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Studies on tetra-amine phthalocyanines

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Abstract

Metal(II) tetranitro phthalocyanines of cobalt, nickel and copper are synthesized in pure state by a novel modified method. The complexes are characterized using elemental, electronic and IR spectral studies. Pure metal(II) tetra-amino phthalocyanines of cobalt, nickel and copper are synthesized by reducing the nitro groups of the above complexes using sodium sulphide. These complexes are also characterized by elemental, electronic, IR spectral and magnetic susceptibility measurements. The nature of the electrical conductivities of the above three metal(II) tetra-amino phthalocyanine derivatives are studied in the temperature range 303–473 K and the data are presented. Among the effect of various substituent groups on the electrical conducting property of phthalocyanine, amine group substituent on the peripheral benzene ring of the phthalocyanine molecule has been found to increase electrical conductivity to a greatest extent. These complexes showed about 10^5–10^6 times higher electrical conductivities compared to their parent phthalocyanine compounds.

Keywords: Metal(II) tetra-amino phthalocyanine; Metal(II) tetranitro phthalocyanine; Magnetic property; Electrical conductivity

1. Introduction

Metal phthalocyanine class of compounds attracted world-wide interest because of their interesting properties like chemical inertness, excellent thermal stability, very high colouring properties, catalytic activity, semiconductivity, photoconductivity and the like [1–5]. Electrical conductivity is one of the important properties of the phthalocyanine compounds which attracted great deal of interest since 1948 [6,7]. Extensive research work has been carried out to improve the electrical conductivity of phthalocyanines via doping mechanism and polymerization methods [3–5,8–13]. The effect of substituents and the peripheral phenyl groups of the phthalocyanine structure seems to yield much information about the nature of electrical conductivity of complexes. However, work done in this direction is meagre. In 1991, Singerski et al. [14] studied the electrical conductivity of nickel (II) tetra-amino phthalocyanine. Among the effect of various substituent groups on the electrical conducting property of phthalocyanine, amine group substituent on the peripheral benzene ring of the phthalocyanine molecule has been found to increase electrical conductivity to a greatest extent [15–20].

The aim of the present work is to improve the method of synthesis with respect to time consuming earlier reported procedure. Properties of metal phthalocyanines are very sensitive to the presence of impurities. So, another aim is to find out the electrical conducting property of the pure tetra-amine metal phthalocyanine derivatives of cobalt, nickel and copper at the room temperature and to study its variations in the optimum temperature range from ambient to 473 K. Pure metal(II) tetra-amine phthalocyanines of cobalt, nickel and copper complexes are synthesized by first synthesizing metal tetranitro phthalocyanines using the novel method and then reducing the same using sodium

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sulphide. These materials are characterized using elemental, UV–Vis, IR, magnetic susceptibility and powder X-ray diffraction studies. Electrical conductivity study has been carried out on the synthesised metal(II) tetra-amino phthalocyanines of the above three metals over the temperature range 303–473 K and the results are presented in this paper.

2. Materials and methods

2.1. Preparation of metal(II) tetra-amino phthalocyanines

2.1.1. Synthesis of metal(II) tetranitro phthalocyanines

Metal tetranitro phthalocyanines of cobalt, nickel and copper are prepared by a novel method. A brief outline of the procedure is as follows.

2.1.1.1. Cobalt(II) tetranitro phthalocyanine. Finely ground mixture of 5.2 g nitrophthalonitrile, 1.75 g ammonium chloride, 2.2 g cobalt sulphate heptahydrate, 1.2 g sodium hydroxide and catalytic amount of sodium methoxide (~0.1 g) was placed in a 100 ml three necked flask provided with a mechanical stirrer, refluxing condenser and thermometer. About 15 ml dimethyl sulphoxide was added to the mixture and it was heated slowly with stirring to 180 K and maintained at 453 ± 5 K for 4 h. Colour of the reaction end product was dark blue. The product obtained was washed with alcohol, then with water several times. It was then dried over phosphorus pentoxide.

Nickel and copper(II) tetranitro phthalocyanines are also prepared using the similar procedure as described above.

Anal. for cobalt(II) tetranitro phthalocyanine, $C_{32}H_{12}N_{12}O_8Co$: Calc. C, 51.14; H, 1.60; N, 22.36; Co, 7.84. Found: C, 51.85; H, 1.88; N, 22.49; Co,7.92%. Electronic absorption, λ_{max}, (nm): 202, 301, 385, 680, 752. IR absorption bands (cm^{-1}): 760s, 846w, 945w, 1052w, 1090w, 1336s, 1532s, 3094w. Yield: 91%.

Anal. for nickel(II) tetranitro phthalocyanine, $C_{32}H_{12}N_{12}O_8Ni$: Calc. C, 51.16; H, 1.61; N, 22.37; Ni, 7.82. Found: C,51.84; H, 1.76; N, 22.57; Ni,7.93%. Electronic absorption, λ_{max}, (nm): 200, 303, 385, 675, 757. IR absorption bands (cm^{-1}): 760s, 852w, 941w, 1050w, 1089w, 1116w, 1332s, 1519s, 3098w. Yield: 88%.

Anal. for copper(II) tetranitro phthalocyanine, $C_{32}H_{12}N_{12}O_8Cu$: Calc. C, 50.83; H, 1.59; N, 22.33; Cu, 8.40. Found: C, 51.18; H, 1.63; N, 22.61; Cu, 8.72%. Electronic absorption, λ_{max} (nm): 200, 303, 385, 668, 740, 764. IR absorption bands (cm^{-1}): 763s, 856w, 936w, 1058w, 1090m, 1118w, 1338s, 1512s, 3098w. Yield: 90%.

2.1.2. Cobalt(II) tetra-amino phthalocyanine 2-hydrate

Preparation of cobalt, nickel and copper phthalocyanine tetra-amine are done by reduction of the nitro derivatives using sodium sulphide as explained earlier [21]. A brief summary of the procedure is given below.

About 4.0 g of finely ground cobalt(II) tetranitro phthalocyanine was placed in 100 ml water. To this slurry, 20 g of sodium sulphide nonahydrate was added and stirred at 323 K for 5 h. The solid product was separated and purified using 0.5 M sulphuric acid and 1.0 M sodium hydroxide. Finally, the complex was washed with water until free from sodium hydroxide and sodium chloride. The dark bluish green product was dried over phosphorus pentoxide.

Metal(II) tetra-amino phthalocyanines of cobalt and nickel are prepared by the above method using the corresponding metal(II) tetranitro phthalocyanines.

Anal. for cobalt(II) tetra-amino phthalocyanine 2-hydrate, $C_{32}H_{24}N_{12}O_2Co$: Calc. C, 57.6; H, 3.6; N, 25.2; Co, 8.8. Found: C,58.1; H, 3.3; N, 25.1; Co, 8.9%. Electronic absorption, λ_{max}, (nm): 210, 302, 380, 740. IR absorption bands (cm^{-1}): 738m, 782w, 825w, 950w, 1058m, 1098m, 1132m, 1254m, 1309w, 1345w, 1420m, 1606m, 3160w, 3280w.

Anal. for nickel(II) tetra-amino phthalocyanine 2-hydrate, $C_{32}H_{24}N_{12}O_2Ni$: Calc. C, 57.6; H, 3.6; N, 25.2; Ni, 8.8. Found: C,57.1; H, 3.7; N, 24.9; Ni, 8.9. Electronic absorption, λ_{max}, (nm): 212, 302, 380, 742. IR absorption bands (cm^{-1}): 733m, 748w, 820w, 862w, 951w, 1052m, 1095m, 1136m, 1248w, 1305w, 1345w, 1412m, 1605m, 3186w, 3278w.

Anal. for copper(II) tetra-amino phthalocyanine 2-hydrate, $C_{32}H_{24}N_{12}O_2Cu$: Calc. C, 57.2; H, 3.6; N, 25.0; Cu, 9.6. Found: C,57.5; H, 3.6; N, 24.9; Cu, 9.8%. Electronic absorption, λ_{max}, (nm): 216, 302, 375, 740. IR absorption bands (cm^{-1}): 730m, 746w, 832w, 865w, 949w, 1052m, 1095m, 1133m, 1252w, 1304w, 1340w, 1409m, 1604m, 3187w, 3280w.

2.2. Elemental analysis

Elemental analysis for carbon, hydrogen and nitrogen were done by Regional Sophisticated Instrumentation Center, CDRI, Lucknow, India. The metal contents of the metal(II) tetra-amino phthalocyanines were determined by decomposing a known amount of the complex using H_2SO_4–HNO_3 mixture, followed by careful evaporation and calcinations [22].

2.2.1. Physical measurements

UV–Vis spectra were recorded in 15 M sulphuric acid using Systronics type – 117 model spectrophotometer with 1 cm silica cells, Systronics, Ahmedabad, India. IR spectra were recorded in KBr using Shimadzu 8201PC FT-IR spectrometer, Japan. Magnetic susceptibility measurements were done using the Gouy magnetic balance consisting of the type NP-53 electromagnet with DC power supply type NP-1053 and a Keroy semimicro balance supplied by Universal Scientific Company, Bombay, India. Pure mercury tetrathiocyanato cobaltate (II) was synthesized and used as a calibration standard [23]. A JEOL-JDX-8P X-ray diffractometer was used to study powder X-ray diffraction of the samples. Powdered metal(II) tetra-amino phthalocyanine derivatives were compressed into pellets of 1.3 cm diameter and thickness ranging from 0.15–0.25 cm, using Perkin–Elmer KBr Die under a pressure of 500 kg/cm^2. The Carver laboratory Press Model – diaton capacity was been used for applying the pressure. The diameter and thickness of the pellets were determined by using a screw gauge readable upto 0.005 cm. Conducting silver paint (ELTECKS preparation No. 1228-C) was coated on both flat surfaces of the pellets and the electrical contacts to the samples were made using the same silver paint to the electrodes. The electrical contacts were checked to verify the ohmic connection and resistance measurements were done from 303 to 473 K using DOT 402 Digital Milli Ohm Meter and DOT 425 Insulation Resistance Tester, Bhandari Electronics and Electricals, Bangalore, India.

3. Results and discussion

Pure metal(II) tetranitro phthalocyanines of cobalt, nickel and copper are synthesized with a very good quantitative yield by a modified procedure as outlined above. In the previous method, tetra-amino phthalocyanines were prepared by first synthesizing metal tetranitro phthalocyanines using urea-phthalic anhydride reagents. In the modified method, metal tetranitro phthalocyanines have been synthesized using 4-nitro phthalonitrile. The yields and purity of the metal tetranitro phthalocyanines are very good in both the methods. However, in the urea-phthalic anhydride method, the purification procedure requires a few days, whereas in the present method it has been reduced to a few hours. The compounds are characterized using elemental analysis, electronic spectral and IR spectral studies. The results of the elemental analysis for carbon, hydrogen, nitrogen and metal agreed fairly with the calculated values. Metal(II) tetra-amino phthalocyanines of cobalt, nickel and copper are obtained by reducing the above compounds using sodium sulphide. The results of the elemental analysis for carbon, hydrogen, nitrogen and metal showed that these complexes are equally pure as obtained by the earlier method [21].

3.1. Electronic spectral and IR spectral study

The electronic spectral data are recorded for metal(II) tetra-amino phthalocyanines of cobalt, nickel and copper complexes in the range 200–800 nm using 30 N sulphuric acid as solvent. These complexes showed absorption bands at 205–220, 285–305 and 730–745 nm in addition, shoulders at 380–385 nm are observed in the spectra of all the complexes. The deep greenish blue colour of the complexes are due to the Q band which may be assigned to the $6e_g \leftarrow 2a_{1u}$ transitions [24].

Two weak absorption bands at 3280–3285 and 3165–3190 cm^{-1} are observed in all the IR spectra of metal phthalocyanine tetra-amine complexes which may be assigned to the ν_{as} and ν_s stretching vibrations of the amino groups. Intense absorption bands are observed at around 1605 cm^{-1} due to the $-NH_2$ in-plane bending vibrations. All the complexes showed absorption bands around 1135, 1095, 1050, 945, 860 and 745 cm^{-1} due to the phthalocyanine skeletal vibrations [25].

3.2. Magnetic susceptibility measurements

Magnetic susceptibility measurements on metal(II) tetra-amino phthalocyanines of cobalt, nickel and copper complexes have been investigated in solid state at the ambient temperature and varying magnetic field strengths ranging from 1.02 to 3.58 kG. The experimental data indicated that copper and cobalt complexes are paramagnetic nature and, the nickel complex is diamagnetic in nature. Effect of magnetic field strength on the magnetic properties of these complexes are reported in Table 1. Fig. 1 shows the variations in the magnetic properties of these complexes with magnetic field strength in these complexes which may be due to the intermolecular co-operative effect [26].

3.3. Powder X-Ray diffraction

The powder X-Ray diffraction study of cobalt, nickel and copper phthalocyanine tetra-amines were done in the range 2θ angles 2 – 40°. The diffraction patterns of these tetra-amine derivatives showed qualitatively similar spectrographs. Out of the three peaks observed, one is sharp peak with maximum intensity and other two are not well resolved broad peaks with less intensity. The interplanar spacings are calculated using the Bragg's equation

$$n\lambda = 2d\ \sin\theta,$$

where n is the integer, λ is the wavelength of X-ray radiation, d is the interplanar distance and θ is the complement of the angle of incidence. The interplanar spacings for the sharp peaks of cobalt, nickel and copper phthalocyanine tetra-amines are found to be 13.52, 13.44 and 15.29. The shapes of the X-ray diffraction spectrograph indicate that these tetra-amines are amorphous in nature.

3.4. Electrical conductivity

The room temperature electrical conductivities observed for the pure metal(II) tetra-amino phthalocyanines

Table 1
Magnetic susceptibility and the electrical conductivity data for metal(II) tetra-amine phthalocyanines

Compound	Magnetic susceptibility		Electrical conductivity $(\Omega\,\mathrm{cm})^{-1}$		Activation energy, E eV (temperature range)
	Field strength (kG)	$\chi_M \times 10^6$ CGS units	303 (K)	473 (K)	
Cobalt(II) tetra-amine phthalocyanine 2-hydrate	1.02	3085	5.7×10^{-7}	8.6×10^{-5}	0.112 (308–358 K)
	1.92	2253			
	2.81	2170			
	3.58	2105			
Nickel(II) tetra-amine phthalocyanine 2-hydrate	1.02	−598	1.3×10^{-6}	2.6×10^{-4}	0.088 (308–378 K)
	1.92	−355			
	2.81	−339			
	3.58	−330			
Copper(II) tetra-amine phthalocyanine 2-hydrate	1.02	1576	7.6×10^{-7}	1.1×10^{-4}	0.106 (313–363 K)
	1.92	1258			
	2.81	1231			
	3.58	1179			

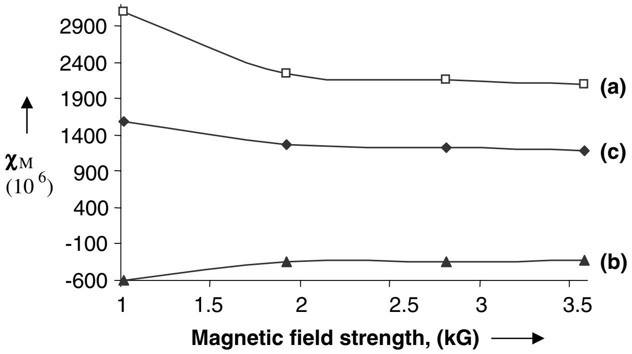

Fig. 1. Variations of magnetic susceptibilities: (a) cobalt; (b) nickel; (c) copper phthalocyanine tetra-amines with field strength.

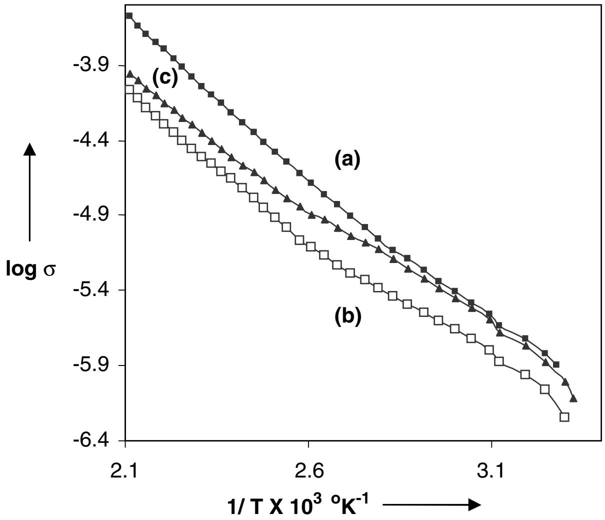

Fig. 2. Variations of electrical conductivities: (a) cobalt; (b) nickel; (c) copper phthalocyanine tetra-amines with temperature.

of cobalt, nickel and copper are found to be 10^5–10^6 times higher compared to their respective parent phthalocyanines. Electrical conducting properties of phthalocyanines are very much sensitive to the presence of impurities. In authors' experience, the electrical conductivities of $\sim 10^8$ order are observed for tetra-amine derivatives of cobalt, nickel and copper when hydrogen chloride has not been removed during the process of synthesis. The variations of electrical conductivity over a temperature range 298–473 K are studied and the conductivity data of metal phthalocyanine tetra-amines are plotted log σ versus $1/T$, Fig. 2. The plots indicated that cobalt, nickel and copper phthalocyanine tetra-amines are semiconducting in nature. The conductivity of cobalt(II) tetra-amine phthalocyanine is found to be linear in the temperature range 308–358 K followed by a gradual increase and, once again becomes linear between the temperature range 383–473 K. Similarly, linear relationship in the conductivity variations are observed for nickel (II) tetra-amino phthalocyanine in the temperature ranges at 298–373 and 378–473 K. In the case of copper tetra amine phthalocyanine linear relationships of the electrical conductivity are observed in the range 313–363 and 368–473 K. These thermally activated varying conductivity with temperature was found to obey the expression:

$$\sigma = \sigma_0 e^{-E/kT},$$

where E is the activation energy, σ is the specific conductivity at T K, σ_0 is a constant and 'k' is Boltzmann constant. The relevant data observed for the electrical conductivity of the three metal phthalocyanine tetra amines are presented in Table 1. The room temperature specific electrical conductivities of cobalt, nickel and copper phthalocyanine tetra amines are 5.7×10^{-7}, 1.3×10^{-6} and 7.6×10^{-7} $\Omega^{-1}\,\mathrm{cm}^{-1}$, respectively. The order of electrical conductivities observed for these phthalocyanine tetra-amines are Ni(II) > Cu(II) > Co(II). This may be explained due to the following considerations. The variations of electrical conductivities of metal phthalocyanine complexes can be expected due to the nature of the central metal atom, the nature of substituent groups at the peripheral benzene rings of the phthalocyanine molecule, overlap of the π-electron systems between the molecules and differences in the stacking arrangements of the phthalocyanine molecules. Differences and the order of electrical conductivities in this case are mainly observed due to the differences in the nature of the central metal atom, interplanar distances between the molecules and differences in stacking arrangements of the molecules. Highest electrical conductivity is observed for nickel phthalocyanine tetra-amine is due to the smaller interplanar spacing between the molecule as well as favourable intermolecular stacking which are expected to lead to the greater π-electron interactions between the molecules resulting highest electrical conductivity. Copper phthalocyanine tetra-amine showing higher electrical conductivity compared to cobalt phthalocyanine tetra-amine though the interplanar distance between the molecules in the former is greater. This may be due to the greater favourable intermolecular stacking between the copper phthalocyanine tetra-amine molecules compared to cobalt phthalocyanine tetra-amine molecules leading to the higher π-electron interactions. The 10^5–10^6 times improved electrical conductivity compared to their respective parent phthalocyanines are due to electron donor amine substituent group. Electron donor substituent amino groups may facilitate for greater intermolecular contact and increase interactions of 3d orbitals with the π-orbitals of the neighbouring phthalocyanine units, thus providing a pathway for charge carriers. The change in activation energies with different temperature ranges may be due to some phase transformations and variation in the intermolecular interactions resulting change in the electrical conductivity.

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