Electrical and thermal studies on copper complexes of phthalocyanine and biphthalocyanine and their derivatives

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Abstract

The electrical and thermal behaviour of metal-free biphthalocyanine and its Cu complex, and of phthalocyanine Cu complex were examined. The effect of chloro and carboxylic substitution was evaluated. The compounds show semiconductivity in the range 278–573 K. The activation energy for conduction was calculated and a conduction mechanism was proposed. The activation energy of the $\alpha \rightarrow \beta$ phase transformation for some compounds was calculated using DTA. Decarboxylation was observed in both d.c. electrical conductivity and DTA measurements.

INTRODUCTION

Phthalocyanine (PC) and its derivatives form an interesting family of compounds with a wide range of properties and, hence, applications. The semiconducting behaviour of these compounds represents a promising source of applications that are not yet exploited. In previous works [1–3], the compounds were prepared and studied with respect to their use as pigments. It was also reported that Cu(PC) has some catalytic activity [4]. The electrical properties of some divalent biphthalocyanine complexes were also investigated [5].

In the present work, the thermal and electrical properties of prepared metal-free biphthalocyanine (biPC), Cu(biPC) and Cu(PC) complexes were investigated. The effect of substitution, namely, by chloro and carboxy groups, on the electrical and thermal behaviour of the compounds was also considered.
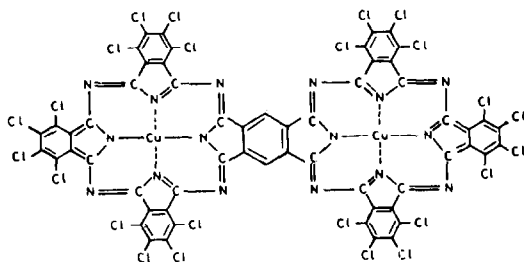
EXPERIMENTAL

The compounds examined (**I–VI**) were prepared and characterised as previously reported [1–3]. The test samples of the purified powders were
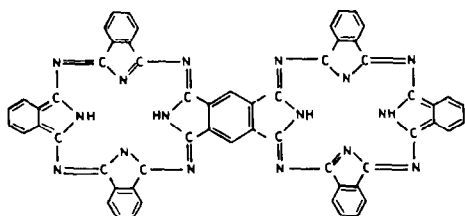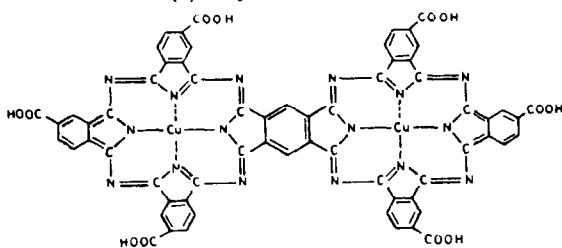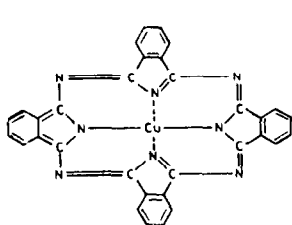
(I) Metal free biphtalocyanine
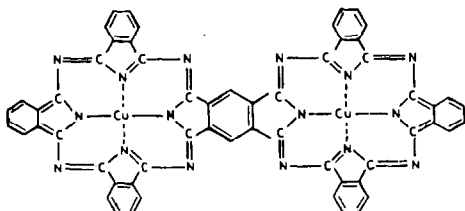
(II) Biphtalocyanine

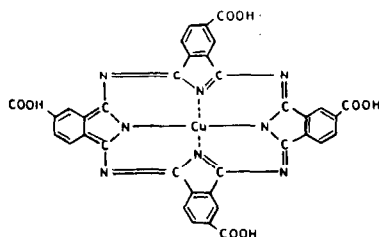

(III) Polychloro bipc Cu

(IV) Hexacarboxy bipc Cu

(V) Cu phthalocyanine   (VI) Tetracaboxy pc Cu

made in the form of pellets 12 mm in diameter and 1–2 mm in thickness. The d.c. electrical conductivity was measured as previously described [6].

The differential thermal analysis (DTA) was performed using a Shimadzu XD-30 thermal analyser. A heating rate of $15\,°C\ min^{-1}$ was used.

RESULTS AND DISCUSSIONS

The variation of the logarithm of the conductivity, log σ (Ω^{-1} cm^{-1}), plotted against the reciprocal of the absolute temperature, $1000/T$ (K^{-1}), for the tested samples is shown in Figs. 1 and 2. The measured conductivity
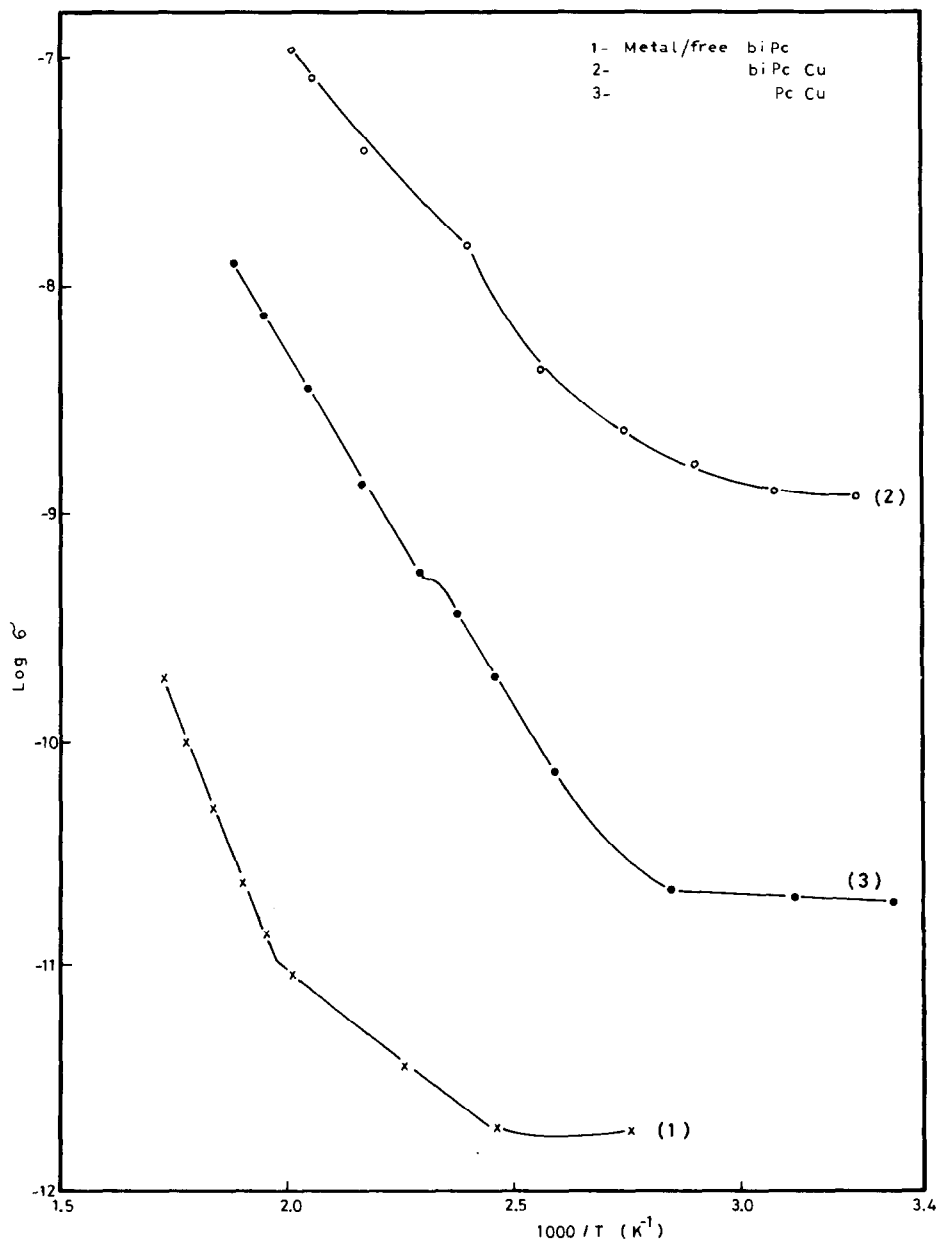

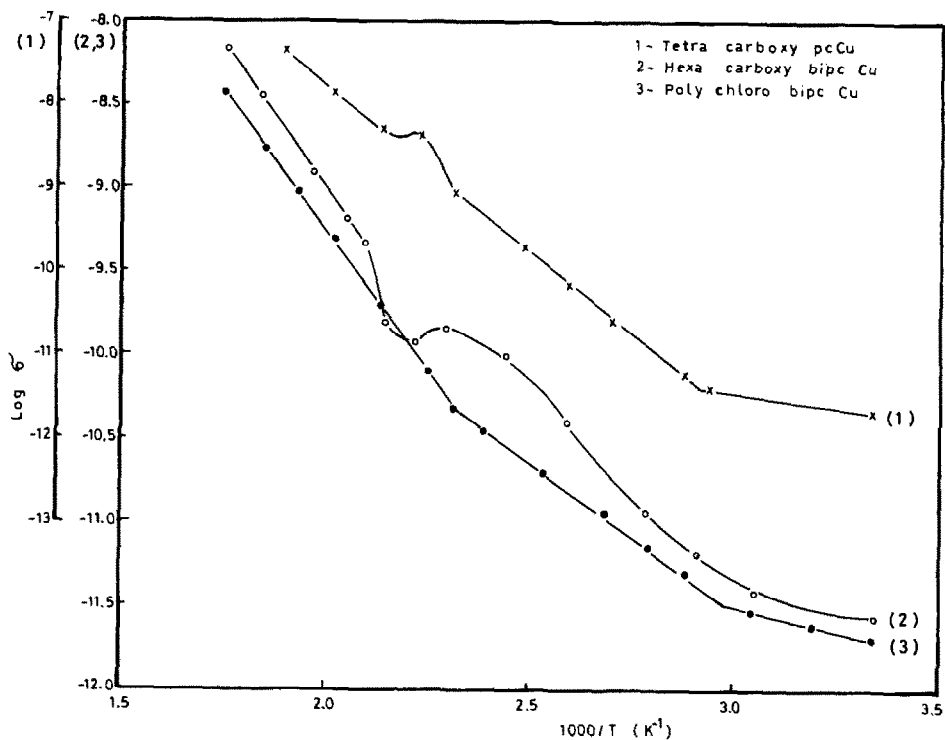Fig. 1. Variation of conductivity log σ ((Ω^{-1} cm^{-1}) vs. reciprocal absolute temperature.

Fig. 2. Variation of conductivity log σ (Ω^{-1} cm^{-1}) vs. reciprocal absolute temperature.

values indicate semiconductivity and fit well with the known relation, $\sigma = \sigma_0 \, e^{-\Delta E/2KT}$ [5]. It is noteworthy that the ligands and their Cu complexes have nearly identical room temperature conductivities. The highest conductivity was for Cu(biPC) complex which was characterised by the lowest activation energy for conduction. This observation leads to the assumption that the conduction takes place according to a band-to-band transition mechanism. In this case, the electrons find conduction paths by transition from the highest filled molecular orbital to the lowest unfilled one. The effect of the substituted groups on the conductivity was observed by investigating the tetracarboxy-PC, hexacarboxy-biPC and polychloro-biPC copper complexes. The substituted complexes have lower conductivities and higher activation energies, as shown in Table 1. It has been reported that PC derivatives containing OH and OCH$_3$ groups and their complexes with Cu, have higher electrical conductivities than the unsubstituted ones [7]. However, the effect of substitution on the conductivity is complicated. The substitution affects the mode and, hence, the efficiency of packing and also the electron density in the conjugated system of the molecule. Thus substitution may assist or oppose conduction.

Another feature that can be observed in Figs. 1 and 2 is the presence of a change in slope of the plot of log σ versus $1000/T$; this indicates a change

TABLE 1

Conductivities and activation energies of the tested compounds

Compound	Conductivity (Ω^{-1} cm^{-1})		Activation energy ΔE (eV)
	Room temp.	523 K	
Metal-free biPC	1.905×10^{-12}	2.455×10^{-11}	1.886
biPC Cu	1.349×10^{-9}	1.995×10^{-7}	0.943
Polychloro-biPC Cu	1.995×10^{-12}	1.122×10^{-9}	1.320
Hexacarboxy-biPC Cu	2.512×10^{-12}	2.239×10^{-9}	1.370
PC Cu	1.995×10^{-11}	1.585×10^{-8}	1.236
Tetracarboxy-PC Cu	1.995×10^{-12}	3.981×10^{-8}	1.733

in activation energy. In the unsubstituted metal-free biPC, this change in slope was observed at around 509 K, while in the complexes, the change occurred at lower temperatures. The change in slope is generally attributed to some physical transformation. It was reported that the change from α- to β-PC occurred at 453 K [8]. The effect of phase transition on the activation energy is the subject of some dispute in the literature. Hamann and Storbeck [9] believe that a phase transition should be associated with a change in activation energy, while Harrison and Ludewig [10] reported that such transitions would have no effect. The change of slope was accompanied by an inversion (a decrease in conduction being followed by an increase) in the case of carboxylic-substituted Cu complexes, see Fig. 2. This observation indicates that a decarboxylation reaction may be occurring in the temperature ranges 435–469 K for tetracarboxy-PC and 435–476 K for hexacarboxy-biPC copper complexes. Table 1 shows a relatively higher value of conductivity for tetracarboxy-PC copper than for PC copper complexes. This trend is reversed at room temperature. This can be correlated with the decarboxylation reaction that occurred in the former.

The DTA curves of biPC and the Cu complexes of both tetracarboxy-PC and hexacarboxy-biPC are shown in Fig. 3. The curves reveal exothermic peaks at 498, 498 and 478 K, respectively, corresponding to the $\alpha \rightarrow \beta$ phase transformation. However, this phase transformation was reported to take place in metal-free PC at 453 K [8]. The peaks observed are broad and, hence, the reaction starts at lower temperatures and continues over a wide temperature range. These features are usually attributed to defects or disorder in the lattice that assist the start of the reaction. The activation energy of the transformation was calculated according to the simple method of Piloyan et al. [11], taking into consideration the precautions required for applying this method [12]. The results are compiled in Table 2. The activation energies were 8.743, 11.252 and 15.759 kJ mol^{-1} for biPC, tetracarboxy-PC copper complex and hexacarboxy-biPC copper complex, respectively. It can be seen that the activation energy increases on complexation and
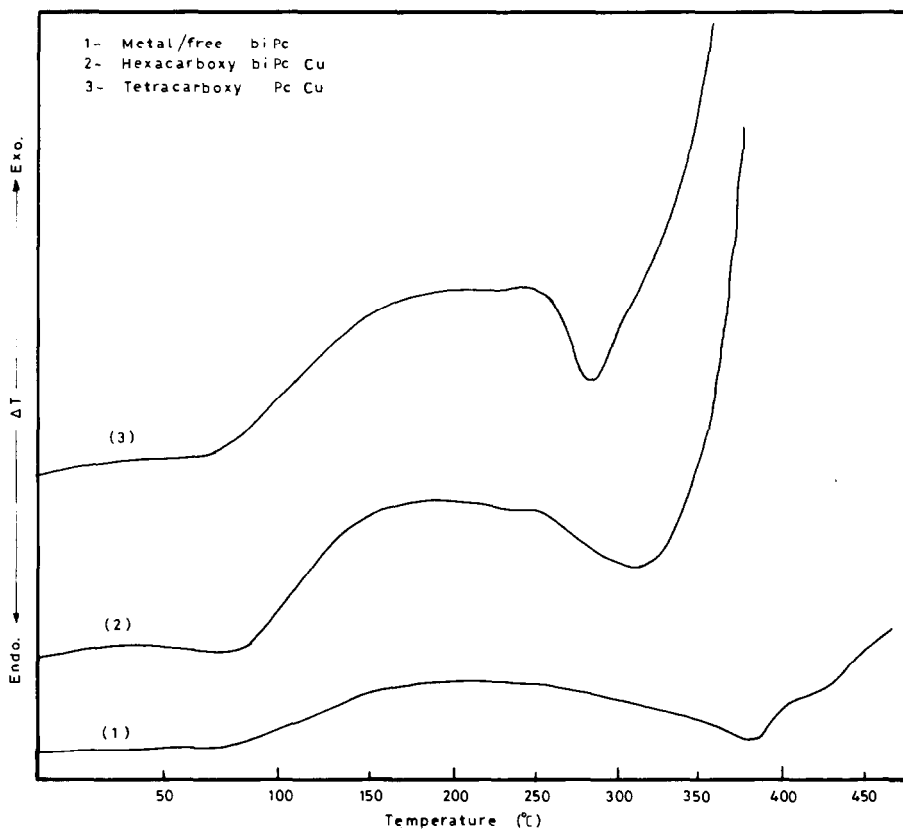
Fig. 3. DTA analysis of metal-free biophthalocyanine, hexacarboxy Cu complex of bi-phthalocyanine and Cu phthalocyanine.

substitution. Both of these factors hinder the solid state phase transformation by complicating the diffusion-controlled growth of the new phase.

Another feature of the DTA curves is the presence of endothermic peaks at relatively higher temperatures. For metal-free biPC, the endothermic reaction is characterised by an activation energy of 20.5 kJ mol^{-1} and takes

TABLE 2

DTA results of metal-free biPC, hexacarboxy-biPC and tetracarboxy-PC complexes

Compound	Exothermic reactions			Endothermic reactions		
	Peak temp. (K)	Start peak (K)	Activation energy (kJ mol^{-1})	Peak temp. (K)	Start peak (K)	Activation energy (kJ mol^{-1})
Metal-free biPC	498	363	8.7	658	638	20.5
Hexacarboxy-biPC Cu	478	373	15.8	578	528	23.1
Tetracarboxy-PC Cu	493	353	11.3	558	543	26.3

place beyond the range of the conductivity measurements, probably indicating the start of a dissociation process. For tetracarboxy-PC and hexacarboxy-biPC copper complexes, the endothermic reactions occur at 558 and 578 K with activation energies of 26.3 and 23.1 kJ mol^{-1}, respectively, and probably correspond to a decarboxylation process.

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