

## COMPLEX COMPOUNDS OF FLUORINATED $\beta$ -DIKETONE DERIVATIVES WITH TRANSITION METALS

**Kuchkorova Rano Rasulovna**

KXH. TSPU named after Nizami

phone +998995275009

e-mail: [rano.qochqorova@bk.ru](mailto:rano.qochqorova@bk.ru)

**Umarov Bako Bafoevich**

BUKhGU.d.kh.s.prof.

phone +998905119040

e-mail: [rano.qochqorova@bk.ru](mailto:rano.qochqorova@bk.ru)

**Kadirova Shakhnoza Ziyodulloevna**

4th year student Tashkent Pharmaceutical Institute

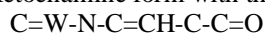
e-mail: [rano.qochqorova@bk.ru](mailto:rano.qochqorova@bk.ru)

phone. +907307126

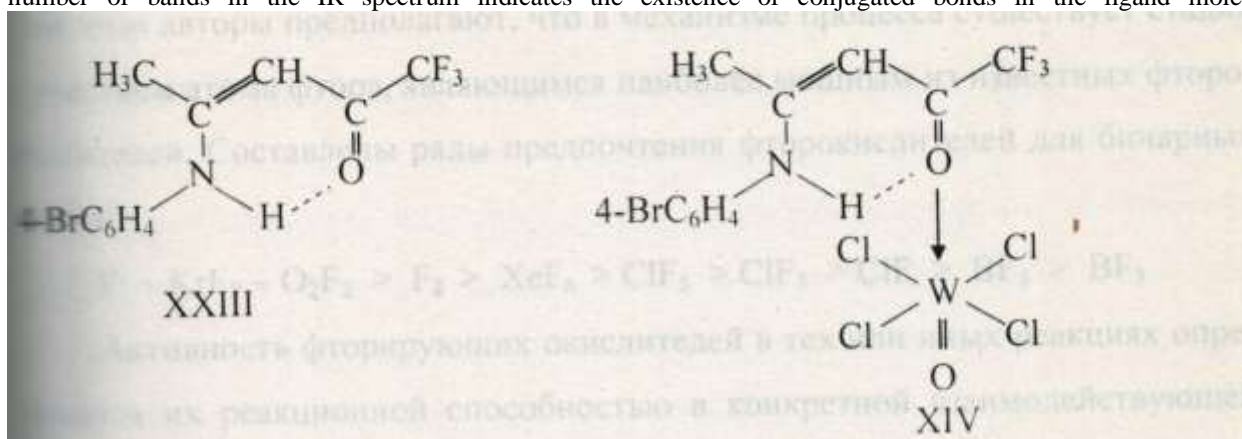
**Annotation:** Investigation of the composition and structure of newly synthesized compounds using modern methods of physicochemical research and the direction of the condensation reaction of aroyltrifluoroacetylmethanes with acid hydrazides, depending on the reaction conditions.

**Key words:** aroyltrifluoroacetylmethanes, 1,1,1-trifluoromethyl-4 (4chlorophenyl) butanedione -2,4, hydrazides, diketone form, cis-enol form, tautomerism,  $\beta$  - diketones.

It was said above that the products of the interaction of fluorinated  $\beta$ -diketones with nitrogen-containing nucleophilic reagents  $\beta$ -enamines are potential prototropic systems with various tautomeric systems. The imine-enamine tautomerism of  $\beta$ -aminovinyl ketones, the possibility of varying the steric properties of fluorinated substituents, and their electronic effects made it possible to synthesize, on their basis, complex compounds of various types with various ways of coordinating ligands to the metal ion (104). The authors of this work described the structure of  $HQS[WOCl_3L^1]$  ( $HL^1 = N$ -phenylacetylacetoneimine), in which the ligand is coordinated in the deprotonated ketoenamine form with the closure of a six-membered metallocycle



In this work (104), the results of the synthesis of the N-mono derivative of  $\beta$ -aminovinylketone and N-(4-bromophenyl)-1,1,1-trifluoroacetylacetone(HL) and its complex  $WOCl_4 \cdot H L^1$  are presented. The ketoamine form is realized in the molecule (XXIII), with the localization of the acidic proton at the nitrogen atom, the presence of a number of bands in the IR spectrum indicates the existence of conjugated bonds in the ligand molecule.



The electroacceptor - group should usually prevent the polarization of the C=O bond and increase the vibrational frequency of this bond [1], but in the spectrum, due to the presence of IMHB, the vibrational frequency of the ketone fragment of the ligand molecule

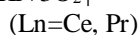
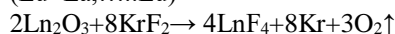
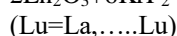
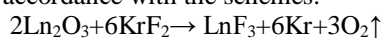
> N-H...O=C< are marked as wide bands near 3180 and ~3390  $cm^{-1}$ . In the IR spectrum of the complex compound  $WOCl_4 \cdot H L^1$ , stretching vibrations  $\gamma$  (N-H) are observed in the region of ~3320  $cm^{-1}$ , which indicates the preservation of WMH during complex formation in the coordinated enamine molecule. In general, based on IR spectroscopic studies, the authors state that in the  $WOCl_4 \cdot H L^1$  complex under consideration, the tungsten atom has an octahedral coordination sphere with a terminal oxo atom, four chlorine atoms, and an oxygen atom of the carbonyl group of the neutral ligand molecule [4].

An analogous type of coordination of  $\beta$ -aminovinyl ketones was noted earlier by the authors [8] in molecular complexes of molybdenum dioxochloride with N-phenyl and N-heptylacetylacetonimines [2]. The problem of synthesizing coordination compounds of d- and f-transition elements in high oxidation states is solved by using fluoride compounds [7]. Currently, these syntheses are carried out in oxidative fluorination reactions [9] with the use of substances that are both fluorinating agents and strong oxidizing agents. When choosing such a reagent, they are guided by the thermodynamics of its dissociation [7]. At the same time, the authors suggest that the mechanism of the process includes a stage involving the fluorine atom, which is the most powerful of the known fluoroxidants. The preference series of fluoroxidants for binary systems are compiled:



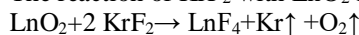
The activity of fluorinating oxidants in certain reactions is determined by their reactivity in a specific interacting system from the point of view of the modes of the fluorination process in low- and high-temperature fluorination reactions (8). It should be noted that this classification is very conditional, however, as a boundary corresponding to it. Fluoroxide reactions must be carried out in special equipment due to the hygroscopicity of the reagents and high reactivity.

The reactions of  $\text{KrF}_2$  with  $\text{Ln}_2\text{O}_3$  ( $\text{Ln}=\text{Ce}, \dots, \text{Lu}$ ) were carried out in the presence of anhydrous HF at room temperature. The suspension was stirred with the gases evolved – krypton and oxygen. The reaction proceeds in accordance with the schemes:

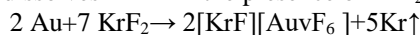


The process is very slow, and the yield of formed fluoride decreases in the following order:  $\text{Pr} \rightarrow \text{Nd} \rightarrow \text{Sm} \rightarrow \text{Eu} \rightarrow \text{Gd} \rightarrow \text{Tb} \rightarrow \text{Dy} \rightarrow \text{Er}$

The reaction of  $\text{KrF}_2$  with  $\text{LnO}_2$  in anhydrous HF proceeds according to the scheme:

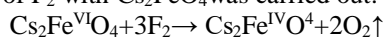


The reaction of  $\text{KrF}_2$  with gold in anhydrous HF at  $20^\circ\text{C}$  proceeds according to the scheme, and gold rapidly dissolves in HF in the presence of  $\text{KrF}_2$ .



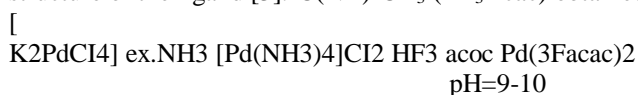
The reaction of  $\text{XeF}_2$  with  $\{\text{MF} + \text{AgF}_2\}$  ( $\text{M}=\text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ) proceeds very slowly (within 12-15 hours) with the formation of  $\text{M}(\text{AgIII})\text{F}_4$  in the range of  $200\text{-}250^\circ\text{C}$ . With a molar ratio of  $\text{Cs}:\text{Ag} = 2:1$  and repeated grinding of intermediate products, it is possible to obtain an  $\text{Ag}(\text{V})$  derivative in the form of a mixed-valent fluoride of the composition  $\text{Cs}_4\text{AgIII AgV F}_{12}$

So experiments were carried out on the synthesis of compounds in high-temperature processes or experiments at a fluorine pressure of  $\sim 500$  atm. At a high fluorine pressure (50-100 atm.) and a temperature of  $100\text{-}200^\circ\text{C}$ , the reaction of  $\text{F}_2$  with  $\text{Cs}_2\text{FeO}_4$  was carried out:

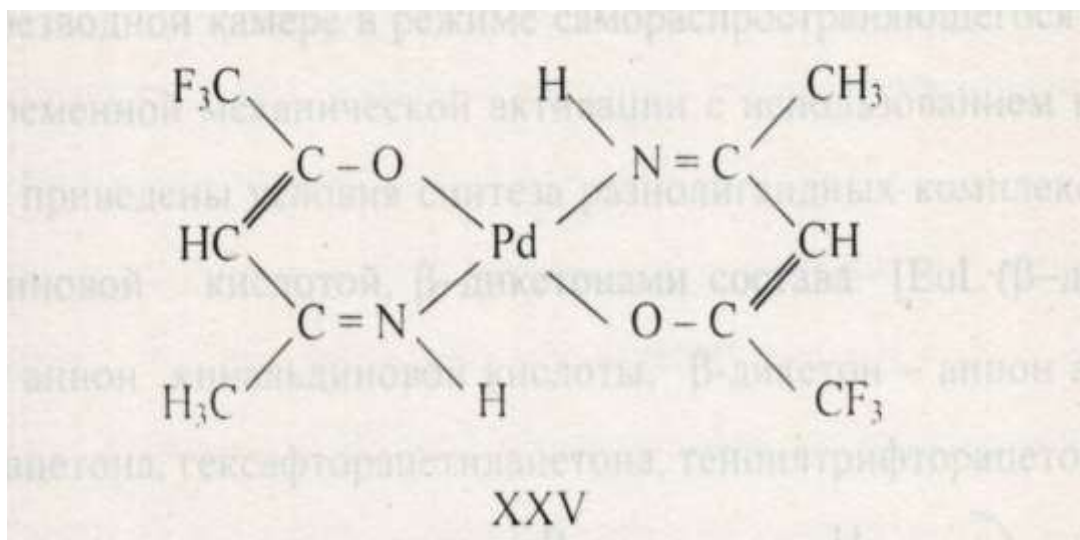


In describing the kinetic side of the reaction for the synthesis of higher fluorides, the authors [103, 111] confine themselves to fixing the difficulties of the kinetic plan and analyzing ways to eliminate them; therefore, a serious substantiation of these reactions and their performance in specially prepared equipment is required.

Studies on the synthesis and study of the volatility and thermal stability of  $\beta$ -diketonates of a number of transition and rare earth elements (REE) have shown that the most promising compounds for the production of palladium, platinum, nickel and copper coatings by vapor deposition are fluorinated  $\beta$ -diketonates of these metals [8, 9]. It has been established that the volatility and thermal stability of metal  $\beta$ -diketonates can vary significantly depending on the structure of the ligand [3].  $-\text{C}(\text{NH})-\text{CH}_3$  ( $\text{HF}_3\text{Acac}$ ) obtained according to scheme



Abstract—The crystal and molecular structure of bis-(trifluoro-imoketone)palladium(II)(XXV) constructed from isolated  $\text{Pd}[\text{3Facac trans-complexes}]$  has been studied. The palladium atom is located in the center of symmetry and has a square planar coordination of two pairs of  $[\text{N}_2\text{O}_2]$  atoms:



In contrast to palladium(II) complexes, the interaction of  $K_2[PdCl_4]$  with HFacac yielded complex compounds: the more volatile fraction  $[Pt(3Facac)_2]$ -highly soluble in chloroform, benzene, and hexane, and the less volatile fraction  $[Pt(3Facac) \cdot H_2O]$ , which in turn is highly soluble in chloroform, worse in benzene. Despite the great similarity of the intermediate complexes  $[Pd(NH_3)_4]Cl_2$  and  $[Pt(NH_3)_4]Cl_2$ , in contrast to the first, labile Pd (II) complex, in the case of kinetically inert Pt (II) complexes, the substitution of coordinated ammonia for another ligand is very difficult. Used together with ammonia and sodium acetate, it was possible to carry out the reaction in a neutral medium [3]. The volatility of chelates of fluorine-containing  $\beta$ -diketones is explained by the fact that the high electronegativity of fluorine atoms leads to disruption of the dense packing of the crystal lattice of the complex and weakening of intermolecular bonds [3].

REE compounds of the LiEF<sub>4</sub> type are of great practical interest as laser materials, the crystals of these complexes have a tetragonal structure with four REE ions in the unit cell, their magnetic susceptibility and heat capacity are well studied, and for some there are EPR data [1, 2]

The yield of the nickel(II) complex compound based on benzoylhydrazone 1,1,1-trifluoromethyl-4-(4-bromophenyl)butanedione-2,4  $NiC_{17}H_{13}N_3O_2BrF_3$  was 0.15 g (36%).

Complex compounds of nickel(II) and copper(II) with a coordinated ammonia molecule in the fourth coordination site of a square planar metalocycle were synthesized similarly. Elemental analysis results in Table 4.

Yields and results of elemental analysis of nickel(II) complex compounds based on benzoylhydrazones of aroyltrifluoroacetylmethanes. Yields and results of elemental analysis of complex compounds of nickel(II) structure.(XLIV) based on benzoylhydrazones of aroyltrifluoroacetylmethanes

Connection	Exit	T. melt °C	Found%				Gross formula	Calculated %			
			Ni(II)	C	H	N		Ni(II)	C	H	N
$NiL^1 \cdot NH^3$	80	141-143	14,01	49,07	2,28	9,79	$NiC_{17}H_{14}N_3O_2F_3$	14,39	50,04	3,46	10,30
$NiL^2 \cdot NH^3$	65	151-152	13,70	51,09	3,51	9,73	$NiC_{18}H_{16}N_3O_2F_3$	13,90	51,26	3,66	9,95
$NiL^3 \cdot NH^3$	69	156-157	12,85	48,96	3,15	9,31	$NiC_{18}H_{16}N_3O_3F_3$	13,40	49,35	3,68	9,60
$NiL^4 \cdot NH^3$	86	105-106	13,17	46,05	2,65	9,24	$NiC_{17}H_{13}N_3O_2ClF_3$	13,26	46,14	2,96	9,50
$NiL^5 \cdot NH^3$	36	229-230	11,93	41,40	2,13	8,03	$NiC_{17}H_{13}N_3O_2BrF_3$	12,04	41,93	2,70	8,63

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