

## PROPERTIES OF COMPLEX COMPOUNDS OF S-ELEMENTS.

**Ospanova Zukhra Sarsenbaevna**

Samarkand State Veterinary Medicine, Animal Husbandry and Biotechnology University,  
Nukus Branch

**Sarsenbaev Ilhambay Eliwbay o'g'li**

Samarkand State Veterinary Medicine, Animal Husbandry and Biotechnology University,  
Nukus Branch

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The chemistry of the S elements of groups I and II is mainly related to the chemistry of the ions, with the exception of lithium and beryllium. The small size of the cations of these two elements makes them very polar, so the chemistry of beryllium can be considered fully covalent and the chemistry of lithium can be considered partially covalent.

The ionic radius is the main factor that determines the coordination number of the cation, its degree of hydration and, therefore, the solubility of salts.

Cations of the main subgroup elements of Group I usually form unstable complexes with oxygen donors. However, there are ammonias that are very unstable but can persist for a long time under certain conditions:

$[\text{Li}(\text{NH}_3)_4]\text{Cl}$ ,  $[\text{Na}(\text{NH}_3)_6]\text{I}$ ,  $[\text{K}(\text{NH}_3)_6]\text{I}$ .

In general, conventional coordination complexes contain neutral solid ligands and simple anionic or chelating anion ligands as well as neutral oxygen donors. Since the interaction between the central ion and the ligand in alkali metal complexes is electrostatic, lithium forms the strongest complexes with all monodentate ligands, all other things being equal.

Alkaline earth metal cations give a much wider range of complexes, due to their smaller radius and higher charge. For the doubly charged cations of the group, the ionic type of metal-ligand bond (ion-ion or ion-dipole) also predominates, since  $\text{Me}^{2+}$  ions do not have the free energy cells necessary to form a ligand donor. Acceptor bond and also (– there are no suitable electron pairs for the formation of a dative bond.  $\text{Be}^{2+}$  - The strongest complexing agent in the  $\text{Ba}^{2+}$  series is the  $\text{Be}^{2+}$  ion due to its small radius and high charge density. Consequently, the most unstable complexes are  $\text{Ba}^{2+}$  complexes .

The unusually high density of the positive  $\text{Be}^{2+}$  charge allows beryllium to form complex compounds with almost all available ligands, which, by the way, explains its great toxicity. In this case, beryllium's bonds with oxygen donor ligands are stronger than with nitrogen donors. Therefore, the ammonia complexes in  $[\text{Be}(\text{NH}_3)_4]\text{Cl}_2$ , which have much higher thermodynamic stability, are rapidly decomposed by water (oxidizing ligands). This is due to water's greater polarity than ammonia.

The ionic interaction between solid  $\text{Be}^{2+}$  and solid oxygen results in the greatest energy gain. The complexation of beryllium is the reason for the amphoteric nature of beryllium hydroxide:  $\text{Be}(\text{OH})_2 + 2\text{NaOH} = \text{Na}_2[\text{Be}(\text{OH})_4]$ .

In contrast to all other cations of the main subgroup II, which prefer oxygen,  $\text{Mg}^{2+}$  binds mainly to nitrogen donors, but ammonia and amine complexes of  $\text{Ca}^{2+}$  are known. In biological

systems,  $\text{Ca}^{2+}$  is coordinated by oxygen atoms (usually several negatively charged carboxyl groups).

The presence of ligands with donor nitrogen atoms leads to preferential binding of  $\text{Mg}^{2+}$ . There is a difference in the structure of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  compounds.  $\text{Mg}^{2+}$  ions form six-coordinate compounds with a regular structure,  $\text{Ca}^{2+}$  ions often have high coordination numbers (7 or 8) and form asymmetric complexes. The inherent flexibility and adaptability of  $\text{Ca}^{2+}$  to ligands means that it binds well to the irregularly shaped centers of biological ligands. In contrast to the  $\text{Mg}^{2+}$  ion, the  $\text{Ca}^{2+}$  ion is more effective as a bridge in the reverse cross-linking of ligands. For small simple ligands, especially weakly acidic anions, the binding of cations is determined by their polarizability. As the ionic radius increases, the bonding decreases. Thus, the formation constants of complexes with acetate result in the following order:  $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$ . In the case of the nitrilotriacetate ligand,  $\text{Ca}^{2+}$  binds more strongly than  $\text{Mg}^{2+}$ . A similar order is observed for most strong acid anions, i.e.  $\text{H} > \text{K}^+ > \text{Na}^+$  and  $\text{Ca}^{2+} > \text{Mg}^{2+}$ . This sequence can be explained by the larger size of the ligand, which displaces several water molecules from the coordination sphere of the cation.

If the cations have the same radius but different charges, the reason for the selectivity lies in the hydration of the cation, the ligand and the complex. A medium with a low dielectric constant destabilizes complexes with a large positive charge than those with a small one. The use of ligands with a hydrophobic outer part increases their selectivity towards monovalent cations. Negatively charged ligands, especially hydrophilic ones, show higher selectivity for divalent cations than for monovalent cations.

There are some ligands that have a very high selective binding capacity. These are macrocyclic ligands: cyclic ethers, cryptands and some natural ionophores, often antibiotics of various structural types and their synthetic analogues. For example, the cyclic peptide valinomycin is one of the best ligands that can form a selective complex with  $\text{K}^+$ . Antibiotics such as valinomycin transport  $\text{K}^+$  into the mitochondria, hence the term "ionophore". The antibiotic actinomycin binds  $\text{Na}^+$  instead of  $\text{K}^+$ . There are macrocyclic ligands for the different binding of divalent metal ions.

All macrocyclic ligands have the following common features: a site for a cation, a hydrophobic appearance, and a flexible structure that allows the successive replacement of water molecules with a metal. The formation constants of complexes with certain crown ethers vary significantly from cation to cation - they depend on the relative size of the cation and the vacancy of the crown ether. For alkali metal cations, a very simple relationship is known between the ionic radius and the number of oxygen atoms in the crown ether, which provides the best agreement:

$\text{Li}^+(4)$ ,  $\text{Na}^+(5)$ ,  $\text{K}^+(6)$ ,  $\text{Cs}^+(8)$ .

The values of the formation constants also depend on the type of solvent and the presence of hydrophobic or hydrophilic substituents on the crown ether. The presence of hydrophobic groups favors the binding of monovalent cations compared to divalent cations, since divalent cations hardly leave water molecules due to their great polarizability. This makes it possible to effectively separate cations of the same size but different charges (e.g.  $\text{Na}^+$  and  $\text{Ca}^{2+}$ ).

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