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## 1-Pentamethylbenzyl-3-<sup>n</sup>buthylbenzimidazolesilver(I)bromide complex: Synthesis, characterization and DFT calculations



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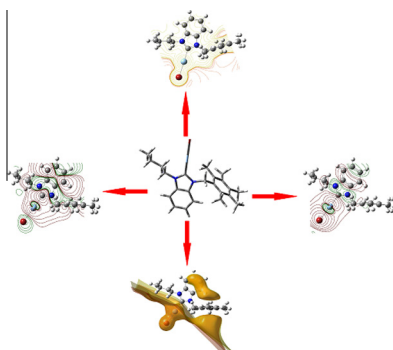
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### HIGHLIGHTS

- The novel silver(I) complex of 1-pentamethylbenzyl-3-<sup>n</sup>buthylbenzimidazolesilver(I) bromide was synthesized.
- The title complex was solved by X-ray diffraction, FT-IR, UV–vis and NMR spectroscopies.
- To obtain further information, DFT calculations were performed on silver(I) complex.
- The NLO, NBO and HOMO–LUMO analysis were carried out on silver(I) complex.
- DFT levels successfully predict the different properties of silver(I) complex.

### GRAPHICAL ABSTRACT

The electrostatic potential, contour plots of HOMO, LUMO and ESP for silver(I) NHC complex.



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### ABSTRACT

A novel NHC complex of silver(I) ion, 1-pentamethylbenzyl-3-<sup>n</sup>buthylbenzimidazolesilver(I)bromide, was prepared and fully characterized by single crystal X-ray structure determination. FT-IR, NMR and UV–vis spectroscopies were employed to investigate the electronic transition behaviors of the complex. Additionally, the molecular geometry, vibrational frequencies, gauge including atomic orbital (GIAO) <sup>1</sup>H and <sup>13</sup>C chemical shift and electronic transition values of silver(I) complex were calculated by using density functional theory levels (B3LYP and PBE1PBE) with LANL2DZ basis set. Also, the vibrational frequencies were supported on the basis of the potential energy distribution (PED) analysis calculated for PBE1PBE level. We were also investigated total static dipole moment ( $\mu$ ), the mean polarizability ( $\langle\alpha\rangle$ ), the anisotropy of the polarizability ( $\Delta\alpha$ ), the mean first-order hyperpolarizability ( $\langle\beta\rangle$ ) of the title complex. Natural bond orbital (NBO) analysis was performed to determine the presence of hyperconjugative interactions, and charge distributions.

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### Introduction

The legendary journey of NHC salts and their transition metal complexes started in 1968. Öfele [1] and Wanzlick and

Schönherr [2] reported the synthesis of the first chromium and mercury NHC complexes uninformed from each other. In 1991, Arduengo et al. [3] isolated the first silver(I) NHC complex. Due to their better sigma donor ability, NHCs have attracted a rising interest from the pioneers of organometallic chemistry world. During the past decades N-heterocyclic carbenes (NHCs) have emerged as a versatile class of dative ligands in metal

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coordination chemistry, particularly in the field of homogeneous catalysis [4,5].

The metal–NHC complexes exhibit excellent catalytic activity for many practically useful organic transformations, notably the C–C and C–N cross coupling reactions [6–9], C–H bond activation [10–11] as well as the extremely useful metathesis reaction [12,13]. Among the NHC–metal complexes, Ag–NHC complexes have been utilized for several purposes.

Because of their facilitation of “fine tuning”, transition metal–NHC complexes have been widely studied for their catalytic activity [14]. The NHC complexes of coinage metals are concessive compounds with their antitumor activity besides being good catalysis. But their costs shadowed the charm. As an affordable alternative to other coinage metals such as platinum and gold, silver has seemed to be a suitable metal to form complexes of NHCs for industrial demands. Silver–NHCs were studied for their antimicrobial activity by Youngs and his co-workers in 2004 [15]. For a long term of study, most researchers synthesized these complexes for mainly two purposes; for transmetallation and for antimicrobial activity. But recently silver–NHCs have given rise to an untouched field of study with their antitumor activity [16] and catalytic activity [17].

Quantum chemical calculation is one of the recent emerging tools in unraveling physical and chemical properties of molecules. The availability of software packages makes the quantum chemical computation a simple task. The molecular structure, harmonic force fields, vibrational wavenumbers, electronic transitions as well as IR intensities and Raman activities of organic molecules have been investigated by using density functional theory (DFT) computations. In our ongoing research, we have recently synthesized Ag(I) NHC complex, and a combined investigation of the geometrical parameters, fundamental frequencies, GIAO  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts and electronic transitions of the silver(I) complex were experimentally investigated. In order to help to make further investigation on the properties of the complex, DFT calculations were performed. Since it meets with the requirements of being accurate, easy to use and fast enough to allow the study of relatively large molecules of transition metal complexes, density functional theory is frequently used to examine the electronic structure. It is well known that the comparison of the experimental and theoretical results is very important in modeling technology. And so, these calculations are valuable for providing insight into molecular analysis.

## Materials and methods

### General remarks

Diffraction data for the complex were collected with Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 296(2)K using graphite monocromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Diffraction data were collected over the full sphere and were corrected for absorption. The data reduction was performed with the Bruker SMART [18] program package. For further crystal and data collection details see Table 1. Structure solution was found with the SHELXS-97 [19] package using the direct-methods and was refined SHELXL-97 [20] against  $F^2$  using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure model on calculated positions. Geometric calculations were performed with Platon [21]. FT-IR was recorded on SHIMADZU IR-PRESTIGE-2 spectrophotometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured in dimethyl sulfoxide- $d_6$  (DMSO- $d_6$ ) on spectrometer at VARIAN Infinity Plus 300 and at 75 MHz, respectively.  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are referenced to the internal deuterated solvent.

**Table 1**

Crystal data and structure refinement parameters for complex.

|   |   |
|---|---|
| Formula   | $\text{C}_{23}\text{H}_{28}\text{CuN}_2\text{BrAg}$               |
| Formula weight (g)                                  | 520.25  |
| Temperature (K)                                     | 296(2)  |
| Wavelength (Mo $\text{\AA}$ )                       | 0.71073   |
| Crystal system                                      | Monoclinic  |
| Space group   | $P2_1/c$  |
| <i>Unit cell dimensions</i>                         |   |
| <i>a</i> ( $\text{\AA}$ )                           | 10.519(2)   |
| <i>b</i> ( $\text{\AA}$ )                           | 15.069(3)   |
| <i>c</i> ( $\text{\AA}$ )                           | 13.819(3)   |
| $\beta$ ( $^\circ$ )                                | 97.427(10)  |
| Volume ( $\text{\AA}^3$ )                           | 2172.0(8)   |
| <i>Z</i>  | 4.00  |
| Calculated density ( $\text{g cm}^{-3}$ )           | 1.591   |
| Absorption coefficient ( $\text{mm}^{-1}$ )         | 2.777   |
| $F(0,0,0)$  | 1048.0  |
| Crystal size (mm)                                   | $0.54 \times 0.29 \times 0.16$                                    |
| $\theta$ ranges ( $^\circ$ )                        | 1.95–28.49  |
| Index ranges  | –14 < <i>h</i> < 13<br>–20 < <i>k</i> < 17<br>–15 < <i>l</i> < 18 |
| Reflections collected/unique                        | 24976/5358 [ $R(\text{int}) = 0.0545$ ]                           |
| Completeness to theta                               | 28.41 99.4%   |
| Absorption correction                               | Integration   |
| Refinement method                                   | Full-matrix least-squares on $F^2$                                |
| Data/restraints/parameters                          | 5358/0/232  |
| Goodness-of-fit on $F^2$                            | 1.108   |
| Final <i>R</i> indices [ $I > 2\sigma(I)$ ]         | $R_1 = 0.0505$ , $wR_2 = 0.1392$                                  |
| <i>R</i> indices (all data)                         | $R_1 = 0.0671$ , $wR_2 = 0.1468$                                  |
| Largest diff. peak and hole ( $\text{e \AA}^{-3}$ ) | 3.486 and –2.112  |

Routine UV–vis spectra were obtained in a quartz cuvette on an Agilent 8453 UV–vis spectrophotometer.

### Synthesis

NHC salt and corresponding silver complex have been synthesized in high yields via the conventional methods in our laboratory. The chemicals such as benzimidazole, 1-bromobutane and pentamethylbenzene were acquired from suppliers and used without further purification. Pentamethylbenzylbromide and other intermediate products were synthesized according to the methods in literatures [22,23]. Silver complex was synthesized via  $\text{Ag}_2\text{CO}_3$  as silver base in a 50 mL schlenk tube and reaction was monitored by disappearing of the insoluble solid particles in reaction mixture. The stages of synthesis are given in Fig. 1.

### Computational details

All calculations were performed by using GAUSSIAN 09 package program [24], and the obtained results were visualized with the aid of Gauss View-5 software [25]. The structural properties and vibration spectra of the silver(I) NHC complex were determined through the application of DFT/B3LYP [26,27] and DFT/PBE1PBE [28] with LANL2DZ basis set [29–31]. B3LYP is the Becke’s three-parameter hybrid model using the Lee–Yang Parr correlation functional. PBE1PBE is the generalized-gradient-approximation exchange–correlation functional of Perdew, Burke, and Ernzerhof. The LANL2DZ effective core potential basis set was used for all of the calculations. The LANL2DZ basis replaces the 1s through 2p electrons of the heavy atoms with a potential field for a considerable computational savings. Moreover, the assignments of vibrational modes of the silver(I) complex were performed on the basis of potential energy distribution (PED) by using VEDA 4 program [32,33].  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR chemical shifts are calculated within GIAO approach [34,35] which is one of the most common approaches for calculating nuclear magnetic shielding tensor. The electronic

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