmaceuticals. Therefore, coordination compounds, including potassium atoms and different organic molecules, are of great interest from the point of view of the diversity of their physical and pharmaceutical properties. In particular, interesting properties are revealed if biologically active ligands: amino acids, peptides and carbohydrates participate in the coordination compound as organic molecules. In connection with the great scientific interest in such compounds, the aim of this article was to analyze the existing data on the coordination compounds of potassium, iodine and some organic ligands.

Among the coordination compounds of potassium, a special class of substances with the participation in the formation of halide or polyhalide structures is allocated [2]. The variety of pharmaceutical and physical properties of these compounds can be initiated, on the one hand, with the peculiarities of interactions of potassium cations with special atoms of organic molecules and halogen polyanions, and, on the other hand, with a variety of crystal structures of these compounds.

In recent years, the coordination compounds with the formation of multi-nuclear structures, especially with heterometallic clusters, have acquired special significance in connection with their intriguing molecular architecture and biological properties [3-5]. Integration of alkali metal ions into heterometallic clusters can lead to new materials with possible application in magnetic ordering, catalytic and biological recognition [6-7]. Cations of alkali metals deserve great attention of researchers because of their low polarizability and variable coordination numbers, which makes it possible to construct polymer stable structures with a predominant ability of selective ion transport [8]. Analysis of literature data shows that chelating ligands containing O- and N- donors tend to coordinate between transition metals and alkali metals, along with other linking groups [9-12]. Complexes of transition and alkaline metals are of paramount importance for the development of chemotherapeutic drugs and the creation of tools for molecular biology for the chemical modification of proteins and nucleic acids [13-16]. A vivid example of a multi-nuclear structure is the complex of Ni<sub>3</sub>-K and ligands of L-proline (figure 1), showing antimicrobial activity. The most interesting feature of this stellar complex is that it is the first example of a heterometallic cluster in which alkali metal cations are connected by three water molecules with six transition metal ions [3].

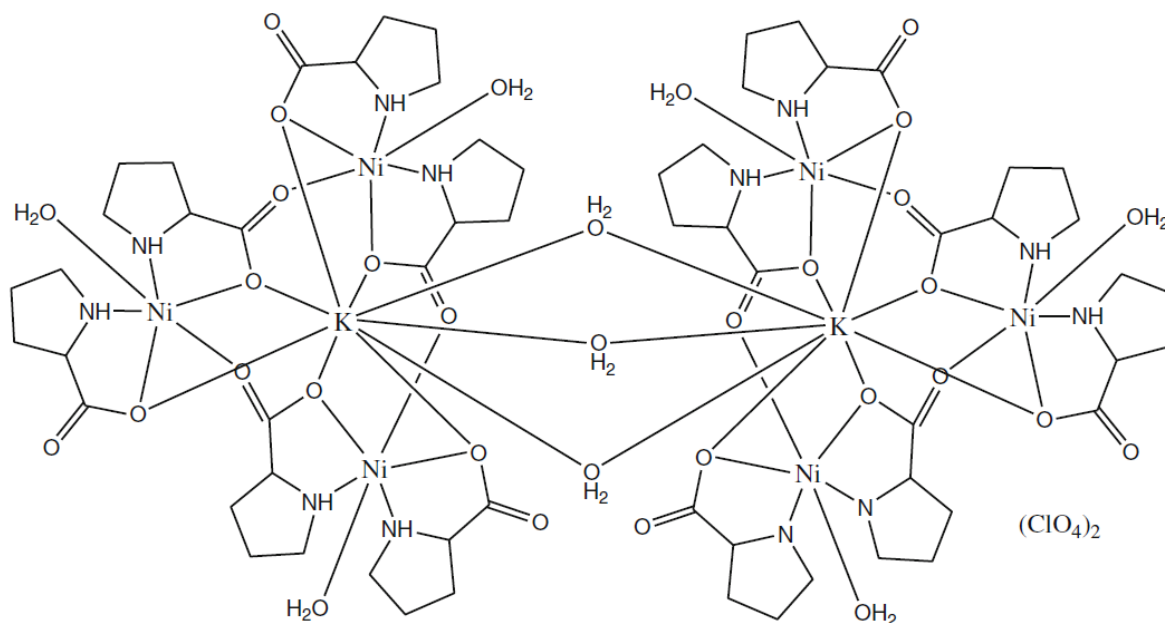


Figure 1 - The heterometallic complex Ni<sub>3</sub>-K [3]

The ionic potassium radius provides a variety of coordinations, from octahedral to decahedral or more. For example, in the structure of betaine potassium bromide dihydrate (C<sub>5</sub>H<sub>11</sub>NO<sub>2</sub>)•KBr•2H<sub>2</sub>O, potassium cations are coordinated by octahedral O atoms and two water molecules [17]. Depending on the temperature near 150 K, a structural phase transition occurs, but no pyroelectric effect was observed in the temperature range 10-300 K, and this compound belongs to the family of dielectrics with the general formula Bet•KX (where, X = Cl, Br, I) [17,18].

In the structures (xanthotoxin)<sub>2</sub>•KI<sub>3</sub> and (glycine)<sub>4</sub>•KI<sub>3</sub> the crystal structure in addition to organic molecules contains potassium cations and triiodide anions. In both structures, the potassium cations are coordinated only by the oxygen atoms of the ligands, and the anions of the triiodide are located in the cavities of the structures, providing compensation for the positive charge of the cations. In the structure (xanthotoxin)<sub>2</sub>•KI<sub>3</sub>, the potassium cations are coordinated by the octahedral six oxygen atoms of the xanthotoxin molecules, and in the (glycine)<sub>4</sub>•KI<sub>3</sub> structure, potassium ions are encapsulated in a distorted Archimedean antiprism of eight oxygens of glycine molecules [19]. The KI<sub>3</sub>/KI<sub>5</sub> complex of the valinomycin antibiotic is another example of a potassium polyhalide compound with a peptide organic ligand, where the cation K is coordinated by the octahedrally six oxygen atoms of the ligand molecules.

Six hydrogen bonds involving amide nitrogen atoms and carbonyl oxygen atoms form a belt around the molecule [20]. Therefore, valinomycin affects the highly specific transport of potassium ions through the cell membrane, which is used in scientific research [21].

Macrocyclic compounds - crown-ethers form stable complexes with alkali metals ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ). In simple ethers, which are weak Lewis bases, sodium and potassium cations are poorly coordinated by oxygen, whereas during the formation of a cycle, metal ions bind more strongly (figure 2).

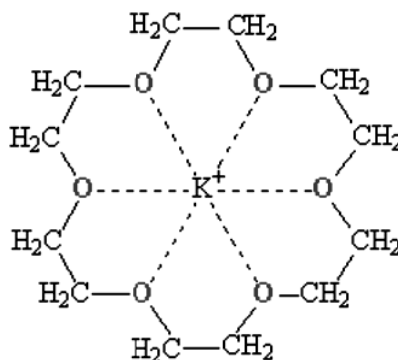


Figure 2 - 18-Crown-6 with coordinated potassium ion

This structure models some antibiotics - ionophores (valinomycin, nigerichin, monensin, salinomycin, gramicidin), which bind the alkali metal cation by the same principle and transport through the cell membrane [21-23].

Chiral crown-ethers are also interesting objects for researchers because of their selective complexation with optically active amino acids or glycosides. The molecular structure of the crown-ether complex containing alpha-beta-glucopyranoside as a chiral moiety with an iodide, is described in [22-24].

The potassium salts of the para-tert-butylcalix[6]arene derivatives of p-bromophenylalanine, in solid form sufficiently large octameric voids, which were detected by X-ray diffraction analysis [25]. The study of self-organizing molecular capsules and molecular cells is an attractive part of supramolecular chemistry [26-28]. These compounds can serve as molecular containers for the inclusion of guest molecules, are used to isolate unstable intermediates [29-31], selective recognition of guest molecules [32-33], and the activation of chemical reactions [34-35]. In the process of self-assembly, the formation of hydrogen bonds and metal coordination play an important role in the creation of unique capsular structures that are large in size. The potassium salt derivatives of p-t-butylcalix[6]-arene and p-bromophenylalanine in the solid state form a new design of octameric capsular structures. In a crystal rich in potassium ions, the driving force of self-organization is coordination and ionic bonds between amino acid residues and potassium ions [25].

Coordination compounds of halides or potassium polyhalides with the participation of saccharides or cyclic polysaccharides as ligands are another interesting name for the semi-organic compounds. Cyclodextrins (CD) are truncated cone-shaped cyclic oligosaccharides, composed of six, seven, eight alpha-1,4-linked D-glucose. They have hydrophobic cavities and primary hydroxyl groups on the narrow sides of macrocycles (heads), as well as secondary hydroxyl groups on the other sides (tail). This deserves special attention, since CDs are able to form stable inclusion complexes with various organic compounds as guest molecules [36,37]. In the crystalline structures, CD molecules often form channels, bonding to each other by weak hydrogen bonds [38]. The size of the channels is determined by the modification of cyclodextrin molecules (alpha, beta or gamma). For example, in the structure  $(\beta\text{-CD})_2 \cdot \text{KI}_7 \cdot 9\text{H}_2\text{O}$  a sufficiently wide channel allows the zigzags of polyiodide  $\text{I}_7^-$  to adapt to the conformation of the channel and to merge in it [39]. The crystal structures of the inclusion complex gamma-cyclodextrin•12-crown-4•LiSCN ( $\text{C}_{48}\text{H}_{80}\text{O}_{40} \cdot \text{C}_8\text{H}_{16}\text{O}_4 \cdot 1/3(\text{LiSCN}) \cdot 7,7\text{H}_2\text{O}$ ) and the inclusion complex gamma-cyclodextrin•12-crown-4•KCl ( $\text{C}_{48}\text{H}_{80}\text{O}_{40} \cdot \text{C}_8\text{H}_{16}\text{O}_4 \cdot 1/3(\text{KCl}) \cdot 9\text{H}_2\text{O}$ ) are described in [40]. Three molecules of gamma-cyclodextrin are folded along the fourth-order rotation axis and form a channel-type structure. The impressive size of gamma cyclodextrins allows them to include a sufficiently voluminous 12-crown-4 molecule with a suitable orientation. These inclusion complexes exhibit a selective inclusion of ions due

to the interactions of cations, crown-ethers and cyclodextrins. For example, due to unusually long distances of  $\text{Li}^+\text{-O}$  and short contacts between 12-crown-4 and gamma-CD molecules in  $(\text{C}_{48}\text{H}_{80}\text{O}_{40}\cdot\text{C}_8\text{H}_{16}\text{O}_4\cdot 1/3(\text{LiSCN})\cdot 7,7\text{H}_2\text{O})$ , normal  $\text{K}^+\text{-O}$  distances and short gamma-CD contacts in  $(\text{C}_{48}\text{H}_{80}\text{O}_{40}\cdot\text{C}_8\text{H}_{16}\text{O}_4\cdot 1/3(\text{KCl})\cdot 9\text{H}_2\text{O})$ , it can be assumed that the compound with lithium is less stable than with the potassium [40].

Thermoelectrochemical elements (TEC) convert thermal energy into electrical potential with an applied temperature difference between two electrodes [41]. It has been shown experimentally that the coordination compound of potassium triiodide and cyclodextrins can be a component of thermoelectrochemical elements [41, 42], having a potential for creating a thermoelectric voltage an order of magnitude higher than semiconductor materials. In the capacity of a redox-active guest molecule, triiodide is used, since  $\alpha$ -CD exhibits an effective host-guest inclusion with this moderately hydrophobic anion of  $\text{I}_3^-$  [43,44]. The supramolecular thermoelectrochemical phenomenon is based on the inclusion-dependent and potential of the oxidation-reduction pair  $\text{I}_3^-$  in the host molecule (cyclodextrin).

Potassium iodide in combination with organic substances also forms new semi-organic materials with nonlinear optical properties. For example, thiourea with potassium iodide forms heat-stable  $\text{K}[\text{CS}(\text{NH}_2)_2]_4\text{I}$  crystals with a second harmonic generation (SHG) efficiency higher than that of KDP [45].

Inclusion of iodine and triiodide in polymers increases the electrical conductivity of complexes of monosubstituted polyacetylenes (up to  $0^{-4} \Omega^{-1} \text{ cm}^{-1}$ ) [46]. Polyiodides have a weak photoactivity, however, polarization can be enhanced by interaction with 3-thiophenemethylamine. As a result, a long chain of polyiodide is formed:  $(-\text{NH}_3\cdot\text{I}\dots\text{I}-\text{I}; -\text{H}\dots\text{I}-\text{I})$ . When the quantum of light is absorbed by iodine, excitons are formed which are ionized in an electric field. Electrons can be transmitted along the polyiodide chain, since the distance between ions becomes shorter than the van der Waals radius [47,48]. This makes it possible to obtain new materials in which molecules of the polyiodide act as electrical current conductors.

Analysis of literature data on coordination compounds of potassium polyiodide shows that, despite the existing interest in the physical and biological properties of these compounds, they still remain a poorly studied class of substances. One expects that a suitable choice of components will allow to obtain new materials with properties of interest to us.

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## CONTENT

<i>Berdibay S.B., Paretskaya N.A., Sabitov A.N., Islamov R.A., Tamazyan R.A., Tokmoldin S.Zh., Ilin A.I., Martirosyan K.S.</i> Phenylalanine – iodine complex and its structure.....	11
<i>Ruzuddinov S., Amiraev U.A., Karkabayeva K.U., Tuhvatshin R.R.</i> Change in cellular and humoral immunity in patients with metallic dentures.....	16
<i>Kabyshev A.M., Kuterbekov K.A., Penionzhkevich Yu.E., Maslov V.A., Mendibayev K., Sobolev Yu.G., Lukyanov S.M., Kabdrakhimova G.D., Aznabayev D.T., Kurmanzhanov A.T.</i> Errors in the total reaction cross sections and energies of incident particles measured using modified transmission technique.....	20
<i>Berdenova B., Kaltayev A.</i> Review of adsorption and thermal characteristics of activated carbon and its application in ang storage and acs systems.....	28
<i>Sotnikov Y.V., Ibraimov V.M.</i> Calculated water demand as the main factor influencing the reliability of hydrogeological forecasts at the evaluation of groundwater elastic reserves..	39
<i>Batpenov N., Ospanov K., Jaxybekova G.</i> Endoprosthesis replacement in deforming arthrosis of the hip joint.....	47
<i>Koigeldina A., Nikolova A., Vassilev A.</i> Drought-induced acclimation changes in young castor ( <i>Ricinus communis</i> L.) plants.....	56

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