

Thermal and spectral properties of di- and trimethoxybenzoates of silver (I)

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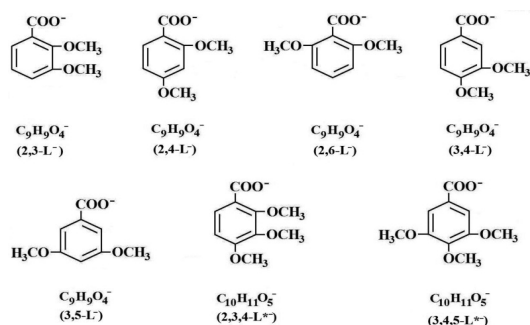
Abstract: The complexes of silver(I) with 2,3-, 2,4-, 2,6-, 3,4-, 3,5-dimethoxy-, and 2,3,4- and 3,4,5-trimethoxybenzoic acid anions have been synthesized and characterized by elemental analysis, IR spectroscopy, thermogravimetric and X-ray studies. Their solubility in water has been also determined at 293K. All analysed complexes were found to be crystalline, anhydrous compounds with low symmetry. The carboxylate groups act as bidentate or monodentate ligands. The thermal stability of compounds has been examined in air in temperature range of 293-1173K. The analysed complexes were found to be stable at room temperature and their solubilities in water at 293K to be in the order of 10^{-4} mol.dm⁻³.

Keywords: complexes of Ag(I); thermal stability; FTIR spectra.

Introduction

The carboxylates of many cations play an important role in inorganic and bioinorganic chemistry and in a great number of various biological processes they are component of several vitamins and drugs [1, 2]. 2,3-, 2,4-, 2,6-, 3,4-, 3,5-Dimethoxy- and 2,3,4- and 3,4,5-trimethoxybenzoic acids are crystalline solids sparingly soluble in water.

Their anions have the following formulae:



In the presented acid molecules there are two kinds of substituents: -COOH and -OCH₃. The first one, as an electron acceptor decreases the electronic density of benzene ring molecule while -OCH₃ as being its donor decreases the acidity of benzoic acid derivatives. These distinct characters of above presented two kinds of substituents influence the properties of methoxybenzoic acid isomers and their compounds. Moreover the mesomeric, inductive and steric effects are known to affect the properties of aliphatic and aromatic compounds. The inductive effects of each methoxy- group causing the delocalization of the electrons in the complex molecule change its energy state and bring about the conjugation of electrons. Furthermore the mesomeric effects caused by those groups rise the energetic changes in the molecule of the organic compound.

The inductive effect created by those substituents influences mainly the electron density in benzene ring in their *meta*- position, while in

their *para*- position both inductive and mesomeric effects play an important role.

In our earlier papers the synthesis of complexes of Co(II), Ni(II) and Cu(II) with various isomers of di- and trimethoxybenzoic acid anions was described and the investigation of their properties was presented [3-12]. Now we decided to present the preparation of di- and trimethoxybenzoates of Ag(I) in the solid state, and the examination of their properties such as: thermal stability in air, solubility in water, the ways of coordination of carboxylate groups and their crystalline form. In this paper we try to present our consideration concerning the influence of *methoxy*- substituents being in various positions in benzene ring on the properties of analysed silver(I) complexes.

Experimental

Synthesis of the complexes

The 2,3-, 2,4-, 2,6-, 3,4-, 3,5-dimethoxy- and 2,3,4- and 3,4,5-trimethoxybenzoic acids and AgNO₃ used for the preparation of complexes were produced by Aldrich Chemical Company. In the experiments the solution of NH₃aq (25 %) produced by Polish Chemical Reagents in Gliwice (Poland) was also used. The 2,3-, 2,4-, 2,6-, 3,4-, 3,5-dimethoxy- and 2,3,4- and 3,4,5-trimethoxybenzoates with Ag(I) were obtained by the addition of equivalent quantities of 0.1 M ammonium 2,3-, 2,4-, 2,6-, 3,4-, 3,5-dimethoxy- and 2,3,4- and 3,4,5-trimethoxybenzoates (pH ≈ 5) to hot solution containing the nitrate(V) of silver(I) and crystallizing at 293 K. The solids were filtered off, washed with hot water and methanol to remove ammonium ions and dried at 303 K.

Instrumentations

Elemental analysis for C, H was performed by using a Perkin-Elmer CHN 2400 analyser. The contents of Ag⁺ ions were established by ASA method with the use of ASA 880 spectrophotometer (Varian) (Table 1). The IR spectra of complexes were recorded over the range 4000-400 cm⁻¹ using M-80 spectrophotometer (Carl-Zeiss, Jena). Samples for IR spectra measurements were prepared as KBr discs (Tables 2, 3). The X-ray diffraction patterns were taken on a HZG-4 (Carl

Zeiss-Jena) diffractometer using Ni filtered CuK_α radiation. The measurements were made within the range $2\theta = 4-80^\circ$ by means of the Debye-Scherrer-Hull method. Thermal stability and decomposition of the complex was determined by Setaram Setsys 16/18 derivatograph recording TG, DTG and DSC curves. The measurement was made at heating rate of 10K·min⁻¹ with full scale. The samples (7.16-7.78mg) was heated in ceramic crucible in air to 1173K (Table 4). The solubilities of analysed complexes in water were measured at 293 K. Saturated solution of the obtained compounds were prepared under isothermal conditions. The contents of Ag(I) were determined by using ASA 880 spectrophotometer (Varian). The values of solubilities are presented in Table 1.

Results and Discussion

The Infrared spectroscopy

The complexes were characterized by elemental analysis (Table 1) and FTIR spectroscopy (Tables 2,3, and Fig. 1). The characterized frequencies related to the carbonyl group are altered markedly in going from acids to the respective salts. The bands of the $\nu(\text{C}=\text{O})$ (from -COOH groups) present in the spectra of the acids, disappear in the spectra of the complexes and two bands arising from asymmetric and symmetric vibrations of the COO⁻ groups are observed (Table 3) [13-17]. According to spectroscopic criteria and especially with regard to that of Nakamoto [13] the carboxylate groups in the analysed complexes show different modes of coordination. In the 2,3-, 2,6-, 3,5-dimethoxy- and 2,3,4-trimethoxybenzoates they may function as bidentate bridging groups, in the 3,4,5-trimethoxybenzoates as bidentate chelating while in the 2,4- and 3,4-dimethoxybenzoates of silver(I) as monodentate. The bands attributed to asymmetric $\nu\text{C-H}$ stretching modes of the -CH₃ groups are observed at 2980-2928 cm⁻¹. The changes in the values of these frequencies are probably connected with the various influences of inductive, mesomeric and steric effects of *methoxy*- groups on the electron density of the aromatic system. The assignments of bands as symmetric $\nu\text{C-H}$ stretching in -OCH₃ groups are

observed at 2840-2832 cm^{-1} . The bands of asymmetric ($\delta_{\text{as}}\text{CH}_3$) and symmetric ($\delta_{\text{s}}\text{CH}_3$) in plane bending of the $-\text{CH}_3$ groups appear at 1468-1416 cm^{-1} , and 1292-1260 cm^{-1} , respectively. The bands corresponding to the silver-oxygen stretching occur at 496 cm^{-1} and 424 cm^{-1} , in the spectra of 2,6- and 3,5-dimethoxybenzoates, respectively, while those for the other analysed complexes are probably below 400 cm^{-1} [13-17].

X-ray diffraction patterns

The analysis of the diffractograms suggests that the 2,3-, 2,4-, 2,6-, 3,4-, 3,5-dimethoxy- and 2,3,4- and 3,4,5-trimethoxybenzoates of silver(I) are polycrystalline compounds [18]. The some of them are presented in Fig. 2. The structures of the compounds were not determined because their single crystals were not obtained.

Thermal analysis

The thermal stability of 2,3-, 2,4-, 2,6-, 3,4-, 3,5-dimethoxy- and 2,3,4- and 3,4,5-trimethoxybenzoates of Ag(I) was studied in air (Table 4, Fig. 3). All the analysed complexes are anhydrous compounds which decompose in two steps (with the exception of 3,4,5-trimethoxybenzoate of silver(I)). At first they form the unstable intermediate product that next, in the second step, are decomposed to Ag_2O being the final product of decomposition. Heated, the anhydrous 3,4,5-trimethoxybenzoate of Ag(I) is directly decomposed to silver(I) oxide. The combustion process of the organic ligand in the analysed complexes is connected with exothermic effect seen on DSC curves. The thermal stability of anhydrous di- and trimethoxybenzoates increases in the order: 2,3- < 3,4,5- \approx 2,4- < 2,3,4- < 3,4- < 2,6- \approx 3,5-. From the comparison of temperature values of the thermal decomposition it follows that the various position of $-\text{OCH}_3$ substituents in benzene ring influences the thermal stability of complexes. Probably it is connected with the different participations of the inductive and mesomeric effects of *methoxy*-groups in the electron density of the system. In our previously published papers [6, 8, 10-12] it was said that the complexes of 3,5-dimethoxybenzoates with Co(II), Ni(II) and Cu(II) were more thermally stable than those of the remaining isomers. The hydrates of 3,5-dimethoxybenzoates

of Co(II), Ni(II) and Cu(II) losing water molecules in one step form the anhydrous compounds that next are decomposed at higher temperatures than dimethoxy- and trimethoxybenzoates of those elements. Their higher thermal stability is caused by the greater arrangements of the molecule structure and the decay of the steric effects. In these compounds the substituents are placed far from each other in benzene ring. Taking into account the structures of the remaining isomer molecules it is possible to state that the steric effects resulting from the close situated substituents in benzene ring may decrease their thermal stability.

Solubility

The solubilities of 2,3-, 2,4-, 2,6-, 3,4-, 3,5-dimethoxy- and 2,3,4- and 3,4,5-trimethoxybenzoates of silver(I) in water were measured at 293 K (Table 1). They are in the order of 10^{-4} $\text{mol}\cdot\text{dm}^{-3}$. The 2,3,4- and 3,4,5-trimethoxybenzoates of Ag(I) are more soluble salts than those of dimethoxybenzoates.

Conclusions

According to the survey of literature the silver(I) complexes are unstable in air, while our investigations appeared them to be stable compounds with thermal stability being comparable with those hydrates of di- and trimethoxybenzoates of Co(II), Ni(II), and Cu(II). The complexes of Ag(I) are anhydrous compounds with carboxylate groups of various dentates resulting from the different influences of inductive, mesomeric and steric effects of $-\text{OCH}_3$ groups on the electron density of the system depending on their position in benzene ring.

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