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ORGANIC METALS FROM SIMPLE AROMATIC HYDROCARBONS:
 PERYLENE RADICAL SALTS

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Abstract Crystal structures, temperature dependent ther-
 mopower and conductivity measurements of several metallic
 perylene radical salt phases are discussed.

Organic metals from simple aromatic hydrocarbons (radical cation salts) have caused considerable interest because of their easy preparation and their special electronic and magnetic properties¹⁻¹². One of the more interesting donors for the preparation of such metals by electrochemical methods is perylene, due to the fact that a large number of different radical salts varying in stoichiometries and crystal structures but with relatively high electric conductivities can be obtained.

The two most important parameters in the electrochemical crystallization which has to be optimized in order to obtain good quality crystals of different radical salt phases are the concentration of the donor molecules or the donor cations in the solution and the solvent. So, e.g. from dichloromethane (CH_2Cl_2) saturated with perylene (pe) and anions like $\text{X} = \text{PF}_6^-$ or AsF_6^- only one type of crystals is obtained: $(\text{pe})_2\text{X}_{1.1} \cdot 0.8 \text{CH}_2\text{Cl}_2$ (1)¹. Using trichloroethane instead of dichloromethane results in isomorphous crystals but due to the large solvent molecules with a different stoichiometry: $(\text{pe})_2\text{X}_{1.4}$ (2). The more polar solvent tetrahydrofuran (THF) dissolves about 10 times as much perylene as the mentioned chloro-

hydrocarbons in order to obtain a saturated solution. In THF a number of different compounds can be obtained, depending on the concentration of the donor during the electrocrystallisation. Crystals of the following compositions have been characterized: $(\text{pe})_6\text{X}_1$ (3), $(\text{pe})_3\text{X}_1$ (4), $(\text{pe})_2\text{X}_1 \cdot 2/3 \text{ THF}$ (5), $(\text{pe})_2\text{X}_{1.5} \cdot 0.5 \text{ THF}$ (6) and $(\text{pe})_1\text{X}_1$ (7). By choosing the right concentration it is possible to prepare only one of those phases which have all different crystal structures and distinct electrical and magnetic properties.

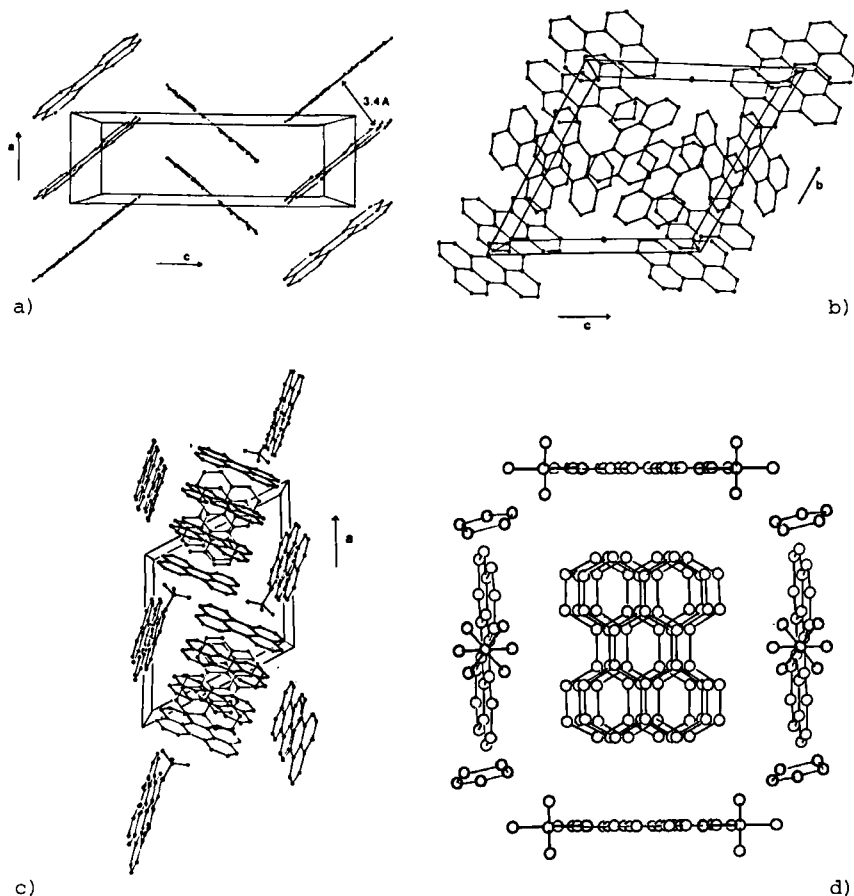


Fig. 1 Structures of: a) 1, 2, 6. b) 3. c) 4. d) 5.

Fig. 1a) shows the perylene stacks in crystals of 1, 2 and 6 projected perpendicularly to the stacking axis¹. A stereo projection of the unit cell of crystals of 3 onto the ac-plane is shown in Fig. 1b)¹³, of 4 onto the ab-plane in Fig. 1c)¹³ and a projection of the unit cell of crystals of 5 onto the ab-plane in Fig. 1d)¹³.

In crystals of 1, 2 and 6 regular perylene stacks occur with the molecules inclined to the stacking axis resulting in a "herring bone" arrangement (Fig. 1a). Those crystals show a metallic behaviour at room temperature with conductivity values up to $1400 (\Omega\text{cm})^{-1}$.

The semiconducting 6:1 phase 3 (Fig. 1b) contains three different pairs of perylene molecules which are arranged in a nearly perpendicular way. In the 3:1 phase 4 (Fig. 1c) two types of perylene molecules are observed. Tetradic stacks of perylene molecules with only a weak overlap between the tetrads occur flanked by other perylene species and by anions¹³. Along the stack direction an electric conduction can be observed. The conductivity ranges at about $0.5 (\Omega\text{cm})^{-1}$.

In the 2:1 phase 5 (Fig. 1d) perylene molecules form nearly regular infinite stacks parallel to the c-axis. Within a stack the molecules are parallel and the crystallographically interplanar distances are identical (3.4 \AA). Additional perylene units nearly perpendicular to the stack molecules form "channel-walls" together with THF-molecules and the anions¹³. The room temperature conductivities of crystals of 5 typically range between 50 and $100 (\Omega\text{cm})^{-1}$.

Crystals of 1, 2 and 6 are quasi one-dimensional organic metals down to about 180 K for 1, and 2 and to about 110 K for 6 as it was shown by several spectroscopic methods^{1,4,6,9,10}. The isomorphous crystals of 1, 2 and 6 with different stoichiometries have almost identical bandwidths of the conduction band but varying bandfillings. The nearly identical bandwidths of the conduction band could be demonstrated by thermopower measurements. Fig. 2a)

and b) show the temperature dependence of the thermopower of typical crystals of 1 and 6.

In a one-dimensional case the thermopower S for an electron gas in a tight binding band $\epsilon_k = 1/2 W \cos(ka)$ is given /14/ by eq. 1)

$$S = \frac{2 \pi^2 k_B \cdot T}{3e \cdot W} \cdot \frac{\cos(\pi/2 \cdot \rho)}{\sin^2(\pi/2 \cdot \rho)} \quad (1)$$

W = bandwidth; ρ = number of holes per site; $\rho = 0.55$ for crystals of 1 and $\rho = 0.75$ for crystals of 6. Using these ρ , the thermopower S of 6 should be smaller than S of 1 as actually found (see Fig. 2a,b). From the linearly dependent parts of S in Fig. 2a) and b) we obtain a bandwidth $W = 1.2$ eV for 1⁹ and $W = 1.35$ eV for 6 in a good agreement with optical reflectance measurements⁶.

Fig. 3a) shows the temperature dependence of the conductivity normalized to the room temperature value for $(\text{pe})_2\text{AsF}_6 \cdot 2/3 \text{ THF}$ (5a) crystals. A very similar conductivity behaviour is observed for $(\text{pe})_2\text{PF}_6 \cdot 2/3 \text{ THF}$ (5b) or $(\text{pe})_2(\text{AsF}_6)_{0.45}(\text{PF}_6)_{0.55} \cdot 2/3 \text{ THF}$ (5c). Nevertheless, a few excellent crystals of the mixed anion type 5c behaved like shown in Fig. 3b). The steep conductivity increase can not be observed in a second temperature cycle.

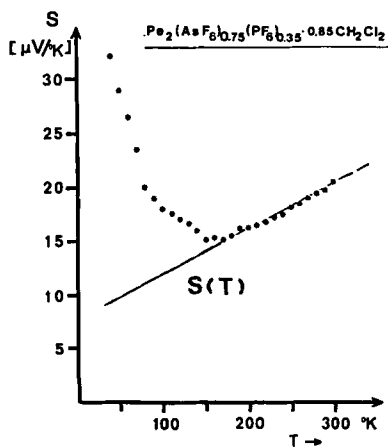


Fig. 2a) Thermopower of crystals of 1.

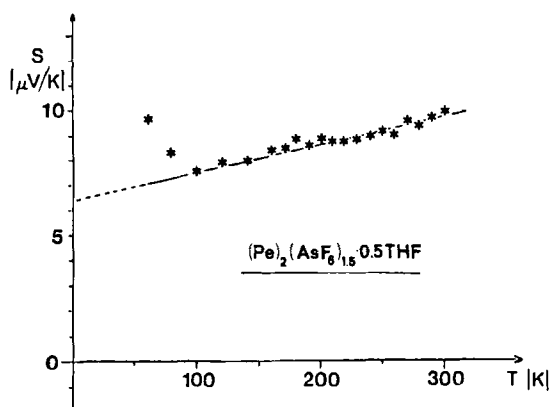


Fig. 2b) Thermopower of crystals of 6.

A similar behaviour was already observed in mixed anion type crystals of 1⁴. There are further indications that crystals of 5c behave special. ESR-experiments show that the specially selected crystals of 5c are exceptionally good quasi one-dimensional systems¹⁵. While the ESR-linewidth of crystals of 5a and 5b are 34 resp. 26 mG those of 5c are typically 17 mG and in specially selected crystals even smaller. Electron spin echo decay experiments of the latter specimens indicate a ratio of the in-stack to out-of-stack diffusion rate of $D_{||}/D_{\perp} > 10^7$ ¹⁵.

The thermopower of crystals of 5c is non-linear in the temperature range in which the conductivity increases (see Fig. 4). This non-linear behaviour resembles very much the phonon drags usually appearing in metals at temperatures below 20 K.

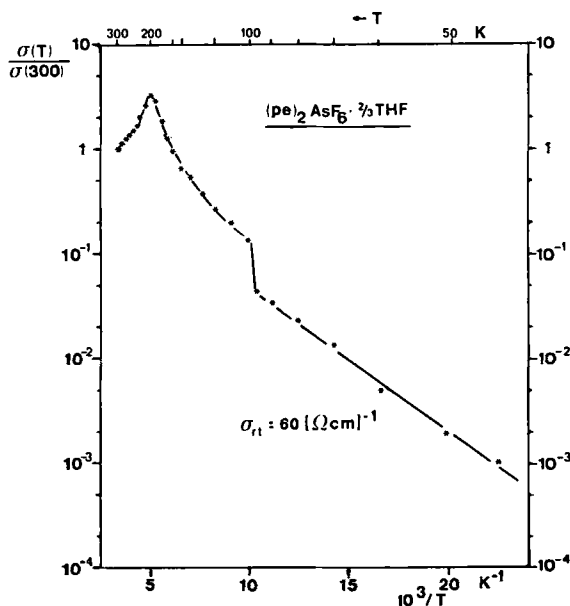


Fig. 3a) Temperature dependent conductivity of crystals of 5a.

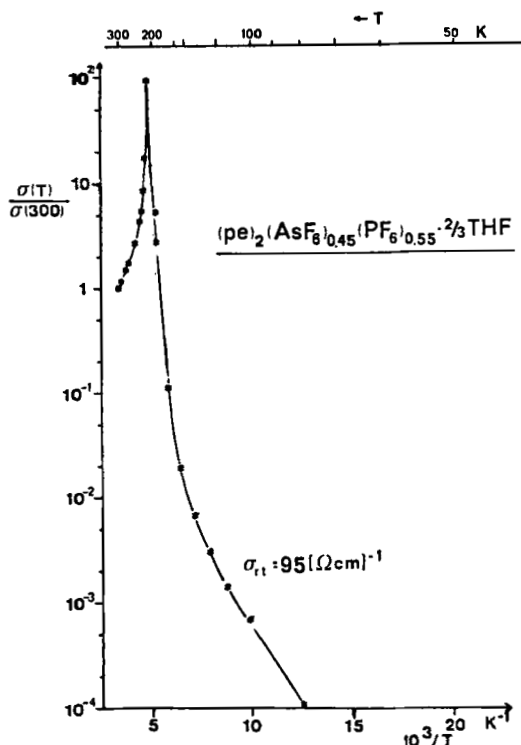


Fig. 3b) Temperature dependent conductivity of exceptionally good crystals of 5c (see text).

It was shown^{16,17} that such a phonon drag-like behaviour can also be expected at high temperatures if electron-libron interactions play a dominant role and if the libron-libron collision time is larger than the libron-electron collision time so that the librions cannot reach thermal equilibrium. In such a case the quadratic electron-libron interactions might explain the steep conductivity increase^{16,17}. The non-linear behaviour of the thermopower below 110 K (Fig. 4) probably is caused by a phase transition which is also evident in the conductivity data (Fig. 3a). The conductivity below 110 K is typically as for a semiconductor.

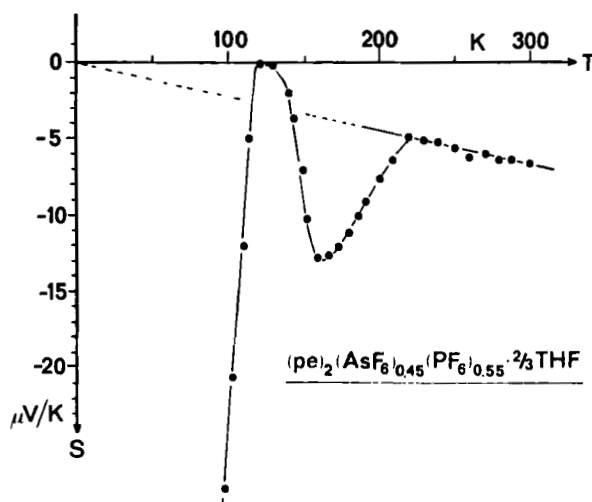


Fig. 4) Thermopower of crystals of 5c.

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