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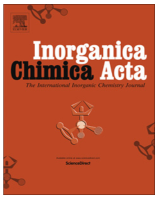

Research paper

Cation-π-complex of Ag(I) ion with 1*H*-indole-5-carboxylic acid – Structural analysis and energetics of the M–L bonds

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This paper aims at filling the gap of governing forces leading to bonded charged Ag^I–ion to unsaturated hydrocarbons comparing with its coordination ability in metal–organics, in particular, carboxylic acids, describing a new, first reported in the literature, very rare case of cation-π–complex of Ag^I–ion with 1H-indole-5-carboxylic acid ($[Ag^I(\eta_2\text{-}C_9H_7NO_2)_3(NO_3)]$) (**1**). Correlation between bonding fusion of Ag^I–ion, examining four interaction modes (π–complex to ethene fragment (I); π–complex to phenyl fragment (II); M–N bond formation (III); and M–O bond formation (IV)) and the energetics of the interacting complex system is carried out. The energetics of M–L bonds is studied using topologic charge density analysis at bond critical points (*bcps*) using experimental crystallographic electron densities. The bond energies are correlated to theoretical quantum chemical bond dissociation energies. The methods of single crystal X-ray diffraction and computational quantum chemistry such as 'atoms in molecules' (AIM); 'natural bond orbital analyses' (NBO) and electrostatic potentials are used. The research takes dual steps associated with: (*i*) increasing the understanding about the molecular forces causing for preferred cation-π–interactions of Ag^I–ions even in presence of classical ligand like a carboxylic acid; and (*ii*) provides a thermodynamic explanation about bonding affinity of Ag^I–ion towards polydentate molecular systems. Clearly then, the paper has fundamental importance for the organometallic and inorganic chemistry. Owing the great significance of the cation-π–interactions in the folding of proteins; neurological signaling in living cells, and many more phenomena in the biological systems, our paper also has an underlined interdisciplinary impact.

1. Introduction

As is mentioned in the 'Abstract' to this paper cation π–interactions, in a general context, play a significant importance in biological systems associated with folding of protein macromolecules, neurological signaling, and many more biological phenomena in the living cells. Thus, they attract significant attention by both experimental and theoretical studies [1]. In particular π–interactions of Ag^I–ion have crucial significance due to the well-known biological activity of the silver both including in its nanoparticle elemental state as well as cationic forms in different oxidation states [2]. Despite the fact that transition metal π–complexes with ethylene and its derivatives have been regarded chemically as among the most important coordination compounds [3] starting with the first organometallic compound of such as type $\{K[PtCl_3(C_2H_4)]\cdot H_2O\}$ (Zeise's salt) isolated in 1827 [3b] determination and structural characterization of π–complexes of Ag^I–ion (or other transition metal ions) are very rare [3]. This lack of knowledge about experimental molecular structure of Ag^I–containing species difficult significantly further understanding the coordination behavior of silver(I) ion; to study in detail nature of M–L bonds; chemical reactivity; thermodynamic stability of the complexes; mechanisms of complex formation, etc. both experimentally and theoretically. Moreover the coordination chemistry of silver(I) ion is further complicated, stabilizing different oxidations states: from elemental Ag^0 to ions having from +1 to +3 oxidation forms. In this context, we go to the note that our study contributes significantly to further understanding of the coordination behavior of silver(I) ion in a so rare known cases of cation-π–complexes. Moreover, in the field of organometallic chemistry of Ag^I–ion many research efforts have been devoted to understanding of coordination behavior of this metal ion and its bonding affinity. However there is a rather lack of knowledge in this field because of in general crystallographic reports are very rate so far. This fact

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difficult significantly a complementary application of crystallographic and quantum chemical methods studying the nature of the Ag–L chemical bond; chemical reactivity of the complexes; their thermodynamic stability; reaction kinetics; mechanisms of complex formation; factors governing the coordination fashion, etc. Moreover only a theoretical analyses and molecular modelling of Ag^I–containing organometallics and metal–organics is a significant research challenge as well. Because of Ag^I–ion exhibits remarkable chemical reactivity and can stabilize diversity of geometries of the metal chromophore, along with its capability to form organometallics and ion···π (η_n)–complexes. In addition, Ag^I–ion, as mentioned above, has great ability to stabilize coordination compounds at different oxidation state from +1 to +3, including Ag^0 in the silver nanoparticles.

2. Experimental

2.1. Analytical methods

The X-ray diffraction intensities were measured on a Bruker Smart X2S diffractometer, using micro source Mo-K_α radiation and employing ω scan mode. An absorption correction based on multiple scanned reflections. The crystal structure was solved by direct methods using SHELXS-97 [1] (Table S1). The structure was refined by full-matrix least-squares refinement against F^2 [4]. Anisotropic displacement parameters were introduced for all non-hydrogen atoms. The hydrogen atoms attached to carbon were placed at calculated positions and refined allowing them to ride on the parent carbon atom. The hydrogen atoms bound to nitrogen and the oxygen were constrained to the positions which were confirmed from the difference map (Fig. S1) and refined with the appropriate riding model, which the exception of the amino and water hydrogen atoms. Structural data block was processed by PLATON and VESTA [4]. The crystallographic refinement parameters are summarized in Table S1. The monopole and multipole ED refinement was carried out by the XD2016 and MoPro v16 program packages [4,5] employing the Hansen–Coppens methodology (Fig. S2). The experimental crystallographic structural factors were further processed by WinGX 2014 [6] towards the data quality. WTANAL and DRK–plot analyses of the structure factors was carried out by the latter program package, in addition to the residual analyse and the THMA one evaluating of the thermal motion on the base on experimentally measured U_{ij}s [7]. The 'bond valence model' and charge density analysis was carried out by WinGX 2014 and Shelxle [8] program packages.

Fig. S5 shows the statistical treatment of the crystallographic data of (**1**). The quality of the data indicators are associated with the data collection and processing of the intensities of the *hkl*–reflections [9,10]. The decision about the multipolar refinement of electron densities is carried out *via* residual analysis. According to the accepted criteria, R-values lower than 10% for high resolution data are accepted as a good quality indicator. The data in Table S1 show R1 = 9.05% for our structure despite the refined disorder (Fig. 1) [10c]. Despite the fact that there are alerts-A in the checkcif file (PLAT 211, https://checkcif.iucr.org/) (See 169-ccdc.cif shown as Supporting information) it is important to note that these alerts are due to the shown data completeness 0.807 (or at about 80%) at θ = 25.35° which has been reduced due to the high number of bad reflections (See the original data collection bi169.raw file shown as Supporting information) collected on the base on quality of the crystals of low dimension 2D thin and stacked objects. On the base on this fact there is difficult to distinguish using the chemometric approaches the atoms types N and C, moreover atoms O1 and Ow2 are disordered. The DRK–plots and correlations between experimentally observed and calculated F_o and F_c values are also indicator for data quality. All deviations are lower than ±2%. In addition, the normal probability plots reveals a Gaussian distribution, which is an indication that there is not systematic error [9,10] (Fig. S5). In this context, the computations of the electronic densities can be regarded as reliable (See Fig. S1 and Table S3). Nevertheless that we operate with a reduced data completeness (above) it is valid to the EDs of all atoms included in the inner coordination sphere of the chromophore (Atoms Ag1/Ag2 (disorder), C4, C18, C21, C22, C24 and C25)). On the other hand the discrepancy between the theory and experiment could also point to bias by the quality of the crystalline samples (plate 2D crystal) [11] and/or perturbation of the atomic positions taking into consideration different coordinates of the disordered atoms (See the coordinates of the complex shown as 169-bomd.pdb, Supporting information).

2.2. Materials and synthesis

The 1*H*-indole-5-carboxylic acid (Sigma-Aldrich) was used for synthesis of (**1**) using equimolar mixture of the acid and $AgNO_3$ (Sigma–Aldrich) preliminary dissolved in 5 mL solvent mixture $CH_3OH:H_2O = 1:1$. The mixture was heated at T = 100 °C for 4 h. To the hot solution are added drops of k.M HCl dissolved in the same solvent mixture. The obtained after a week colorless crystals were filtered off, washed with CH_3OH and dried on P_2O_5 at 298 K. Yield 50%. Chromatographic and mass spectrometric data were obtained as independent verification of the obtaining of (**1**).

2.3. Theory/computations

See Supporting information.

3. Results and discussion

3.1. Crystal structure of (**1**)

Following the general description of the crystallographic analysis of (**1**), we must begin with the fact that the compound (**1**) crystalizes in a centrosymmetric triclinic space group (Table S1, Fig. 1). The coordination fashion of the metal chromophore is $\{[Ag^I\text{-}(\eta_2\text{-}C_9H_7NO_2)_3]^-\}$ interacting with the ethene fragment of the 1H-indole-5-carboxylic acid at molar ratio metal-to-ligand 1:3. In addition the Ag^I–ion is bonded to NO_3^- anion thus forming an Ag^I-C_6O chromophore. On the contrary the bidentate coordination affinity of the nitrate ligand in Ag^I–complexes which has been already described [12] in complex (**1**) inorganic ligand acts as monodentate species. It is important to mention that a ratio M:L = 1:3 in π–complexes not only of silver(I) but other transition metal complexes with ethene [3,1b,13] so that (**1**) is an examples where even increasing of complexity of molecular scaffold of the π–dentate chromophore, the interaction with Ag^I–ion leads to formation of cationic $\{[Ag(\eta_2\text{-}C{=}C)_3]^+\}$ metal ion containing fragment in the organometallics. Nevertheless that there have been reported scarce data about isolation of $\{[Ag(\eta_2\text{-}C{=}C)]^+\}$ chromophore in substituted ethene containing organics as well [13]. The $Ag^I\cdots O(NO_2)^-$ bond length is 2.464 Å, while $Ag^I\cdots\pi$–interactions have lengths within 2.229–2.767 Å. The corresponding bond angles ∠C–Ag–O and ∠C–Ag–C are within 99.1(0)–106.7(1) and 96.5(1)–102.5(6)°, respectively. Nevertheless that disposition of the COOH group in the ligands in (**1**) is suitable for intramolecular hydrogen COOH···O=C(OH) formation, there is found that the two complex units $[Ag^I(\eta_2\text{-}C_9H_7NO_2)_3(NO_3)]$ in the unit cell of (**1**) form dimer *via* intermolecular COOH···O=C(OH) interactions (Fig. 2) with bond lengths COOH···O=C(OH) ∈ 2.536–2.714 Å.