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LETTERS TO THE EDITOR

Synthesis and Structure of Copper(II) Complex with Comenic Acid

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Comenic (5-hydroxy-4-oxo-4*H*-pyran-2-carboxylic) acid is a component of Baliz drug and determines the therapeutic effect of the latter [1]. It affects the function of slow sodium channels and can be used as a component of drugs for pain syndrome treatment [2], anti-stress therapy, and treatment of the consequences of opiates administration [1, 2]. The data on comenic acid properties and complex compounds have been scarce and contradictory [3–6].

As a typical oxyoxocarboxylic acid, comenic acid dissociates in two stages in aqueous solutions; pK_1 = 1.77–2.34 and pK_2 = 7.70–7.86 [3–6] (Scheme 1).

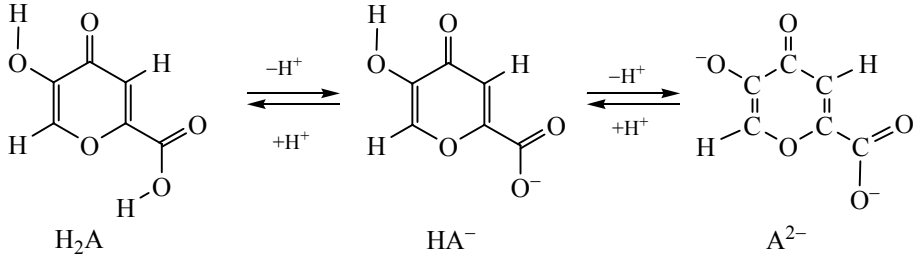
Owing to the presence of several coordination sites, comenic acid forms a variety of complex compounds. We have earlier studied its complexes with alkali and alkaline earth metals [3, 4]. Here we describe a complex of comenic acid with copper(II).

Comenic acid was isolated from Baliz drug via liquid chromatography (an Altex-112 instrument, an Ultra-sphere ODS column, an Optilab Multiger 902B differential detector). The acid formed white crystals turning yellow in air, moderately soluble in water and insoluble in ethanol. The acid and its copper complex were identified using IR spectroscopy and thermal analysis data.

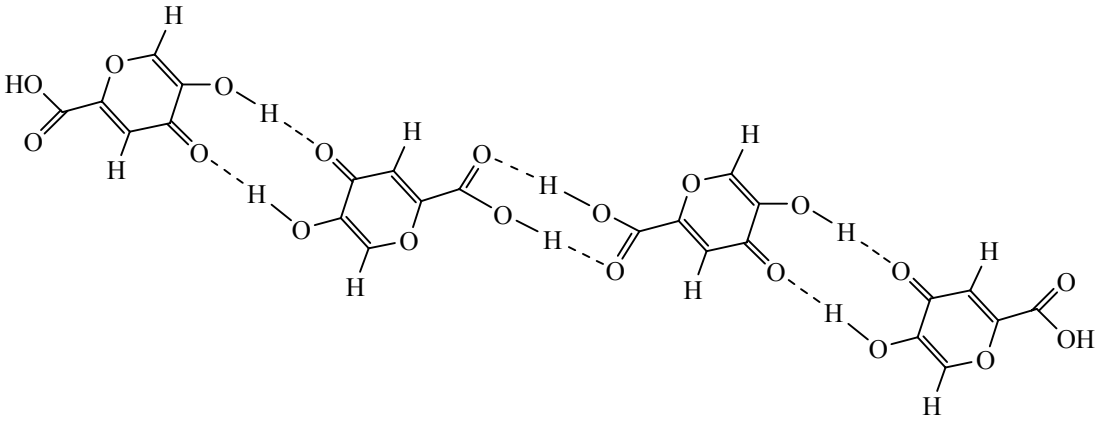
The complex was prepared by mixing equal volumes of 0.1 mol/L solutions of comenic acid and copper(II) chloride at 80°C and pH 3.6. The solution was kept during 1 day till the formation of the fine-crystalline precipitate; the crystals were filtered off, washed with ethanol, and dried in a dessicator over calcium chloride to a constant mass.

Thermal analysis of the prepared complex revealed the following transformations: evaporation of the adsorbed water (up to 107°C, mass loss of 0.3%), two-step elimination of coordination water (up to 170°C, mass loss of 22.2%), and pyrolysis (325–348°C, exothermic).

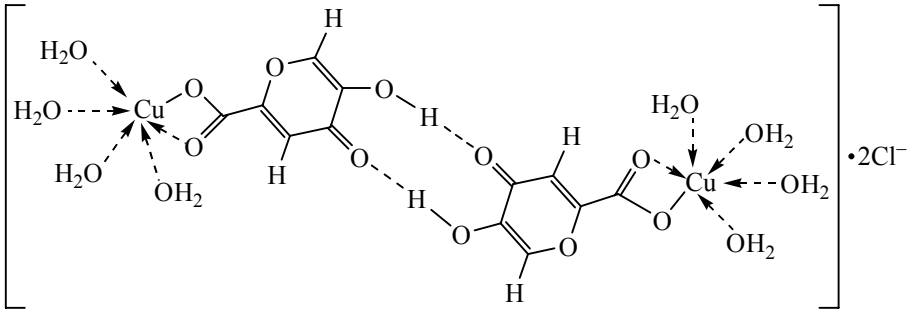
Scheme 1.



Scheme 2.



Scheme 3.



IR spectrum of comenic acid contained the characteristic absorption bands at 3300–2600 (OH) and 1650 (C=O) cm^{-1}. The hydroxy group in the position *5* (3320 cm^{-1}) formed an intramolecular hydrogen bond with the keto group (1728 cm^{-1}), the intermolecular bonding (dimer formation) was confirmed by the presence of the bands at 2950 and 2600 cm^{-1} (Scheme 2).

The group of the bands at 2500–2700 cm^{-1} assigned to the carboxylic groups dimer disappeared in the IR spectrum of the complex; hence, the complex formation involved exclusively the carboxylic group of comenic acid.

According to elemental analysis, the complex formula was as follows: $[Cu(H_2O)_2HA]Cl{\cdot}2H_2O$. Found, %: C 22.11; Cl 10.12; Cu 20.42. Calculated, % : C 22.64; Cl 11.15; Cu 19.98.

A binuclear complex was likely formed, containing two copper ions linked to the carboxylic groups of a pair of anions of comenic acid, the latter being in turn united in a dimer via interaction of the hydroxyl and the keto group. The suggested structure of the complex is given in Scheme 3.

Thermogravimetric analysis was performed using a NETZSCH STA 409 PC/PG instrument in air at linear heating at 10 deg/min from room temperature to 1000°C. IR spectra (KBr pellets) at 350–4000 cm^{-1} were recorded using a Shimadzu IR-Prestige Fourier spectrometer.

REFERENCES

1. Kazakov, V.N., Panova, T.I., and Panova, L.E., *Neurophysiol.*, 2003, vol. 35, no. 5, p. 392.
2. Kondratenko, R.V., Chepkova, A.N., and Shurygin, A.Ya., *Bull. Exp. Boil. Med.*, 2003, no. 5, p. 464.
3. Pirogova, A.N., Gorokhov, R.V., Kolokolov, F.A., Saradzhyan, A.A., Shurygin, A.Ya., and Bukov N.N., *Izv. Vuzov, Ser. Khim. Khim. Tekhnol.*, 2009, vol. 52, no. 12, p. 30.
4. Volynkin, V.A., Pachuev, A.V., Pirogova, A.N., Panyushkin, V.T., and Shurygin, A.Y., *J. Struct. Chem.*, 2011, vol. 52, no. 5, p. 892.
5. Rogachevskii, I.V. and Plakhova, V.B., *Russ. J. Gen. Chem.*, 2006, vol. 76, no. 11, p. 1820. DOI: 10.1134/S1070363206110272.
6. Agafonov, A.V., Udalova, A.M., and Grishina, E.P., *Russ. J. Phys. Chem. (A)*, 2005, vol. 79, no. 3, p. 403.