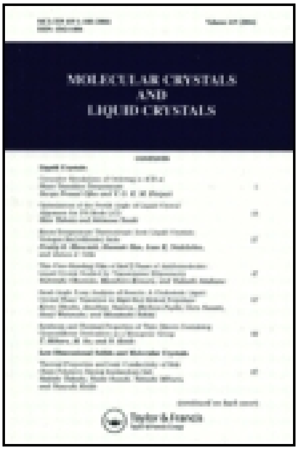

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METAL-INSULATOR TRANSITIONS IN THE PERYLENE-DITHIOLATE FAMILY

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Abstract In the family of the isostructural perylene-dithiolate organic conductors with general formula (perylene)$_2$M(mnt)$_2$, (mnt = 1,2 dicyanoethylene-1,2-dithiol), (M = Pt, Pd, Au), the platinum and palladium compounds undergo clear metal-insulator transitions at 6.5 K and 28 K respectively and the gold one a broad transition with a minimum in the resistivity at 55 K. In these materials, electrons are itinerant on the segregated perylene stacks and appear to be localized on the dithiolate stacks which are magnetic (one unpaired electron) for M = Pt, Pd and diamagnetic for M = Au. This difference appears to be related to the fact that 1 D structural fluctuations are observed well above the transitions, by X-ray diffuse scattering, in both materials where the dithiolate stack is magnetic, and are not detected in the other. The nature of these transitions will be discussed on the basis of the available data.

INTRODUCTION

The family of perylene-dithiolate complexes has proved to be particularly suited for the study of the importance of magnetic interactions related to metal-insulator transitions in highly conducting organic materials. The complexes of this series, derived from the metal bis(cis-1,2-dicyanoethylene-1,2 dithiolene), abreviately known as M(mnt)$_2$ have the general formula (Per)$_2$M(mnt)$_2$ where M = Ni, Cu, Pd, Pt and Au. A particularly interesting situation results from the fact that in the isostructural Pt, Pd and Au complexes the conducting radical cation stacks run parallel to the dithiolate anion chains which are magnetic when M = Pt and Pd and diamagnetic when M = Au. They exhibit metallic behavior down to very low temperatures, followed by metal-insulator transitions accompanied by magnetic transitions.

Usually in organic metals, the high conductivities are due to transport along a radical cation or anion linear chain with Pauli type magnetic susceptibility, the counter-ions being diamagnetic.

On the other hand, linear chains of paramagnetic species usually appear in insulators. Insulating dithiolate complexes with magnetic one-dimensional character and undergoing spin-Peierls transitions have, in fact been described by Interrante et al.[1]. Conductors derived from $M(mnt)_2$ with no peculiar magnetic behavior have also been reported by Underhill and Ahmad[2]. $Li_{0.82}Pt(mnt)_2 \cdot 2H_2O$ undergoes a simple Peierls transition at 215 K.

The combination of perylene, as a donor, with 1,2-dithiolate transition metal complexes, as acceptors, was first reported by Schmitt et al.[3]. The molecular packing in this perylene-nickel bis(cis-1,2-ditrifluoromethylethylene-1,2-dithiolene), complex of formula $(Per)\,|Ni(S_2C_2(CF_3)_2)_2|$, consists of true alternate stacks with regular spacing and the compound is a semiconductor with a conductivity of the order of 10^{-5} $ohm^{-1}\,cm^{-1}$, measured in a single crystal. Studies on the family of the highly conductive perylene--dithiolate complexes followed, and the first results were reported in 1974 and 1976[4,5]. Since then, we have been studying the electrical and magnetic properties of the $(Per)_2M(mnt)_2$ complexes with M = Pt, Pd, Au and we will now try to give a general view on the nature of their metal-insulator transitions considering the magnetic behavior in the neigbourhood of those transitions.

SURVEY OF EXPERIMENTAL RESULTS ON THE $(PER)_2M(MNT)_2$ FAMILY

Structure

$(Per)_2M(mnt)_2$, with M = Pt, Pd and Au is an isostructural series crystallizing in the monoclinic system (space group $P2_1/c$). A detailed structure, for the $(Per)_2Pt(mnt)_2$ was reported earlier[6]. Latice parameters are a = 16.612 A, b = 4,194 A, c = 30,211 A, β = = 118.70°. The perylene and the $Pt(mnt)_2$ molecules form segregated regular stacks in a skew arrangement, along the b axis. The perylene molecules are 3.32 A apart along the chain and the

$Pt(mnt)_2$ molecules are separated by 3.65 A, the distance between Pt atoms being 4.19 A. In the ac plane the stacking is close to an hexagonal array, with 6 perylene stacks surrounding a dithiolate stack, Fig.1. Both species are tilted relative to the b axis, the perylene molecular planes forming an angle of 37^{o} with the b axis and the dithiolate molecules, an angle of 29^{o} in the oposite sense.

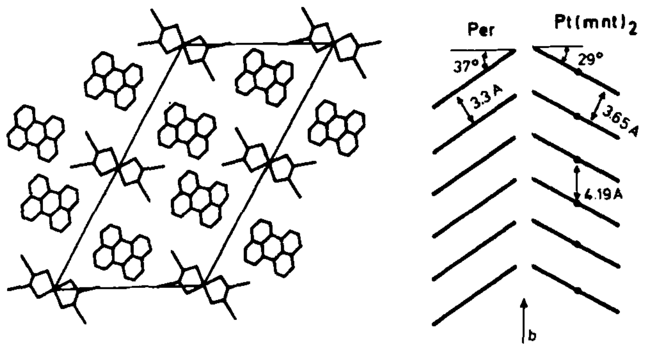

FIGURE 1 Projection of the structure of Per_2 $Pt(mnt)_2$ along the b axis (left), and schematic representation of the stacking (right).

Electrical resistivity and X-ray diffuse scattering

We have recently reported detailed resistivity measurements and X-ray diffuse scattering results on the members of this family of organic metals[7]. In Fig.2, typical conductivity results are shown.

The platinum and the palladium compounds undergo clear metal-insulator transitions at 6.5±0.5 K and 28±1 K respectively, and the gold one a broad transition with a minimum in the resistivity at approximately 55 K .

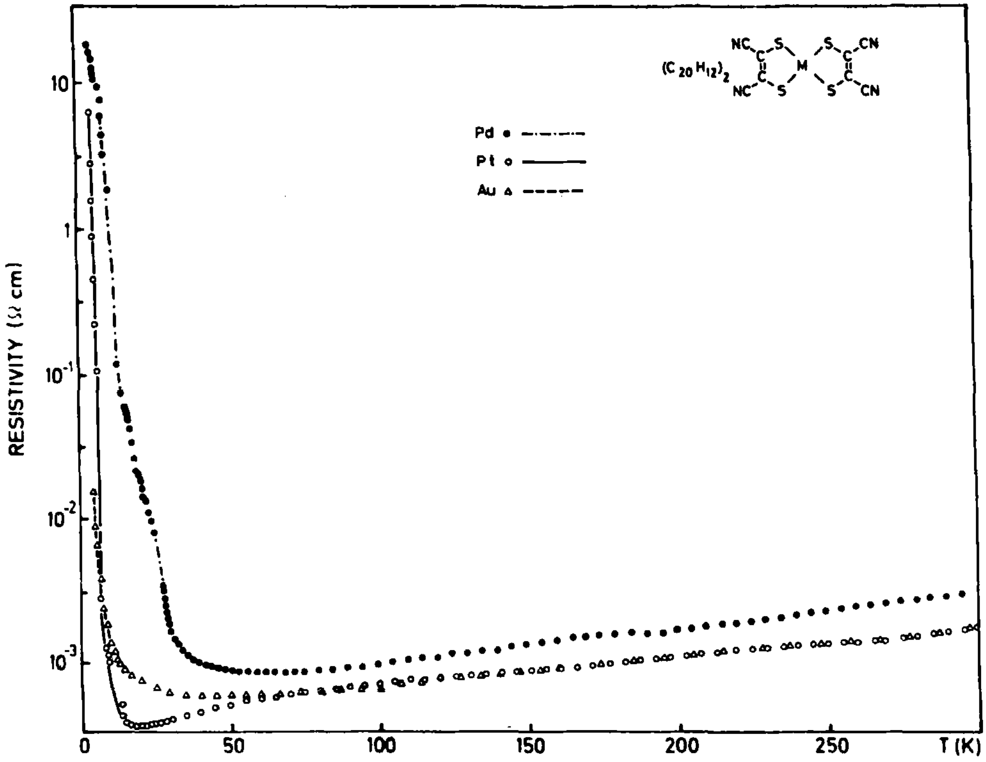

FIGURE 2 Temperature dependence of the resistivity for Per_2 $M(mnt)_2$, M=Pd, Pt, Au.

In $(Per)_2$ $Pt(mnt)_2$, the resistivity increases sharply around the transition temperature, by 5 orders of magnitude, and then decreases again from 2.5 K down to the limit of our measurement which was 1.3 K. The maximum in the conductivity is observed at ~20 K and its value is around 3×10^3 $ohm^{-1}cm^{-1}$. At room temperature the anisotropy of the conductivity is of order $\sigma_b/\sigma_a \simeq 10^3$.

In $(Per)_2$ $Pd(mnt)_2$, a second transition at approximately 11 K is apparent from the resistivity and a tendence to bend down, is also apparent from the data.

The X-ray diffuse scattering results show that for $(Per)_2Pd(mnt)_2$

diffuse planes at $q = b^*/2$ are visible starting at about 100 K and clearly condensing at ~30 K. Similar behavior is observed for $(Per)_2\ Pt(mnt)_2$ for which those diffuse planes start to be visible at 25 K showing at 10 K a visible tendency to condensate. In our equipment the lowest temperature atainable was 10 K.

Contrary to the behavior in these two first compounds, in $(Per)_2\ Au(mnt)_2$no diffuse planes are observed down to 10 K.

Magnetic Properties

The magnetic properties of $(Per)_2\ Pd(mnt)_2$ have been reported earlier[5]. From bulk static magnetic susceptibility measurements and powder e.s.r. spectra, it could be proven that spin exchange interaction takes place between the spins localized on the perylene stack and those on the $Pd(mnt)_2$ stack. Here, we should recall that $Pd(mnt)_2^-$ and $Pt(mnt)_2^-$ are paramagnetic species, while $Au(mnt)_2^-$ is diamagnetic. $(Perylene)^+$ is, of course a paramagnetic cation radical. It was indeed shown that in $(Per)_2\ Pd(mnt)_2$ the powder e.s.r. spectra had averaged g values, $\bar{g}_i(Per_2\ Pd(mnt)_2) = x\ g_{Per} + (1 - x)\ g_i\ (Pd(mnt)_2^-)$; the subindex i referring to each of the three components of the anisotropic g tensor, for both $(Per)_2\ Pd(mnt)_2$, and $Pd(mnt)_2$ in (tetrabutylammonium) $Pd(mnt)_2$, as indicated. The g value for perylene was taken as isotropic ($g = 2.0026$). From spectra at different temperatures, in the range of 77 to 300 K, x values were computed for each temperature. Using those and the bulk static paramagnetic susceptibility data in the same temperature region the contribution to the susceptibility due to the perylene stack could be separated from the contribution due to the $Pd(mnt)_2$ stack.

It was shown that the perylene stack had an almost temperature independent susceptibility of the Pauli type (of order 3×10^{-4} emu) in that temperature range, while the $Pd(mnt)_2$ species behaved as a Curie Weiss paramagnet corresponding to 0.11 spins per formula unit.

More recently, we have focused on the magnetic properties of the other members of the series. Preliminary results on the bulk static magnetic susceptibility of $(Per)_2Pt(mnt)_2$[6] show a Curie-Weiss type behavior from 300 K down to around 30 K, at which temperature an anti-ferromagnetic-like interaction appears to begin taking place, the susceptibility goes through a maximum at about 20 K and then it decreases sharply. An atempt was made to separate the perylene stack component, at that time. This proved to be correct as our most recent results from e.s.r. spectra show that, at least in the high temperature region, a spin exchange interaction takes place between the perylene spins and those localized on the $Pt(mnt)_2$. Another interesting feature of the e.s.r. results which are presented in more detail at a poster in these proceedings, is the fact that in both the Pd ant Pt complexes, for $H \perp b$ an e.s.r. line appears at $g = g_y(M(mnt)_2^-)$ below the metal-insulator transition. In $(Per)_2$ $Pt(mnt)_2$, with $H \perp b$, the intensity of the single crystal e.s.r. line with $g = 2.016$ which we interprete as the result of exchange between the perylene spins ($g = 2.0026$) and the $Pt(mnt)_2^-$ spins ($g_x = 2.067$) has a maximum at around 20 K and decreases sharply below 10 K , in agreement with the static susceptibility data.

$(Per)_2$ $Au(mnt)_2$ exhibits a single e.s.r. line corresponding to the perylene spins which slowly decreases in intensity down to around 7 K, when it starts to increase sharply, with sharply decreasing linewidth.

CONCLUSIONS

It is clear that conduction occurs through the perylene stacks and that the electrons on the dithiolates are localized. A positive thermopower which at room temperature is of the order of 28 $\mu V K^{-1}$ for all three members of the family is an indication that the dominant charge carriers are the holes on the perylene stacks. The Curie-Weiss type magnetic susceptibility for the platinum and palladium complexes in the high temperature region is an indication that electrons are localized on the dithiolate anions although their spins are exchanging with those on the perylene stacks giving a Pauli type susceptibility on those stacks. All this agrees with the formula $(Per)_2^+ M(mnt)_2^-$ with 1/2 hole per perylene molecule and one electron per dithiolate anion with $S = 1/2$ for $M = Pt$ and Pd, and $S = 0$ for $M = Au$.

The palladium and platinum complexes undergo true metal-insulator transitions driven by one-dimensional structural fluctuations on the dithiolate stacks ($q_b = 0.5\ b^* = 2\ K_F$), where the electrons appear to be localized, from the magnetic measurements. The magnetic data at low temperatures is still insufficient to determine the real nature of those phase transitions, but the 1D structural fluctuations observed well above the transition temperatures reflecting the presence of 1D spin fluctuations and the behavior of the metal-insulator transition observed in the platinum complex point towards spin-Peierls type transitions. A more detailed study of the magnetic properties in the vicinity of those transitions is under way and we hope to be able to clarify this very interesting situation in the near future.

In the case of $(Per)_2\ Au(mnt)_2$ the fact that $Au(mnt)_2^-$ is a closed shell anion explains the absence of diffuse lines in the diffuse X-ray scattering if the driving force for dimerization in the other compounds is of magnetic origin. The transition in this material, also appears to be of a different nature. The broad transition could be due to a gradual electron localization when the temperature decreases.

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