Novel Molecular Conductors, $(DIETS)_4M(CN)_4$ (M = Ni, Pd, Pt): Highly Reticulated Donor···Anion Contacts by –I···NC– Interaction

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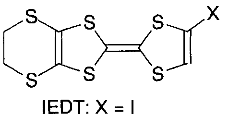
The novel molecular conductors, $(DIETS)_4M(CN)_4$ (M = Ni, Pd, Pt) where reticulated donor···anion contacts are constructed using the strong and directional –I···NC– interaction, are synthesized and characterized.

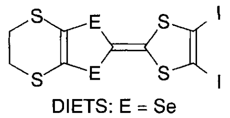
It is well known that the variety of crystal and electronic structures in molecular conductors depends not only on the structure of the molecule with the frontier orbitals but also on cation···anion interactions. We have proposed that an introduction of the strong and directional cation···anion interactions would control the molecular arrangement and therefore the electronic structure.[1,2] Our idea is based on the one-dimensional chain structure in the crystal of *p*-iodobenzonitrile directed by the strong and directional –I···NC– interactions.[3,4] We have already synthesized some iodine-bonded unsymmetrical π-donors[1] and accumulated unique examples of the molecular conductors the crystal structures of which are directed by the strong and directional –I···X– (X = CN, Br or S) type cation···anion interactions.[1,2] According to the information obtained from the iodoethylenedithiotetrathiafulvalene 'IEDT' salts, we now step into the improvement of the electrical conductivity and the development of the new molecular packing using the selenium containing π-donor, 'DIETS' (diiodoethylenedithiodithiadiselenafulvalene) which has two iodine atoms on the edge of the skeleton.

In this paper, we report the synthesis and properties of $(DIETS)_4M(CN)_4$ (M = Ni, Pd, Pt) salts and the novel crystal structure of the $Pd(CN)_4$ salt. The crystal structure of the $Pd(CN)_4$ salt is governed by the highly reticulated –I···NC– network of donor and anion molecules.

Black elongated plates of $(DIETS)_4M(CN)_4$ (M = Ni, Pd, Pt) were obtained by galvanostatic oxidation (1.0 μA) of a solution containing DIETS (*ca.* 8 mg)[5] and $(Bu_4N)_2[M(CN)_4]$ (M = Ni, Pd or Pt) (*ca.* 20 mg) in CH_2Cl_2 (20 ml) under an argon atmosphere at 20 °C. Temperature-dependent resistivities of these three salts are shown in Fig. 1. They are metallic > 80–100 K, and below this undergo moderate metal–semiconductor transitions. This is in contrast to the semiconductive behaviour (from room temperature) of the all-sulfur analogues diiodoethylenedithiotetrathiafulvalene ('DIET') salts with the same anions.[1,8] The selenium substitution in the parent TTF skeleton has effectively improved conducting property. It is also noted that the temperatures of the metal–semiconductor transitions are lowered with the increase in atomic number of the central metal in the counter anion.



IEDT: X = I
EDT-TTF: X = H



DIETS: E = Se
DIET: E = S

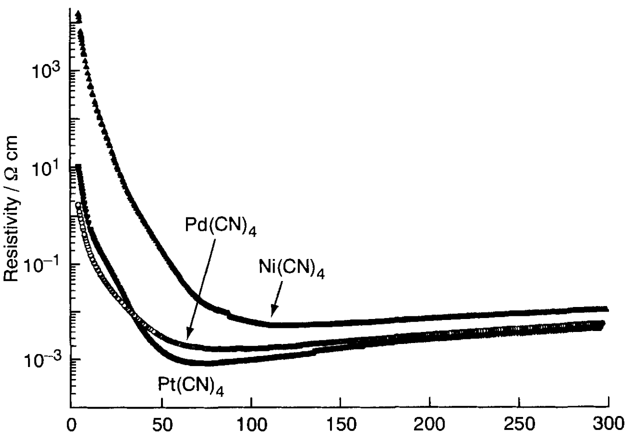


Fig. 1 Temperature dependences of the resistivities for $(DIETS)_4M(CN)_4$ (M = Ni, Pd, Pt)

X-Ray diffraction studies have revealed that these three salts have similar cell parameters.† Molecular packing of the $Pd(CN)_4$ salt is shown in Fig. 2. Two crystallographically independent donor molecules are on the mirror plane and the ethylenedithio groups are disordered. Donor molecules are stacked along the *c* axis. Two iodine atoms on the donor molecule and four cyano groups on the counter anion are fully connected and form an infinite chain of anions and quadruple donors along the *b* axis. There are two kinds of short I···N distances [2.95(1) and 3.11(1) Å] between DIETS and $Pd(CN)_4$. Both interactions are more than 12–16% shorter than the sum of the van der Waals radii (3.53 Å: Bondi, 3.65 Å: Pauling) and this characteristic shortening indicates the existence of the strong intermolecular –I···NC– interactions. Furthermore, the I···N–C angles [I(1)···N(1)–C(11) 143(1)°, I(2)···N(1)–C(11) 106.7(8)°] suggest that these two –I···NC– interactions are different. The p_σ LUMO on the iodine atom is concerned with both interactions, while the shorter interaction [I(1)···N(1)] is associated with the lone pair on the cyano group and the longer one [I(2)···N(1)] with the p_π triple bond of the cyano group. Usually, unsymmetrical π-donors are stacked alternatively. In this case, however, the donors in the column are arranged in the same direction (Fig. 3). We can easily understand that this comes from the strong –I···NC– interactions. Owing to this unique stacking feature, we can also see the I···I chains along the stacking direction. The I···I distances [4.265(1) and 4.179(1) Å] are almost the same as the sum of the van der Waals radii (3.96 Å: Bondi, 4.30 Å: Pauling). There exist many chalcogen···chalcogen short contacts among columns and the

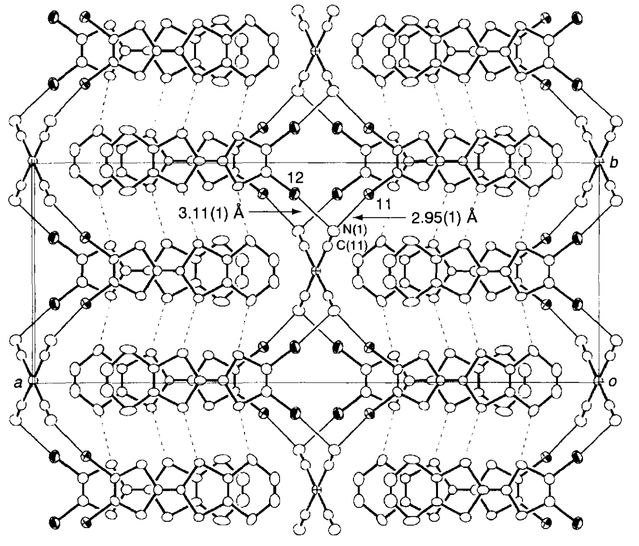


Fig. 2 Packing diagram of $(DIETS)_4Pd(CN)_4$ viewed from the crystallographic *c* axis. Dotted lines indicate the short chalcogen···chalcogen contacts.

intermolecular overlap integrals of HOMOs in DIETS show that inter-column interactions are almost isotropic and are *ca.* 1/5–1/7 of the intra-column ones. These ratios are smaller than those in β-(EDT–TTF)$_2$AsF$_6$ (the ratios are *ca.* 1/7–1/40 and the Fermi surface consists of two pairs of warped planes).[9] Simple tightbinding band calculation indicates that there exist two pairs of quasi two-dimensional opened Fermi surfaces.

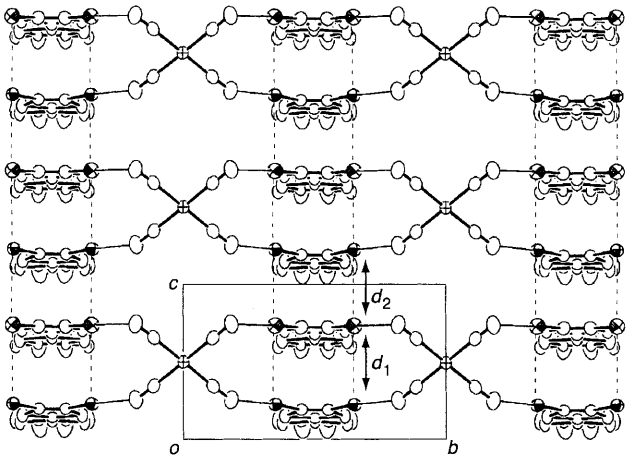


Fig. 3 Donor···anion network viewed from the crystallographic *a* axis. Interplaner distances are: d_1 = 3.67, d_2 = 3.85 Å. Dotted lines indicate the short I···I contacts.

There should be various applications of the strong and directional donor···anion interactions based on iodine-bonded π-donors. For example, an application to systems including anions with localized magnetic moments, would be of special interest from the aspect of the interaction between the itinerant π-electrons and the localized spins.

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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 2θ = 60°. The intensities were corrected for Lorentz and polarization effects and an analytical absorption correction was carried out. The structure was solved by the direct method and refined by full-matrix least-squares methods using reflections with $I \geqslant 3\sigma(I)$. Anisotropic thermal parameters were used for non-hydrogen atoms. All calculations were performed with use of a TEXSAN program package of MSC.

Crystal data for (DIETS)$_4$Pd(CN)$_4$: $C_{36}H_{16}N_4I_8PdS_{16}Se_8$, M_W = 2770.83, monoclinic, space group *C*2/*m*, a = 32.560(7), b = 12.755(3), c = 7.595(2) Å, β = 90.49(2)°, V = 3154(1) Å^3, Z = 2, D_c = 2.917 g cm^{-3}, F(000) = 2516.0, R = 0.064, R_w = 0.083, GOF = 2.47 for 3271 observed reflections out of 4817 unique reflections. *Cell parameters* for (DIETS)$_4$Ni(CN)$_4$: a = 32.433(8), b = 12.699(3), c = 7.626(2) Å, β = 90.32(2)°, V = 3141(1) Å^3, Z = 2. *Cell parameters* for (DIETS)$_4$Pt(CN)$_4$: a = 32.590(6), b = 12.758(2), c = 7.625(2) Å, β = 90.54(2)°, V = 3170(1) Å^3, Z = 2.

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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