

ОРГАНИЧЕСКАЯ И БИООРГАНИЧЕСКАЯ ХИМИЯ

STUDY OF THE COMPLEXATION OF GOLD (III) WITH 1-VINYLMIDAZOLE

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It has been found by X-ray diffraction that the crystal structure of the complex of 1-vinylimidazole with HAuCl_4 consists of AuCl_4^- polyanions and $(\text{C}_5\text{H}_7\text{N}_2)^{+1}$ polycations. Herewith, the interaction between polyanions and polycations, in addition to the ionic bond, is also carried out by hydrogen bonds of the $\text{Cl} \cdots \text{H}-\text{C}$ type [the length of the donor-acceptor bond is 3.7049 (7) Å] and $\text{Cl} \cdots \text{H}-\text{N}$ [the length of the donor-acceptor bond is 3.2727 (7) Å], forming infinite chains [100] alternating in the directions [011] and [0-11]. The vinyl fragment of 1-vinylimidazole is not involved in coordination.

To assess the thermal stability and possible pathways of the complex decomposition, a thermal study was conducted under dynamic heating. The decomposition of the complex proceeds at a temperature above 88°C and ends at 300°C with a loss of 21.5% of the mass, which corresponds to the cleavage of one ligand molecule.

Figs. 4, table 1, references 22.

N-vinylazoles are an important class of azole derivatives that can form radical polymerization and copolymerization products [1-3]. Many azole-based complex compounds exhibit biological activity and serve as effective drugs [4-7].

In [8-9] articles, we showed that the alkylation reaction of azoles in the N-methyl-morpholine N-oxide/ H_2O (NMO/ H_2O) system to the site of

various phase transfer catalysts is not inferior in reaction yields during phase transfer catalysis (PTC). Further, our studies on the alkylation of imidazole with dichloroethane using phase transfer catalysts (quaternary ammonium salts) in an aqueous solution of N-methylmorpholine-N-oxide (NMO/H₂O) were carried out.

According to published data, there are many examples of N-alkylation of imidazole (1) under PTC conditions [10-13], but there is no alkylation of imidazole with dichloroethane.

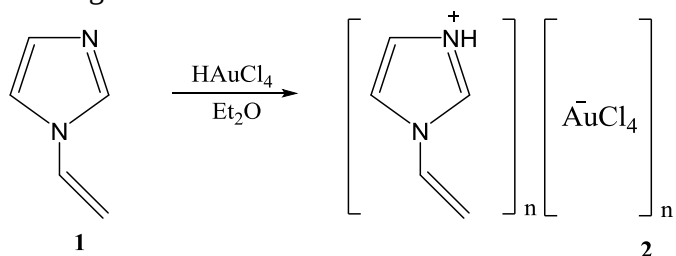
The need for development was dictated by the fact that 1-(2-chloroethyl)imidazole (2) is simultaneously an intermediate product in the synthesis of an important class of 1-vinylimidazole, on the other hand, 1-vinylimidazole and its derivatives are still obtained under acetylene pressure at a temperature of 130°C and higher [14].

It is known from the literature that 1-vinylimidazole (1), when interacting with transition metal chlorides, forms donor-acceptor complexes due to the free pair of electrons of the nitrogen atom in position 3 and the vacant metal orbital [15-18].

Coordination compounds of gold⁺ in HAuCl₄ with 1-vinylimidazole, in contrast to transition metal complexes, are not known in the literature.

A simple route for the synthesis of 1-vinylimidazole (1) in the PTC/NMO system [19] motivated us to study its complexation with HAuCl₄.

At room temperature, when mixing an ether solution of HAuCl₄ with an ether solution of 1-vinylimidazole (1), ion-type complexation instantly proceeds according to the scheme:



The study of the IR spectra of 1-vinylimidazoles (1) has shown that the complexation of the latter with HAuCl₄ is manifested in large displacements, the vibration frequency of the hetero ring from 1530 to 1550 cm⁻¹. A change in the vibrational frequency of the vinyl group (ν=1680 cm⁻¹) is not observed in the IR spectra, although the intensity of the double bond band decreases. According to published data [20], this indicates that the vinyl fragment of 1-vinylpyrazole is not involved in the coordination with HAuCl₄. Despite this, the results of X-ray diffraction analysis show that the vinyl fragment binds to chlorine atoms by non-classical hydrogen bonds. The short-wavelength shifts of the vibrational band of the hetero ring of compound 2 indicate the coordination of the heterocycle with HAuCl₄, which is consistent with the results of X-ray diffraction.

In the ^1H NMR spectrum of complex **2**, a weak-field shift of the 3-H and 5-H protons is observed ($\Delta\delta$ 0.79; 0.95). Weak-field shifts are also observed for the proton signals of H_A , N_B , and N_C of the vinyl substituent ($\Delta\delta$ 0.15; 0.48; 0.29, respectively) compared with ligand **2**.

Weak-field displacements of hetero ring proton signals confirm the participation of the imidazole cycle in HAuCl_4 coordination [7, 20].

The results of X-ray diffraction analysis show that, in the crystal structure, AuCl_4^- polyanions bind to $(\text{C}_5\text{H}_7\text{N}_2)^{+1}$ polycations with $\text{Cl}\cdots\text{H-C}$ type bonds (the length of the donor-acceptor bond is 3.7049 (7) Å) and $\text{Cl}\cdots\text{H-N}$ (the length of the donor-acceptor bond 3.2727 (7) Å). Herewith, each polyanion is, on the one hand, bound to a vinylimidazole molecule by a $\text{Cl}\cdots\text{H-C}$ type hydrogen bond, and, on the other hand, a $\text{Cl}\cdots\text{H-N}$ type hydrogen bond. Violation of the alternation of types of hydrogen bonds leads to a disordered distribution of vinylimidazole molecules in two positions (Fig. 1).

In 3D, using hydrogen bonds, infinite chains alternating in the direction are formed, spreading in directions (Fig. 2). The bonds between the chains can mainly be described by the Van der Waals interactions.

Thermogravimetric analysis of the synthesized complex **2** was performed on a TG/MS NETZSCH STA 449 (TG), QSM403 (MS) instrument, under dynamic heating conditions (Fig. 3). The initial stage of sample mass loss (green curve) begins at 88°C and ends at approximately 112°C. It is interesting that it is in the temperature range 88-112°C that very distinct exothermic effects with maximum values appear on the DSC curve (blue curve). We suppose that in this stage, the ligand is cleaved and then polymerized. The decomposition of complex **2** ends at 300°C, and the weight loss of the sample corresponds to the amount of vinylimidazole in the complex of ~ 21.5%, which matches with the mass spectrum data.

The character of the thermogravimetric curve with an increase from 112°C to about 300°C has a complex form, and, possibly, both the decomposition of the HAuCl_4 salt and partial oxidative decomposition of the formed polymer take place. According to the TG curves after 300°C, the residue is approximately 39.83%, which corresponds to the percentage of Au in the complex.

Thus, X-ray diffraction analysis shows that in compound **2** there is no covalent bond of the donor-acceptor type, in contrast to transition metal chlorides. AuCl_4 binds to the molecules of 1-vinylimidazole by hydrogen bonds of the type $\text{Cl}\cdots\text{H-C}$ and $\text{Cl}\cdots\text{H-N}$.

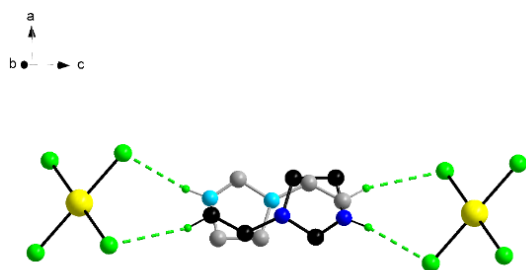


Fig. 1. Scheme of a disordered vinylimidazole molecule depending on the types of hydrogen bonds. For clarity, one orientation of the molecule is represented by dark colors (black, blue), and the other by light colors (gray, light blue).

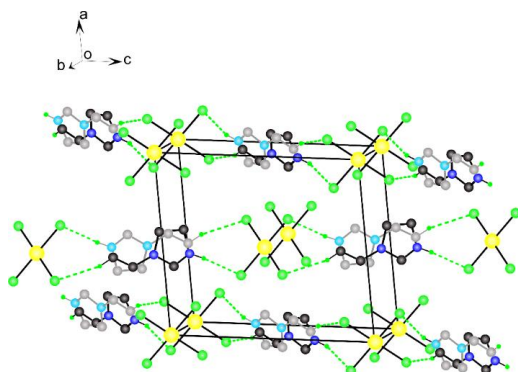


Fig. 2. 3D packaging of the AuCl_4^{-1} , $(\text{C}_5\text{H}_7\text{N}_2)^{+1}$ complex. The chains formed by hydrogen bonds are visible.

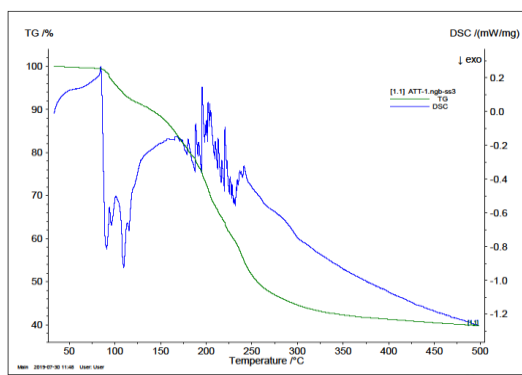


Fig. 3. Thermogravimetric analysis curves for complex 2.

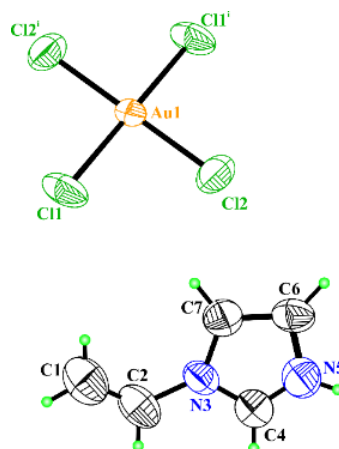


Fig. 4. Atomic model of the structure of the AuCl_4^{-1} complex with the vinylimidazole molecule $(\text{C}_5\text{H}_7\text{N}_2)^{+1}$. For clarity, only one orientation of disordered vinylimidazole is shown. Ellipsoids of anisotropic thermal vibrations are carried out at the level of 50% probability.

Experimental Section

IR spectra were recorded on a Termo Nicolet Nexus spectrometer in liquid paraffin. ^1H NMR spectra were recorded on a Varian Mercury-300VX spectrometer (300 MHz) at a temperature of 300 K in a $\text{DMSO-d}_6\text{-CCl}_4$, 1: 3 solution, internal standard TMS. Elemental analysis was performed on an Evrovector EA-3000 instrument. X-ray diffraction studies were performed on a “CAD4 Enraf-Nonius” diffractometer. Thermogravimetric studies were carried out on a “TG/MS NETZSCH STA 449 (TG), QSM403 (MS)” derivatograph, heating rate 5 *deg/min*, temperature range 20-500°C. Imidazole and HAuCl_4 were purchased from Sigma-Aldrich and used without further purification.

Synthesis of the complex $[\text{HAuCl}_4]$ (2). To 0.55 g (0.00126 mol) of HAuCl_4 , 50-100 ml of dry ether was added until HAuCl_4 was completely dissolved. Then, 0.15 g (0.016 mol) of 1-vinylimidazole (**1**) was added. The resulting yellow crystals were filtered off and dried, mp. 35-120°C. The yield of complex **2** is 0.3 g (45%) based on 1-vinylimidazole. IR spectrum, ν , cm^{-1} : 1530 (ring), 1650 (C=C). ^1H NMR spectrum, ppm, J (Hz): 5.40 dd (1H, =CH₂, J = 8.8 and 2.2), 5.97 dd. (1H, =CH₂ J = 15.7 and 2.2), 7.31 dd. (1H, =CH₂ J = 15.7 and 8.8), 7.80 br.s. (1H, NCH), 8.18 br.s. (1H, NCH), 9.41 br.s. (1H, NCHN). Spectrum ^{13}C δ_c , ppm: 105.2 (C=CH₂), 120.5 (C=H), 130.6 (N-CH), 131.2 (N=CH), 140 (NCHN). Found, %: C 13.53; H 1.72; N, 6.61. $\text{C}_5\text{H}_6\text{N}_2\text{Cl}_4\text{Au}$. Calculated, %: C 13.79; H 1.60; N 6.43.

X-ray diffraction analysis of compound **2** was carried out at room temperature on an Enraf-Nonius CAD-4 autodiffractometer (graphite monochromator, $\text{MoK}\alpha$ radiation, λ = 0.71069 Å, θ / 2θ scan). Unit cell parameters were determined and refined by 25 reflections with $12.0^\circ < \theta < 15.5^\circ$. The absorption was calculated using the ψ -scanning method [21]. The structure was decrypted by the direct method. The coordinates of the hydrogen atoms were determined by geometric calculations and refined according to the riding model: C–H = 0.93 Å, $\text{Uiso}(\text{H}) = 1.2\text{Ueq}(\text{C})$ and for N–H = 0.86 Å, $\text{Uiso}(\text{H}) = 1.2\text{Ueq}(\text{N})$. The parameters of non-hydrogen atoms were refined by full-matrix least squares in the anisotropic approximation. All structural calculations were performed using the SHELXTL software package [22]. The atomic coordinates and other structural parameters of the AuCl_4^{-1} , $(\text{C}_5\text{H}_7\text{N}_2)^{+1}$ complex were deposited with Cambridge Crystallographic Data Centre (CCDC № 1860896); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif. The main crystallographic data of the AuCl_4^{-1} , $(\text{C}_5\text{H}_7\text{N}_2)^{+1}$ complex are shown in Table. The structure of complex **2** is shown in Fig. 4.

**Crystallographic data, experimental parameters, and structure
refinement of AuCl_4^{-1} , $(\text{C}_5\text{H}_7\text{N}_2)^{+1}$ AuCl_4^{-1} , $(\text{C}_5\text{H}_7\text{N}_2)^{+1}$**

Parameter	Value
Syngonia	Monoclinic
Space group	$P2/n$
a , Å	10.633(2)
b , Å	4.1689(8)
c , Å	12.364(3)
β , deg	93.61(3)
V , Å ³	547.0(2)
Z	2
$\rho(\text{calc.})$, g/cm ³	2.634
$\mu(\text{MoK}\alpha)$, mm ⁻¹	14.374
$T_{\min}/T_{\max}$	0.49892/0.89506
$F(000)$	396
Crystal size, mm	0.3×0.06×0.06
Temperature, K	293
θ data collection area, deg	2.5–30.0
Reflection index intervals	$0 \leq h \leq 14$, $-5 \leq k \leq 5$, $-17 \leq l \leq 17$
The number of measured reflections	3322
The number of independent reflections	1585
The number of observed reflections with $I > 2\sigma(I)$	1225
The number of specified parameters	88
R , wR_2 , S	0.0281, 0.0720, 1.16
$\Delta\rho_{\max}/\Delta\rho_{\min}$, $e \text{ Å}^{-3}$	-1.35/ 0.71

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**1-ՎԻՆԻԼԻՄԻԴԱԶՈԼՈՎ ՈՍԿՈՒ (III) ԿՈՄՊԼԵՔՍԱԳՈՅԱՑՄԱՆ
ՌԻՍՈՒՄՆԱՍԻՐՈՒԹՅՈՒՆԸ**

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Ռենտգենկառուցվածքային անալիզի միջոցով պարզվել է, որ 1-վինիլիմիդազոլի և HAuCl_4 -ի կոմպլեքսի կառուցվածքը բաղկացած է AuCl_4 -պոլիանիոններից և $(\text{C}_5\text{H}_7\text{N}_2)^{+1}$ պոլիկատիոններից:

Ընդ որում, պոլիանիոնների և պոլիկատիոնների միջև փոխազդեցությունը իրականացվում է, բացի խոնական, նաև $\text{Cl}\dots\text{H}-\text{C}$ [դոնորակցեպտորային կապի երկարությունը 3,7049(7) Å] և $\text{Cl}\dots\text{H}-\text{N}$ [դոնորակցեպտորային կապի երկարությունը 3,2727(7) Å]

տիպի ջրածնական կապերի միջոցով, առաջացնելով տարածության մեջ ուղղորդվող անվերջ շղթաներ [100], որոնք տարածվում են [011] և [0-11] ուղղություններով: 1-Վինիլիմիդազոլի վինիլային հատվածը չի մասնակցում կոորդինացման մեջ:

Ջերմակայունության և կոմպլեքսի քայքայման հնարավոր ուղիների դնահատման համար իրականացվել է Ջերմային հետազոտություն դինամիկ տաքացման պայմաններում: Կոմպլեքսի քայքայումը ընթանում է 88°C -ից բարձր և ավարտվում է 300°C ջերմաստիճանում 21.5% զանգվածի կորստով, ինչը համապատասխանում է մեկ լիգանդի մոլեկուլի պոկմանը:

ИССЛЕДОВАНИЕ КОМПЛЕКСООБРАЗОВАНИЯ ЗОЛОТА (III) С 1-ВИНИЛИМИДАЗОЛОМ

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Методом РСА установлено, что кристаллическая структура комплекса 1-винилимидазола с HAuCl_4 состоит из полианионов AuCl_4^- и поликатионов $(\text{C}_5\text{H}_7\text{N}_2)^{+1}$. При этом взаимодействие между полианионами и поликатионами, помимо ионной связи, также осуществляется водородными связями типа $\text{Cl}^{\cdots}\text{H}-\text{C}$ [длина донорно-акцепторной связи 3,7049(7) Å] и $\text{Cl}^{\cdots}\text{H}-\text{N}$ [длина донорно-акцепторной связи 3,2727(7) Å], образуя чередующиеся в направлении [100] бесконечные цепочки, распространяющиеся в направлениях [011] и [0-11]. Винильный фрагмент 1-винилимидазола не участвует в координации.

Для оценки термостабильности и возможных путей распада комплекса проведено термическое исследование в условиях динамического нагрева. Распад комплекса протекает выше 88°C и заканчивается при 300°C с потерей 21.5% массы, что соответствует отщеплению одной молекулы лиганда.

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