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# SYNTHESIS AND STRUCTURAL STUDIES OF METAL(II) 4,9,16,23-PHTHALOCYANINE TETRAAMINES

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**Abstract**—Preparation of pure metal(II) 4,9,16,23-phthalocyanine tetraamine 2-hydrates of copper, cobalt, nickel and zinc are reported. Elemental analysis, electronic spectra, FT-IR spectra, powder X-ray diffraction, magnetic-susceptibility measurements, dynamic thermogravimetric MS and GC–MS spectral studies are carried out to check the purity, structural integrity, thermal stability and mode of fragmentation of these complexes. Magnetic-susceptibility measurements showed a variation in the magnetic moments of these complexes with magnetic field strength, indicating the presence of a co-operative intermolecular effect.

Metal phthalocyanines and their derivatives are of great technological importance for the manufacture of blue-green pigments.[1–3] Currently intensive research is going on in producing phthalocyanine compounds useful for applications[1] as catalysts, photoconductors, photosensitizers, electrical conductors, photovoltaic materials, and thermally stable polymers.[1–7] Incorporation of the phthalocyanine structure either in the polymeric backbone or as curing agent to epoxy resins is expected to increase thermal stability, chemical resistance and fire retardance. The polymers prepared from phthalocyanines did not give the thermal stability expected from the stable phthalocyanine structure.[8–13] The use of phthalocyanine carboxylic acids and copper phthalocyanine to cure epoxy resins has been described in the literature.[14,15] However, those phthalocyanine derivatives and copper phthalocyanine are insoluble, react heterogeneously and remained as discrete particles even after curing. Because of this major disadvantage of insolubility, complete realization of their thermal stability and the chemical resistance of phthalocyanines were not seen in the cured resins. This is because phthalocyanine and its metal derivatives are insoluble in water and most common organic solvents. But the solubility can be altered by substituting suitable functional groups in the peripheral benzene rings of the phthalocyanine structure. Among the thermally stable soluble phthalocyanine compounds, amine groups substituted metal phthalocyanine derivatives are found to be promising. The amine derivatives of metal phthalocyanines have been previously synthesized mostly for the preparation of inks, dyes and pigments.[1,16–21] The procedures described often give impure compounds and these compounds have not given clear solutions in aprotic solvents. An efficient method was developed for the synthesis of analytically pure metal(II) 4,9,16,23-phthalocyanine tetraamines with the structure shown in Fig. 1.

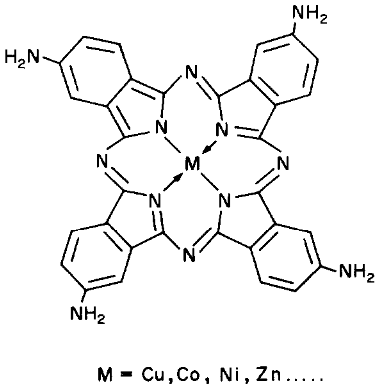

Fig. 1. Structure of metal(II) 4,9,16,23-phthalocyanine tetraamines.

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The present work describes the synthesis and structural investigations of pure metal phthalocyanine tetraamines (MPTAs). The synthetic procedure has been adapted from the methods outlined to synthesize various other types of metal phthalocyanine derivatives.[16–25]

## EXPERIMENTAL

### *Materials*

4-Nitrophthalic acid, ammonium chloride and ammonium molybdate are A.C.S. reagents from Aldrich Chemical Co., U.S.A. All other chemicals were of analytical grade. Metal(II) 4,9,16,23-phthalocyanine tetraamine 2-hydrates of copper, cobalt, nickel and zinc are prepared as follows.

(1) *Copper*(II) *4,9,16,23-tetranitrophthalocyanine*. 12.0 g copper sulfate pentahydrate, 37.0 g 4-nitrophthalic acid, 4.5 g ammonium chloride, 0.5 g ammonium molybdate and excess urea (50–60 g) were finely ground and placed in a 500-cm$^3$ three-necked flask containing 25 cm$^3$ of nitrobenzene. The temperature of the stirred reaction mixture was slowly increased to 185°C and maintained at $185 \pm 5$°C for 4.5 h. The solid product was finely ground and washed with alcohol until free from nitrobenzene. The product was added to 500 cm$^3$ of 1.0 N hydrochloric acid saturated with sodium chloride, boiled for about 5 min, cooled to room temperature and filtered. The resulting solid was treated with 500 cm$^3$ 1.0 N sodium hydroxide containing 200 g sodium chloride and heated at 90°C until the evolution of ammonia ceased. The solid product after filtration was treated with 1.0 N hydrochloric acid and separated by centrifugation. Alternate treatment with hydrochloric acid and sodium hydroxide was repeated twice. The copper(II) 4,9,16,23-tetranitrophthalocyanine was washed with water until chloride-free. The blue complex was dried at 125°C.

(2) *Copper*(II) *4,9,16,23 - tetraaminophthalocyanine 2-hydrate*. About 10 g of finely ground copper(II) 4,9,16,23-tetranitrophthalocyanine was placed in 250 cm$^3$ water. To this slurry 50 g of sodium sulfide nonahydrate was added and stirred at 50°C for 5 h. The solid product was separated by centrifuging the reaction mixture and treated with 750 cm$^3$ of 1.0 N hydrochloric acid. The bulky blue precipitate of copper(II) tetraaminophthalocyanine hydrochloride was separated by centrifugation. It was then treated with 500 cm$^3$ of 1.0 N sodium hydroxide, stirred for 1 h and centrifuged to separate the dark green solid complex. The product was repeatedly treated with water, stirred and centrifuged until the material was free from sodium hydroxide and sodium chloride. The pure copper complex was dried *in vacuo* over $P_2O_5$.

Metal(II) tetranitrophthalocyanines of cobalt, nickel and zinc were prepared by the same method using cobalt, nickel and zinc salts in place of the copper salt of procedure (1). The corresponding metal phthalocyanine tetraamines are obtained by using procedure (2) as described above.

### *Methods*

Beckman Model DB spectrophotometer with 1-cm silica cells, from Beckman Instruments Inc., U.S.A., was used for UV and visible spectral studies. IR spectra were recorded using a Nicolet MX-1 FT-IR spectrometer. Carbon, hydrogen and nitrogen elemental analyses were done by Huffman Laboratories Inc. Co., U.S.A. The metal contents in the MPTAs were determined by decomposing a known amount of the complex using a sulphuric acid–nitric acid mixture followed by careful evaporation and calcination to constant weight. Thermogravimetric studies were carried out with a Du Pont Model 990 thermal analyzer and a 951 thermogravimetic module. A heating rate of 10°C min$^{-1}$ was used in air and nitrogen atmospheres with a flow rate of 100 cm$^3$ min$^{-1}$. The Gouy magnetic balance consisting of a type NP-53 electromagnet with a DC power supply type MP-1053 and a semimicrobalance supplied by Universal Scientific Co., India, was used. A mercury tetrathiocyanato cobaltate(II) complex was used as the calibration standard. The JDX-8P JEOL X-ray diffractometer was used to study the X-ray diffraction pattern of the samples. The spectra were obtained with the following conditions: target Fe (Mn filter), voltage 30 kV, current 30 mA, time constant 4, chart speed 10 mm min$^{-1}$, channel width 0.7, and channel center 1.0.

A Hewlett–Packard model 5980 mass spectrometer equipped with a data acquisition system provided mass spectra of the individual components of the pyrolysis products at 70 eV. Two direct inlet probes (DIPs) were used. The low-temperature DIP can heat to 470°C at a heating rate of 50–100°C min$^{-1}$ below 350°C and 10–50°C min$^{-1}$ above 350°C. The high-temperature DIP was attached to a solid pyrolizer. The sample was heated for 1 min at each of the following temperatures: 700, 800, 900 and 1000°C. A Hewlett–Packard model 5830A gas chromatograph was used to study the volatile gaseous products formed during the thermal treatment. A sample of 1–2 mg of MPTA was inserted inside the platinum coil of the pyroprobe. The sample was

Table 1. Elemental, magnetic and spectral data of metal(II) 4,9,16,23-phthalocyanine tetraamine 2-hydrate ($MPTA \cdot 2H_2O$)

| Name of compound | Field strength (G) | Magnetic susceptibility $(\chi_m \times 10^{-6})$ | $\mu_{\text{eff}}$ (BM) | UV–visible absorptions: wavelength (ε) | IR spectral data ($cm^{-1}$) | Elemental analyses (%): found (calc.) |
|---|---|---|---|---|---|---|
| $CuPTA \cdot 2H_2O$ | 1024 | +1792.60 | 2.093 | 214 (5.7776) | 3282, 3188, 1604, 1411, 1343, 1303, 1251, 1136, 1098, 1053, 951, 863, 833, 744 and 831 | C: 57.5 (57.2) |
| | 1960 | +1679.54 | 2.022 | 300 (5.5267) | | H: 3.6 (3.6) |
| | 2816 | +1560.42 | 1.946 | 382 (5.1547) | | N: 24.9 (25.0) |
| | 3584 | +1423.13 | 1.862 | 749 (5.4678) | | Cu: 9.8 (9.6) |
| | 4352 | +1311.42 | 1.790 | | | |
| | 4792 | +1304.42 | 1.783 | | | |
| | 5632 | +1257.58 | 1.747 | | | |
| | 6144 | +1198.64 | 1.709 | | | |
| $CoPTA \cdot 2H_2O$ | 1024 | +3269.73 | 2.822 | 212 (5.6931) | 3284, 3180, 1607, 1420, 1345, 1309, 1254, 1134, 1097, 1060, 950, 863, 822, 780 and 736 | C: 58.1 (57.6) |
| | 1960 | +2956.77 | 2.683 | 298 (5.5603) | | H: 3.3 (3.6) |
| | 2816 | +2629.67 | 2.530 | 388 (5.1521) | | N: 25.2 (25.2) |
| | 3584 | +2602.47 | 2.518 | 738 (5.2844) | | Co: 8.9 (8.8) |
| | 4352 | +2469.46 | 2.452 | | | |
| | 4792 | +2269.30 | 2.354 | | | |
| | 5632 | +2222.47 | 2.332 | | | |
| | 6144 | +2169.67 | 2.302 | | | |
| $NiPTA \cdot 2H_2O$ | 6144 | −460.782 | — | 208 (5.6991) | 3280, 3186, 1605, 1412, 1344, 1308, 1251, 1135, 1098, 1056, 950, 864, 822, 748 and 733 | C: 56.8 (57.6) |
| | | | | 302 (5.6212) | | H: 3.5 (3.6) |
| | | | | 380 (5.1538) | | N: 24.8 (25.2) |
| | | | | 738 (5.5251) | | Ni: 8.9 (8.8) |
| $ZnPTA \cdot 2H_2O$ | 6144 | −468.284 | — | 214 (5.7416) | 3279, 3165, 1602, 1401, 1340, 1299, 1248, 1133, 1095, 1045, 936, 864, 823, 743 and 728 | C: 56.1 (57.0) |
| | | | | 302 (5.5430) | | H: 3.7 (3.6) |
| | | | | 384 (5.1515) | | N: 24.5 (25.0) |
| | | | | 742 (5.4249) | | Zn: 9.6 (9.4) |

then kept in the pyrolysis chamber which was kept at 250°C. The sample was pyrolyzed at 900°C for 1 min. The volatile products were flushed with helium carrier gas to the GC separation column. The GC column used was 2 m long with a 2 mm i.d., glass column packed with 3% OV101 on 80/100 supelcoport. During the analyses the column temperature was held at 60–280°C and then maintained at the upper limit for 8 min. The helium gas flow was 20 $cm^3 \, min^{-1}$.

## RESULTS AND DISCUSSION

The procedures described above are simple, commercially realizable and give pure compounds with almost quantitative yields ($\simeq$ 90%) except in the case of the zinc compound where the yield was only 30–40%. In this case the zinc complex seems to undergo degradation when it is heated in the presence of sodium hydroxide solution. These MPTAs have a metallic lustre and a deep greenish black colour. They give clear solutions in aprotic solvents such as dimethylsulphoxide, dimethylformamide and dimethylacetamide. The method of synthesis is applicable to the preparation of MPTAs of metals whose ionic radii[26] are about 0.8 Å. The preferred metals are copper, cobalt, nickel, zinc, iron, platinum, aluminium and vanadium. The most preferred metals are copper, cobalt and nickel. The results of the elemental analyses for carbon, hydrogen, nitrogen and metal agreed fairly well with the calculated values and were consistent with the structures shown in Fig. 1 with two water molecules.

### *Electronic absorption spectra*

Metal(II) 4,9,16,23-tetraaminophthalocyanines of copper, cobalt, nickel and zinc showed absorption bands at 208–218, 288–306 and 732–746 nm in 30 N sulphuric acid (Table 1). In addition, shoulders are observed around 380–384 nm in all the absorption spectra of the complexes. The deep greenish blue colour of the derivatives may be due to the $e_g \leftarrow a_{2u}$ transitions. A small dependence of the spectrum upon the central metal ion may be due either to the involvement of the $p\pi(a_{2u})$ orbitals in the $\pi$-bonding of the phthalocyanine ring system or more probably to the inductive effect.[27] In comparison with the spectra of the corresponding parent phthalocyanines the two peaks in UV regions around 208–218 and 288–306 nm remained almost unaffected in the spectra of the corresponding MPTAs. The peaks in the parent metal phthalocyanines around 424–438 nm appeared as shoulders at 380–384 nm with a blue shift. The peaks in the longer-wavelength region (732–746 nm) showed a bathochromic shift with increasing intensity with respect to the corresponding parent phthalocyanines. This is due to the auxochromic —$NH_2$ group present in the benzene portion of the complexes.

### *IR spectra*

The FT-IR spectral data were recorded in KBr discs and the results are presented in Table 1. Two weak broad absorption bands at 3279–3284 and 3165–3188 $cm^{-1}$ are observed in all the spectra of the MPTAs. These absorptions may be assigned to the $\nu_{as}$ and $\nu_s$ stretching vibrations of the amino groups. Intense —$NH_2$ group in-plane bending vibrations are observed at 1602–1607 $cm^{-1}$. Peaks around 1340–1345, 1299–1309 and 1248–1251 $cm^{-1}$ indicated the presence of C—N aromatic stretching. The bands at 1133–1136, 1095–1098, 1045–1060, 936–951, 863–864 and 743–750 $cm^{-1}$ may be assigned to the various phthalocyanine skeletal vibrations.[27]

### *Dynamic thermogravimetric studies*

The nature of the analytical curves (Fig. 2) indicated that these amine derivatives of copper, cobalt, nickel and zinc phthalocyanines are degraded mainly in two steps. The weight loss (5–5.4%) which takes place between 50 and 130°C corresponds to the loss of two water molecules. The second weight loss is very catastrophic in an oxidizing atmosphere and is about 76–77% which is equivalent to the degradation of the unmetallated phthalocyanine structure. The final products in the oxidizing atmospheres are CuO, CoO, NiO and ZnO. The stability of the MPTAs in the oxidizing atmosphere is in the order CoPTA > CuPTA > NiPTA > ZnPTA. The second step of weight loss is very resistant in a nitrogen atmosphere and the weight loss seems to be due to some other mode of degradation. This weight loss is gradual in the temperature range 500–900°C and the char yields vary from 65 to 79%, depending on the MPTA. The stability in the inert atmosphere is found to follow the order NiPTA > CoPTA > CuPTA > ZnPTA.

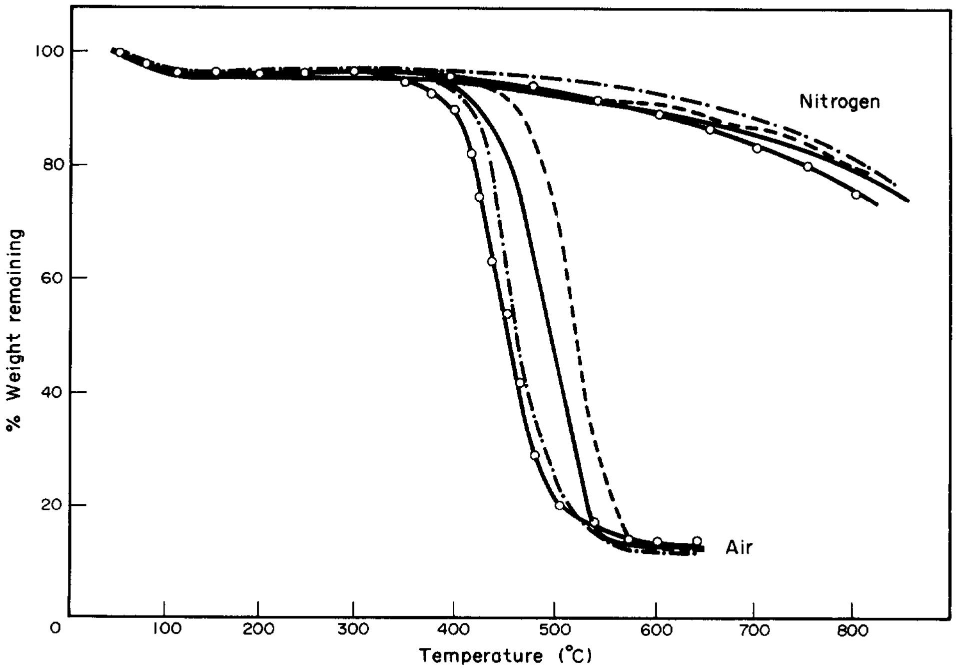

Fig. 2. Dynamic thermogravimetric analytical curves of: (1) CuPTA · $2H_2O$ (——), (2) CoPTA · $2H_2O$ (– – – –), (3) NiPTA · $2H_2O$ (— · — · —), and (4) ZnPTA · $2H_2O$ (— ○ — ○ —).

### *Magnetic-susceptibility measurements*

The magnetic-susceptibility data for metal(II) 4,9,16,23-phthalocyanine tetraamines of copper, cobalt, nickel and zinc are consistent with the paramagnetic nature of the copper and cobalt complexes and the diamagnetic nature of the nickel and zinc complexes. The complexes are square planar with molecular symmetry $D_{4h}$. A summary of the magnetic properties over the range of magnetic field strengths 1025–6144 G are reported in Table 1. The magnetic moment parallels that of other spin-paired square planar cobaltous derivatives with a moment considerably above that expected for one unpaired electron. This may be due to the orbital contribution which could arise by mixing the ground state $(b_{2g})^2\,(e_g)^4\,(a_{1g})^1$ and higher orbitally degenerate states such as $(b_{2g})^2\,(e_g)^3\,(a_{1g})^2$. CuPTA has a moment corresponding to the spin-only value at a higher magnetic field strength and this value is very close to the 1.9 BM observed in most of the copper complexes. The variation in the magnetic moments with magnetic field strength has also been observed in the case of metal phthalocyanine sulphonic acid and metal phthalocyanine tetracarboxylic acid complexes. The variations in these complexes may also be due to the intermolecular co-operative effect.[25]

### *Powder X-ray diffraction*

X-ray diffraction spectrographs of CuPTA, CoPTA, NiPTA and ZnPTA recorded through a range of angles (5–90°) showed similar patterns. All these complexes showed one broad sufficiently intense diffracted peak and the interplanar spacings calculated based on these data gave values (in Å) of 13.05, 12.32, 12.32 and 12.32 for CuPTA, CoPTA, NiPTA and ZnPTA, respectively.

### *Mass and GC–mass spectral studies*

The mass spectra recorded at various temperatures indicated that the concentrations of the volatile products observed are very low even at a very high temperature. At 500°C, $m/z$ of 18, 14, 64, 91, 118 and 143 appeared in more than 20% relative abundance with $m/z = 118$ being the base peak. At higher temperatures (700–1000°C) $m/z$ of 28, 32, 44, 64, 82, 96, 128, 160, 192 and 256 (base peak) are seen in the mass spectra of the MPTAs. The gas chromatograms of the pyrolysed products of the MPTAs showed only trace quantities of volatile materials. The products identified are $N_2$, $N_2H_4$, $C_6H_6$, $C_6H_5NH_2$, $C_6H_5CN$, $C_6H_5(CN)_2$ and $C_6H_4(CN)(NH_2)$. The peak corresponding to $m/z = 44$ in mass spectra of MPTAs seems to be unusual. However, this is possible if the tetraamines have the property of adsorbing carbon dioxide gas. The study to support this is under further investigation.

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