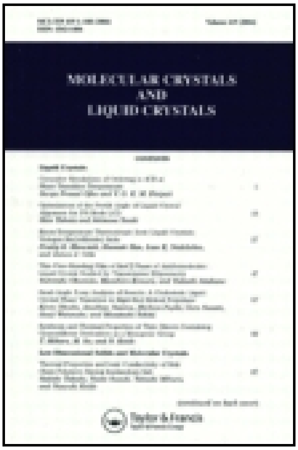

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Structure, Spectra and Conductivity of Oxidized Zinc Phthalocyanine Single Crystals

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STRUCTURE, SPECTRA AND CONDUCTIVITY OF OXIDIZED ZINC PHTHALOCYANINE SINGLE CRYSTALS.

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Abstract Electrode grown ZnPcCl and $ZnPcCl_xBr_{(1-x)}$ crystals have been characterized by X Ray crystallography, Infra red absorption spectroscopy and elemental X Ray analysis. Their semi conductive properties are discussed on the basis of the helical stack and intermolecular overlaps between macrocyclic ligands.

PREPARATION

Single crystals of a novel modification of stacked macrocyclic complexes have been grown on Pt anode from organic solutions of Zinc phthalocyanine in the presence of chloride or/and bromide electrolytes.

CRYSTALLOGRAPHY

Figure 1 shows the helical mode of stacking in the tetragonal (P4/n nc) lattice cell of ZnPcCl which has been completely characterized[1]. Two stricking features are to be singled out in this compound : (i) the macrocycles are closely combined in staggered bimolecular units (fig.2), (ii) the metallic atom resides on the axis but at a distance of 0.59 Å of the tetrapyrrolic centre. While all reported pentacoordinate MPcL complexes show tent-like deformation of the aromatic ring[2-3] phthalocyanine ligands are rigorously planar and mutually parallel and perpendicular to the tetragonal axis.

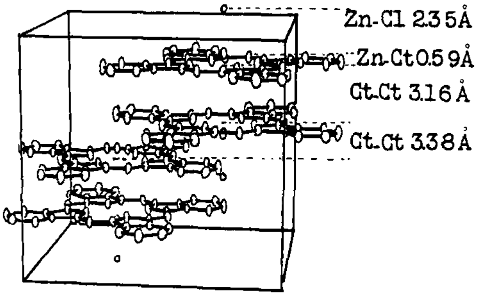

FIGURE 1 Ortep drawing, view along the a axis showing the distance in the stacking. Ct : center of the four pyrrolic N square.

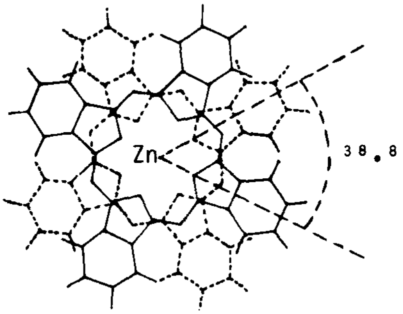

FIGURE 2 Scheme of the dimere unit, view along the c axis, showing the staggering angle between the two phthalocyanine planes.

CONDUCTIVITY

Obvious Pc-Pc overlap in Zn_2Pc_2 units (3.16 Å) explains good conductive potentiality while distances between adjacent units (e.g. plane to plane 3.32 Å, C_5 (benzo)-aza N = 3.40 Å) are short enough to justify the semi conductive mobility of electrons in the material[1]. This, with the integer oxidation number, accounts for the mediocre conductivity ($\sigma = 10^{-1}\ \Omega^{-1}\ cm^{-1}$) and the modest activation energy (0.16 - 0.19 eV). The temperature dependence curves of the conductivity (fig; 3) show that transition points appear at c.a. 230 K($ZnPc^+Cl^-$)or 200 K $ZnPc^+(Br0.9\ Cl0.1)^-$ and allow to distinguish the chloride compound which is an intrinsic semi-conductor and the mixed anion compounds whose behaviour at low temperature is similar to doped materials.

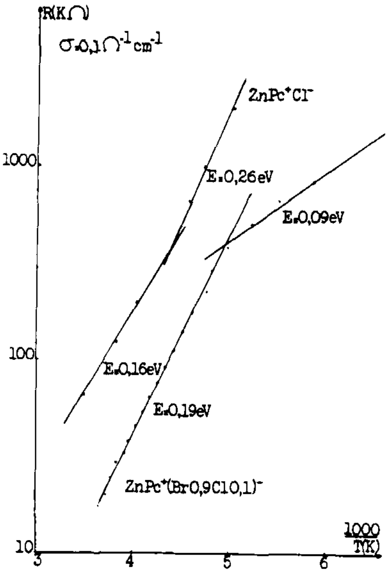

FIGURE 3 Temperature dependence curves ot the conductivity

I.R. SPECTRA

When possible the I.R. absorption spectra have been recorded. The new material appears to be well defined and distinct from the α or β modifications of ZnPc.

TABLE Comparison between ZnPcCl and ZnPc I.R. frequencies

Absorption	ZnPc		ZnPcCl	
Metal dependent	1487	st.	1486	w.
	1410	m.	1402	w.
	1290	m.	1289	sh.
	1061	st.	1061	m.
	888	m.	887	w.
	257	m.	261	v.w.
	241	m.	246	w.
	98	st.	87	w.
Stacking dependent	1061	st.	1061	m.
	1080	st.	1078	m.
	1117	st.	1117	w.
	1067	m.	1063	w.
Peripheral mode	1005	w.	1006	w.
	947	w.	950	w.
	509	st.	499	st.
Zn-Cl stretching			277 or 219?	st.

st : strong ; m : medium ; sh : shoulder ; w = weak ; v.w. : very weak

shifted broadened bands with a large decrease of intensity appear for metal and stacking dependent absorptions while almost identical bands remain for peripheral CH and C-C vibrations.

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