Theoretical investigation of the pressure-induced insulator-to-metal-to-insulator transitions in one-dimensional bis(dimethylglyoximato) platinum(II), $\text{Pt}(\text{dmg})_2$

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Abstract

The electrical resistivity of one-dimensional bis(dimethylglyoximato) platinum(II), $\text{Pt}(\text{dmg})_2$, exhibits unexpected insulator-to-metal-to-insulator (I-M-I) transitions under the high pressure. The interesting but complicated nature of these pressure-induced I-M-I transitions is approached by the density functional theory calculations on a kind of stacking model. After optimization of one monomer, a set of stacking models with different intermolecular distances (metal-metal bond) are built from 8 units of monomers to simulate the various stages during pressure increasing in experiment. As the metal-metal bond lengths decrease, the calculated HOMO and LUMO energy gaps become narrow and reach the minimum value (0.27 eV) when the metal-metal bond length is 2.4 Å. If the metal-metal bond length is continually decreased for simulating even higher pressure, the energy gaps were found to be enlarged again, at the same time, the natural charge analysis of the models shows the intra-molecular charges transfer from Pt atom to N atoms rather than the inter-molecular one. The entire energy gap change of these stacking model systems is well consistent with the electrical resistivity change in experiment. This similar tendency also indicates that the change of metal-metal bond length and the following unique charge transfer may be the main reason to the pressure-induced I-M-I transitions of $\text{Pt}(\text{dmg})_2$ complexes.

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Introduction

Conductivity of materials is one of the hottest topics of material research and design. During these studies, the metal to insulator (M-I) and/or insulator to metal (I-M) transition easily occurs, especially for the transition metals involved materials. However, the mechanism of the transition is always not easily understood. For example, the reason to the M-I transition of stoichiometric VO_2 at ambient pressure has been debated for decades until recently it has been clearly explained [1-5]. By the knowledge of the nature of this transition, the M-I transition of VO_2 has been successfully controlled by modifying orbital occupancy in experiment [6], which exhibits enormous potential of applications.

Since graphene becomes a sparkling rising star on the horizon of material science for its various potential applications [7, 8], the researches of low-dimensional electron systems have led to a renewal of interest in polymers composed of platinum complexes [9, 10]. Actually, the platinum complexes were well synthesized over 150 years ago, but their fantastic properties were recognized gradually from the twentieth century, such as, the optical properties [11-20], the magnetic properties [21], and the significant usage as the anticancer drugs [22]. Among these various platinum complexes with interesting abilities, the title complex, bis(dimethylglyoximate) platinum(II), $\text{Pt}(\text{dmg})_2$, has attracted a lot of interests not only for its nanostructure within well-organized one-dimensional metal chain [23] but also for its reversible but abnormal pressure-induced electrical conductivity change in experiment [24-26].

The $\text{Pt}(\text{dmg})_2$ is a d^8 square-planar complex and stacking upon each other with a Pt-Pt distance ($d_{\text{Pt-Pt}}$) of 3.26 Å from the experiment data (See Figure 1a and 1b) [27, 28]. The experiment of $\text{Pt}(\text{dmg})_2$ finds that there is a two-step transition of $\text{Pt}(\text{dmg})_2$ complex from insulator to metal to insulator (I-M-I) as the pressure increasing from ambient pressure up to 10 GPa. Because of its one-dimensional structure, the $\text{Pt}(\text{dmg})_2$ is a suitable model system for the mechanism research of the pressure-induced I-M-I transitions by means of theoretical calculations. At an early stage of research here we build a model system and theoretically investigate the relationship between the Pt-Pt metal bond lengths ($d_{\text{Pt-Pt}}$) and the electronic structure change with assuming under the high pressure. Finally, we will discuss the relation of our results with the experimentally reported electrical resistivity change under the high pressure.

Figure 1. Structure of $\text{Pt}(\text{dmga})_2$ (a) monomer, (b) stacking model of 8 monomers.

Computational details

According to the calculations of platinum (II) complex [29, 30], the mPW1PW91 [31] density functional is employed for the one unit $\text{Pt}(\text{dmga})_2$ monomer geometry optimizations without any symmetry constraint. The LANL2DZ [32] is only employed for the Pt atom, and the 6-31G(d, p) basis set for the other elements. The local minimum structure is confirmed by a successive frequency calculation with the same basis set for the geometry optimizations.

The stacking model systems are built from stacking of monomers with different metal bond lengths, and a 90° rotated between the adjacent monomers, which are corresponding to the X-ray diffraction data [26-28]. During building our stacking model systems the effects of methyl group to the structural geometry are not taken into consideration, although the rotation of methyl group and interaction with adjacent chains under high pressure have been observed in experiment [28]. It is pointed out by the theoretical calculations of Kovács that the rotations of methyl group have negligible effects on the geometrical parameters of the bis(glyoximate)-metal skeleton in monomer [33]. Moreover, there is no condensation of molecular plane in our stacking models. In other words, when we build the stacking model system structures, only the $d_{\text{Pt-Pt}}$ is changed during stacking, while the other parameters of geometry are kept the same as those in monomer without another optimization for the whole stacking geometries. Here we only consider the pressure-induced bond length change in one direction for simplification.

The necessary number of monomer is examined by the Mulliken net charge distributions of selected atoms from the calculations with different number of monomers. As an enough size at which net charge becomes stable on the stacking, 8 units of monomer are employed for the following calculations; the details will be described in the next section. A set of 8 units of monomer are built with different Pt-Pt metal bond ($d_{\text{Pt-Pt}}$) to simulate the different stage of the complex under pressures, shown in Figure 1b. All the calculations were carried out with GAUSSIAN 09 program package [34] equipped with Natural Bond Orbital (NBO) program suite [35].

Results and discussion

A reasonable geometry of monomer is significant to the following stacking complex calculations, therefore the differences in geometry are carefully examined. The optimized geometry of monomer $\text{Pt}(\text{dmg})_2$ is compared with experiment data from X-ray diffraction [28] and another theoretical calculations by Kovács [33] at B3P86 functional with LANL2DZ with f polarization functions [36] for Pt atom and 6-311+(+)G(d, p) for other atoms. The optimized structure information is summarized in the Table 1. Compared with the experimental data, especially for those bond lengths and bond angles that metal atoms are involved, current functional and basis set give very reasonable results. The slightly large difference in N-O and C-N bond lengths and O-H...O bond angle between theoretical calculations and experimental data should be attributed to the interactions in the isomorphous crystals (lone pairs of O and rotation of methyl group) and the approximations used in theoretical calculations. Although a little better agreement can be obtained from the theoretical calculations by Kovács because of somewhat larger valence basis set employed [33], the maximum difference between their and our calculations in bond lengths and angles are only 0.008 Å and 1.3°, respectively. Moreover, considering the cost of following stacking model systems calculations, the more economical 6-31G(d, p) basis set would be more suitable.

Table 1. Selected geometrical parameters of Pt(dmg)₂ complex (Units in angstrom or degree).

Method	Exp. ^a	Cal. ^b	Our results
M–N ₃ ^c	1.976(12)	1.976	1.984
M–N ₆	1.995(13)	1.994	2.002
N ₃ –O ₂	1.354(24)	1.351	1.347
N ₆ –O ₇	1.351(18)	1.279	1.277
O ₂ –H ₁	1.06(15)	1.014	1.014
O ₂ ...O ₁₄	2.638(19)	2.666	2.661
H ₁ ...O ₁₄	1.63(15)	1.667	1.660
N ₃ –C ₄	1.282(29)	1.299	1.299
C ₄ –C ₅	1.425(29)	1.461	1.464
C ₅ –N ₆	1.308(24)	1.316	1.318
C ₄ –C _{4'}	1.510(30)	1.487	1.490
C ₅ –C _{5'}	1.467(31)	1.487	1.490
N ₃ –M–N ₆	78.2(7)	79.5	79.6
N ₆ –M–N ₁₀	101.8(7)	100.5	100.4
M–N ₃ –C ₄	116.8(14)	116.4	116.1
M–N ₆ –C ₅	115.9(12)	115.4	115.1
N ₃ –O ₂ –H ₁	111.9(80)	103.6	103.4
C ₄ –N ₃ –O ₂	123.2(15)	121.1	121.8
C ₅ –N ₆ –O ₇	125.0(14)	124.6	125.0
O ₂ –H ₁ ...O ₁₄	159(13)	167.4	168.7
N ₁₃ –O ₁₄ ...H ₁	-	106.0	105.6
C ₅ –C ₄ –N ₃	115.3(19)	114.6	114.9
C ₄ –C ₅ –N ₆	113.9(18)	114.0	114.2
C ₅ –C ₄ –C _{4'}	124.1(19)	122.8	122.4
C ₄ –C ₅ –C _{5'}	126.6(19)	124.1	123.8

^a. Exp. means the experiment data from ref.[27].

^b. Cal. means the calculations data by Kovács at B3P86/6-311+(+)(G(d, p) level of theory from ref.[33].

^c. See Figure 1 for the atomic numbering.

In order to obtain an appropriate number of units for stacking, the calculations are first carried out for monomers stacking from 2 units to 8 units, and the $d_{\text{Pt-Pt}}$ is changed from 2.2 Å to 3.2 Å ($\Delta d=0.2$ Å). The Mulliken net charge distributions of selected N and Pt atoms in the 2nd unit by different $d_{\text{Pt-Pt}}$ are plotted in Figure 2. It is well known that the Mulliken net charge is not very accurate, since it is highly sensitive to the atomic basis set. However, we still can find some useful information, for example, on the tendency by considering the relative changes of Mulliken populations when the same basis set is employed. It shows that if the unit size is more than 6 units, the Mulliken net charge distributions of selected N and Pt atoms become stable. The same stabilities of

charge distributions are also found for the other atoms and these in other units. With the feasible computational resources, therefore, 8 units of monomer are employed for the following calculations.

Figure 2. Mulliken charge of the selected atoms in the 2nd unit under the stacking effect.

The $\text{Pt}(\text{dmg})_2$ complexes of 8 units were calculated from 2.1 Å to 3.3 Å ($\Delta d = 0.1$ Å for more detailed analysis) to examine the potential pressure effect on the energy gaps of complex. The selected orbital energies (from the HOMO-4 to LUMO+4, total 10 orbitals) are shown in Figure 3. The longest metal bond ($d_{\text{Pt-Pt}}$) of model structure is equal to 3.3 Å, which is responding for the experimental data (3.26 Å) at ambient pressure. The calculated orbital energy gap of $d_{\text{Pt-Pt}}$ at 3.3 Å is 2.78 eV, which is somewhat larger than the experiment data (about 2.05 eV) [37, 38]. This large energy gap of $d_{\text{Pt-Pt}}$ at 3.3 Å indicates the model system is an insulator, which is consistent with the experimental

observation at ambient pressure [26]. The calculated orbital plots of $d_{\text{Pt-Pt}}$ at 3.3 Å show that the HOMO almost comes from $5d_{z^2}$ orbitals of Pt atoms. While the LUMO consists of the $6p_z$ orbitals of Pt atoms and the p orbitals of the ligands, shown in Figure 4. The HOMO and LUMO plots in our calculations are supported by the electron transition experiments [24-26].

Figure 3. Selected orbital energies (from HOMO-4 to LUMO+4, the star marked (*) indicates a degenerated orbital.) with different metal-metal bond length.

Figure 4. Orbital plots of HOMO and LUMO at metal bond length ($d_{\text{Pt-Pt}}$) is equal to 3.3 Å, which is corresponding to the $\text{Pt}(\text{dmg})_2$ complexes at ambient pressure in experiment.

When the metal-metal bond length ($d_{\text{Pt-Pt}}$) is decreasing from 3.3 Å to 2.4 Å, the corresponding energy gaps dramatically become narrow from 2.78 eV to 0.27 eV. The only 0.27 eV of energy gap for $d_{\text{Pt-Pt}}$ at 2.4 Å indicates the quasi-metallic behavior of the complex system. This tendency of energy gap narrowing agrees well with the electrical resistivity of experiment results that the electrical resistivity decreases dramatically from $10^4 \Omega\cdot\text{cm}$ to $10^{-1} \Omega\cdot\text{cm}$ as the pressure is increasing to 6 GPa [26]. However, the magnitude of these changes in energy gap and resistivity are not compared, because of several approximations in theoretical calculations. For instance, the molecule is condensed at all directions under the increasing pressure in experiment, while only one direction, where the metal bond is alone with, is compressed in calculations. One can expect from the similar tendency that the change of energy gaps dominate the insulator to metal transition in experiment. The nature of HOMO and LUMO is continued with pressure but the orbital plots are given complicated as a mixing between them. Moreover, the frontier orbitals are localized around in the terminals in such a finite system, though crystal orbital calculations always provide as delocalized and uniformed phases because of periodic boundary condition. This fact would suggest under high pressure that electron transfer between adjacent chains between localized terminals might be more responsible for conductivity rather than that within intra-chain in such a limited stacking system. Another possibility is that electron transition from the valence band to the conduction band that has phases around the middle of the chain might contribute on the conductivity. To make the conduction mechanism clear, huge calculations on three-dimensional systems of several stacking alignments and additionally excited states calculations would be required. However, here we focus on the electronic structure change accompanied with pressure in one-direction as such huge stacking system requires huge amount of calculations even with recent advanced super-computers.

When the $d_{\text{Pt-Pt}}$ continually decreases, the energy gap is going to be enlarged again. When the $d_{\text{Pt-Pt}}$ is equal to 2.1 Å, the corresponding energy gap is changed back to 0.55 eV. The reason to this enlarged energy gap is examined by the natural net charge changes of selected atoms from NBO analysis (Pt, N3 and N6 atoms, see Figure 1a for the atomic numbering), which is shown in Figure 5. Because of the symmetry of 8 units, the charge distribution is the same in each pair units (unit 1 and 8, unit 2 and 7, unit 3 and 6, unit 4 and 5, in total of 4 pairs). The similar values of the charges of selected atoms in all units indicate the similarity of each unit in the one-dimensional complex chain though each orbital population of Pt atom provides different electron distributions. When the $d_{\text{Pt-Pt}}$ is less than 2.7 Å, the natural net charges of Pt atoms increase dramatically in all units. Meanwhile, the corresponding ones of the N atoms (N3 and N6) significantly decrease. The changes of corresponding atoms suggest the pressure will

induce the intra-molecular charge transfer from the central metal to ligand atoms (MLCT). Table 2 shows that the occupation number of the anti-bonding π^* orbitals of selected C=N bond is continuously increasing, as the metal bond length is decreasing. This increasing of occupation number should be attributed to (1) The repulsions from d orbitals of metals, when the $d_{\text{Pt-Pt}}$ bond length becomes shorter, (2) the delocalization within each molecular plane, which is gradually enhanced by the interactions from adjacent units, especially when the molecular layer becomes closer. This kind of intra-molecular MLCT, which is essential to the relaxation processes of excitons of $\text{Pt}(\text{dmg})_2$ system,[38] is also observed by the pump-probe spectroscopy in experiment [39-41].

Figure 5. Natural net charge changes of selected atoms (Pt, N_3 and N_6 atoms) within each unit. U_n means the atoms in the n th unit. See Figure1 for the atomic numbering.

Table 2. Occupation number of the anti-bonding π^* orbitals of selected C=N bond in each unit.

$d_{\text{Pt-Pt}}$ (Å)	Occupation number of π^* orbitals of C(12)=N(13) ^a			
	U1 & U8	U2 & U7	U3 & U6	U4 & U5
3.3	0.436	0.424	0.425	0.425
3.2	0.435	0.424	0.424	0.424
3.1	0.436	0.423	0.424	0.424
3.0	0.437	0.423	0.424	0.424
2.9	0.440	0.424	0.425	0.426
2.8	0.445	0.429	0.430	0.430
2.7	0.454	0.440	0.439	0.439
2.6	0.460	0.457	0.466	0.471
2.5	0.467	0.462	0.469	0.475
2.4	0.474	0.470	0.474	0.485
2.3	0.477	0.493	0.501	0.500
2.2	0.483	0.513	0.524	0.513
2.1	0.494	0.542	0.555	0.532

^a Number in bracket is the atomic number, see Figure 1 for details.

Figure 6. Natural net charge summed up for each unit with different metal-metal bond length.

The pressure-induced charge transfer between units (inter-molecular charge transfer) is also examined by the sum of natural net charge of each unit, plotted in Figure 6. The change in net charges becomes more active when the $d_{\text{Pt-Pt}}$ is less than around 3.0 Å. However, it was found that the inter-molecular charge transfer is not zero but considerably small compared with the intra-molecular charge transfer as shown in Figure 5. This small charge change between units also indicates the similarity of each unit, and thus strong charge density wave (CDW) is not observed. Therefore, the planar intra MLCT should be the main reason to the disappearance of $5d_{z^2}-6p_z$ transition of $\text{Pt}(\text{dmg})_2$ when the pressure above 5 GPa in experiment. In addition, it's also pointed out by Kovács from theoretical calculations that among the donor-acceptor interactions in the framework of the Lewis mode, the most important one is the σ -donation from the lone pair of N atoms to unfilled s and d^* valence orbitals of metal from the NBO analysis of monomer calculations at ambient pressure [33]. Because of the continuously pressure-induced planar MLCT, consequently, this hindered donation may lead the disappearance $5d_{z^2}-6p_z$ transition. There is also a new absorption (540 nm) suddenly appeared under high pressure in experiment, which is different from the absorptions at ambient pressure. Actually, there are three strong absorptions of UV-vis spectrum of $\text{Pt}(\text{dmg})_2$ film observed at 275, 328 and 681 nm in experiment at ambient pressure, which are assigned to the $\pi-\pi^*$, MLCT and d-p transitions [19, 42, 43]. Therefore, the sudden appearance of the new absorption when the pressure is above 5 GPa may not be simply assigned to any of the three types of transitions observed at ambient pressure. Considering the very short $d_{\text{Pt-Pt}}$ (less than 2.4 Å) in the model system at high pressure, the strong electron-electron repulsion of Pt atoms and the pressure enhanced hybridization of orbitals from both metal and ligand may result in this new appeared absorption, which may also be responsible to the enlarged energy gap changes at high pressure [44, 45]. Actually, the experiment results show that the metal bond length $d_{\text{Pt-Pt}}$ is 2.9 Å at 5 GPa and reaches 2.8 Å at 10 GPa (the radius of Pt cluster is about 1.4 Å at ambient pressure). This short metal bond implies strong core-valence overlap and even significant core-core overlap between neighboring Pt atoms. In addition, the ligands are also crucial to the localization of valence electrons, not only for its enhanced delocalization of the bis(glyoximato)-metal skeleton but also the possible intra-molecular hydrogen bonding at high pressure.

Conclusions

We presented here a set of theoretical models, in which only the metal bond direction of the complex is gradually compressed for computational simplification, to simulate the various stages of $\text{Pt}(\text{dmg})_2$ systems under increasing pressures in experiment. Although the values of metal bond length and energy gaps are somewhat

different from the experimental data, especially the metal bond length is much shorter than experimental data; the tendency of energy gap change of these models is well consistent with the electrical resistivity change in experiment. This consistence indicates that the pressure-induced I-M-I transition of $\text{Pt}(\text{dmg})_2$ complex should be mainly attributed to the change of metal bond length.

When the $d_{\text{Pt-Pt}}$ is decreasing from 3.3 Å to 2.4 Å, the corresponding energy gap is reduced from 2.78 eV to 0.27 eV. This energy gap change simulates to the insulator-metal transition of experimental observation, when the pressure is below about 6 GPa. If the metal bond length is continuously decreasing, a serial of enlarged energy gaps are obtained from the theoretical calculations, accompanied with charge transfer from central metal atoms to ligands within each unit rather than inter-molecular charge transfer. The enhanced hybridization of orbitals from metal and those from ligand and the strong electron-electron repulsion of metals at high pressure may be the reason to the successive metal-insulator transition in experiment when the pressure is above 6 GPa. A further detail of this transition is still under investigation and will be discussed in the next stage.

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Pressure

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In
experiment

*Graphical abstract - synopsis

The conductivity change of one-dimensional $\text{Pt}(\text{dmg})_2$ in experiment has been reproduced by the energy gap change in theoretical calculation on a serial stacking models with different metal-metal bond lengths. This consistence indicates that the change of metal-metal bond is essential to the conductivity of one-dimensional $\text{Pt}(\text{dmg})_2$.