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Low dimensional molecular semiconductor: the radicalar bis-phthalocyaninato lutetium Pc2Lu.CH2Cl2 (*)

P. Petit, K. Holczer and J.-J. André
Institut Charles Sadron, 6, rue Boussingault, 67083 Strasbourg Cedex, France

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Résumé. — Les cristaux de bis-phtalocyanine de lutétium solvaté, Pc2Lu.CH2Cl2, sont des semiconducteurs moléculaires intrinsèques (\( \sigma_{\text{R.T.}} = 6 \times 10^{-5} \ \Omega^{-1}. \text{cm}^{-1} \), \( E_{\text{act.}} = 0.32 \text{eV} \)). La structure cristalline et les propriétés magnétiques montrent le caractère unidimensionnel de ce système radicalaire. Contrairement aux propriétés magnétiques qui sont profondément perturbées par la présence d’oxygène, les propriétés de transport y sont insensibles. Ceci est caractéristique d’un couplage entre spins de la molécule de dioxygène adsorbée et de la molécule radicalaire concernée.

Abstract. — Crystals of solvate bisphthalocyaninato-lutetium, Pc2Lu.CH2Cl2, are shown to be intrinsic molecular semiconductors (\( \sigma_{\text{R.T.}} = 6 \times 10^{-5} \ \Omega^{-1}. \text{cm}^{-1} \), \( E_{\text{act.}} = 0.32 \text{eV} \)). Both crystallographic determinations and magnetic properties demonstrate the one-dimensional character of this radicalar material. While dioxygen has drastic and reversible effects on the magnetic properties, it has not anyone on transport properties. This is characteristic of spin coupling between the adsorbed oxygen and the radicalar host molecule, Pc2Lu.CH2Cl2.

1. Introduction.

Organic semiconductors have been intensively studied [1-3]. However, as far as molecular semiconductors are defined as materials composed of a single kind of molecules which may crystallize and form thin films showing an intrinsic conductivity in the range \( 10^{-6}-10^{-1} \ \Omega^{-1}. \text{cm}^{-1} \), none of the organic compounds presenting an apparent semiconducting behaviour can be considered as an intrinsic molecular semiconductor [3]. The only exceptions are bis-phthalocyanine derivatives recently reported [4-8]. While the conduction properties of different rare earth diphthalocyanines were reported [9-11], the intrinsic character was demonstrated for the Lu derivative [5-8]. In particular for this system, a conductivity at room temperature of \( 10^{-5} \ \Omega^{-1}. \text{cm}^{-1} \) has been reported and its ability to be doped by electron donor or acceptor has been proved [5, 6]. The elaboration of associated devices such as Schottky or p-n junctions is now in progress [7].

The peculiar conduction properties of Pc2Lu are related to the exceptional redox properties of this radicalar (neutral) system [12]; indeed, as far as the hopping transport is concerned, the smaller the difference between the oxidation and reduction potentials, the smaller is the thermal activation energy and the higher the room temperature conductivity [4, 6, 8, 13].

The synthesis of Pc2Lu was first reported by Moskalev and co-workers [14-16] and its radicalar nature is now well established [17-19]. Single crystals of Pc2Lu may be obtained by recrystallization or electrocrystallization. However a polymorphism is observed leading to very different stackings depending on the preparation conditions [20, 21].

This system may then be studied in a great variety of phases with various anisotropy, dimensionality of packing and type of organisation. Apart single crystals, amorphous or polycrystalline thin films or even columnar liquid crystals when using substituted derivatives may be obtained [5, 6, 22]. This paper deals with magnetic and electrical properties discussed in terms of dimensionality and disorder, of one of the possible crystalline structures shown by Pc2Lu; drastic effects of oxygen are described.

Pc2Lu is prepared from dichloromethane solution as Pc2Lu.CH2Cl2 solute. As this peculiar crystalline...
form is obtained by recrystallization, the only tractable samples are composed of a few aligned single crystals (referred to as oriented polycrystals in the following). The structure of the PC2Lu molecule is shown in figure 1 [21]. The lutetium atom (Lu(III)) is eight-fold coordinated by the isoindole nitrogen atoms of the two staggered phthalocyanine macrocycles (A and B), one of them rotated by 45° with respect to the other. The mean-values of the distances between the Lu atom and the four Niso of both rings A and B are 1.35 Å and 1.34 Å respectively. Both macrocycles are convex but one of them (A) deviates more from planarity than the other one (B).

![Fig. 1. — Molecular structure of bis-phthalocyaninato lutetium (III) after [21].](image)

In this crystalline form, the phthalocyanine molecules are regularly stacked and parallel in the c direction, which is the growing axis of the crystal (Fig. 2). The planes of the macrocycles in this stack make an angle of 36° with the c axis. The interaction between two consecutive molecules distant of around 3.8 Å is favored. Molecules belonging to neighbouring stacks are parallel in the b direction and tilted by an angle of 72° with respect to each other in the a direction. This structure shows a bidimensional arrangement of parallel molecules. The interactions of π-electrons between molecules belonging to successive (bc) planes should be very weak. From the crystallographic structure, it can then be deduced that the interactions in this material must be strongly anisotropic:

\[ J_a < J_b < J_c. \]

The included CH₂Cl₂ molecules of the solvent of crystallization are located in the crystallographic mirror plane and surrounded by four PC₂Lu molecules.

From the crystallographic data, no indication may be deduced concerning the radicalar nature of the molecule in the crystal and the electron localization on one or both macrocycles of the molecule. These points may only be clarified for isolated molecules from their magnetic behaviour in solution [23].

In various solvents (dichloromethane, chloroform, tetrachloromethane, chloronaphtalene, toluene), PC₂Lu shows an E.S.R. spectrum composed of one unresolved line near the free electron confirming the π-nature of the unpaired electron. In all cases, its intensity corresponds to one spin 1/2 per PC₂Lu, as expected for this neutral radical (green form).

2. Magnetic properties of PC₂Lu.CH₂Cl₂ in solid state.

In solid state, the E.S.R. line shape becomes nearly Lorentzian and the linewidth is drastically reduced, indicating a strong spin exchange interaction in the material. The signal exhibits an intensity corresponding to one spin 1/2 per PC₂Lu molecule.

The temperature dependence of the unpaired π-electrons magnetic susceptibility determined by integration of the E.S.R. signals is in total agreement.

![Fig. 2. — Schematic crystal packing in PC₂Lu.CH₂Cl₂ structure (ac plane) after [21]. NMET = Methine Nitrogen Atom ; NISO = Isoindole Nitrogen Atom.](image)

![Fig. 3. — Inverse of normalized magnetic susceptibility as a function of temperature of a PC₂Lu.CH₂Cl₂ polycrystalline sample determined from E.S.R.](image)
with the one obtained from static susceptibility measurement previously reported on similar crystals [18]. As already published [5], this dependence follows a Curie-Weiss law on the whole temperature range (4.2-300 K) with a spin exchange temperature of about 6 K (Fig. 3).

3. Oxygen effect.

The peak to peak linewidth is around 1 gauss (depending on the orientation) for oriented polycrystals and 2 gauss for powder samples. However, this linewidth is strongly affected by the presence of air [5] and decreases instantaneously by a factor two when pumping on the sample, whereas the intensity of the signal remains unchanged. This effect, fully and immediately reversible, is related to an adsorption phenomenon of dioxygen molecules on the surface of the sample rather than a complexation similar to that observed for non radical phthalocyanine derivatives and polyacetylene [24]. In this last case the conductivity would be drastically modified whereas the electrical characteristics of Pc$_2$Lu.CH$_2$Cl$_2$ remain unaffected by the presence of oxygen. As observed for some TCNQ salts [25], the line is broadened by a supplementary relaxation process due to spin exchange of the sample with the magnetic moment of the dioxygen molecules. At each temperature ($T > 300$ K), a polycrystalline sample was exposed to air and then pumped off. The effect of oxygen on the linewidth disappears at about 500 K (Fig. 4). Since the exchange coupling between neighbouring Pc$_2$Lu ($J = 6$ K) is relatively small, either oxygen may diffuse rapidly inside the crystals or the surface in contact with oxygen is large. Since this crystalline form is compact (density 1.64), the oxygen effect has then been interpreted as issued from a high specific area related to the presence of many cracks, usually observed for organic systems containing solvent molecules.

A more detailed study of the linewidth has been performed in the low temperature range (4.2-300 K). In presence of helium gas, an anomaly occurs on powder samples at 55 K, corresponding to the melting temperature of O$_2$, trace of which being unavoidable. This singularity disappears for vacuum sealed samples (Fig. 4). The same study was carried out on a crystal and preliminary results pointed out that a splitting of the E.S.R. line appears at low temperature (between 4.2 and 50 K) [5] and is maximum for a peculiar angle between the crystal c axis and the applied magnetic field $H_0$. The two lines collapse for an angle of 55-60°. However, this effect does no more occur for a vacuum sealed sample, the spectrum being composed of only one of these lines in the whole temperature range whatever the orientation. One of this line is clearly linked to the presence of oxygen and shows a much more anisotropic g-factor than the other one. The existence of both signals is clearly due to two types of spins, both localised on the phthalocyanines, but with two different magnetic environments. This splitting is not due to misorientation of a part of the polycrystalline samples.

4. Dimensionality of Pc$_2$Lu.CH$_2$Cl$_2$.

The anisotropy of the linewidth as a function of the orientation with regard to the magnetic field has been carried out on a vacuum sealed crystal. Whereas no anisotropy is observable when the sample growing axis (c axis) is parallel to the r.f. field $H_1$, the variation of the linewidth is characteristic of a low dimensional system when c axis is perpendicular to $H_1$ (Fig. 5). It has been shown that

![Fig. 4. — Oxygen effect on a powder sample.](image)

![Fig. 5. — Variation of $\Delta H_{1/2}$ expressed in gauss as a function of the orientation between the crystal c axis and the magnetic field.](image)
the E.S.R. linewidth is expressed, for a one-dimensional system as [26]:

\[ \Delta H = \alpha |3 \cos^2 \theta - 1|^{4/3} + \beta \]  \hspace{1cm} (1)

and for a two-dimensional one as [27]:

\[ \Delta H = \alpha' (3 \cos^2 \theta - 1)^2 + \beta' \]  \hspace{1cm} (2)

where \( \alpha, \beta, \alpha', \text{ and } \beta' \) are constants.

In our case, equation (1) fits the curve much better than equation (2), but the polycrystalline character of the samples prevents the complete analysis of the line shape at the peculiar angles (0°, 55° and 90°). Nevertheless, at 55° and in the whole temperature range, the ratio \( (\Delta H_{pp})/(\Delta H_{1/2}) \), where \( \Delta H_{1/2} \) is the half-width at half maximum of the absorption line, is almost constant and close to \( 2/\sqrt{3} \), characteristic of a pure Lorentzian shape as expected for this peculiar orientation [27] (Fig. 6). Note that the anisotropy remains important on the whole temperature range.

\[ \text{Fig. 6. — Comparison between } \Delta H_{1/2}(0) \text{ and } \Delta H_{pp}(x) \text{ expressed in gauss as a function of temperature for the } 55^\circ \text{ orientation (magic angle).} \]

5. Electrical properties of \( \text{Pc}_2\text{Lu.CH}_2\text{Cl}_2 \).

Electrical conductivity measurements, with both two and four contacts, have been performed on \( \text{Pc}_2\text{Lu.CH}_2\text{Cl}_2 \), along the c axis, in the temperature range 200-450 K (Fig. 7). The contacts have been realized with silver paint and 10 \( \mu \) diameter gold threads.

The results obtained by the two methods are identical because of the high enough resistivity of the materials. The room temperature conductivity is:

\[ \sigma_{\text{R.T.}} = 6 \times 10^{-5} \text{ } \Omega^{-1} \text{ } \text{cm}^{-1}. \]

It is at least six orders of magnitude higher than those found for all the other metallo-phthalocyanines [3] studied at this time and they are not affected by the presence of oxygen. In this system, oxygen does not play a role of electron acceptor.

As a function of temperature, an activation energy of 0.32 eV has been found, assuming that the conductivity follows an exponential law of the type:

\[ \sigma = \sigma_0 \exp(-E_{\text{act.}}/kT) \]

where \( k \) is Boltzman's constant.

This transport property does not significantly depend on the samples and is nearly frequency independent \( (\sigma(10 \text{ GHz}) = 10^{-4} \text{ } \Omega^{-1} \cdot \text{cm}^{-1} \) at room temperature). In consequence, these values are considered as intrinsic characteristics of \( \text{Pc}_2\text{Lu.CH}_2\text{Cl}_2 \) crystals.

6. Discussion.

From crystallography and E.S.R. measurements, it has been shown that \( \text{Pc}_2\text{Lu.CH}_2\text{Cl}_2 \) is a highly anisotropic system (1D) in which the spin exchange interactions dominate the line shape. Furthermore, as well in solution as in solid state, the magnetic susceptibility remains unchanged. No electronic delocalization then arises in solid state, i.e., the overlap between two consecutive molecules is not
strong enough to overcome the Coulomb repulsion of two electrons on the same site. For these reasons, it is to be expected that the conduction comes from the hops of electrons from site to site along the chains forming the material in the c direction. In a simple Hubbard model approach (28):

\[ H = U \sum_i n_{i,\uparrow} n_{i,\downarrow} + t \sum_{i,\sigma} (a_{i+1,\sigma}^\dagger a_{i,\sigma} + a_{i,\sigma}^\dagger a_{i+1,\sigma}) \]

(where \( t \) is the hopping integral between the two consecutive molecules, \( a_{i,\sigma}^\dagger \) and \( a_i \) the creation and annihilation operators, \( n_i \) the occupation operator). The Coulomb energy \( U \) being supposed to derive from the activation energy \( (U = 2 E_{\text{act}}) \) a bandwidth of \( 4t = 0.050 \text{ eV} \) may be estimated through the relation \( J = \frac{2t^2}{U} \).

For such a system, contrary to the magnetic properties, the transport ones are not drastically depending on the stacking details, except if the dimensionality is affected, as expected for other reported crystalline structures of \( \text{Pc}_2\text{Lu} \) [23].

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