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Periodic DFT Study of Molecular Crystals

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***Abstract* — Two molecular crystals have been studied using the first-principles density functional theory calculations within the generalized gradient approximation (GGA). It was found that the Perdew–Burke–Ernzerhof (PBE) GGA exchange-correlation functionals are adequate for the mentioned systems. Obtained results show that it is possible to reproduce very well the geometry of at least some molecular crystals if computational parameters are chosen adequately. In addition to reproducing crystalline structures of the compounds in close agreement with the available experimental data, the present work reports analysis on the chemical bonding in the materials and gives total and partial density of states of these molecular crystals for the first time.**

***Index Terms*—Molecular crystals; Structure; Electronic properties; DFT.**

I. INTRODUCTION

Organometallic compounds recently have found numerous applications in different areas: silver(I)-N and silver(I)-O bonding compounds are known as potential bioinorganic materials [1]. Silver(I) ions have long been known to have inhibitory and bacterial effects [2]. Silver(I) complexes also show antimicrobial activities [2].

Despite a progress in experimental synthesis and molecular design of different silver(I) complexes [3] it is needed a better understanding of these systems at the fundamental quantum level. In the present research, a quantum mechanical treatment has been carried out through the density functional theory (DFT) computations. On the other hand, prediction of molecular crystal structures computationally has been considered an impossible mission. In particular, there are exist some suggestions that DFT cannot deal accurately with systems like molecular crystals due to inadequate treatment of Van der Waals forces, which are the weak intermolecular forces arising from quantum induced instantaneous polarization multipoles in molecules and are dominant forces in molecular organic crystals at ambient state. Nevertheless, in the present work, we apply standard DFT technique to study Bis(1*H*-imidazolium-κN^3)silver(I) nitrate and cyclic amide complex $Ag_2(C_4H_4NO_2)_2(H_2O)$, and show that this approach is adequate for the molecular compounds if corresponding computational parameters such as cut-off energy, *k*-point grid as well as pseudopotentials are carefully chosen and optimised for a given system. If periodic DFT computations are able to reproduce sufficiently good the geometry of a given molecular crystal, then it allows performing very precise studies on electrical, electronic, magnetic and other features which could be of interest for the future scientific and technological applications.

II. OUTLINE OF THE METHODOLOGY

Vienna *ab initio* Simulation Package (VASP) [4] based on the DFT approach has been utilized in the present work. The interaction between the core electrons and the valence electrons is implemented through the projector augmented wave (PAW) method [5] while the PBE [6] exchange-correlation functionals are used throughout the work.

In case of the Bis(1*H*-imidazolium-κN^3)silver(I) nitrate, a cut-off kinetic energy of 800 eV is used by converging the total energy to < 1 meV. Γ-centred Monkhorst-Pack (MP) grid with a 0.035 $Å^{-1}$ separation was applied, which corresponds to a *k*-point mesh of 6x3x2 for the exploited 92-atom supercell of the this crystal possessing orthorhombic $P2_12_12_1$ crystalline lattice. The above-mentioned parameters were obtained through the atomic relaxation until all the forces were < 0.008 eV/Å and equilibrium state of the system was achieved. For the $Ag_2(C_4H_4NO_2)_2(H_2O)$ crystal, a cut-off energy of 900 eV was used by converging the total energy to < 1 meV. Γ-centred Monkhorst-Pack (MP) grid with a 0.03 $Å^{-1}$ separation was applied, which corresponds to a *k*-point mesh of 5x5x2 for the exploited 100-atom supercell. The crystalline lattice is monoclinic $P2_1/n$. The previously mentioned parameters were obtained through the atomic relaxation until all the forces were < 0.01 eV/Å.

In order to take into account strong electronic correlation of the Ag-*d* electrons, we included an intra-site Coulomb repulsion *U*-term on the *d* projector of the Ag atom [7]. Value of *U* parameter ($U = 3.5$ eV) was optimised within the present study by fitting crystal structure results to the experimental data.

III. RESULTS

A. Bis(1H-imidazolium-κN3)silver(I) nitrate

Bis(1*H*-imidazolium-κN^3)silver(I) nitrate consists of $[Ag(C_3N_2H_4)_2)]^+$ cations and $(NO_3)^-$ anions. The Ag(I) atom

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exhibits a AgN_2 linear coordination geometry arising from two N atoms of imidazole molecules. The uncoordinated nitrate anion interacts with imidazole by hydrogen bonding, generating a one-dimensional supramolecular chain. Through the DFT+U calculations we managed to reproduce quite well the equilibrium geometry of this crystal. The orthorhombic crystalline lattice parameters were found to be equal to $a = 5.08$ Å, $b = 11.04$ Å and $c = 18.43$ Å, which are rather close to the experimentally obtained numbers [8] being equal to $a = 4.9941$ Å, $b = 10.9250$ Å and $c = 18.0729$ Å. Computationally obtained cell volume is about 1034.22 Å^3, which is only 4.8% larger compared to the experimentally reported figure of 986.07 Å^3 [8]. Larger lattice parameters and cell volume are obtained due to larger hydrogen-bond lengths found in the theoretical calculations. As one can see from Table I, computed C-C, C-N and O-N bond lengths practically matched the experimental ones, the Ag-N bond length only slightly exceeds the one acquired from the X-ray data whereas the N-H and C-H bond lengths are considerably larger compared to those found experimentally.

TABLE I.
BONDS AND ANGLES

Bond	Calculated (Å)	Experimental (Å)
Ag–N	2.16	2.112
C–H	1.34	0.930
C–C	1.38	1.348
C–N	1.37	1.371
N–H	1.04	0.860
O–N	1.26	1.240
Angles	**Calculated (°)**	**Experimental (°)**
N–Ag–N	173.57	172.62
C–N–C	106.15	105.8
C–N–Ag	130.95	126.3
C–N–H	126.36	126.1
O–N–O	120.41	121.5
N–C–N	110.66	111.2

Selected bond-lengths and angles formed by the chemical bonds obtained by the DFT+U computations in comparison to the experimental X-ray measurements [8], of the Bis(1H-imidazolium-κN3)silver(I) nitrate molecular crystal.

Table I also shows data on main angles between the chemical bonds in the system. The computed angles are in very good concordance with the experimental data, which implies that the DFT indeed can be applied to at least some molecular crystals describing satisfactorily intermolecular interactions. The effectiveness of DFT approach might depend, however, on careful selection of some computational parameters. Two imidazole ligands are reproduced to be planar according to the experimental findings. As shown elsewhere [9], the relative orientation of the imidazole ligands might be influenced by many factors. Usually, internal electrostatic interactions and steric constraints of the ligand could be of significance to determine ground state binding orientation. Rather long axial Ag-N bonds in the Bis(1*H*-imidazolium-κ*N*^{3})silver(I) nitrate could lead to very weak π-bonding between the imidazole and nitrogen and consequently relative parallel orientation of the imidazole pairs.

Total density of states (DOS) is depicted in Fig. 1. A strong peak around -21 eV is formed by the N 2s AOs with a considerable admixture of the C 2s states and some smaller contributions from the C 2p AOs and N2p AOs and O 2s states. N 2s as well as C 2s and C 2p AOs are responsible for a narrow peak observed around -17 eV. An energy band which can be considered as the upper valence band (VB) is formed by a number of sub-bands, the widths of which range from 0.5 eV to 1.8 eV. The first sub-band is noticeable between -10.5 and -8.5 eV and is predominantly composed of the N 2p and C 2p states. Further up in energy, a strong peak is observed at -7.2 eV with important contributions from the N 2p as well as both O 2s and O 2p AOs. A sub-band between -6.0 and -4.5 eV is due to the N 2p and C 2p AOs with an admixture of H 1s states as well. At higher energies, a strongest sub-band is found being situated between -3.2 and -1.9 eV. The composition of this sub-band is predominantly due to the O 2p AOs with a strong admixture of the N 2p and Ag 4d states. The top of the upper VB including the highest occupied molecular orbital (HOMO) is formed primarily by the C 2p states. The conduction band (CB) bottom shows a sharp peak around 3 eV originating from the mixture of the N 2p and O 2p AOs. The higher CB states, situated between 4 and 9 eV are due to the N 2p, C 2p as well as both Ag 5s and Ag 5p AOs. The energy region between the upper VB and the unoccupied CB states results in the forbidden energy-gap with a width of approximately 3.0 eV. The value of band-gap width implies that the crystal might be considered as a wide band-gap semiconductor. However, in order to exhibit electrical conductivity similar to inorganic wide band-gap semiconductors, the molecular crystal should possess free electrons or free holes since typical current carriers in organic semiconductors are holes and electrons in π-bonds. Although normally organic compounds are insulators their constituent molecules have π -conjugate systems, and electrons can move via π -electron clouds, especially by hopping, tunnelling or some another related mechanism. In order to create free electron or free hole states in the Bis(1*H*-imidazolium-κ*N*^{3})silver(I) nitrate it would be necessary to apply some doping mechanism which would be worth of a separate study.

Bader population analysis [10] has been exploited to calculate charges on atoms. It was deduced that oxygens have charges between -0.43 *e* and -0.52 *e* depending on atom, it is necessary to state that all O atoms form chemical bonds with the N atoms. Nitrogens are positive, i.e. their charges are between 0.61 *e* and 0.65 *e*, if they form chemical bonds with the O atoms. On the contrary, the N atoms having chemical bonds with C atoms are negative, i.e. their Bader charges are between -1.05 *e* and -1.16 *e*, respectively. Carbons themselves are found to have charges between 0.27 *e* and 0.44 *e* in case of the C-C bonds; whereas the corresponding charges on C atoms are between 0.81 *e* and 0.96 *e* if they are situated between two N atoms. Charges on the H atoms are between 0.05 *e* and 0.14 *e* if they form bonds with the C atoms whereas the corresponding numbers

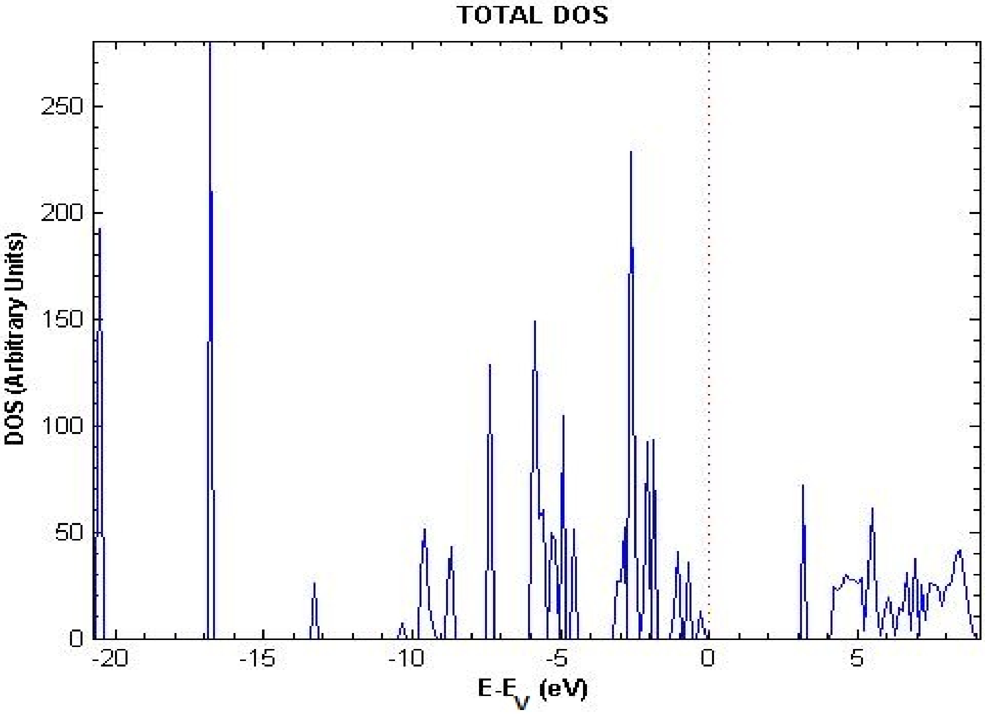

Fig. 1. Total DOS of the Bis(1H-imidazolium-κN3)silver(I) nitrate molecular crystal. The band-gap width is found to be approximately 3.0 eV

are between 0.46 *e* and 0.49 *e* if they are connected to the N atoms. Finally, the atomic charge on each one of the Ag atoms is equal to 0.40 *e*. The chemical bonding between the metal (Ag) atom and its closest N atoms are essentially ionic. N atoms, which find themselves to be close to one of the Ag atoms, have charges between -1.05 e and -1.16 e while the Ag atoms are rather positive as stated before. The same implication can be drawn from the electronic density map (Fig. 2) which shows the region surrounding one of the Ag atoms. Electronic density mainly is concentrated on the two Ag-closest N atoms.

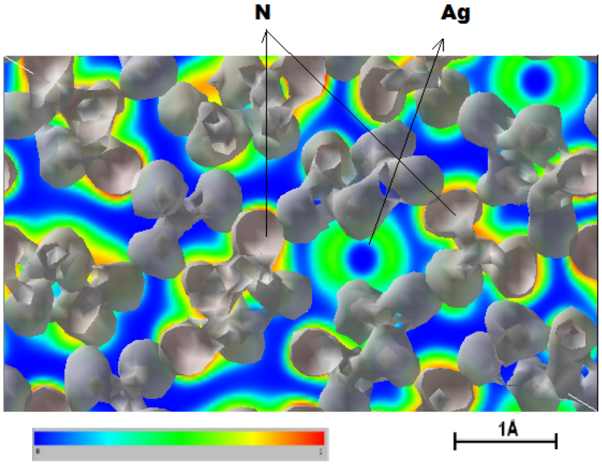

Fig. 2. Electronic density plots are taken around one of the Ag atoms and projected on the (011) plane. The electronic density of chemically active valence electrons is mainly concentrated on the Ag-nearest N atoms showing the significance of ionic character in the chemical bonding between the metal (Ag) atom and its vicinity. Isosurfaces (in grey) that encloses a specific fraction of the atom´s electron probability are shown additionally.

B. Silver cyclic amide complex Ag2(C4H4NO2)2(H2O)

Silver cyclic amide complex $Ag_2(C_4H_4NO_2)_2(H_2O)$ structure has a butterfly-shaped $[Ag(C_4H_4NO_2)_2]$ dimer containing an eight-membered-ring. One of the Ag atoms is four-coordinate, with only Ag-O bonds, meanwhile the other Ag atom is two-coordinate, with Ag-N bonds exclusively. In this crystal, the multiple bonding capabilities of the groups in the system ease multiple ligand-Ag^+ contacts, which include intermolecular bonding via an Ag-O bond [11]. The DFT+*U* calculations managed to reproduce satisfactorily the geometry of the compound. The monoclinic crystalline lattice parameters were obtained to be equal to a = 8.74 Å, b = 8.09 Å, c = 17.83Å. The corresponding experimental data [11] are a = 7.6776 Å, b = 8.0431 Å, c = 17.8184 Å. Generally, chemical bond-lengths are found somewhat larger than the experimental results (Table II). The computed volume of the cell is 1258.94 Å^3, which is also larger compared to the experimental value of 1089.85 Å^3 (15.5%), mainly due to the larger a parameter. Nevertheless, main reason of larger lattice parameters and cell volume are due to larger hydrogen-bond lengths found in the theoretical calculations. In experimental measurements [11] methylene H atoms are placed within the crystal using a riding model, which might produce mistake in determining real H sites. Table II also gives the angles found between the chemical bonds in the system. Most of the obtained angles are in concordance with the experimental results, but there are some discrepancies as well. In general, structure of the computed compound is rather close to the experimental findings.

DOS pattern of the $Ag_2(C_4H_4NO_2)_2(H_2O)$ crystal is shown in Fig. 3. The C 2s and 2p AOs with a considerable

TABLE II
CHARGES AND DISPLACEMENTS

Bonds	Calculated (Å)	Experimental (Å)	Bonds	Calculated (Å)	Experimental (Å)
Ag1-N1	2.12	2.077	Ag2-O2	2.56	2.365
Ag1-N2	2.12	2.095	Ag2-O4	2.30	2.38
Ag1…Ag2	3.26	3.1418	Ag2-O5	2.17	2.41
Ag1…Ag1	3.31	3.2261	Ag2-O1	2.44	2.447
Angles (º)	**Calculated (Å)**	**Experimental (Å)**	**Angles (º)**	**Calculated (Å)**	**Experimental (Å)**
N1-Ag1-N2	162.00	165.55	O2-Ag2-O1	118.92	123.74
O2-Ag2-O4	116.21	134.2	O4-Ag2-O1	78.81	74.98
O2-Ag2-O5	88.17	79.03	O5-Ag2-O1	76.56	87.71
O4-Ag2-O5	147.07	146.73			

Selected bond-lengths and main angles in the Ag2(C4H4NO2)2(H2O) molecular crystal obtained by the DFT+*U* computations in comparison to the experimental measurements [11].

admixture of the O 2s and O 2p states are forming a strong peak around -21 eV. There are contributions for both α and β spin sub-systems. The next peak is around -18 eV being composed mainly by the N 2s states, with some contributions of the O 2s states, but only for the α spin. Around -14 eV there is a peak that has only contributions for β spin sub-system and is composed predominantly by the C 2s and H 1s states. These states are also contributing to the peak at about -11 eV. For the energy range between -10 eV and -5 eV, the band is formed from the C 2s, C 2p and N 2p states. Further up in energy, from -5 eV to the top of the upper VB, it is finally possible to see contributions from the Ag atoms. These contributions are mainly from the Ag 4d AOs with some admixture of O 2p AOs as well. The top of the VB is mainly due to the O 2p AOs. The gap from the HOMO to the LUMO is around 3.5eV. This value, known as the band-gap width, implies that the crystal could be considered as a wide band-gap semiconductor similar to the previously described Bis(1*H*-imidazolium-κN^3)silver(I) nitrate. The conduction band is composed mainly of the Ag 5s and Ag 5p states with admixture from the C 2p and O 2p AOs.

The Bader population analysis shows that the O atoms have charges between -0.42 *e* and -0.96 *e* depending on their neighbours. The atoms forming chemical bonds with an Ag atom are more negative (-0.90 *e* to -0.96 *e*) compared to those O atoms of a H_2O complex (-0.42 *e*). The N atoms have a charge between -0.90 *e* and -0.96 *e*. There are two

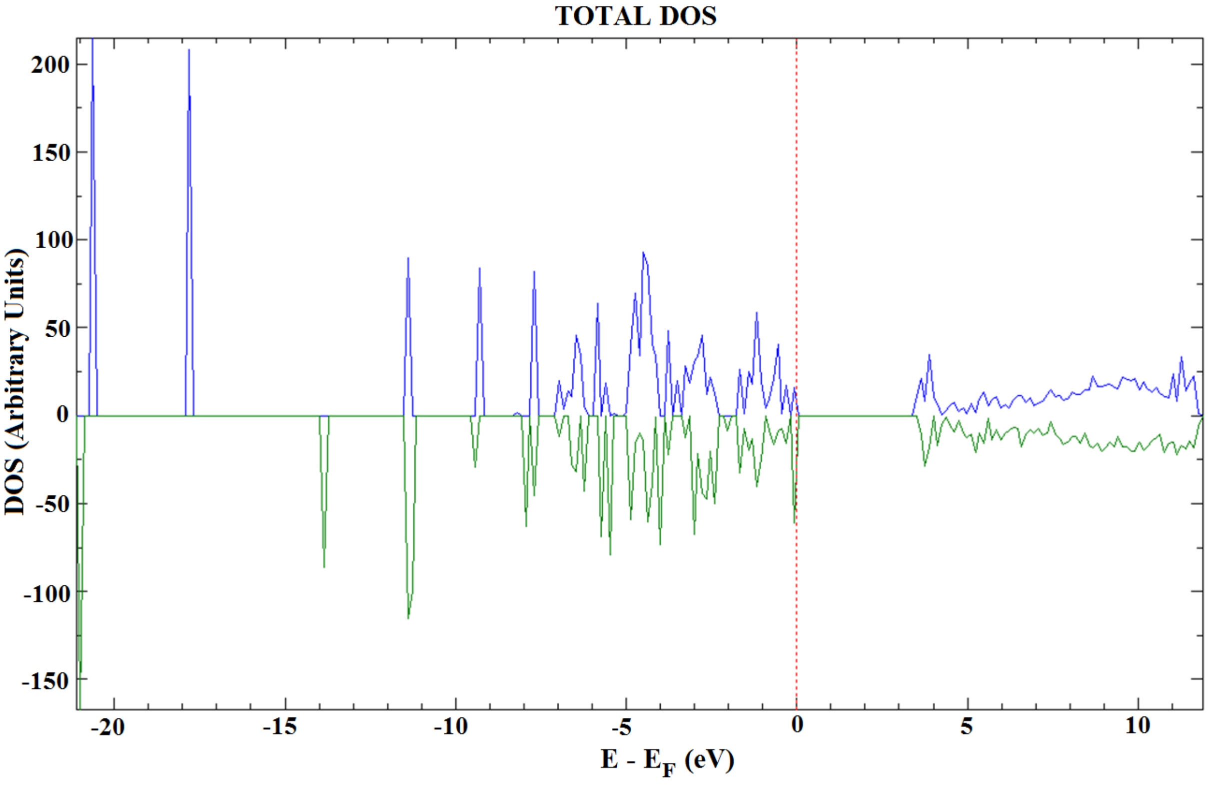

Fig. 3. Total DOS of the Ag2(C4H4NO2)2(H2O) molecular crystal. The band-gap width is found to be approximately 3.5 eV.

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types of C atoms: some of them are C-N and C-O bonded, and the rest are C-C and C-H bonded. For the first type of C atoms, charges are between 0.89 *e* and 1.09 *e*, whereas the other type C atoms have charges between 0.01 *e* and 0.08 *e*. The Bader population analysis implies that the first type C atoms are more ionic compared to those forming second type bonds, which are more covalent. The H atoms have rather small charges close to 0.0 *e*. Finally, the atomic charges on the Ag atoms are between 0.42 *e* and 0.72 *e*.

The important result of our investigation is discovery of local magnetic moments on some of the O atoms situated close to two metal (Ag) atoms. The magnitude of magnetic moments on these oxygens is found to be around 1.03 μ_B. The Ag atoms also exhibit magnetic moments being equal to 0.28 μ_B and 0.12 μ_B for Ag atoms forming chemical bonds with N and O atoms, respectively. This outcome underlines the importance of using periodic model in study of molecular crystals.

IV. CONCLUSIONS

Using first-principles DFT+*U* approach, electronic structure of two molecular crystals has been studied. We demonstrate that periodic DFT methodology can be applied successfully to at least some molecular crystals since we reproduce very well the structure of both systems. The bond lengths and angles between the principal chemical bonds are also found in agreement with the existing experimental results. The only disagreement is for the H bonds which are larger compared to the corresponding experimental numbers. Notwithstanding, this discrepancy does not necessarily mean that our results are wrong since the experimental estimation of the H positions can be erroneous.

The computed density of states of these systems implies that they can be considered as a wide band-gap semiconductors with the band-gap widths being close to 3.0 eV and 3.5 eV for the Bis(1*H*-imidazolium-κN^3)silver(I) nitrate and $Ag_2(C_4H_4NO_2)_2(H_2O)$ crystal, respectively. Valence electronic density plots as well as Bader charges on atoms indicate that the metal (Ag) atom has strong ionic bonding with its neighbouring either O or N atoms.

The main conclusion of our paper is that a periodic DFT model can be used to reproduce rather well crystalline structure and the main geometrical parameters of at least some of the molecular crystals, if computational parameters are chosen adequately. The availability of periodic DFT models for molecular systems allows to study electrical, electronic, magnetic and the other features at more precise level and thus opens new possibilities in research of these systems at the fundamental quantum level.

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