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NOTE

Infrared Studies of Cu-Phthalocyanine Dye

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The infrared spectra of Cu-phthalocyanine were recorded. The analysis has been carried out by assuming C_{4h} point group symmetry. The vibrational frequencies appeared are lesser than expected.

The spectroscopic study of molecular structure of polyatomic macro-molecules requires good theoretical as well as high quality experimental approaches. The study of literature shows that Cu-phthalocyanine is coplanar[1] and tetradentate with the four coordinating N-atoms occupying the corners of a square. All the C—N bonds within the 16 membered central ring are approximately equal, the system being continuously conjugated[2] with the C—N distance 1.38 Å. The four isoindole N-atoms are shifted 0.04 Å, towards the Cu-atom relative to their position in the phthalocyanine ligand while the angle at the isoindole N-atom decreases from 108° to 99°. The unique structural features of Cu-phthalocyanine, catalytic effect[3] and its uses in pigment technology[4] motivated us to undertake the detailed vibrational analysis[5] of Cu-phthalocyanine dye. The molecule under investigation has been discussed with a view to examining the structural pattern and nature of bonding.

The copper-phthalocyanine was made available from M/s Fluka, Switzerland and used as such without any further purification. The infrared spectrum was recorded on Perkin-Elmer (Model 577) double beam grating spectrophotometer in the range 4000–200 cm^{-1} using KBr pellets. The source of continuous radiation was Nernst Glower and the detector was a permanently evacuated thermopile. The mesurements of bands were accurate within the range ±4 cm^{-1}

The infrared spectrum of copper phthalocyanine shows the regionwise absorption bands which are shown in Table-1.

The infrared data given in Table-1 as well as the known structure of copper phthalocyanine revealed the following features:

TABLE-1

S.No.	Region (cm^{-1})	Nature of the bond	Indication
1.	*ca.* 3330	No absorption	absence of —O—H
2.	*ca.* 2200	No absorption	absence of ≡C
3.	1780–1650	Medium absorption	>C=O absent
4.	1230–1050	Sharp and intense	due to C—N
5.	840–690	Strong absorption	C—H out-of-plane bending

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The molecule does not contain —OH or N—H group and hence no absorption around 3300 cm^{-1}. Absorption at 3300 cm^{-1} is attributed to —CH stretching (with sp^2 hybridised carbon). The bands around 2900 cm^{-1} in the regions (2) and (4) of the table, the absorption at 2500 cm^{-1} is absent rightly because there is neither C≡C nor >C=O. The region (4)-1230–1050 cm^{-1} is attributed to C—N band. There are bands around 700 cm^{-1} (attributed to C—H out-of-plane bending) as well as at lower wavenumbers.

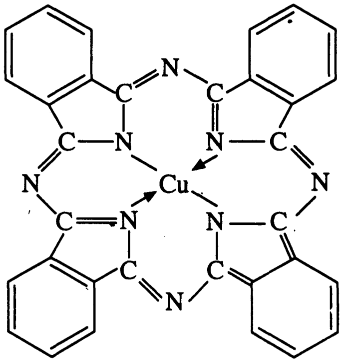

Fig. 1.

The structure of copper phthalocyanine (Fig. 1) suggests all the vibrations to be of skeletal type, *i.e.*, belonging to the entire structure. The number of bands observed in the spectrum is far less than the expected and total 24 frequencies (cm^{-1}) appearing as follows:

3300 w, 3010 w, 2900 m, 2840 m, 1680 s, 1620 s, 1595 w, 1510 m, 1470 s, 1422 s, 1350 m, 1335 s, 1290 s, 1162 s, 1122 s, 1065 m, 940 m, 900 s, 875 s, 795 m, 765 s, 750 s and 715 s.

The very weak absorption at 3400–3300 cm^{-1} is due to the presence of some impurities. The strong absorption at 2900 cm^{-1} is assigned to C—H stretching vibrations. The C—H group is present in all the four benzene rings of the molecule. The present data confirm the reasonable expectation that the C—H stretching modes of some heterocyclic compounds will be essentially similar to those of aromatic compounds of similar structure. However, some such compounds like pyridine and picolines[6–9] show C—H absorption in the range somewhat higher than in the Cu-phthalocyanine. Below 2000 cm^{-1} to 1500 cm^{-1} there is one weak and one very sharp and strong absorption which may be assigned to the presence of aromatic ring only because the presence of an aromatic type structure is best recognized by the presence of =C—H stretching vibrations near 3030 cm^{-1} range. Such vibrations are already detected in the present molecule.

In these regions the absorption bands due to C=C vibrations can also throw light on the presence of conjugation[10] with the double bonds of the ring. Wright[11] included it as a definite medium intensity band occurring in the ring.

The 1595 cm^{-1} band is a normal aromatic vibration but is always weak and difficult to detect unless it is made stronger by external conjugation, when it becomes a readily recognizable band of medium intensity. The other bands between 1600 and 1500 cm^{-1} can be expected for phenyl ring to occur in such polycyclic molecules. Theoretically although, as bond fixation occurs in such materials and not all the bands are of equal strength[12], it is to be expected that there may be some broadening of the overall ranges in which they can occur. A sharp band at about 1470 cm^{-1} appears perhaps due to the presence of a number of cyclic aromaticities in the molecule and this is evidenced by Orr and Thomson[13].

There are some strong and some weak bands between 1470 and 1100 cm^{-1}, which are assignable to either C—N or C—C vibration in the molecule. The strong absorption at 1890 cm^{-1} is due to the C—C—C in-plane deformation vibration of the molecule. The region 1290–910 cm^{-1} is supposed to contain bands due to C—H in-plane bending vibrations. The remaining characteristic region is that between 900 and 700 cm^{-1} in which deformations occur. The strongest band in this region originates in the out-of-plane vibrations of the H-atoms in the molecule. The presence of some bands around 500 cm^{-1}, *i.e.*, low frequency bands has been observed and they are assigned to Cu—N bonding.

REFERENCES

1. A.B.P. Lever, *Adv. Chem. Radiochem.*, **7**, 28 (1965).
2. E.L. Knopa and J.J. Romer, U.S. Patent 25, 13098 (1950).
3. M. Polanyi, *Trans. Faraday. Soc.*, **34**, 1191 (1938).
4. R.P. Linstead and J.M. Robertson, *J. Chem. Soc.*, 1736 (1936).
5. Venkat Raman, *Ana. Chem. of Redox Dyes*, 446 (1972).
6. Kline and Turkeritch, *J. Chem. Phy.*, **12**, 300 (1944).
7. Roberts and Szware, *J. Chem. Phy.*, **16**, 981 (1948).
8. Marion, Ramsay and Jones, *J. Am. Chem. Phy. Soc.*, **73**, 305 (1951).
9. Conbon, Hales and Herington, *J. Chem. Soc.*, 2125 (1951).
10. L.J. Bellamy, The Infrared Spectra of Complex Molecules, Methuen, London, Vols. I and II (1980).
11. N. Wright, *Industrial Eng. Chem. Analyst. Edn.*, 113 (1941).
12. C.F. Bridger, *Quart. Reviews*, 147 (1951).
13. Orr and Thompson, *J. Chem. Soc.*, 281 (1951).

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