

METHODS OF SYNTHESIS OF COORDINATION COMPOUNDS WITH MIXED LIGANDS

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Abstract. This article provides information on synthesis methods of coordination compounds with mixed ligands, complex compounds, structural formulas of synthesized coordination compounds, synthesis of quinazolon-4 and its potassium and sodium salts.

Keywords: bidentate ligand, complex compound, oxalate ion, monodentate, polydentate, xinzolone-4, tautomerism, UV- and IR-spectroscopy, alcohol, DMSO, DMFA.

Academician Yu. N. Kukushkin gave the following definition to complex compounds: "A complex compound should be understood as compounds that have a central atom surrounded by ligands, whether in a crystalline state or in a solution.

The phenomenon of complex formation does not occur only in some elements, but is characteristic of most elements of D. I. Mendeleev's periodic system.

Tassir was the first to form the complex $\text{CoCl}_2 \cdot 6\text{NH}_3$ in 1798. The study of complex compounds shows that the phenomenon of complex formation is an important phenomenon that belongs to most of the elements in D. I. Mendeleev's periodic system, rather than to some elements.[5].

A complex compound is a compound whose molecule has a central atom surrounded by several ions or molecules, that is, ligands.

A ligand can occupy one or several positions around the central atom. For example: ligands such as Cl^- , Br^- , I^- , CO , H_2O , NH_3 each take one place.

They are called monodentate ligands. Oxalate ion and ethylenediamine occupy two places. Such ligands are called bidentate ligands. Diethylenetriamine is a tridentate ligand. Triaminotriethylamine is an example of a four-dentate ligand.

A complex compound tends to maintain its independence even in solutions. It dissociates to a small extent into ions. If the positive charge of the central ion exceeds the sum of the negative charges of the surrounding ligands, such a complex is a cation complex; if the charge of the central ion is less than the sum of the negative charges of the ligands surrounding it, then it is an anion complex; if the difference between the charge of the central ion and the sum of the charges of the ligands is equal to zero, it is called a neutral complex compound. Complex compounds are of great importance in technology, medicine, agriculture, and science.

Complex compounds are widely distributed in nature. For example, chlorophyll, which is in the green part of plants and carries out photosynthesis, is a complex combination of magnesium. The substance that supplies living cells with oxygen is a complex combination of blood hemoglobin and iron. Many minerals consist of complex compounds of aluminosilicates.

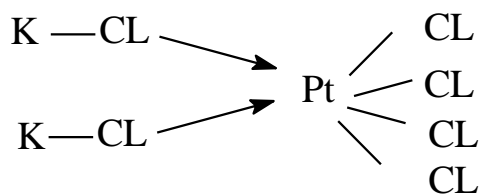
In order to understand the essence of the processes by which complex compounds are formed, we will familiarize ourselves with the coordination theory proposed by the Swedish

chemist A. Werner in 1894 and supplemented by L. A. Chugayev, I. L. Cherniyayev, A. A. Grinberg and other scientists [11].

The main points of this theory are as follows:

1. One of the ions or atoms in complex compounds is the central ion and is called the complex former.
2. Oppositely charged ions or polymolecules, i.e. ligands, of a certain ion are placed around the central ion forming a complex, in other words, they are coordinated.
3. The central ion or atom forms the inner sphere of a complex compound with ligands, the inner sphere is written in square brackets.
4. The number of ligands directly connected to the central ion or atom, that is, the coordination number of the central atom, has values equal to 2, 4, 6, 8.
5. Most elements have additional valences in addition to their basic valences.
6. Each element seeks to satisfy its main and additional valences.
7. The additional valences of the central atom have a specific direction in space.

A. Werner's theory is a coordination theory. According to A. Werner, compounds of the first order are formed at the expense of basic valence, and complex compounds are formed at the expense of additional valence. For example: Pt and Cl atoms that combine with PtCl_4 and KCl to form $\text{PtCl}_4 \cdot 2\text{KCl}$ exhibit additional valences in addition to their basic valences:



Here, the closed lines show the main valence, and the lines indicated by the arrow show the additional valence, that is, the coordination bond.

Complex compounds have specific liquefaction, boiling, decomposition temperatures, solubility in certain solvents, especially water, electrical conductivity and other properties.

The ability of this or that element to form a coordination compound depends on the structure of the surface electron shell of the superelement atom and its position in the periodic table. Ions are included. A particle forming a coordination compound acts as an electron pair acceptor. If the central atom participates in chemical bonding with its empty s-orbitals, then only d(σ)-bonding, if empty p-orbitals also participate, d- and p-bonds occur (when it participates with p-, d- or f-orbitals, d- and p-bonds also arise). The table below shows which orbitals the central atoms participate in forming a coordination compound [6], [27].

Table 1

Types of orbitals involved in the formation of a complex compound

Periods	Central atoms	Interacting empty orbitals			
		s	p	d	f
1	H-He	+	-	-	-
2	Li-Ne	+	+	-	-
3	Na-Ar	+	+	+	-
4	K-Kr	+	+	+	-
5	Rb-Xe	+	+	+	-

6	Cs-Rn	+	+	+	+
7	Fr-Ku	+	+	+	+

We can see from the table that the number of empty orbitals involved in complex formation of coordination compounds increases as the period number increases. Elements of period I participate in formation of coordination compound only with s-orbitals, elements of period II with s- and p-orbitals. In the elements of the third and fourth period, in addition to s- and p-, d-orbitals are also involved, and in the elements of the sixth and seventh period, f-orbitals are also involved. Therefore, when moving to any new period, the possibility of forming a coordination combination of the elements of the previous period remains. Table 2 below lists the coordination numbers specific to the central atom.

Table 2

Coordination numbers specific to the central atom

Periods	Central atoms	Coordination numbers of the central atom in the formed coordination compounds								
		2	3	4	5	6	flat square	7	8	9
1	H-He	+	-	-	-	-	-	-	-	-
2	Li-Ne	+	+	+	-	-	-	-	-	-
3	Na-Ar	+	+	+	+	+	+	-	-	-
4	K-Kr	+	+	+	+	+	+	+	+	-
5	Rb-Xe	+	+	+	+	+	+	+	+	+
6	Cs-Rn	+	+	+	+	+	+	+	+	+
7	Fr-Ku	+	+	+	+	+	+	+	+	+

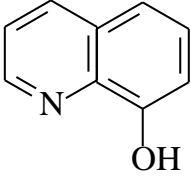
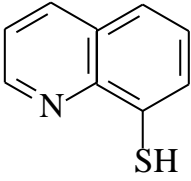
We can see from the table that the coordination number of elements increases when moving from one period to another. The coordination number of elements of the first period is equal to 2. Elements of the second period can take part in one s-orbital and three p-orbitals. Their coordination number is 4. When moving to the atoms of the elements of the third period, since d-orbitals can also participate, their coordination number can be equal to 6 (accounting for s, p and d-orbitals), and for the atoms of the elements of the sixth and seventh period, the coordination number has a higher value. numbers are found [11], [8].

As ligands, anions (F^- , OH^- , CN^- , SCN^- , NO_2^- , CO_3^{2-} , CrO_4^{2-} , etc.) neutral molecules (H_2O , NH_3 , CO , N_2 , NO , N_2H_4 , $NH^2-(CH_2)^2-NH_2$ etc.) is involved. Each ligand has one or several unshared (free) electron pairs. Sometimes molecules that do not have unshared electron pairs, but have electrons that can participate in p-bonding, also act as ligands. As a result of the interaction of the s- and p-orbitals of the ligand with the empty orbitals of the central atom, d-bonds appear, between the p- and d-orbitals of the ligand and the empty orbitals of the central atom, p-bonds appear. (but when s- and px-orbitals overlap each other, a d-bond is always formed). The donor properties of ligands are due to electron pairs in their s and p-orbitals; and acceptor properties are realized due to empty p- and d-orbitals. The table below shows the atoms that act as electron donors of ligands [9], [12], [13].

Table 3

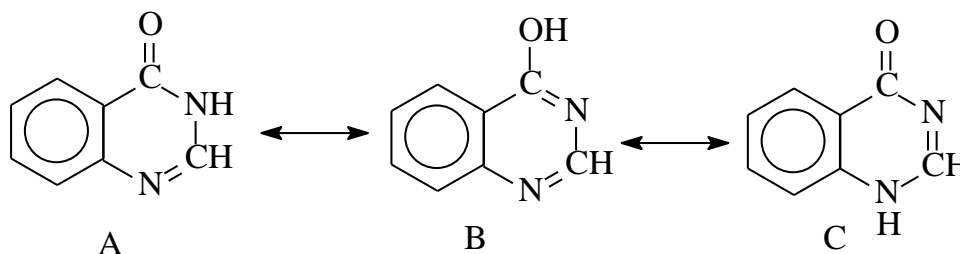
Ligands and their electron donor atoms

in the ligand electron	Ligands of molecular type		Ion turdagi ligandlar	
	monodentate	polydentate	monodentate	polydentate

donor atoms				
H, F, Cl, Br, I	-	-	H ⁻ , F ⁻ , Cl ⁻ , Br ⁻ , I ⁻	-
C	CO, C ₂ H ₄	C ₆ H ₆	CN ⁻	-
N	NH ₃ , C ₅ H ₅ N, RCN, RNH ₂	NH ₂ (CH ₂) ₂ -NH ₂	NO ₂ ⁻ , N ₃ ⁻ , SCN ⁻	-
O	H ₂ O	R-CO-CH ₂ -CO-R	O ⁻² , OH ⁻	CO ₃ ⁻² , SO ₄ ⁻² , RCOO ⁻ , C ₂ O ₄ ⁻²
S	R ₂ S	R-CHSH-CH ₂ - CHSH-R	SCN, S ⁻²	-
O yoki N	-		ONO ⁻	H ₂ NCH ₃ COO ⁻
O va N	-	EDTA	-	-
S va N	-		-	-

1.1. Xinzolone-4 and its potassium and sodium synthesis of salts

The presence of donor atoms (N, S, O) in the composition of xinzolone-4 and its derivatives, their formation into various tautomers and coordination with metals at the expense of these donor atoms are of both theoretical and practical interest. Xinzolone-4 is a white crystalline substance and can exist in several tautomeric states:

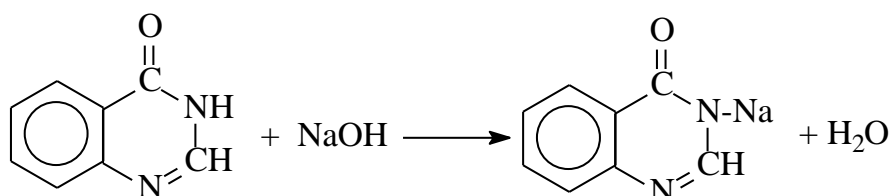
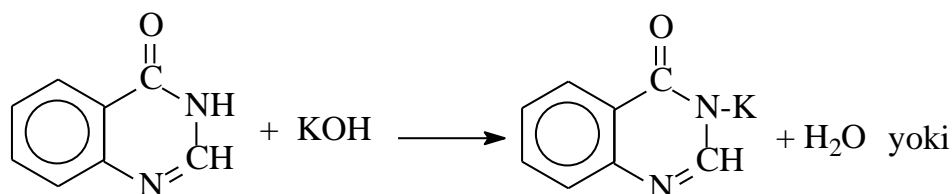


The result of the experiments was found to be in the ratio A:B:C=7:2:1 [19].

Xinzolone-4 is treated with alkali in an alcohol solution in a ratio of 1:1, and xinzolone-

4

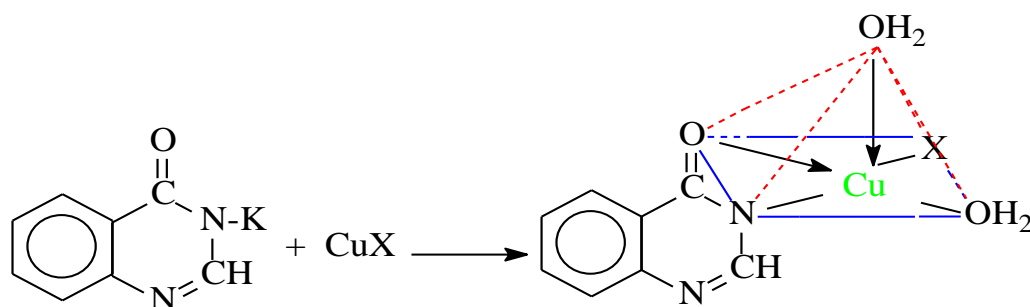
It is possible to obtain potassium and sodium salts, which are soluble in relation to:[24]



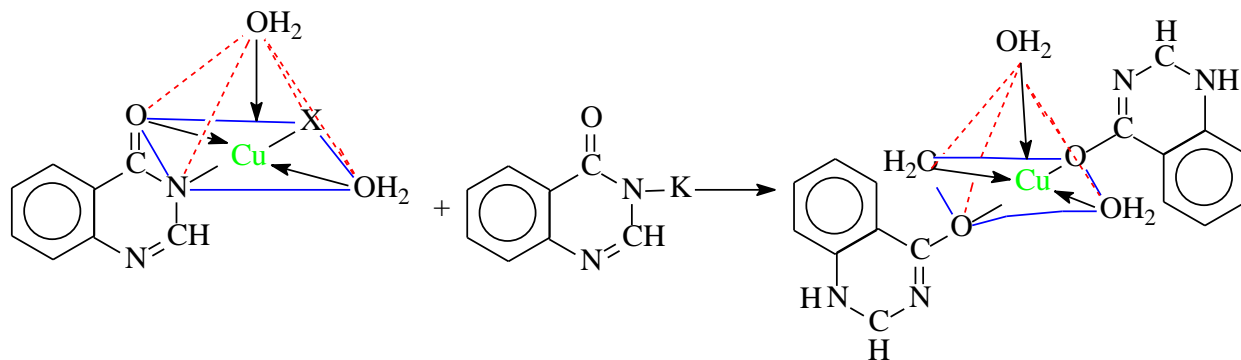
Potassium and sodium salts of xinzolone-4 dissolve well in alcohol and form a pale yellow solution. It is possible to synthesize complex compounds of various concentrations by adding the required amount of 3d-metal salts to these salts of xinzolone-4.

1.2. Xinzolone-4 with copper (II) salts in three different compositions complex compounds

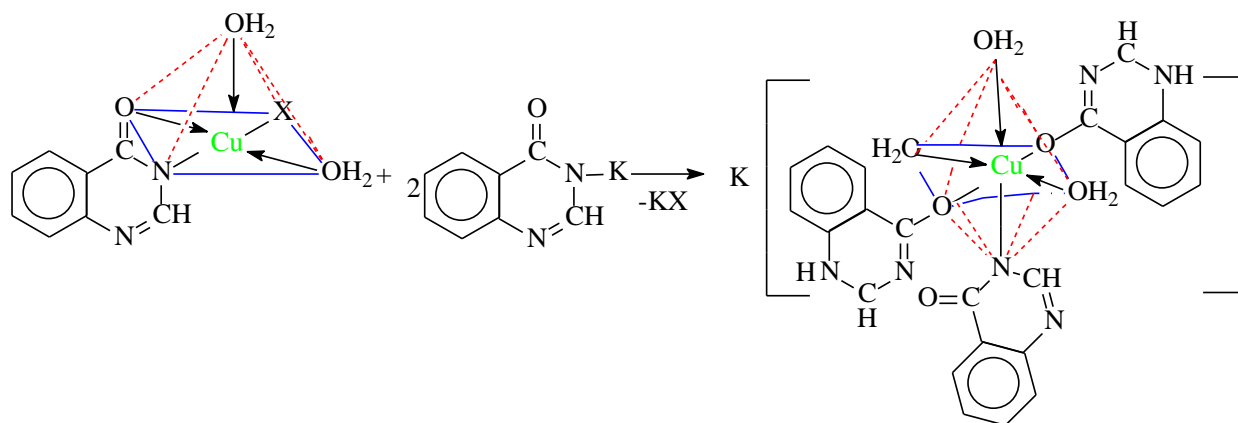
By exposing xinzolone-4 to its potassium or sodium salts (KX) in a ratio of 1:1 from an alcoholic solution of copper salts $\text{Cu}(\text{NO}_3)_2$, $\text{Cu}(\text{CH}_3\text{COO})_2$, CuCl_2 , CuSO_4 , a difficult-to-dissolve dark green color $\text{CuX} \cdot \text{Xz} \cdot 2\text{H}_2\text{O}$ ($\text{X}=\text{NO}_3^-$, CH_3COO^- , Cl^- , SO_4^-) precipitation, that is, simple ligand complex compounds with 1:1 composition were synthesized [23].



If xinzolone-4 is added to the complex compound (precipitate) with the same composition ($\text{CuX} \cdot \text{Xz} \cdot 2\text{H}_2\text{O}$) from a solution of potassium salt in alcohol in a ratio of 1:2, an air-colored solution, i.e., a complex compound with a simple ligand with a composition of 1:2 is formed. The reaction mechanism can be expressed as follows:



When adding xinzolone-4 from the solution of potassium salt in alcohol to the air-colored $\text{Cu}(\text{Xz})_2 \cdot 3\text{H}_2\text{O}$ complex compound with a composition of 1:2 and more, an ink-colored solution is obtained, i.e., with a composition of 1:3 a complex compound is formed:



The infrared spectra of the three complexes synthesized above are similar, and the reduction of $\nu(\text{C}=\text{O})$ in the ligand from 1710 cm^{-1} to 1690 cm^{-1} is accompanied by absorption lines related to valence vibrations of N-H bonds at 3200 cm^{-1} of the complex absence of observation in the IR-spectra of the compounds indicates that xiazolone-4 is bidentately combined with copper metal through nitrogen in the third position and oxygen in the fourth position [24].

The formation of 1:1, 1:2, and 1:3 complex compounds can be determined by color change, precipitation, elemental analysis, and comparison of the intensity of absorption lines in IR spectra. Some physicochemical properties of quinazolon-4 and its complex compounds are presented in Table 6 below.

Table 6

Some physicochemical properties of xiazolone-4 and its complex compounds

№	Compounds	Color	Molecular mass	Amount of elements (%)				
				Me	C	N	S	H
1	Xiazolone-4	white	146	-	65,05 65,75	19,24 19,17	-	4,2 4,3
2	$\text{CuNO}_3 \cdot \text{Xz} \cdot 2\text{H}_2\text{O}$	Sharp green	306	20,63 20,91	31,14 31,37	13,75 13,72	-	3,0 2,9
3	$\text{Cu}(\text{Xz})_2 \cdot 3\text{H}_2\text{O}$	Blue	406	15,32 15,76	47,03 47,29	13,56 13,80	-	3,9 3,9
4	$\text{K}[\text{Cu}(\text{Xz})_3 \cdot 2\text{H}_2\text{O}]$	Ink color	571	11,41 11,20	50,33 50,42	14,53 14,61	-	3,4 3,3
5	$\text{Cu}(\text{Xz})(\text{OXz}) \cdot \text{H}_2\text{O}$	Open green	404	16,76 16,85	47,81 47,72	13,84 13,82	-	3,4 3,2
6	$\text{Cu}(\text{Xz})(\text{AXz}) \cdot \text{H}_2\text{O}$	Sharp Blue	386	16,12 16,18	49,42 49,64	18,33 18,82	-	3,4 3,2
7	$\text{Cu}(\text{Xz})(\text{TPP}) \cdot \text{H}_2\text{O}$	Gray color	432	14,81 14,77	50,00 49,94	12,96 12,88	7,4 7,8	3,7 3,9
8	$\text{Cu}(\text{Xz})(\text{AAXz}) \cdot \text{H}_2\text{O}$	Air color	409	16,82 16,76	51,12 51,24	16,94 16,88	-	2,9 3,0
9	$\text{Cu}(\text{Xz})(\text{KMAXz}) \cdot \text{H}_2\text{O}$	Open green	425	15,24 15,18	50,58 50,46	16,34 16,53	-	2,8 2,9

The EPR spectra of copper complex compounds were studied, and the resulting anisotropic parameters ($g \parallel = 2.221$, $A = 13\text{g}$ and $g \perp = 2.067$) were studied. The information obtained from the IR spectrum also confirms that copper complex compounds have a square pyramidal structure. The electrical conductivity of the formed complex compounds was studied and it was determined that they are low electrical conductivity ($18 \div 25 \text{ cm}^{-1} \cdot \text{om}^2 \cdot \text{mol}^{-1}$) [4].

CONCLUSION

Based on the received information, the following conclusions were reached:

1. Formation of complex compounds of 1:1, 1:2 and 1:3 composition of xiazolone-4 with copper salts was studied using elemental analysis UV- and IR-spectroscopy.
2. Xiazolone-4 was found to coordinate bidentate with the central ion through nitrogen in the 3rd position and oxygen in the 4th position, forming a four-membered metallocycle.
3. It was found that the NO_3^- ion contained in the complex compound $\text{CuNO}_3 \cdot \text{Xz} \cdot 2\text{H}_2\text{O}$ can be exchanged for xiazolone-4 or its derivatives, and complex compounds with mixed ligands were synthesized.
4. During the synthesis of complex compounds with mixed ligands, it was found that xiazolone-4 is more active than the rest of its derivatives.
5. In complex compounds with mixed ligands, bidentate coordination of 2-oxoxiazolone-4 and 2-thioxoquinazolone-4 with copper ion was studied, forming a four-membered metallocycle through nitrogen in the third position and oxygen in the fourth position.
6. The solubility of the synthesized complex compounds was checked; good solubility of the ligand in alcohol, DMSO, DMFA, and water was observed.
7. $\text{Cu}(\text{Xz})(\text{OXz}) \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{Xz})(\text{AXz}) \cdot \text{H}_2\text{O}$, $\text{Cu}(\text{Xz}) \cdot (\text{TPP}) \cdot \text{H}_2\text{O}$, $\text{Cu}(\text{Xz})(\text{AAXz}) \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{Xz})(\text{KMAXz}) \cdot \text{H}_2\text{O}$ mixed ligand complex compounds were synthesized.
8. Based on the obtained results, the structural formulas of the synthesized coordination compounds were proposed.

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