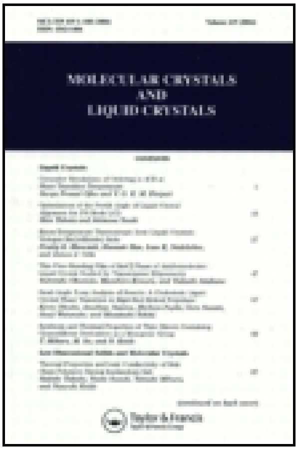

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Septet Spin State in the Lithium Phthalocyanine π-Radical Compound. Role of Dioxygen

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SEPTET SPIN STATE IN THE LITHIUM PHTHALOCYANINE π-RADICAL COMPOUND. ROLE OF DIOXYGEN.

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Abstract The lithium phthalocyanine π-radical compound is a molecular semiconductor which exhibits exceptional magnetic properties. These latter are interpreted as resulting from two distinct spin species. One species is delocalized and its behaviour may be interpreted in the frame of itinerant magnetism. It is responsible of an extremely narrow ESR line. The other species is due to localization of the PcLi spins interacting with molecular oxygen. At low temperature this magnetic coupling is shown to stabilize a septet spin state which involves indirect ferromagnetic coupling between neighbouring π-spins. The experimental results obtained up to now on this unexpected spin state are presented and discussed.

INTRODUCTION

The search for bulk ferromagnetic properties in organic compounds has gained much interest during the last years.[1] Such a challenge has lead different workers to suggest some basic rules about the possible ways to obtain molecular ferromagnetism.[1-6] For example in some materials the stabilization of a high spin multiplicity in the molecular ground state seems to be a necessary condition. However in order to achieve bulk ferromagnetism it is of course necessary to couple, in some way, ferromagnetically such high spin states. Three basically different classes of organic compounds have been investigated up to now, namely: i) segregated stacks[6] or mixed-stacks[5] charge-transfer complexes; ii) polymeric materials[3,4] and organic radicals[7]; and iii) organometallic compounds.[8] In class i)the magnetic properties of the first unambiguous organic bulk ferromagnet[9] have been interpreted in the frame of the ideas first proposed by McConnell.[2] High spin multiplicities have been obtained in polymers and radicals[7,10-12] and the search for bulk ferromagnetism is in progress.[6,12]

The present work deals with a molecular band semiconductor, the lithium phthalocyanine π-radical compound, PcLi.[13-16] In the following it will be shown that PcLi may interact with dioxygen, O_2, without involving complexation or charge-transfer mechanisms. The resulting septet spin-state observed at low temperature is interpreted as originating from indirect ferromagnetic exchange coupling between neighbouring PcLi π-spins; this coupling is favoured by the presence of the localized triplet spin ground state of O_2. Both ESR experiments and measurements of magnetization and susceptibility with the help of a SQUID susceptometer suggest the existence of such an exchange coupling. These results are analyzed in relation with the crystalline structure of PcLi.[17]

SAMPLE PREPARATION

The synthesis of PcLi has been previously reported.[13] Various samples were stable over a long period of time (more than two years) under usual packaging conditions with regards to temperature and atmosphere. They were obtained through different chemical routes leading to the obtention of pure PcLi.

The sample preparation for the SQUID experiments was recently described.[16] It is worth noting that these samples are polycrystalline because the required amount of PcLi is at least a few tens of mg in order to achieve the best experimental resolution. The great sensitivity of the ESR technique allows to work with only one single crystal ($m \leq 1$ μg).

At the present time only the extreme conditions with regards to the O_2 content were studied, i.e. air exposed samples and samples held under vacuum. The amount of O_2 present in the samples could not be determined accurately up to now.

ELECTRON SPIN RESONANCE STUDIES (AT 9.5 GHz)

Linewidth and g-factor

At room temperature and under the ambient atmosphere the peak-to-peak ESR linewidth ΔB_{pp} of PcLi is about 1 Gauss both for powders and for single crystals. A strong line narrowing is observed on pumping with ΔB_{pp}, decreasing down to a few mG for a crystal (fig. 1a,b). Such a narrowing effect has been attributed to strong exchange interactions[14]; this effect is instantaneous and reversible.

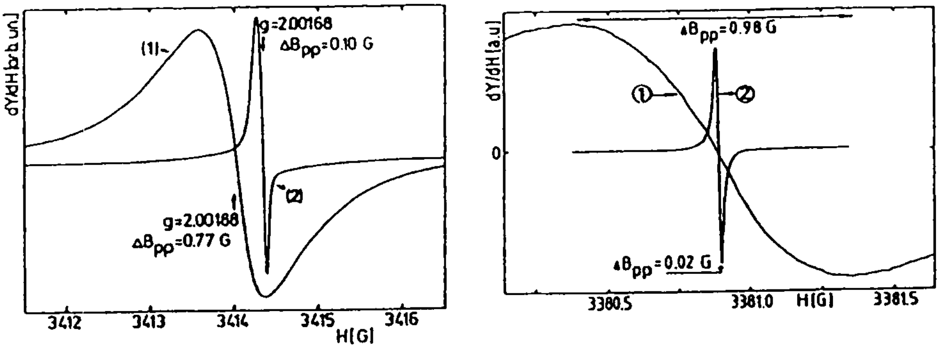

Figure 1. Modification of the ESR signals of a powder (left side) and of a crystal (right side) of PcLi when 1) air exposed, and 2) under vacuum.

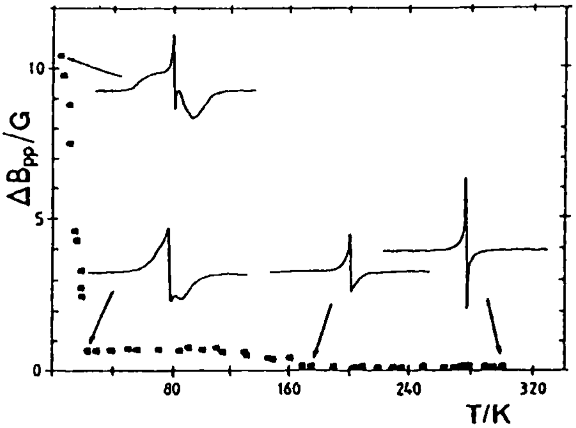

Figure 2. Thermal variation of the peak-to-peak linewidth of PcLi powder held under vacuum. Some typical shapes of the ESR spectra are shown for different temperature ranges.

For the polycrystalline samples held under vacuum (≈ 10^{-2} mbar) the spectrum consists in two superposed lines whose relative intensity is temperature dependent (fig. 2). It should be noticed that both linewidths increase as the temperature decreases: this may be an indication for a localization of the spins. The two components, i.e. the broad and the narrow ones, are observed for a given orientation of a single crystal at low temperature and under vacuum (see caption of fig. 3).

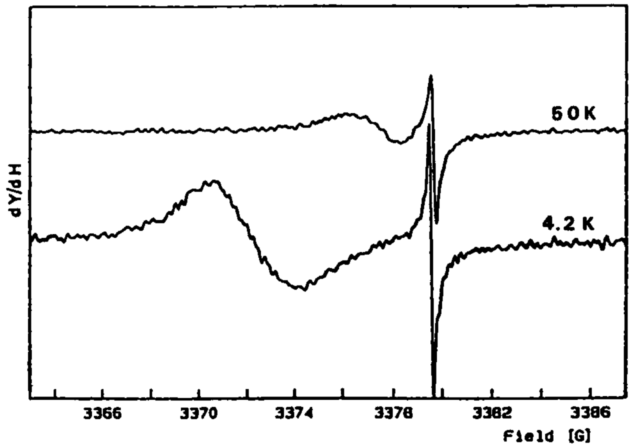

Figure 3. Splitting of the broad component from the narrow component of the ESR spectra for a single crystal held under vacuum (θ=0 degree, T=4.2 K and 50 K).

In Fig. 3 the rotation angle θ is the angle between the direction of the growing axis of the crystal (which is the molecular stacking axis) and the direction of the applied static field H_0. The two components may be observed separately in a crystal, due to a large anisotropy of the g-factor of the broad line (g_B) at low temperature. The g-shift for g_B is specific of a low temperature magnetic behaviour of the spin species involved in the broad ESR line whereas the g-factor for the narrow line (g_N) is close to the free electron g-value. It has a very low anisotropy over the whole investigated temperature range (4-300 K) (Table I).

TABLE I Values of the g-factor for the broad line and for the narrow line at different temperatures and for given orientations of a single crystal held under vacuum.

θ [deg.]	Temperature [K]	g_{Broad}	g_{Narrow}
0	4.2	2.0041_5	2.0023_2
90		2.0013_5	——
0	25	2.0038_5	2.0023_5
90		2.0018_5	——
0	50	2.0028_1	2.0023_3
90		2.0022_3	——
0	300	——	2.0024_1
90		——	2.0023_9

Spin susceptibility

The spin susceptibility of a PcLi powder held under a primary vacuum exhibits a Curie-Weiss behaviour at low temperature.[14]

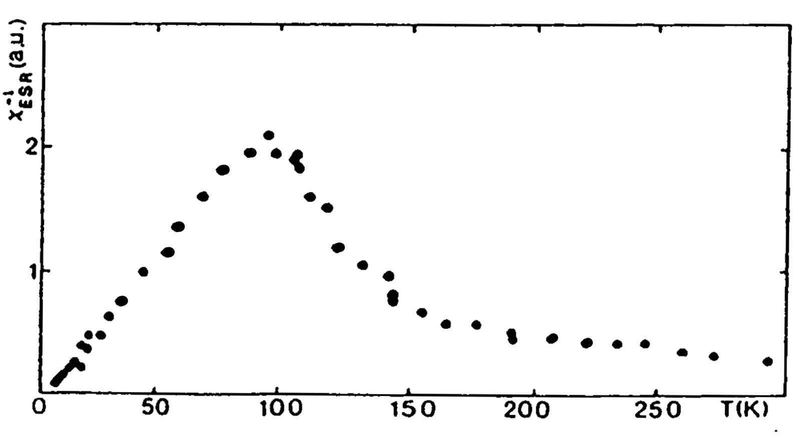

Figure 4. Thermal variation of the reciprocal ESR susceptibility for a single crystal held under vacuum.

The thermal variation of the ESR susceptibility of a crystal held under vacuum is Curie-Weiss like from 6 K up to c.a. 100 K where a cusp is observed (in χ^{-1} in fig. 4), then the susceptibility increases up to room temperature. This behaviour has to be related to the previous observations of two lines in the ESR spectra. The total susceptibility of PcLi is the sum of two distinct contributions: the first one exhibits a Curie-Weiss like behaviour and becomes the increasingly important contribution to the intensity of the ESR signal as the temperature decreases (broad ESR line) whereas the second one decreases with temperature (narrow line). These competing behaviours are responsible of the cusp of χ^{-1} at around 100 K in fig. 4.

SQUID STUDIES

Susceptibility

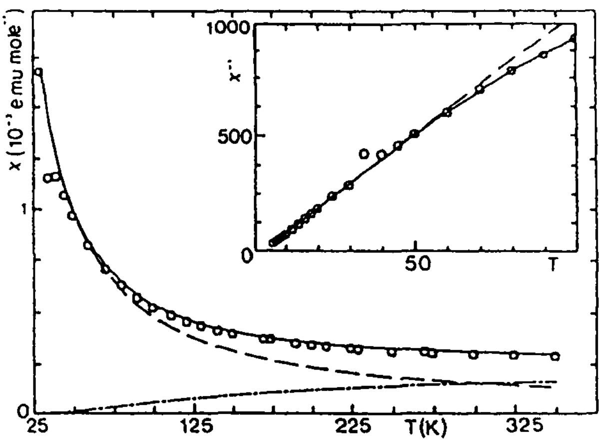

Figure 5. Thermal variation of the spin susceptibility determined at 1 kOe (SQUID susceptometer) for a polycrystalline sample of PcLi held under vacuum (m≃26 mg);— — — low temperature Curie-Weiss component (see also in the inset the reciprocal susceptibility);—·—·thermally activated component; ——— resulting fit of the total susceptibility.

The spin susceptibility of a polycrystalline sample held under vacuum, determined after substraction of the diamagnetic contribution to the total measured susceptibility, exhibits a behaviour qualitatively similar (fig. 5) to the one previously described in the ESR experiments performed on a single crystal. In the low temperature range, a Curie-Weiss like contribution is observed with $\theta_C \simeq 2$ K and a Curie constant $C \simeq 0.05$ emu.K.mole^{-1}. At temperature higher than about 50 K, a departure from the Curie-Weiss law is observed. A fit which takes account of the ESR observations and describes quite well the observed temperature dependence has been performed[16,18] (fig. 5). The remaining contribution, after substraction of the Curie-Weiss contribution, is shown to be thermally activated. This has been recently interpreted as resulting from delocalized spins whose magnetic properties may be analyzed in the frame of itinerant magnetism.[16,18] We now focus on the low temperature magnetic behaviour that we ascribe to the broad component of the ESR signal.

Magnetization

TABLE II Values of the saturation magnetization and of the O_2 content deduced from the Brillouin fit of the magnetization curves for different samples held under vacuum.

Sample	Weight [mg]	Temperature [K]	Saturation magnetization [erg.Oe^{-1}.mole^{-1}]	O_2 content [% mole^{-1}]
I*	10.9	6	2200	6.6
	11.3	10	1407	4.2
II**	25.8	6	418	1.3
III***	850.8	1.9-4.2 7.3-11.1	112	0.3

*powder grown in acetone; **one batch of crystals grown in acetonitrile; ***same than sample II with five different batches.

The variation of the magnetization with the magnetic field has been determined at low temperature for different samples (Table II). For all samples we have studied the corresponding experimental data fit well on a single curve depicting a saturation behaviour (fig. 6): the magnetization is well described by a Brillouin function for a septet spin state. The different curves in fig. 6 are drawn once the value of the saturation magnetization (M_S) has been optimized in the least-squares sense for J=3.

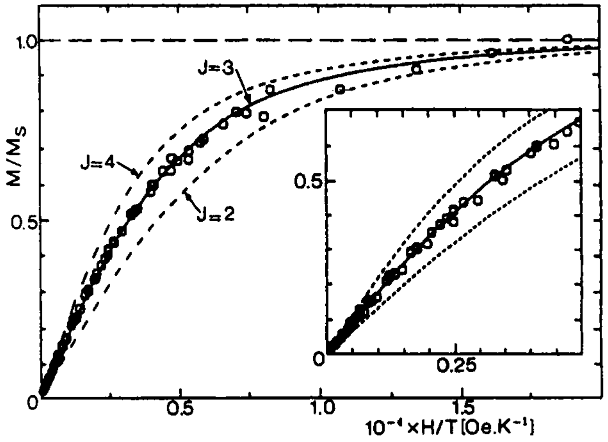

Figure 6. Field dependence of the magnetization normalized to the saturation magnetization performed at different temperatures for different polycrystalline samples of PcLi held under vacuum (see Table II). The magnetization is shown in the inset for the lowest ratio of the field to the temperature. The fitted curves represent the Brillouin function for the indicated values of J.

In the following we neglect the orbital angular moment since we are dealing with π-electrons orbitals. The magnetization data corresponding to the susceptibility drawn in fig. 5 are those given in table II for sample II. Using the ratio of the Curie constant, estimated from the low temperature susceptibility, to the saturation magnetization, in order to estimate the value of J, we find that J is likely to be 3/2 or 2. Since the accuracy of the experiments is higher in the case of the magnetization measurements and owing to the observed similar saturation behaviour for different chains of macrocycles are far apart so that it may be reasonably assumed that they do not interact. Therefore we can consider, as a first step, the system as a 1-D crystalline system. Of great interest is the existence of broad free channels between the chains. In particular it is shown that these channels are well suited for host molecules. This is illustrated in fig. 7 were the extension of the Van der Waals outlines is represented for the peripheral atoms of the macrocycles. The molecule of oxygen may easily diffuse into the available free space; this is also true for other molecules such as water. The molecular oxygen is the only spin carrier in the ambient atmosphere and it has a triplet spin ground state. All results previously described and with special emphasis on the strong effects of air exposure or air evacuation on the ESR spectra are then consistently interpreted as resulting from magnetic coupling between O_2 and PcLi. The O_2 content in the different studied samples has been estimated from the values of M_s (Table II), considering a septet spin value. It is found to be less than 7 %, so that O_2 molecules act as impurities in the samples studied under vacuum. The septet-spin species found at low temperature may be analyzed as resulting either from: i) a ferromagnetic coupling between four 1/2 π-spins of PcLi (S_1) and one spin 1 of O_2 (S_2), or from ii) an antiferroma-gnetic coupling between eight S_1 and one S_2. A rough analysis of the symmetry of the π-orbitals of PcLi and of O_2 suggests that the case ii) is probably preferred. In both cases the S_1 belonging to adjacent chains are parallel. This interaction scheme is an indirect ferromagnetic exchange coupling induced by O_2. The π_x, π_y orbitals of O_2 overlap the π_z orbitals of those C atoms of PcLi which strongly interacts within the stacks. Preliminary results based on the measurements of the Overhauser shift of the ESR line[19] suggest that there exist some conduction channels between these C atoms. It may be noticed that the possibility for indirect ferromagnetic exchange interaction has been previously considered on a theoretical point of view in the case of m-polydiphenylcarbene.[20]

samples in these experiments, the discrepancy between the susceptibility data and the magnetization data is attributed mainly to the low accuracy of the estimated susceptibility. Another explanation would take account of the possibility of a statistical distribution of differents spin multiplets in the samples as it has been proposed in order to interpret the magnetization behaviour of some galvinoxyl radicals.[7] Although this cannot be excluded "a priori" the septet spin state will be considered hereafter since its origin may be understood in view of the structural informations (see below).

ROLE OF DIOXYGEN

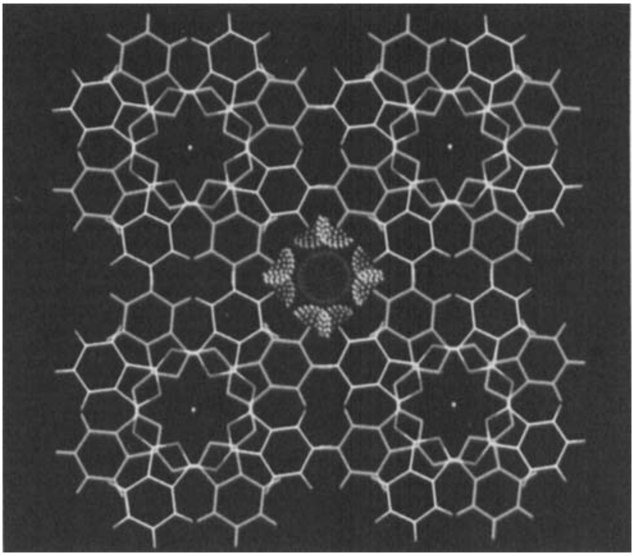

Figure 7. Projected view of the crystalline structure of Pcli along the stacking axis. The O_2 molecule is represented into the free channels defined by the Van der Waals outlines of the peripheral atoms of the macrocycles.

The crystalline structure of PcLi is tetragonal with a=b=19.575 Å and c=6.491 Å, c being the stacking axis.[17] The molecules are staggered by 38.7° along c, the nearest neighbours distance being 3.245 Å: this is less than the Van der Waals distance and it implies strong intermolecular interactions within the chains. The

CONCLUSION

The analysis of the results concerning ESR lines, ESR susceptibility, static susceptibility and magnetization on the ground of the structural information available for PcLi has been shown to be consistent with a local ferromagnetic coupling between those neighbouring macrocycles which surround a molecule of O_2. The experiments reported here have been performed on samples held under vacuum, i.e. at low contents of O_2. The measurements of the susceptibility and of the magnetization for samples encapsulated under ambient atmosphere are under progress.

It should be mentioned that another phthalocyanine based compound, the metal-free phthalocyanine doped by sodium, H_2PcNa_x, has recently been reported in the frame of organic ferromagne-tism.[21]

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