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Electrical properties of monoazacrown ether-substituted phthalocyanines

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D.c. conductivities of polycrystalline monoazacrown ether-substituted phthalocyanines (M = 2H, Ni, Zn, Pb, Cu) and diphthalocyanine (M = Lu) are measured as Au–MPc–Au sandwiches to be of the order 10^{-10}–10^{-12} S m^{-1}. Chemical doping with oxidants (e.g. $NOBF_4$) and enhancing the stacking of planar phthalocyanine moieties through the formation of alkali metal adducts with sodium and potassium ions leads to increase in conductivity of the order 10^1–10^2. The low conductivity and the diamagneticity of the bis(phthalocyaninato)-lutetium can be ascribed to the lack of radical nature in $LuH(Pc)_2$. For the a.c. conductivities, lead and lutetium complexes form a group with higher conductivities and the rest show lower conductivity. The conduction activation energies calculated from Arrhenius plots exhibit the lowest value (0.40 eV) for the lutetium compound.*

1. Introduction

The electrical properties of phthalocyanines have attracted considerable interest in recent years, especially in relation to the development of various devices including thin film chemical sensors [1, 2], solar cells [3], photoconductors [4] etc. Although the electrical conductivity of many metallo-phthalocyanines is relatively low (the order being 10^{-10}–10^{-12} S m^{-1}), it can be improved by some treatments which include the formation of low dimensional compounds by a stacked cofacial arrangement with a suitable interplanar distance or partial oxidation (doping) of macrocycles [5, 6]. The intrinsic conductivity of bis(phthalocyaninato)lutetium and lithium phthalocyanine is exceptionally high and it is attributed to their radical nature [7, 8].

In contrast to the thermal stability of phthalocyanines (Pc), their insolubility in common solvents causes difficulties for many applications. Peripheral substitution of Pcs with long alkyl chains or bulky groups enables one to overcome these difficulties [9]. In this context, utilization of crown ether substituents have led to soluble products which have additional functionalities such as binding alkali metal ions or forming stacked structures in the presence of certain cations [10–13]. Also, the order of molecules in the condensed phases has indicated the formation of ion channels through the crown ether moieties capable of conducting alkali metal cations [14].

Recently we have reported a new soluble phthalocyanine carrying monoaza-15-crown-5 substituents [15, 16]. In the present paper, the electrical properties of these new phthalocyanines, their alkali metal complexes and doped derivatives are investigated as pellets. While measurements on high quality single crystals or LB films would obviously be more desirable, such samples are not available for these monoazacrown ether-substituted phthalocyanines and polycrystalline conductivity data can still be informative. This is especially true for a systematic investigation of chemically related series of materials having the same precursor and similar compositions.

2. Experimental

Starting from *N*-acetyl-4′,5′-dibromo-monoazabenzo-15-crown-5 (**1**), dicyano-derivative (**2**) was obtained by the Rosenmund von Braun reaction with CuCN in anhydrous tetramethylurea. Cyclotetramerization to the phthalocyanines was accomplished by the reaction of **2** with hydroquinone in the case of metal-free compound (**3**) or with the corresponding metal salts ($NiCl_2$, $ZnCl_2$ PbO, $CuCl_2$ or Lu $(OAc)_3 \cdot 3H_2O$) for the metal phthalocyanines (**4**–**8**) (Fig. 1).

The alkali metal complexes of copper phthalocyanine (**7**) were prepared by treating its solution in chloroform/ethanol (5:3) with excess KSCN or NaSCN in absolute ethanol. The elemental analysis results and spectral data are consistent with CuPc·2KSCN (**7a**) and CuPc·4NaSCN (**7b**).

The structure of the samples was a Au–MPc–Au sandwich in the configuration commonly used for such studies [17, 18]. To prepare the samples for the electrical measurements, the materials were powdered

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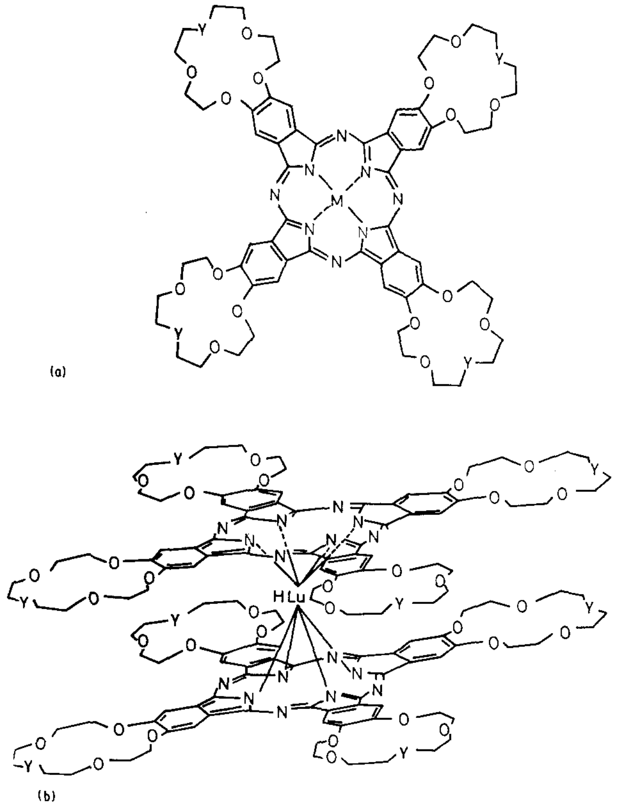

Figure 1 (a) Phthalocyanines with M = 2H (**3**), Ni (**4**), Zn (**5**), Pb (**6**) and Cu (**7**); (b) bis (phthalocyaninato)lutetium (**8**) (Y = $NCOCH_3$).

in a mortar and pressed at a load of 10 tons for 4 min in disc-shaped compacts with a diameter of 14 mm and a thickness of 0.45 mm. Evaporated gold electrodes were applied using a Varian R&D 3119 coater. Samples were mounted in the chamber of a cryostat.

Current–voltage (I–V) characteristics and d.c. conductivity of the samples were measured with a Keithley 617 electrometer in air and in vacuum (1×10^{-1} Pascal). A.c. conductance and parallel capacitance were measured with a Hewlett Packard 4192A impedance analyser of frequency range 10 Hz–10 MHz in parallel circuit mode. All the conductivity measurements were carried out at room temperature.

The conductivity activation energies, E_a, were calculated from conventional Arrhenius plots of temperature dependence of conductivity $\sigma = \sigma_0 \exp[-E_a/kT]$.

3. Results and discussion

The results of the d.c. conductivity measurements of monoazacrown ether-substituted metal-free phthalocyanine (**3**), its metal derivatives (**5**–**7**), the alkali metal adducts (**7a**–**7b**) and partially oxidized derivative (**7c**) of Cu-phthalocyanine and the sandwich type bis(phthalocyaninato)lutetium compound (**8**) are summarized in Table I. The room temperature d.c. conductivities of the metal-free and metal phthalocyanines are rather low and of the order 10^{-10}–10^{-12} $S\,m^{-1}$ *in vacuo* (1×10^{-1} Pascal), but comparable with the values obtained in the case of other substituted phthalocyanines [8]. Although an increase in the conductivity is observed for the measurements in air, the values are of the same order (Table I).

TABLE I D.c. conductivity of phthalocyanines in vacuum and in air at room temperature and their activation energies

Sample	D.c. conductivity (σ_{dc}) (Sm^{-1})		Activation energy, E_a (eV)
	In vacuum	In air	
3	7.5×10^{-12}	26×10^{-12}	0.93
4	6.3×10^{-11}	24×10^{-11}	0.88
5	2.7×10^{-10}	8.6×10^{-10}	0.69
6	7.8×10^{-12}	13×10^{-12}	0.51
7	2.9×10^{-11}	4.6×10^{-11}	0.96
7a	7.6×10^{-10}	17×10^{-10}	0.79
7b	6.8×10^{-9}	14×10^{-9}	0.72
7c	2.4×10^{-10}	35×10^{-10}	0.80
8	4.3×10^{-11}	90×10^{-11}	0.40

Partial oxidation of the planar phthalocyanine molecules in stacks is one of the possibilities to increase the electrical conductivity [5]. Chemical (iodine, bromine, $NOBF_4$) or electrochemical treatment is reported for this process. In the present work, monoazacrown ether-substituted Cu-phthalocyanine is partially oxidized with $NOBF_4$ to observe the change in conductivity. The measurements under identical conditions indicate an increase in σ_{dc} of the order 10^1.

Azacrown ether-substituted phthalocyanines provide a completely new opportunity to induce the stacking of planar phthalocyanine moieties. According to the size of the polyether ring, 1:1 or 1:2 (metal/macrocycle) adducts are formed with alkali metal salts. For 15-crown-5, sodium ion is encapsulated into the ring, while potassium ion prefers 1:2 sandwich formation. Therefore in the case of monoazacrown ether-substituted phthalocyanine (**7**), potassium ion leads to a stack formation with crown ether groups one on top of the other, while staggered conformation is possible with sodium ions bound in each macrocycle.

The effect of alkali metal complexation on electrical properties is investigated through NaSCN and KSCN adducts of Cu-phthalocyanine (**7**). Elemental analysis results indicate a host–guest ratio of 2:1 for K^+ (**7a**) and 1:1 for Na^+ (**7b**). The increase in electrical conductivity after complexation with alkali metal is substantial (Table I) and it can be attributed to the change in the conduction pathway from ligand centred by holes to metal centred by the interaction of the *d*-orbitals of the transition metals [19]. In this context, the staggered arrangement of sodium adducts (**7b**) might cause a closer interaction of planar phthalocyanine moieties than the sandwich-type potassium derivatives (**7a**).

In contrast to the reported values and our previous works with crown ether-substituted phthalocyanines, the d.c. conductivity of Lu-diphthalocyanine (**8**) is of the same order as the other metal and metal-free derivatives [7, 8, 20], but the increase in the conductivity values obtained in air is somewhat higher (Table I). This phenomenon can be explained by the lack of radical character in **8** which is diamagnetic. Since Lu is almost always trivalent, then each of the phthalocyanine moieties should be in the oxidation state of (− 2), so the product **8** is $LuH(Pc)_2$, a reduced form of

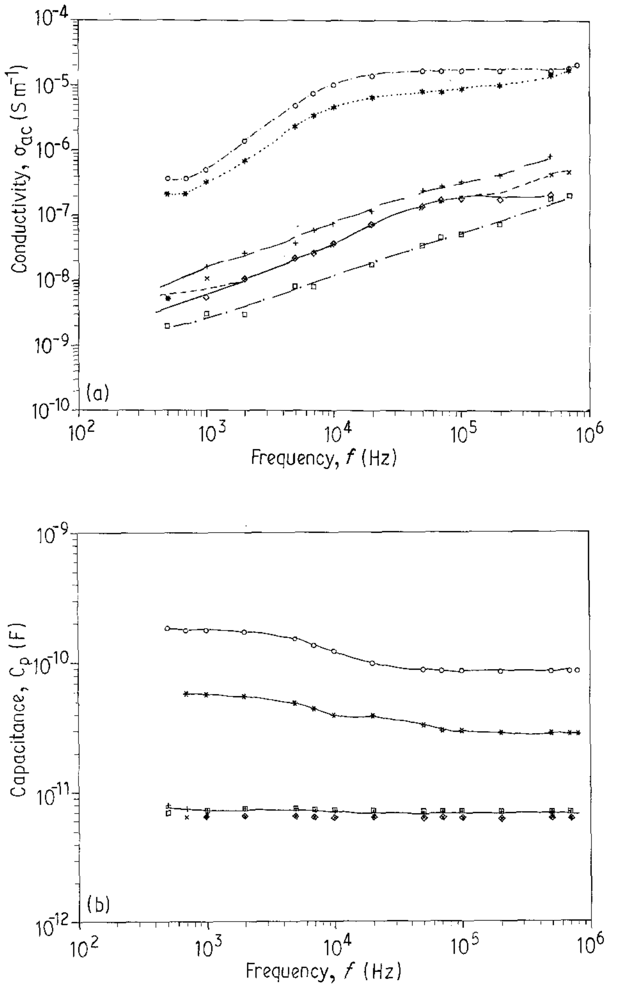

Figure 2 Dielectric spectra of the phthalocyanines (**3**–**7**) and bis(phthalocyaninato)lutetium (**8**) at room temperature. □, **3**; +, **4**; ×, **5**; *, **6**; ◇, **7**; ○, **8**. (a) Conductance as a function of frequency; (b) capacitance as a function of frequency.

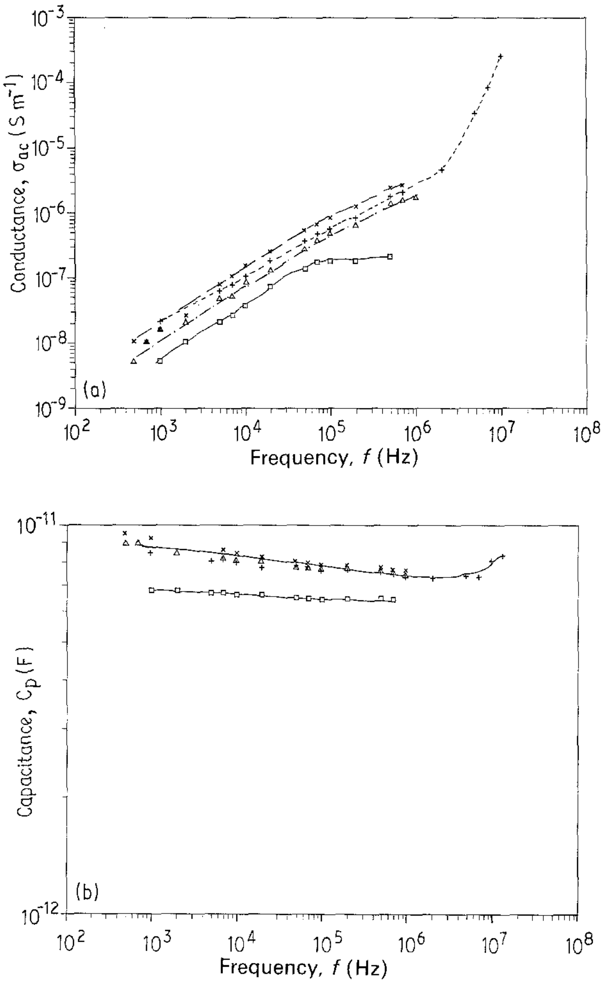

Figure 3 Dielectric spectra of copper phthalocyanine (**7**), its alkali metal adducts (**7a** and **7b**) and partially oxidized derivative with $NOBF_4$ (**7c**) at room temperature. □, **7**; +, **7a**; △, **7b**; ×, **7c**. (a) Conductance as a function of frequency; (b) capacitance as a function of frequency.

neutral radical lutetium diphthalocyanine. The ^1H nuclear magnetic resonance (NMR) data also confirm these observations [16]. Consequently, no intrinsic conductivity can be expected from **8** and the more pronounced increase in the conductivity values obtained in air is a result of partial oxidation to $Lu(Pc)_2$.

The a.c. electrical properties of the phthalocyanines were also determined between two planar Au electrodes. The conductivity and capacitance as a function of frequency in the range 500 Hz–1 MHz are displayed in Figs 2 and 3. Here the samples can be classified into two groups: i) Pb and Lu complexes show higher conductivities in all frequency ranges; ii) 2H, Ni, Zn and Cu form the second group with lower conductivity (Fig. 2a).

The value of σ_{ac} of **8** at lower frequencies is rather low and only one order of magnitude higher than other phthalocyanines. At higher frequencies, while σ_{ac} of **8** becomes constant, a continuous rise is observed for the other phthalocyanines (Fig. 2a). No distinct difference in σ_{ac} has appeared after doping **7** chemically with $NOBF_4$. The values of σ_{ac} of the alkali metal adducts **7a** and **7b** closely follow each other up to a frequency of 1 MHz and the Na complex shows a further increase (Fig. 3a).

The hopping conduction mechanism has been postulated also to explain the charge carrier transports in planar phthalocyanine molecules [8]. The empirical formula given for frequency dependent conductivity is

$$\sigma(\omega) = A(T)\omega^{n(T)}$$

where $0.5 < n(T) < 1.0$. For **8** $n(T) \approx 0.9$ in the frequency range of 1–50 kHz and for the other phthalocyanines $n(T) \approx 0.7$ in the same frequency range. Also the capacitance curves are almost constant (Figs 2b, 3b). This evidence indicates the electronic nature of the conduction mechanism.

The conduction activation energies, E_a, required for intermolecular electron hopping between phthalocyanine units, have been calculated from Arrhenius plots and listed in Table I; E_a is the lowest for the Lu-compound.

4. Conclusions

Although the conductivities of monoazacrown ether-substituted phthalocyanines are relatively low as in the case of other unsubstituted parent compounds, they can be enhanced by processes such as insertion of various transition metals, partial oxidation or alkali metal complexation. The electronic nature of a.c. conductivities can be explained by a hopping conduction mechanism.

References

1. TH. SAUER, W. CASERI, G. WEGNER, A. VOGEL and B. HOFFMAN, *J. Phys. D: Appl. Phys.* **23** (1990) 79.
2. J. D. WRIGHT, *Prog. Surf. Sci.* **33** (1989) 1.
3. S. SIEBENTRITT, ST. GÜNSTER and D. MEISSNER, *Verhandlungen der Deutschen Physikalischen Gesellschaft VI* **26** (1991) DS30.2.
4. Y. KANEMITSU and S. IMAMURA, *J. Appl. Phys.* **67** (1990) 3728.
5. M. HANACK, S. DEGER and A. LANGE, *Coord. Chem. Rev.* **83** (1988) 115.
6. B. N. DIEL, T. INABE, N. K. JAGGI, J. W. LYDING, D. SCHNEIDER, M. HANACK, C. R. KANNEWURF, T. J. MARKS and L. H. SCHWARTZ, *J. Amer. Chem. Soc.* **106** (1984) 3207.
7. M. MOUSSAVI, A. DE CIAN, J. FISCHER and R. WEISS, *Inorg. Chem.* **27** (1988) 1287.
8. Z. BELARBI, C. SIRLIN, J. SIMON and J.-J. ANDRE, *J. Phys. Chem.* **93** (1989) 8105.
9. M. HANACK, A. GÜL, A. HIRSCH, B. K. MANDAL, L. R. SUBRAMANIAN and E. WITKE, *Mol. Cryst. Liq. Cryst.* **187** (1990) 365.
10. A. R. KORAY, V. AHSEN and Ö. BEKAROĞLU, *J. Chem. Soc. Chem. Commun.* **1986**, 932.
11. V. AHSEN, E. YILMAZER, M. ERTAS and Ö. BEKAROĞLU, *J. Chem. Soc. Dalton Trans.* **1988**, 401.
12. V. AHSEN, E. YILMAZER, A. GÜREK, A. GÜL and Ö. BEKAROĞLU, *Helv. Chim. Acta* **71** (1989) 1616.
13. A. I. OKUR, A. GÜL, A. CIHAN, N. TAN and Ö. BEKAROĞLU, *Synth. React. Inorg. Met.-Org. Chem.* **20** (1990) 1399.
14. C. SIRLIN, L. BOSIO, J. SIMON, V. AHSEN, E. YILMAZER and Ö. BEKAROĞLU, *Chem. Phys. Lett.* **139** (1987) 362.
15. V. AHSEN, A. GÜREK, E. MUSLUOĞLU and Ö, BEKAROĞLU, *Chem. Ber.* **122** (1989) 1073.
16. E. MUSLUOĞLU, V. AHSEN, A. GÜL and Ö. BEKAROĞLU, *ibid.* **124** (1991) 2531.
17. H. PAGNIA and N. SOTNIK, *Phys. Status Solidi* (*A*) **108** (1988) 11.
18. A. AHMAD and R. A. COLLINS, *ibid.* **123** (1991) 201.
19. O. E. SIELCKEN, H. C. A. van LINDERT, W. DRENTH, J. SCHOONMAN, J. SCHRAM and R. J. M. NOLTE, *Ber. Bunsenges. Phys. Chem.* **93** (1989) 702.
20. Z. Z. ÖZTÜRK, E. MUSLUOĞLU, V. AHSEN and Ö. BEKAROĞLU, *Verhandlungen der Deutschen Physikalischen Gesellschaft VI* **25** (1990) MO2.7.

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