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Synthesis, characterization and DFT studies of two new silver(I) complexes with 3,4-lutidine

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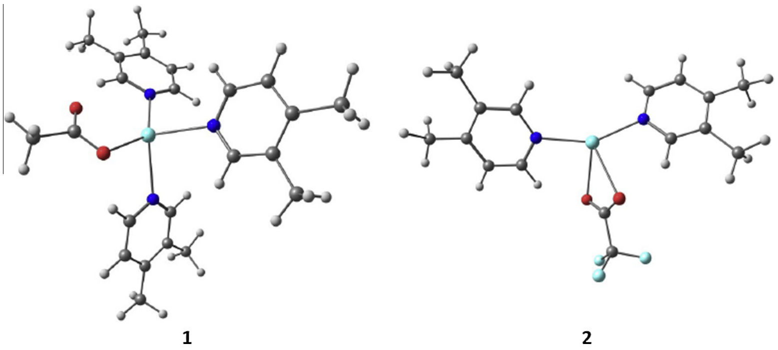
HIGHLIGHTS

- The $[Ag(34lut)_3(OAC)]$; **1** and $[Ag(34lut)_2(TFA)]$; **2** were synthesized and identified.
- Both complexes having distorted tetrahedral coordination geometry around silver ion.
- The OAC is monodentate in **1** while the TFA is bidentate in **2**.
- NBO analyses confirmed the coordination behavior of the COO group in **1** and **2**.
- **1** is predicted to have higher NLO properties than **2**.

GRAPHICAL ABSTRACT

The optimized molecular structure of complexes **1** and **2**.



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ABSTRACT

The synthesis, characterization and molecular structure of two new Ag(I) complexes with 3,4-lutidine (34lut) have been reported. The $[Ag(34lut)_3(OAC)]$; **1** and $[Ag(34lut)_2(TFA)]$; **2** complexes, where OAC and TFA are acetate and trifluoroacetate respectively, have been characterized using elemental analysis, FTIR, NMR and mass spectra. Their molecular structures were calculated using DFT quantum chemical calculations. Both **1** and **2** were found to have distorted tetrahedral geometry around the Ag(I). The spectroscopic properties of the studied complexes have been calculated using the same level of theory. The Infrared vibrational frequencies of the COO stretches confirmed that the OAC is monodentate in **1** while the TFA is bidentate in **2**. The calculated polarizability (α_0) and HOMO–LUMO energy gap (ΔE) values indicated that **1** has higher NLO activity than **2**. The electronic spectra of these complexes are calculated using the TD-DFT calculations. The calculated ^1H NMR chemical shift values using GIAO approach showed good correlations with the experimental data. The interaction energies using the second order perturbation theory have been used to study the different intramolecular charge transfer interactions in the studied complexes. The NBO calculations indicated that both the Ag—O bonds are almost identical in **2** but not in **1**.

Introduction

The use of silver salts in medicine was well known since the 400 B.C [1]. For centuries, silver compounds have been known to possess interesting biological properties and potent antibacterial activities [2–8]. Furthermore, silver compounds have reemerged

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as a viable treatment option for infections encountered in burns, open wounds and chronic ulcers [9–13]. The drug silver sulfadiazine ([Ag((4-aminophenyl)sulfonyl)(pyrimidin-2-yl)azanide]$_n$ in 1968 was used as antibacterial topical cream on burns [13]. Thus, the biological activity of new silver(I) complexes is potentially important [14–25]. Moreover, antibacterial experiments have shown broader antimicrobial activity spectra for silver complexes with Ag—O and Ag—N bonds than with Ag—P and Ag—S bonds [26,27] due to distinctive weak Ag—O and Ag—N bonds in their structures [14,28]. It should be mentioned that, the combination between silver and organic ligands enhances both the antibacterial activity and also decrease the risk of random chemical reactions in wound fluids. From this point of view, there is more need to synthesize more effective and less-toxic Ag-complexes [29,30].

From structural point of view, Ag(I) coordination compounds have received a great deal of attention because this metal ion is known to adopt various coordination numbers and geometries such as linear, trigonal-planar or tetrahedral coordination geometries due to the presence of vacant s and p orbitals. In the recent decades, attention has moved toward finding more applications for such coordination compounds based on functional properties displayed by these materials [31–33]. One such property that has attracted much interest is in the area of non-linear optics (NLO) [32–39]. It was reported by Jin et al. that silver(I) complexes have promising activity as potential NLO materials [40]. These complexes were found to have better nonlinear optical properties than the free ligand. Important factors that affect the NLO activity of a compound are related to its electronic and spectroscopic properties such as dipole moment, polarizability and the ability of electronic excitation.

In the present work we aimed to synthesize and characterize two new silver(I) complexes of 3,4-lutidine (34lut) with acetate and trifluoroacetate anions. The synthesized complexes were characterized using different spectroscopic techniques such as FTIR, NMR and mass spectra. Their molecular structures, spectroscopic and electronic properties have been calculated using DFT calculations. NBO analyses were used to calculate the stabilization energies of the different intramolecular charge transfer interactions (ICT) occur in their structures. Moreover, the NBO calculations were used to describe the coordination behavior of the carboxylate group in the studied complexes. Also, the ^{1}H NMR chemical shifts were calculated using GIAO method and correlated with the experimental data.

Experimental details

Synthesis

All chemicals were reagent grade and used without further purification.

Silver acetate and silver trifluoroacetate were prepared by the same method reported by Logvinenko et al. [41]. The [Ag(34lut)$_3$(OAc)]; **1** and [Ag(34lut)$_2$(TFA)]; **2** complexes were synthesized by mixing 10 ml of the aqueous silver(I) salt (1.0 mmol) solution with 15 ml ethanolic solution of the 3,4-lutidine ligand in the proper molar ratio (2 mmol for **1** and 3 mol for **2**). The resulting white precipitate is dissolved by adding few drops of the corresponding acid of the silver salt. After few days white amorphous plates were obtained and the products were filtrated off and washed with 1:10 water ethanol solution then air dried to give 0.371 g, 76.04% for **1** and 0.303 g, 69.56% for **2** with respect to the ligand.

Analytical data (%):

Complex 1: Calc: C, 56.56; H, 6.19; N, 8.60; Ag, 22.09. *Found:* C, 56.33; H, 6.47; N, 8.56; Ag, 22.42. ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 2.50–2.51$ (18H, 6CH$_3$ substituents), $\delta = 3.501–3.73$ (3H, 1CH$_3$of acetate), $\delta = 7.42–7.76$ (9H, heteroaromatic CH). MS *m*/*z* 488 [M]$^+$.

Complex 2: Calc: C, 44.16; H, 4.17; N, 6.44; Ag, 24.79. *Found:* C, 44.50; H, 4.361; N, 6.78; Ag, 24.488. ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 2.25$ (12H, 4CH$_3$), $\delta = 7.26–8.34$ (6H, heteroaromatic CH). MS *m*/*z* 435 [M]$^+$.

Physical measurements

The elemental analyses of carbon, hydrogen and nitrogen were carried out using Perkin–Elmer analyzer in the centre of mycology and biotechnology at El-Azhar University. The silver content was measured by the inductively coupled plasma (ICP) in the City of Scientific Researches & Technological Applications, Alexandria University. The Infrared spectra were recorded on a Brucker IFS-125 model FTIR spectrophotometer as KBr pellets in the range of 400–4000 cm^{-1} in the central lab, faculty of science, Alexandria University. The ^{1}H NMR spectra measured using 300 MHz JEOL NMR spectrometer using dimethylsulfoxide (DMSO-d_6) as solvent (Fig. S1 Supplementary materials). The mass spectra in DMSO as solvent were carried out using Shimadzu 5050 QA at the central lab, Cairo University (Fig. S2 Supplementary materials).

Computational details

All calculations for the [Ag(34lut)$_3$(OAc)] and [Ag(34lut)$_2$(TFA)] complexes were carried out using Gaussian 03W software [42]. The quantum chemical calculations have been performed using the B3LYP level of theory supplemented with the 6-31G(d,p) basis set for all nonmetal atoms and ECP/LANL08 for silver [43]. All molecular structures were visualized using Chemcraft [44] and GaussView [45] softwares. The geometries were optimized by minimizing energies with respect to all geometrical parameters without imposing any molecular symmetry constraints. The infrared vibrational frequencies and intensities were calculated using the same level of theory at the optimized geometry of the studied compounds. The calculated vibrational wavenumbers are scaled down using single scaling factor [46]. Also, the electronic spectra of the studied compounds were calculated using TD-DFT method. The natural bond orbital (NBO) calculations [47a] were performed using NBO 3.1 program as implemented in the Gaussian 03W package at the DFT/B3LYP level. The second order Fock matrix was carried out to evaluate the donor–acceptor interactions in the NBO basis [47b].

Results and discussion

Molecular structure

The optimized molecular geometries of the studied complexes are shown in Fig. 1 while the optimized geometric parameters (bond distances and bond angles) are given in Table 1. For complex **1**, the Ag(I) is coordinated to three 34lut ligands through the ring nitrogen and one acetate group through one of its oxygen atoms. The Ag—N3, Ag—N13 and Ag—N50 bond distances are calculated to be 2.557 Å, 2.384 Å and 2.516 Å respectively. The Ag—O18 and Ag—O19 bond distances are 2.837 Å and 2.307 Å respectively. The former distance is too long and so, the acetate group in **1** acting as monodentate ligand through one oxygen atom [48]. Hence, distorted tetrahedral coordination geometry around silver ion is predicted. The calculated N3—Ag—N13, N3—Ag—N50 and N13—Ag—N50 bond angles are predicted to be 120.1°, 98.4° and 98.2° respectively. The O19—Ag—N50, O19—Ag—N3 and O19—Ag—N13 bond angles are calculated to be 113.1°, 87.6° and 134.9° respectively. These results are in good agreement with the