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Dimer Complexes of Mixed Ligands of Platinum.

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ABSTRACT

We obtained biologically active single-core and dual-core Mixed-Ligand Coordination Compounds of platinum (II) with ethylenediaminediacetate and mercaptoethanol by creating optimal conditions. Their compositions and structures were researched via various physical and chemical methods. Ethylenediaminediacetate, in the single-core platinum complex, is coordinated bidentate in cis position, which consequently leads to the forced cis coordination of mercaptoethanol. In the dual-core complex of platinum, mercaptoethanol, which functions as a bridge among the metal atoms, is coordinated monodentate to the sulfur atom, whereas the OH⁻ group of the ligand is not involved in coordination. Two ethylenediaminediacetate atoms in terminal position bidentate coordinating with nitrogen atoms form two metalchelate cycle. Carboxylic groups of ethylenediaminediacetate do not participate in coordination regardless of their conditions.

Keywords: dimer complex, dual-core complex, ethylenediaminediacetate, mercaptoethanol, platinum complex.

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INTRODUCTION

The study of mixed ligand complexes has drawn more attention in medicine and engineering recently. On one hand, platinum-based individual and some mixed ligand complexes are used in the comprehensive chemical treatment together with other organic based drugs [1]. On the other hand, it is possible to obtain exceptional thin metal sheets for electronic units as a result of thermal decomposition using complex compounds of mixed sulphur-containing ligand platinum and other transition elements [2].

The study of the structure of the composition and other properties of platinum complexes with various functional biologically active ligands which contain sulphur, nitrogen and oxygen donor atoms (II) is of great importance in modern coordination and bio-coordination chemistry.

Individually, both ethylenediaminediacetate – $\text{HOOCCH}_2\text{CNCH}_2\text{CH}_2\text{NCH}_2\text{COOH}$ (EDDA) and mercaptoethanol – $\text{HSCH}_2\text{CH}_2\text{OH}$ [3] ligands have properties of detoxicant. The studies of structure, composition and other properties of complexes formed as a result of their joint coordination in platinum coordination sphere have been of great interest to chemists and other specialists.

EXPERIMENTAL PART

Synthesis of $\text{Pt}(\text{EDDA})(\text{SCH}_2\text{CH}_2)\text{OH}_2$ complex. During synthesis of these and other complexes, various salts of platinum were used as the starting material.

Firstly, 0.4621 g (1.1132 mmol) is taken of $\text{K}_2[\text{PtCl}_4]$ complex and then, it is dissolved in 20 ml of water and afterwards, filtered through the paper sieve and heated up to 90°C . Then, 0.1959 g (1.1132 mmol) of EDDA ligand calculated in stoichiometric proportions (M:L; 1:1) is dissolved in 15 ml of water and then heated up to that temperature, where both reagents are mixed in hot states. In this stage, the obtained dark yellow solution is mixed in magnetic stirrer for 30 minutes at 70°C .

0.1738 g (2.2259 mmol) of mercaptoethanol is added onto complex formed during the reaction in solution based on theoretical calculation at the very temperature.

Reaction mixture is stirred at 70°C for three hours and then, it is cooled then to room temperature. This is when light yellow colored crystals cипitates from the solution and the solution is filtered through filter glass following the completion of the settling process. The formed material is washed with cold water, spirit and ether. Then, first, it is dried in air and afterwards in vacuum over CaCl_2 until the weight is constant.

Synthesis of $[\text{Pt}_2(\text{EDDA})_2(\text{SCH}_2\text{CH}_2\text{OH})_2]\text{Cl}_2$ complex. Complex $[\text{Pt}_2(\text{NH}_3)_4(\text{SCH}_2\text{CH}_2\text{OH})_2]\text{Cl}_2$ referenced in literature [4] is taken in a weight of 0.4537 g (0.6640 mmol) and suspension is prepared from that in 20 ml of water at 50°C temperature. In accordance with theoretical calculations, 0.2338 g (1.3279 mmol) of ethylenediaminediacetate is taken and dissolved in 15 ml of water mixture (pH=6.2) with HCl in proportions of (3:1). The hot solution of ligand is mixed and added on ready suspension. The total pH of reaction mix is brought to 4 and then heated up to 70°C and homogenous transparent solution is formed at this temperature after 1.5 hour. The formed homogenous solution is filtered and poured in ceramic container and a syrop-shaped solution is obtained when evoporated at 40°C temperature in small volumes. After the cooling reaction mixture is processed with chloroform–ether mixture (2:1), and as a result, dark yellow sediments are formed. The sediments are filtered. Firstly it is washed by cold water and then by spirit and ether. A complex is first dried in air and then in vacuum over CaCl_2 to constant weight.

RESULTS AND DISCUSSION

The yield equaled to 0.1686 g (82%) at the synthesis of $\text{Pt}(\text{EDDA})(\text{SCH}_2\text{CH}_2)\text{OH}_2$ complex.



common $\text{C}_{10}\text{H}_{20}\text{N}_2\text{S}_2\text{O}_6\text{Pt}$ formula

Calculated, %: Pt – 37.28; N – 5.35; S – 12.35; C – 22.95; H – 3.82
 Founded, %: Pt – 37.41; N – 5.45; S – 12.26; C – 23.11; H – 3.99.

The yield equaled to 0.5693 g (89%) at the synthesis of [Pt₂(EDDA)₂(SCH₂CH₂OH)₂]Cl₂ complex.



For C₁₆H₃₀S₂N₄O₁₀Pt₂Cl₂ formula

Calculated, %: Pt–40.50; S–6.65; N – 5.81; Cl – 7.35; C – 19.94; H – 3.11.
 Founded, %: Pt–40.61; S – 6.76; N – 5.93; Cl – 7.745; C – 19.764; H – 3.23.

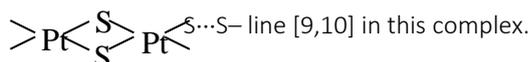
The ratio of the reagents used during the synthesis of complexes and the created conditions ought to be optimal, which would make it possible to obtain clean, individual and high-yielded substance. In order to determine the structure of the newly formed complexes, IR spectra of metal salts and ligands taken initially for synthesis are weighed and interpreted accordingly. In the next stage, IR spectra of these new complex compounds obtained on the basis of these substances were weighed and were analysed on comparative basis.

At IR-spectrum of free ligand, β-mercaptoethanol –SH and –OH are characterized by 2542 and 3660 cm⁻¹ absorption bands correspondingly. This specific absorption bands are also similar to the literature materials [5]. A single asymmetric 1712 cm⁻¹ absorption band of ethylenediaminediacetate (EDDA) in IR spectrum has been attributed to free carboxyl groups of ligands[6]. The absorption band relevant to SH functional group is not registered in IR spectrum of all complexes obtained with the participation of mercaptoethanol and EDDA, which indicates the de-protonation of HS functional group of ligand. On the other hand, unambiguous assertion of their non-participation in coordination is customary not taking into consideration the minor changes in absorption band belonging to the carboxyl groups in IR spectrum.

Furthermore, two absorption bands 354 and 366 cm⁻¹ observed at absorption zone in slow frequencies (200–500 cm⁻¹) of the IR spectrum of complex [Pt(EDDA)(SCH₂CH₂OH)₂] have been attributed to the ν_{Pt-S} valence bond. The observation of one valence bond with two absorption bands shows their location in cis - position with respect to each other according to C_{2v} selection order[7]. Consequently, at – [Pt (EDDA)(SCH₂CH₂OH)₂] complex mercaptoethanol makes monodentant coordination with platinum through sulphur atom in the cis-position, whereas hydroxyl group of ligand does not participate in coordination. Obtained results are similar with literature materials [8].

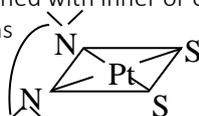
Two nuclear [Pt₂(EDDA)₂(SCH₂CH₂OH)₂] Cl₂ complex compound is obtained by the way of changing the reaction conditions and other parameters. Very interesting facts were registered in IR spectrum of [Pt₂(EDDA)₂(SCH₂CH₂OH)₂]Cl₂ complex. For example, metal-sulphur valence bond is accompanied by two absorption bands in IR spectrum of mononuclear cis-structure complex [Pt(EDDA)(SCH₂CH₂OH)₂], whereas, in the IR spectrum of two-nuclear complex, the corresponding absorption band is observed with three 336, 340 and 348 cm⁻¹ bands. The given absorption bands were attributed clearly to Pt–S valence bond that play the role of a bridge.

Observation of one valence bond in complex [Pt₂(EDDA)₂(SCH₂CH₂OH)₂]Cl₂ with three absorption bands allows us to assume that metal chelate cycle bends along the –



Another fact is worth to be noted that in IR spectrum of mononuclear complex ν_{Pt-N} valence bond is observed with – 420, 424 and 410 cm⁻¹ absorption bands.

To our mind, it can be explained with inner or outer extrusion of flatness due to uneven distribution of electronic dense in flat square flattens of platinum [11,12].



But, in IR spectrum of two nuclear complex, $\nu_{\text{Pt-N}}$ valence bond is observed with one 470 cm^{-1} absorption band, which has led to non-decomposition of absorption band in $300\text{--}500 \text{ cm}^{-1}$ zone after being equally distributed along the $>\text{N}\cdots\text{N}<$ system of electronic dense in five-member metal chelate cycle in complexes with twin conformation.

The absorption bands of free carboxyl group of EDDA not involved in coordination remains unchanged in IR spectrum of both complexes.

So, mercaptoethanol forms both mono- and dimer structure mixed ligand complexes. In both complexes, mercaptoethanol coordinates monodentate with only a sulphur atom, whereas hydroxyl group of ligand does not participate in coordination. However, ethylenediaminediacetate, in all cases, coordinates bidentate with the central atom and forms five-member metalchelate cycle. Carboxyl groups of ligand are not involved in coordination. It was determined that these type chelate-mixed complexes are more stable in aqueous solutions compared to other individual complexes containing mercaptoethanol and they are thermally stable as well.

Unlike with other sulphur-containing ligands, ability of mercaptoethanol to form dimer structure complex compounds, i.e., to become a bridge with sulphur atom, has been proven in chemical methods. Determined values of electrical conductivity 49 and $224 \text{ Ohm}^2\text{cm}^2\text{mol}$ of water-alcohol solutions of the complexes prove the given formulas right. The study of thermal stability of complexes indicated that both of them were stable up to 250°C and their decomposition in the following stage occurred incrementally without melting.

The medication made from both complexes for experiment purposes has shown positive effects in the treatment of skin diseases and therefore, extended research in this field is currently underway.

CONCLUSION

1. Mercaptoethanol forms both mono- and dimer structure mixed ligand complexes. In both complexes, mercaptoethanol coordinates monodentate with only a sulphur atom, whereas hydroxyl group of ligand does not participate in coordination. However, ethylenediaminediacetate, in all cases, coordinates bidentate with the central atom and forms five-member metalchelate cycle.
2. It was determined that these type chelate-mixed complexes are more stable in aqueous solutions compared to other individual complexes containing mercaptoethanol and they are thermally stable as well.

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