Search for potential minimum positions in metal-organic hybrids, $(C_2H_5NH_3)_2CuCl_4$ and $(C_6H_5CH_2CH_2NH_3)_2CuCl_4$, by using density functional theory

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Abstract. The ab-initio density functional theory analysis was applied to metal-organic hybrids, $(C_2H_5NH_3)_2CuCl_4$ (EA) and $(C_6H_5CH_2CH_2NH_3)_2CuCl_4$ (PEA), in order to estimate possible muons stopping positions. Six potential minimum positions and eight ones were revealed in PA and PEA, respectively. Those potential minimum positions can be regarded as initial stopping positions of injected muons. All of expected potential minimum points in EA were near and around the apical Cl and the CuCl$_6$ plane of the CuCl$_6$ octahedra. Instead, in the case of PEA, two of eight positions were close to the phenyl ring giving a possibility that there would be muon states which couple surrounding electrons via a radical formation.

1. Introduction

Metal-organic hybrids which consist of organic and inorganic components have recently attracted much attention because these materials have lots of possibilities for tailoring functionalities and physical properties such as optical, electrical and magnetic properties by adjusting its organic and/or metal building blocks [1]. The organic component functions not only to bind the metal component but also to control the dimensionality and the connectivity in metal components [2]. One of the interesting series is the magnetic hybrid with perovskite-type transition metal salt with chemical formula such as $(C_2H_5NH_3)_2CuCl_4$ (EA) and $(C_6H_5CH_2CH_2NH_3)_2CuCl_4$ (PEA) [3]. Figure 1 shows the crystal structures of EA and PEA. Both hybrids have the orthorhombic crystal structure with the space group $Pbca$. Lattice constants of EA are $a = 7.4789$ Å, $b = 7.1731$ Å, and $c = 21.2406$ Å [4]. In the case of PEA, those are $a = 7.2099$ Å, $b = 7.2664$ Å, and $c = 38.238$ Å. The Cu atom has a spin half and forms the CuCl$_6$ octahedra with surrounding six Cl atoms. The CuCl$_6$ octahedra forms a 2D network of Cl-Cu-Cl and determines the magnetic property of those systems. The distance between CuCl$_6$ planes is about 10 Å for EA and 20 Å for PEA respectively. The orthorhombic crystal structure is due to the buckling of the CuCl$_6$
octahedra along the c-axis with angles of 7.74° and 6.63° for EA and PEA, respectively. Organic parts of EA and PEA consist of the double layer of ethylammonium and phenylethylammonium ions respectively and their charged ends of the ion, which is the nitrogen atom, are oriented to the nearest CuCl$_6$ plane. The EA contains no double bond between C atoms while PEA has aromatic phenyl rings in organic parts.

![Crystal structures](image)

**Figure 1.** Crystal structures of (C$_2$H$_5$NH$_3$)$_2$CuCl$_4$ (EA) and (C$_6$H$_5$CH$_2$CH$_2$NH$_3$)$_2$CuCl$_4$ (PEA). Views of EA (a) along the b-axis and (b) along the c-axis. Views of PEA (c) along the b-axis and (d) along the c-axis. The distance between CuCl$_6$ octahedra layer is about 10 Å in the case of EA and 20 Å in the case of PEA.

The in-plane magnetic correlation between Cu spins was estimated to be ferromagnetic for EA and PEA while the inter-plane magnetic correlation is expected to be much smaller than that of the in-plane one due to the far away distance between CuCl$_6$ layers. Although the magnetic property of both EA and PEA is expected to be 2D like, the appearance of a 3D magnetic state was confirmed in both systems around 10 K by magnetic susceptibility measurements [5, 6, 7]. Our $\mu$SR measurements on EA and PEA revealed the appearance of the clear muon-spin precession in the zero-field condition in magnetically ordered states. This observation evidenced the formation of a coherent long-range magnetic order of Cu spins. The internal field at the muon site was determined from the muon-spin precession frequency to be around 200 G at 4 K in both systems. In the case of PEA, a fast depolarized component in an earlier time region was observed from room temperature down to 4 K. This fast depolarized component was not decoupled even in fields of a couple of Tesla showing the existence of a possible muon state which strongly coupled with surrounding electrons via a radical formation. On the other hand, such a state was not observed in EA. Those experimental results will be published in a separated paper [8].

The dipole-dipole interaction is too weak to trigger the 3D magnetic ordered state through the far away distance between CuCl$_6$ layers, so that the mechanism of the magnetic interaction between layers is still unknown. In addition to this, the alignment of Cu spins in the magnetically ordered state has not yet been determined for EA and PEA. In order to approach those problems
and to get hints to argue the magnetic properties of EA and PEA, we are now trying to reveal the muon positions by using computational techniques. We can determine the spin alignment from the comparison between experimental results and muon positions estimated from computational techniques on the basis of the assumption that internal fields at the muon site are caused by dipole fields from surrounding magnetic moments. In this paper, we present results of the first trial to apply the density functional theory (DFT) method [9, 10] to EA and PEA in order to reveal minimum energy points which could be possible preferences for injected muons to be initially trapped. We found six potential minimum positions in EA and eight ones in PEA. All of expected potential minimum points in EA were near/around the CuCl$_6$ octahedra. Instead, in the case of PEA, two of eight positions were close to the aromatic phenyl ring giving a possibility that there are muon states which couple surrounding electrons via a radical formation.

2. Computational details
The estimation of the potential minimum positions was carried within the DFT framework as implemented in the Vienna Ab-initio Simulation Package (VASP) [11, 12]. We divided the unit cell into 90 × 90 × 265 grids for EA and 90 × 90 × 480 grids for PEA along a-, b-, and c-axes, respectively. The electrostatic potential energy was calculated putting H$^+$ on each grid. The projector augmented wave (PAW) pseudo-potentials was used [13] with the cutoff energy of 500 eV. The generalized gradient approximation (GGA) with the interpolation formula according to Vosko Wilk and Nusair was applied as the exchange correlation potentials [1]. We used the Monkhorst-Pack grid of $k$-points for the Brillouin-zone integrations for the single unit cell [1]. Local lattice relaxation effects which could be driven by injected muons were not included in order to make calculations simpler as the first trial. Potential maps and isosurface plots were generated using Visualization for Electronic and Structural Analysis (VESTA).

3. Results and Discussions
Figure 2 shows calculation results of potential minimum positions in EA. The strategy for finding energy minima consisted in a search for a regions enclosed by the lowest-energy isosurface contours. We firstly found three minimums around the apical Cl atom of the CuCl$_6$ octahedra. Figure 2(a) indicates those three positions by using isosurface areas. Figures 2(b) and (c) are expanded pictures of those three positions around the apical Cl atom. We named those positions to be A1, A2 and A3 from the lower energy side. The A1 and A2 are located symmetrically against the apical Cl atom. The difference of the potential energy between those two positions is due to the tilting of the CuCl$_6$ octahedra. With increasing the energy, another minimum appeared near A2 as shown in Fig. 2(c). This position was named as A4 and would be a counter position to A3. Two more positions were achieved in between two Cl atoms on the CuCl$_2$ plane. Since those two other positions were relatively far away from the apical Cl atom, we marked those two positions as B1 and B2. In total, we found six minimum positions in EA. We could not find out any more minimums at the higher energy region. Each position has the similar potential energy of about -6 eV and the difference in the energy among them was about a couple of hundred meV.

Figure 3 exhibits calculation results on PEA. As was done in the case of EA, we searched minimum potential positions from the lowest potential energy. With increasing the energy level, four minimum potential positions were found around the apical Cl atom of the CuCl$_6$ octahedra. Those positions are shown in the unit cell in Fig. 3(a) and in an expanded view of the CuCl$_6$ octahedra, Fig. 3(b), by isosurfaces. In the higher energy region, two more potential minimum positions were found in between two in-plane Cl atoms in the CuCl$_2$ plane. This finding of six potential minimum positions in PEA was the same tendency with that found in EA. Actually, each position has the similar potential energy of around -6 eV and the difference in the energy among them was about a couple of hundred meV as well as the case of EA. Accordingly, those
Figure 2. (a) Calculation results of the potential energy by using the density functional theory on (C$_2$H$_5$NH$_3$)$_2$CuCl$_4$ (EA). (b)(c) Expanded picture of the CuCl$_6$ octahedra with estimated minimum potential positions which are drawn by isosurfaces. Isosurfaces in (b) and (c) show the potential energy areas which are 337 and 455 meV higher than from the minimum potential position A1, respectively.

positions were named as A1 to A4 and B1 to B2 following the same definition in the case of EA as indicated in Fig. 3(b) and (c).

In addition to those six potential minimum positions, two more positions appeared in and on the phenyl ring of PEA. Those two positions are shown in Fig. 3(d) named as C1 and C2. The C1 position is almost on the C-H bond of the phenyl ring. The C2 position is within the phenyl ring. Potential energies at C1 and C2 sites were about 0.5 eV higher than others and the difference in the potential energy between the two position was about 0.1 eV.

Comparing results achieved in EA and PEA, it was found that positions from A1 to A3, B1 and B2 are quite similar in those systems. This fact means that the electrostatic potential around the CuCl$_6$ octahedra is similar in both of EA and PEA. It can be supposed that muon positions around CuCl$_6$ octahedra are similar and that surrounding organic parts do not affect muon positions around CuCl$_6$ octahedra. Since differences in the potential energy among estimated positions are not so big and was about a hundred of meV, all positions around CuCl$_6$ octahedra can be preferences for injected muons to be initially trapped. Those positions are expected to correspond to those which show the muon-spin precession in the zero-field condition as observed in our previous $\mu$SR experiment [8]. It should be noted that the final muon positions must be different from those estimated in the current study. We have not yet taken into account local relaxation effects of lattice which are caused by injected muons. We also did not include the effect of the zero-point vibration motion of the muon itself. Those effects relax initial muon positions and lead to the deformation of the crystal structure minimizing the total energy and
Figure 3. (a) Calculation results of the potential energy on \((\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3)_2\text{CuCl}_4\) (PEA). (b)(c) Expanded pictures of the \(\text{CuCl}_6\) octahedra with estimated minimum potential positions which are drawn by isosurfaces. (d) Expanded picture of organic components around the phenyl ring. Two potential minimum positions in and on the phenyl ring are drawn by isosurfaces as well. Isosurfaces in (b), (c) and (d) show potential energy areas which are 195, 425 and 1,025 meV higher than that of the minimum potential position, respectively.

to the relaxation of muon positions. More calculation efforts are being undertaken to estimate final muon positions in EA and PEA taking into account those local relaxation effects.

On the other hand, C1 and C2 which are estimated in PEA around the phenyl ring can give different muon states from others. As has been well discussed, the injected muon prefers to form a radical state around the phenyl ring on which \(\pi\) electrons are delocalized over the ring [14]. Such a radical state can make a large internal field at the muon site via the Fermi contact interaction. Thus, the muon state identified in our \(\mu\)SR experiment with a large hyperfine field [8], must be the one that forms a radical state around the phenyl ring. However, the estimation of the final muon state around the phenyl ring is not so easy and straightforward. This is because, the phenyl ring has at least about 10 crystallographic orientations which are ortho-, meta- and parapositions and their inequivalences on both sides of the ring. This complicated local structure of the phenyl ring and delocalized \(\pi\) electrons over the ring make the estimation difficult. Local relaxation effects are also very important in the more accurate estimation of muon positions around the the phenyl ring in PEA.

4. Conclusions
We applied the density functional theory analysis to estimate the electrostatic potential energy in metal-organic hybrids of \((\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4\) (EA) and \((\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3)_2\text{CuCl}_4\) (PEA) in order to estimate local minimum potential positions as preferences for injected muons to be initially trapped. We found six potential minimum positions around the \(\text{CuCl}_6\) in EA. The similar positions were found in PEA as well. Four of them were around the apical \(\text{Cl}\) atom and two of them were in between in-plane \(\text{Cl}\) atoms on the \(\text{CuCl}_2\) plane. Those muon positions
can be candidates to show the muon-spin precession behavior in the zero-field condition in magnetically ordered states in both EA and PEA. Two more minimum potential positions were found in PEA in and on the phenyl ring of the organic part causing possible muon states bound with surrounding electrons via a radical formation having large hyperfine fields as identified in our $\mu$SR study [8]. Differences in the potential energy among those estimated positions were not so large and all estimated positions could be those which injected muon would prefer to be initially trapped.

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