Molecular metals based on silicon phthalocyanine complexes

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The complexes dichlorophthalocyanino)silicon, [SiPcCl₂], and bis(p-nitrophenoxy)phthalocyanino)silicon, [SiPc(p-NPO)₂] exhibit enhanced electrical properties on iodine doping. This may be due to the arrangement of the planar phthalocyanine molecules with decreased interplanar distance along with crystallographically similar environments and the presence of non integral formal oxidation state.

The silicon-phthalocyanine complexes are of great importance because of their attractive properties like high tinctorial power, semiconductivity, photoconductivity, catalytic activity, chemical inertness and high thermal stability1-12. Synthesis and study of electrically conductive mono-molecular as well as polymeric substances are currently of great importance. Most of the studies reported so far have focussed on polymeric silicon phthalocyanines13-23. Substituted silicon phthalocyanines have been relatively less studied with respect to the electrical conductivity24, 25. In addition to the apparent hexa-coordination of silicon, study of the structural features, effect of doping and the electrical properties may help in suitably modifying phthalocyanine complexes for use as electronic devices. In the present work, two silicon phthalocyanine derivatives have been synthesized in pure state and effect of iodine doping on the electrical properties of the complexes has been studied for the first time. These complexes are characterized using elemental, electronic, IR, magnetic susceptibility measurements, X-ray diffraction and TGA studies both before and after iodine doping.

Experimental

Preparation of dichlorophthalocyanino)silicon, SiPcCl₂

Pure dichlorophthalocyanino)silicon was prepared by using the procedure described elsewhere26: 1,3-Diminoisoindoline (9 g, 0.062 mol), silicon tetrachloride (12 ml, 0.07 mol) and quinoline (100 ml, 0.85 mol) were taken in a round-bottomed flask fitted with a water condenser and a mechanical stirrer. The mixture was slowly heated to reflux and the refluxing conditions were maintained for 30 min. On cooling the mixture, a purple crystalline product was obtained which was washed with quinoline, benzene, methanol and acetone. The dried product was recrystallised from 1-chloronaphthalene.

SiPcCl₂, C₃₂H₁₆N₆SiCl₂ [Calc: C, 62.85; H, 2.64; N, 18.32. Found: C, 62.88; H, 2.75; N, 18.41 %], yield 75 %. IR absorption bands (cm⁻¹): 732s, 760m, 784w, 914m, 1062m, 1080s, 1120m, 1164w, 1192b, 1209m, 1336s, 1430s, 1532w. X-ray diffraction data, d(Å): 10.16, 12.06, 8.56, 7.41, 5.86, 5.31, 4.65, 3.62, 3.31 and 3.21 (10.09, 5.31, 4.47 and 3.31). Values inside the bracket represent those obtained after iodine doping.

Bis(p-nitrophenoxy)phthalocyanino)silicon, SiPc(p-NPO)₂

Dihydroxyphthalocyanino)silicon was prepared by adapting the procedure described elsewhere27. Dihydroxyphthalocyanino)silicon (5 g, 0.009 mol) and p-nitrophenol (10 times molar excess) finely ground, were heated slowly to 200 °C and this temperature was maintained for about 2 h. The reaction mixture was cooled and sufficient amount of distilled water was added. The insoluble phthalocyanine compound so obtained was filtered off, washed with water until the washings were colourless. Then the product was boiled with distilled water and filtered. The product was finally washed with acetone and dried at 100 °C for 1 h. SiPc(p-NPO)₂, C₃₂H₁₆N₆O₄Si, [Calc: C, 64.70; H, 2.96; N, 17.15. Found: C, 64.75; H, 3.01; N, 17.20 %], yield 96 %. IR absorption bands (cm⁻¹): 735s, 760w, 915m, 1082s, 1165m, 1182m, 1284m, 1336s, 1428w, 1515m, 1530m, 1580m. X-ray diffraction data, d(Å): 12.32, 9.25, 7.41, 6.18, 5.86, 5.31, 4.85, 4.29, 3.86 and 3.31 (11.17, 4.85 and 4.65). Values inside the bracket represent those obtained after iodine doping.

Doping procedure28

The finely ground (0.5 g) silicon phthalocyanine complex was taken in a closed container containing 100 ml of iodine-saturated chlorobenzene solution and the con-
tents were stirred for 48 h. The peacock blue colour of the complex changed to dark brownish colour after iodine doping; it was collected by centrifugation, washed with several portions of hexane and dried in vacuo.

**Physical measurements**

Electronic absorption spectral measurements of the complexes in 15M sulphuric acid were done using a JASCO Model UVIDEC-610 UV-Vis spectrophotometer. A Gouy magnetic balance comprising type NP-53 electromagnets with DC power supply type MP-1053 and a semimicrobalance supplied by Universal Scientific Company, Bombay, India, was used for the magnetic susceptibility measurements. Pure Hg[Co(SCN)]

_\text{I}_2 was used as a calibration standard. A JEOL-JDX-8P X-ray diffractometer was used to study powder X-ray diffraction pattern of the samples. TGA studies were carried out using a Du Pont Model 990 thermal analyzer with a 951 thermogravimetric module. The data were obtained with the following conditions: sample size 5-10 mg, temperature range ambient to 800 °C, heating rate 10 °C min⁻¹ and nitrogen atmosphere with a flow rate 100 cm³ min⁻¹. Perkin Elmer KBr die, and Carver Laboratory Press Model C-12 were used to prepare the pellets. The diameter and thickness of the pellets were determined by using a screw gauge readable up to 0.005 cm. Conducting silver paint (ELTECS Conductive silver preparation No. 1228/c) was coated on both sides of the pellets and the electrical contacts of the samples were made using the same silver paint to the electrodes. The electrical contacts were checked to verify the Ohmic connection and the conductivity measurements were done at ambient temperature using a Philips Model PM 6303 RCL Meter.

**Results and discussion**

The general structure of silicon phthalocyanine complexes is shown in Fig. 1. Elemental analyses of C, H and N agree fairly well with the calculated values and are consistent with this structure.

**Electronic absorption spectra**

The electronic transitions characteristic of the phthalocyanine ring are assigned as Q, B, N, L and C bands. These bands are also observed in the two silicon phthalocyanine derivatives (Table 1). The Q band (770-851 nm) due to $a_{1u} \rightarrow e_g$ transition was found to show bathochromic shift as well as hyperchromic effect in the case of these silicon phthalocyanines after iodine doping. This band is due to the monomeric species and is found to be slightly affected by the nature of substituents. The multiplicity of this band towards the higher energy side, particularly around the region 670-695 nm observed for these complexes after iodine doping is due to the configurational interaction between the phthalocyanine molecules leading to the formation of dimeric species in solution. The intensity of this band depends upon the concentration of the dimer formed. Also this indicates the greater tendency of the partially oxidized molecules for aggregation in solution. The solution spectra of all the complexes both before and after iodine doping showed absorptions at 370-427 nm of comparable intensity with the Q band. The strong acidic medium may reduce the D₄₇ symmetry of the molecule to C₆₀, which may account for the band around the above region. The B (Soret) band around 305 nm which may be assigned to the $a_{1u} \rightarrow e_g$ transition is found to be not much affected with respect to the position in the electronic spectra of the complexes both before and after iodine doping. But with respect to intensity, a hyperchromic effect is shown after iodine doping. In the electronic absorption spectrum of the complex SiPcCl₂ in 15 M sulphuric acid, the C band was absent both before and after iodine doping. Not much change in the position of the C band has been observed for SiPc(p-NPO), but hyperchromic effect is shown after iodine doping. The bands N and L are expected to be in between the bands B and C. These bands are not well-resolved in the spectra of the complexes both before and after doping.
Table 1- Magnetic susceptibility, electronic spectral and electrical conductivity data of dichloro(phthalocyanino) silicon, SiPcCl₂ and bis(p-nitrophenoxo) phthalocyanino silicon, SiPc(p-NPO)₂.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Field strength (kG)</th>
<th>$\chi_M \times 10^5$ (log $\mu$)</th>
<th>$\lambda_{max}$ nm (log $\epsilon$)</th>
<th>Conductivity (Ω cm)$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiPcCl₂</td>
<td>1.92</td>
<td>-1241.4</td>
<td>771(4.69), 695(4.86)</td>
<td>6.59 x 10$^6$</td>
</tr>
<tr>
<td></td>
<td>[1763.10, 2.06]</td>
<td></td>
<td>430(4.39), 306(4.62)</td>
<td></td>
</tr>
<tr>
<td>C₁₉H₁₈N₄SiCl₂</td>
<td>2.82</td>
<td>-990.68</td>
<td>220(4.61)*</td>
<td>9.54 x 10$^7$</td>
</tr>
<tr>
<td>SiPcCl₂</td>
<td>[1892.09, 2.14]</td>
<td></td>
<td>[814(4.56), 770(4.72)]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.58</td>
<td>-599.30</td>
<td>670(4.77), 427(4.56)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[2001.24, 2.20]</td>
<td></td>
<td>305(4.77), 225(4.84)</td>
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<tr>
<td></td>
<td>4.35</td>
<td>-403.61</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>[2100.47, 2.25]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁₉H₁₈N₄O₁₀Si</td>
<td>2.82</td>
<td>-269.55</td>
<td>306(4.83), 220(4.61)*</td>
<td>3.82 x 10$^5$</td>
</tr>
<tr>
<td>SiPc(p-NPO)₂</td>
<td>[2397.71, 2.40]</td>
<td></td>
<td>[851(4.97), 770(4.90)]</td>
<td>[7.33 x 10$^{-1}$]</td>
</tr>
<tr>
<td></td>
<td>3.58</td>
<td>-57.18</td>
<td>702(4.97), 675(4.88)</td>
<td></td>
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<tr>
<td></td>
<td>[2421.66, 2.42]</td>
<td></td>
<td>360(4.97), 305(5.00)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.35</td>
<td>-32.67</td>
<td>253(4.60)<em>, 225(4.67)</em></td>
<td>208(5.12)*</td>
</tr>
<tr>
<td></td>
<td>[2505.49, 2.46]</td>
<td></td>
<td></td>
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</tbody>
</table>

Note: 1) * Shoulder; 2) Values inside the square brackets represent those obtained after-iodine doping. 3) $\chi_M$ and $\chi'_M$ are in cgs units and $\mu_{eff}$ values are in B.M. units.

**IR spectra**

In the IR spectra of SiPcCl₂ and SiPc(p-NPO)₂ complexes, phthalocyanine skeletal vibrations are found to be affected to a small extent with respect to positions but considerable decrease in intensity and broadening of the peaks are observed after iodine doping. For example, the absorptions at 1163, 1076, 950, 883, 783 cm$^{-1}$ assignable to phthalocyanine skeletal vibrations observed in the case of two silicon phthalocyanine derivatives are found to be at 1161, 1121, 1072, 950, 908 and 725 cm$^{-1}$ respectively after iodine doping with considerable decrease in intensity and broadening.

**Magnetic susceptibility measurements**

The investigation on magnetic susceptibility properties of these two complexes has been carried out in solid state at ambient temperature and varying magnetic field strengths from 1.92 to 4.35 kG. The $\chi_M$, $\chi'_M$ and $\mu_{eff}$ values are given in Table 1. The magnetic moment values are calculated using the corrected susceptibility data. The variations of magnetic properties with the magnetic field strengths for SiPcCl₂ and SiPc(p-NPO)₂ before as well as after iodine doping are presented in Fig. 2. These complexes are diamagnetic in nature and diamagnetism decreases with increasing magnetic field strength before iodine doping. But after iodine doping these complexes are found to be paramagnetic and paramagnetism increases with increase in magnetic field strength (Table 1). These variations of the magnetic property with magnetic field strength may be due to the intermolecular co-operative effects. The difference in the magnetic susceptibility values of the silicon phthalocyanine complexes after iodine doping may be due to the partial oxidation of phthalocyanine complexes with iodine and arrangement of planar phthalocyanine molecules in closer proximity.
Fig. 2 - Variations of magnetic susceptibilities with field strengths 1. SiPcCl$_2$ and 2. SiPc($p$-NPO)$_2$. [(A) before I$_2$-doping and (B) after I$_2$-doping].

Fig. 3 - X-ray diffraction spectra of SiPcCl$_2$(A) and SiPc($p$-NPO)$_2$(B). [(1) before I$_2$-doping and (2) after I$_2$-doping].
X-ray diffraction studies

The data relating to the powder X-ray diffraction study of the complexes SiPcCl, and SiPc(p-NPO), both before and after iodine doping are presented in the experimental section. The interplanar spacings were calculated using the Bragg's equation, 2d sinθ = nλ. All the sharp lines except the broad scattering were found to disappear after iodine doping. This can be explained on the basis of the transformation of crystalline phase to amorphous phase, Fig. 3.

TGA studies

TGA analytical curves indicated the loss of iodine content of the doped phthalocyanine in the temperature range 130-200 °C. The iodine contents are found to be 38 % for SiPcCl, and 31.56 % for SiPc(p-NPO). These values indicate the presence of three iodine atoms in each of the doped complexes. It is observed that iodine volatilizes slowly with time from the doped material. So care must be taken to run the TGA data soon after synthesizing the iodine doped materials for obtaining the correct iodine content.

Electrical conductivity studies

The observed electrical conductivities of the silicon phthalocyanine complexes, both before and after doping with iodine, are reported in Table 1. Effect of iodine doping on the electrical conductivity of these complexes has been studied for the first time in the present investigation. The 10^-10^4 times increased electrical conductivity observed after iodine doping may be explained to be due to the arrangement of the planar molecules in close facial proximity with sufficient intermolecular overlap and the existence of the fractional oxidation state in the arranged molecular stacking 38,39.

References

2 Moser F H & Thomas A L, Phthalocyanine compounds (Reinhold, New York), 1963.