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*A.A. Roman, E.V. Zinchenko, A.A. Golichenko, A.V. Shtemenko***COMPLEX COMPOUND OF DIRHENIUM(III) WITH METHIONINE****Ukrainian State University of Chemical Technology, Dnipropetrovsk**

Chemistry of the dirhenium(III) compounds is rich and versatile, they may retain a metal-metal bond in many reactions including substitution of the ligands and oxidation. The interaction of tetrabutylammonium octachlorodirhenate(III) $(\text{NBu}_4)_2\text{Re}_2\text{Cl}_8$ with proteinogenic amino acid – methionine has been studied. The method of synthesis of complex compounds dirhenium(III) with methionine was elaborated. The composition and structure of $\text{cis-}[\text{Re}_2(\text{Met})_2\text{Cl}_4 \cdot 2\text{CH}_3\text{CN}]\text{Cl}_2$ have been confirmed by elemental analysis, infrared and electronic spectroscopy. Availability quadruple bond rhenium-rhenium can be established using electron spectroscopy, since for each structural type of dirhenium(III) halogenocarboxylates in the visible region there are characteristic absorption maxima which correspond to $\delta \rightarrow \delta^*$ electronic transition. IR-spectra proves the bridging coordination of the carboxyl group to the cluster Re_2^{6+} , shown the presence of stretching vibrations of the protonated $^+\text{NH}_3$ -group at 3449 cm^{-1} and other characteristic bands of methionine. The complex compound of dirhenium(III) with methionine is promising for potential use in medicine.

Introduction

The present stage of development of the coordination chemistry is characterized by increased interest in metal complexes that exhibit biological activity. Chemistry of the dirhenium(III) compounds is rich and versatile, they may retain a metal-metal bond in many reactions including substitution of the ligands and oxidation. [1–2]. In addition, such compounds may be used in medical practice, because possess antitumor, antihemolytic, antiradical and other types of biological activity [3–6].

The relative lability of the equatorial ligand (for example, chloride vs. bridging carboxylate) is essential for ease of substitution, while weak interactions at the axial positions are sensitive to the overall charge of the complex. In this view, a suitable molecular arrangement may be found for the cationic complex, combining around the dirhenium core, a set of bridging carboxylate and more labile chloride ligands. In this context we have examined methionine for the preparation of cationic complex compound of

dirhenium(III). It was important to explore whether the introduction of the amino acid would influence the antitumor activity. Methionine belongs to essential ionogenic amino acid, which is included in the composition of proteins and has nephroprotective properties, reduces the toxicity of many toxic substances and helps to restore the functions of the liver [7]. Moreover, it is involved in the synthesis of adrenaline, creatine, activates the action of a number of hormones, enzymes, neutralizes some toxic substances by methylation [8]. In this regard, promising in terms of biological action may be a new dirhenium(III) compound with methionine. Previously was synthesized the compounds of Cu(II), Ni(II) and Zn(II) with methionine [8], but in this work provides the first complex, where methionine is coordinated as a ligand to a cluster center, containing the multiple bond metal-metal.

Experimental

$(\text{NBu}_4)_2\text{Re}_2\text{Cl}_8$ was prepared as described in [9] and used as the starting materials for the synthesis

of complex compound with amino acid. L-methionine, acetonitrile, acetone, concentrated hydrochloric acid, hexane qualification «analytical grade» was used without further purification.

In order to identify the obtained compound using elemental analysis, infrared and electronic spectroscopy's was used.

Infrared spectra in the 500–4000 cm^{-1} region were recorded on a Fourier spectrometer “Thermo Nicolet Nexus 870 FTIR” (in KBr tablets).

Electronic absorption spectra in the range 56000–10000 cm^{-1} were recorded on a spectrophotometer «Specord M-40».

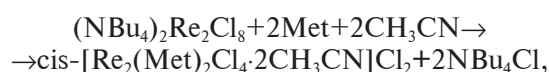
Elemental analyzes for rhenium and chlorine were performed by a gravimetric method using standard procedure [10,11].

The interaction of 0.0029 g (0.0025 mmol) $(\text{NBu}_4)_2\text{Re}_2\text{Cl}_8$ with 0.0038 g (0.0254 mmol) methionine (molar correlation 1:10) in mixture of acetonitrile (1 ml), acetone (3.85 ml) and HBF_4 (0.05 ml) at 70°C under an inert atmosphere was studied. EAS of resulting reaction solution has the band at 16700 cm^{-1} corresponds to the $\delta \rightarrow \delta^*$ electronic transition for quadruple bond rhenium-rhenium in cis-tetrachlorodi- μ -carboxylate of dirhenium(III) [2]. The described method of synthesis can be used as a model of interaction of $(\text{NBu}_4)_2\text{Re}_2\text{Cl}_8$ with methionine but we could not isolate the resulting complex compound from the reaction solution due to destruction during hydrolysis and later replaced HBF_4 on concentrated HCl .

Synthesis of bis-acetonitrile-cis-tetrachlorodi- μ -methioninatodirhenium(III) chloride

0.0655 g (0.4382 mmol) methionine (Met , $\text{CH}_3\text{-SCH}_2\text{-CH}_2\text{-CH}(\text{NH}_2)\text{-COOH}$) was placed into a conical flask and was dissolved in mixture of acetone (15 ml) and conc. HCl to the inhibition of hydrolysis of dirhenium(III) complex compound. Then the solution of 0.05 g (0.0438 mmol) $(\text{NBu}_4)_2\text{Re}_2\text{Cl}_8$ in 5 ml acetonitrile was added and the resulting mixture was stirred under an inert atmosphere during 20 hours at a temperature of about 60°C. During heating the color of the solution changed from green to blue. The blue powder of complex compound (with 64% yield) was obtained after evaporation of solvents in a desiccator with sulfuric acid, recrystallization from acetone and washed with hexane. The resulting substance is soluble in polar organic solvents and water.

The described conversions may be represented by the following reaction:



where $\text{Bu}=\text{C}_4\text{H}_9$.

Results and discussion

Composition of the obtained compound confirmed by elemental analysis:

Found, %: Re – 37.7; Cl – 21.8. Calc'd for $\text{cis-}[\text{Re}_2(\text{Met})_2\text{Cl}_4 \cdot 2\text{CH}_3\text{CN}]\text{Cl}_2$, %: Re – 38.6; Cl – 22.

Availability of rhenium-rhenium quadruple bond was proved using electron spectroscopy, since in the visible region there is characteristic absorption maxima which correspond to $\delta \rightarrow \delta^*$ electronic transition for each structural type halogenocarboxylate dirhenium(III) [2]. In the visible spectra of $\text{cis-}[\text{Re}_2(\text{Met})_2\text{Cl}_4 \cdot 2\text{CH}_3\text{CN}]\text{Cl}_2$ (acetone solution) (fig. 1) we can see absorption band at 16129 cm^{-1} , which confirms to obtaining cis-tetrachlorodi- μ -carboxylate of dirhenium(III) with methionine.

In UV spectra (fig. 2), there is a band at 31250 cm^{-1} corresponds to electron transition with charge transfer $\text{L}^p_{\text{Cl}} \rightarrow \text{Re}$ [12] and confirms the presence of equatorial chlorine atoms as ligands in environment of cluster unit Re_2^{6+} .

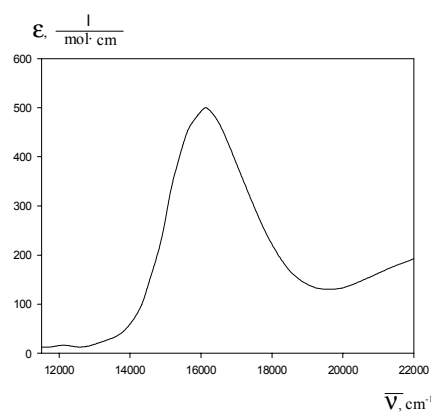


Fig. 1. EAS of $\text{cis-}[\text{Re}_2(\text{Met})_2\text{Cl}_4 \cdot 2\text{CH}_3\text{CN}]\text{Cl}_2$ in acetone

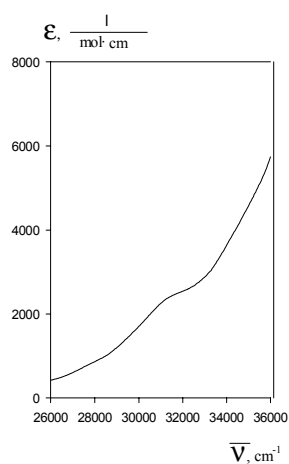


Fig. 2. Fragment of EAS in the UV range $\text{cis-}[\text{Re}_2(\text{Met})_2\text{Cl}_4 \cdot 2\text{CH}_3\text{CN}]\text{Cl}_2$ in acetone

In the IR-spectra of $\text{cis-}[\text{Re}_2(\text{Met})_2\text{Cl}_4 \cdot 2\text{CH}_3\text{CN}]\text{Cl}_2$ is absent the band of uncoordinated carbonyl group of methionine at 1635 cm^{-1} , this band is shifted to the region of 1478 cm^{-1} , what proves the bridging coordination of the carboxyl group to the cluster

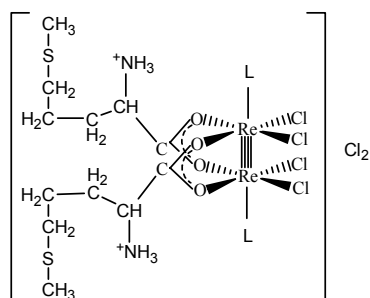
Re_2^{6+} [13]. Also was shown the presence of stretching vibrations of the protonated $^+\text{NH}_3$ -group at 3449 cm^{-1} and other characteristic bands of methionine [14].

On the represented proposed structure shows that four Cl atoms are located in the inner sphere of the complex compound, and two – in the outer sphere. This conclusion is confirmed by the investigation of the molar electric conductivity of an aqueous solution of $\text{cis-}[\text{Re}_2(\text{Met})_2\text{Cl}_4\cdot 2\text{CH}_3\text{CN}]\text{Cl}_2$. The obtained values are in the ranges of $230\text{--}260\text{ Ohm}^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$, that proves the identity of complex compound of dirhenium(III) with methionine to the electrolyte type 1:2 according [15].

On the fact that the two ions of chlorine located in the outer sphere of complex also indicates the precipitation of AgCl in the reaction of the acidified solution of $\text{cis-}[\text{Re}_2(\text{Met})_2\text{Cl}_4\cdot 2\text{CH}_3\text{CN}]\text{Cl}_2$ with a silver tetrafluoroborate according scheme:



Thus, as a result of this study a complex compound of dirhenium(III) with methionine was synthesized. Its composition and structure (fig. 3) was proved by elemental analysis, infrared and electronic spectroscopy:



where $\text{L}=\text{CH}_3\text{CN}$ or other electron donating groups.

Fig. 3. Structure of $\text{cis-}[\text{Re}_2(\text{Met})_2\text{Cl}_4\cdot 2\text{CH}_3\text{CN}]\text{Cl}_2$

Acetonitrile can be replaced by other ligands in axial position with a large value $\text{DN}(\text{SbCl}_5)$ according to the Gutman series of electron-donating properties [13], while retaining the characteristic band at 16129 cm^{-1} in EAS with the increase in its intensity and indicate the stability of the equatorial ligands environment of the Re_2^{6+} cluster unit.

Since for the same derivative with γ -amino-butyric acid the presence of antitumor, antiradical and other biological activities [5] previously was proved, then the resulting compound is promising for potential use in medicine.

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Keywords: rhenium; complex compounds; methionine; biological activity; quadruple bond.

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