Synthesis and Crystal Structure of the Molecular Metal Based on Iodine-bonded π-Donor, (IEDT)[Pd(dmit)$_2$]

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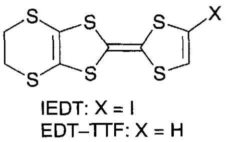
A novel molecular metal, which exhibits strong and directional –I···S– donor–acceptor interaction has been developed using I-bonded π-donor IEDT and the transition metal complex Pd(dmit)$_2$.

Crystal structure control would be the breakthrough in making molecular conductors, but despite the recognition of the close relationship between physical properties and intermolecular cation–anion interactions, very few studies have been done to control whole crystal structures, that is, arrangements of both ions.[1,2] We have already reported the first application of the strong and directional –I···X– (X = CN or halogen atom) type cation–anion interaction to molecular conductors using an I-bonded unsymmetrical donor molecule IEDT (iodo-ethylenedithiotetrathiafulvalene).[1] Such an –I···X– intermolecular interaction is known in the one-dimensional crystal structure of *p*-iodobenzonitrile.[3] This type of interaction originates in the large coefficient of the pσ LUMO on the iodine atom which interacts with the lone pair on the nitrogen or halogen atom. In the course of our study to explore other types of the I-based cation–anion interactions in molecular conductors, we have examined a combination of IEDT with transition metal complexes derived from dmit (dmit^{2-} = 2-thioxo-1,3-dithiole-4,5-dithiolato). The M(dmit)$_2$ [M = Ni, Pd, Pt, Au] unit forms a number of conducting (or superconducting) salts with organic donors, including the donor molecule EDT–TTF (EDT–TTF = ethylenedithiotetrathiafulvalene).[4,5] In this paper, we report the preparation of the first molecular metal based on the I-bonded donor molecule, (IEDT)[Pd(dmit)$_2$] **1** and characterization of its unique crystal structure.

Long, thin black plates of **1** were obtained by galvanostatic oxidation of a solution containing IEDT (*ca.* 8 mg)[1] and (Bu$_4$N)[Pd(dmit)$_2$] (*ca.* 20 mg) in 1,2-dichloroethane (20 ml) under argon atmosphere at 20 °C. Crystal structure of the salt **1** was examined by X-ray diffraction.† The shortest I···S distance between the IEDT and the Pd(dmit)$_2$ molecules is 3.308(4) Å as shown in Fig. 1. It is more than 13% shorter than the sum of the van der Waals radii (3.78 Å: Bondi, 4.00 Å: Pauling). This characteristically short distance indicates the existence of a strong intermolecular –I···S– interaction. This interaction affects the C=S double bond distances in the dmit ligand; the one which interacts with the IEDT molecule is longer than the other [C(1)–S(1) = 1.61(2) Å, C(2)–S(2) = 1.66(2) Å]. Moreover, an examination of bond angles ∠C(S)=S(2)···I = 127(1)° and ∠S(2)···I–C(11) = 168.8(9)° indicates an overlap of the lone pair on the sulfur atom with the pσ LUMO of the iodine atom. This means that the –I···S– interaction is fully directional. Molecular packing in the IEDT layer is shown in Fig. 2(*a*). The IEDT molecules are stacked in the dimeric mode, which is similar to the one in the organic superconductor β-(BEDT–TTF)$_2$I$_3$ [BEDT–TTF = bis(ethyleneditiho)tetrathiafulvalene].[6] Modes of overlap in the IEDT column are: 'bond-over-ring' type in the dimer and 'longitudinal slipping' between the dimers. The Pd(dmit)$_2$ molecules are stacked in a strongly dimeric manner [Fig. 2(*b*)] and the overlapping modes are: 'atom-over-atom' in the dimer and 'longitudinal slipping' between the dimers. The most interesting feature is the stacking direction of the donor and the acceptor, that is, the IEDT



IEDT: X = I
EDT–TTF: X = H

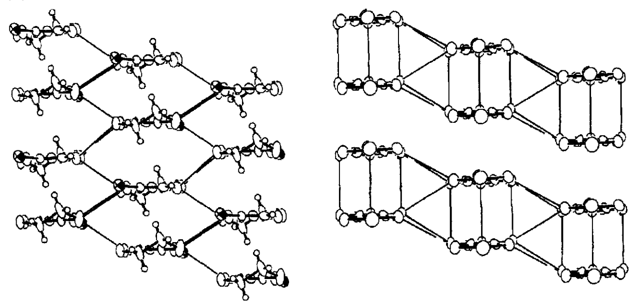


Fig. 2 Packing diagram of the donors and the acceptors: (*a*) IEDT layer (*b*) Pd(dmit)$_2$ layer

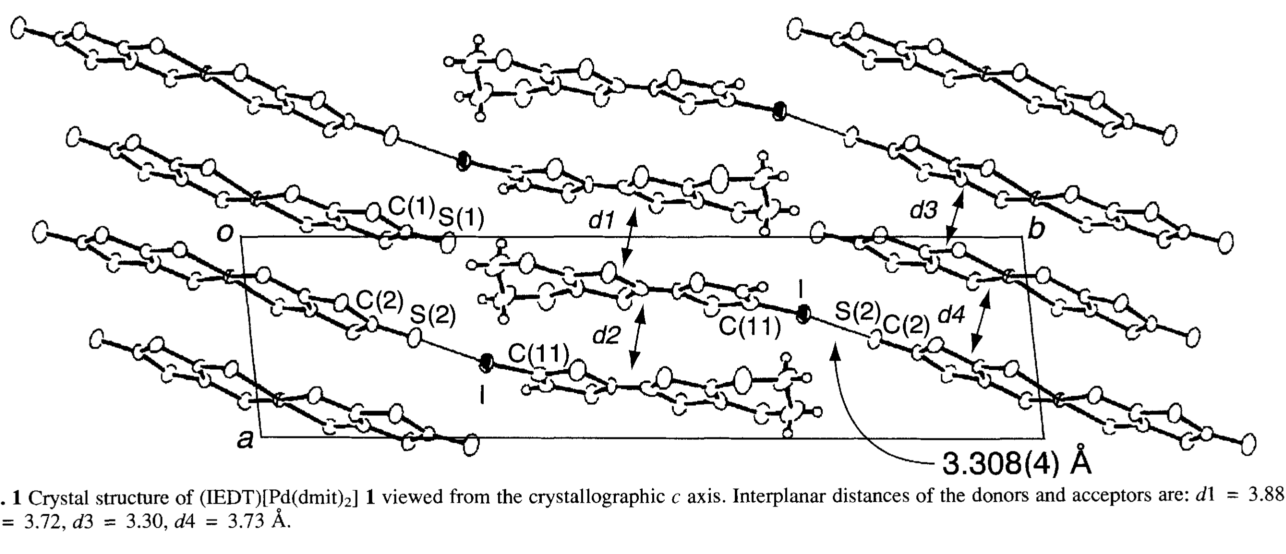


Fig. 1 Crystal structure of (IEDT)[Pd(dmit)$_2$] **1** viewed from the crystallographic *c* axis. Interplanar distances of the donors and acceptors are: *d*1 = 3.88, *d*2 = 3.72, *d*3 = 3.30, *d*4 = 3.73 Å.

molecules and the Pd(dmit)$_2$ molecules form 'parallel' columns along the *a* axis. On the other hand, the (EDT–TTF)[Pd(dmit)$_2$] system[7,8] where the iodine atom is replaced by the hydrogen atom, forms 'solid crossing' column structure (α'-phase);[9] the stacking direction of the donor is different from that of the acceptor. These stacking features suggest that a basic unit in the crystal of **1** is the strongly interacting IEDT–Pd(dmit)$_2$ pair, which restricts the donor and acceptor from constructing the 'solid crossing' column structure. Indeed, we could find no phase with the 'solid crossing' column structure in this system.

Temperature dependence of the resistivity of the salt **1** is metallic down to 4.2 K (Fig. 3), where γ-(EDT-TTF)[Pd(dmit)$_2$], with similar 'parallel' columns exhibits the resistivity anomaly accompanied by the CDW formation.[9] Preliminary tight-binding band calculations show two types of closed Fermi surfaces associated with the HOMO of IEDT and the HOMO of Pd(dmit)$_2$, respectively. There exist small but significant interactions between the IEDT and Pd(dmit)$_2$ layers (about one third of the inter-column interactions within each layer). These values are almost two or three times larger than those in α-(EDT-TTF)[Ni(dmit)$_2$] with the 'solid crossing' column structure.[10] The largest inter-layer overlap integral is observed between IEDT and Pd(dmit)$_2$, which is located on the iodine-bonded side.

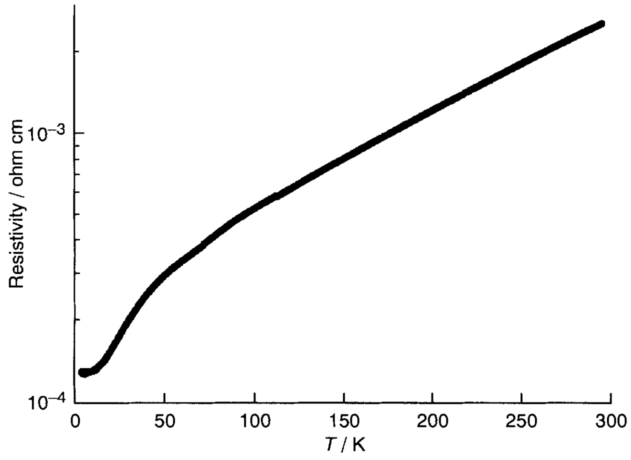


Fig. 3 Temperature dependence of the resistivity for (IEDT)[Pd(dmit)$_2$] **1**

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Footnote

† X-Ray diffraction data were collected on a MAC Science automatic four-circle diffractometer with monochromated Mo-Kα (λ = 0.71069 Å) radiation up to $2\theta = 60°$. The intensities were corrected for Lorentz and polarization effects. The analytical absorption correction was carried out. The structure was solved by direct methods and refined using full-matrix least-squares analyses using reflections with $I \geqslant 4\sigma(I)$. Anisotropic thermal parameters were used for non-hydrogen atoms. All calculations were performed using TEXSAN (MSC).

Crystal data for **1**: $C_{14}H_5IPdS_{16}$, $M_W = 919.57$, triclinic, space group $P\bar{1}$, $a = 7.8763(9)$, $b = 27.872(5)$, $c = 6.344(1)$ Å, $\alpha = 95.33(1)$, $\beta = 110.18(2)$, $\gamma = 82.39(2)°$, $V = 1294.1(4)$ Å^3, $Z = 2$, $D_c = 2.359$ g m^{-3}, $F(000) = 888.0$, $R = 0.084$, $R_w = 0.086$, GOF = 3.99 for 4600 observed reflections out of 7537 unique reflections.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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