Synthesis and Molecular Structure of a Lithium Complex of the Phthalocyanine Radical

Hiroshi Sugimoto,*[a] Masayasu Mori,*[a] Hideki Masuda,[b] and Tooru Taga[b]

[a] *Department of Chemistry, Faculty of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka, 558, Japan*
[b] *Faculty of Pharmaceutical Sciences, Kyoto University, Shimoadachi-cho, Yoshida, Sakyo-ku, Kyoto 606, Japan*

Controlled potential electrolysis of the dilithium salt of phthalocyanine, $Li_2(pc^{2-})$, at 0.15 V *vs.* saturated calomel electrode in acetonitrile gave a lithium complex of the phthalocyanine radical, the crystal structure of which shows that it contains a unit cell with four nearly planar $Li(pc^{\cdot-})$ molecules of S_4 symmetry, stacked metal-over-metal with an Li–Li spacing of 3.245(2) Å, and staggered by 38.7(3)°; its effective magnetic moment decreased from the room temperature value of 1.3 μ_B to 1.0 μ_B at 150 K, but upon further cooling it increased to approach the free-spin value.

Fully or partially oxidized phthalocyanines or their metal complexes are attracting attention as new materials.[1] We have already reported[2] the synthesis of stable radicals of phthalocyanine and their basic characterization by i.r., Raman, e.s.r., and reflectance spectroscopy, as well as their magnetic moments. Their unusual nature, particularly their lower than normal magnetic moments, prompted us to examine them in more detail, and to investigate the molecular structures by *X*-ray crystallography.

In order to obtain single crystals for *X*-ray crystallography, the dilithium salt of phthalocyanine,[3] $Li_2(pc^{2-})$, was electrolysed in anhydrous acetonitrile, using tetraethylammonium

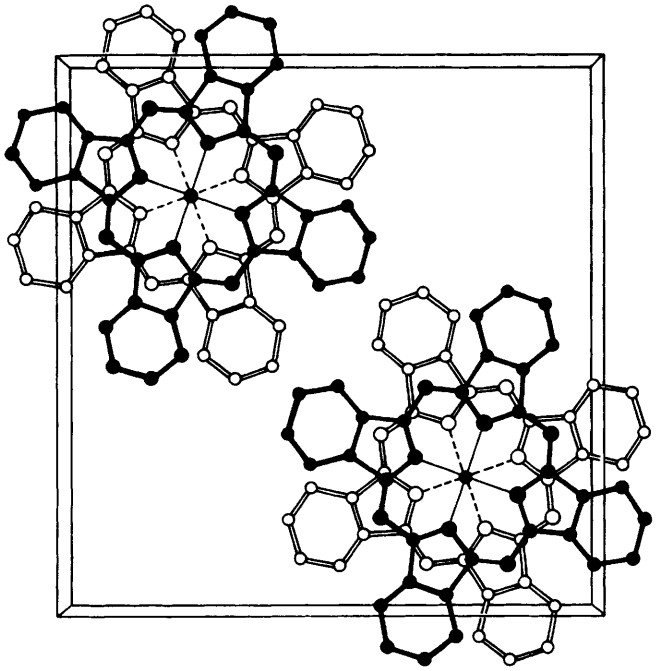

Figure 1. View down the *c* axis of the unit cell of lithium complex of phthalocyanine radical. Hydrogen atoms have been omitted for simplicity. Dimensions: Li–Li 3.245(2), Li–N 1.942(5) Å.

perchlorate, and platinum or gold wire (30 mm long, 1 mm in diameter) as the supporting electrolyte and the working electrode, respectively. The initial concentration was about 2 mM, and the oxidation potential was controlled at 0.15 V (*vs.* saturated calomel electrode). It took 6—7 days for completion, giving almost quantitative yields. The dark-brown needle-like crystals obtained had the characteristic spectroscopic properties described previously,[2] and were used for the crystallographic study.† As shown in Figure 1, the lithium ion is located at the centre of the inner four nitrogen atoms of a nearly planar Li(pc$^{\cdot-}$) molecule having crystallographically imposed $\bar{4}$ (S_4) symmetry. These Li(pc$^{\cdot-}$) molecules are stacked metal-over-metal so that their mean molecular planes are perpendicular to the crystallographic *c* axis. The interplanar distance [3.245(2) Å] is significantly shorter than those of neutral aromatic compounds such as benzene derivatives or graphite (3.35—3.5 Å),[4] probably owing to π electron deficiency on the planes, as proved by a narrow e.s.r. signal at $g = 2.002$ without any hyperfine structure caused by nitrogen atoms.[2] The stacked radical planes are rotated by 38.7(3)° from an eclipsed conformation around the Li–Li axis. The structure has a close similarity to that of nickel or cobalt phthalocyanine iodide which is reported to be highly electrically conductive,[1,5] the distance and the angle of tilt between successive complex radicals being, respectively, 3.244 Å and 39.5° in Ni(pc)I, and 3.123 Å and 40° in Co(pc)I.

† *Crystal data:* $C_{32}H_{16}N_8Li$, M_r = 519.48, space group *P4/nnc*, tetragonal, a = 19.575(3), c = 6.491(3) Å, Z = 4, D_c = 1.387 g/cm^3, U = 2487.9(27) Å^3, μ = 6.49 cm^{-1}. 453 Reflections measured (with 2 $\theta < 60°$) on a Rigaku AFC-5 diffractometer (Mo-K_α) had $F_o > 3\sigma(F_o)$ and were used in the refinement of the structure. The hydrogen atom positions were calculated (C–H = 1.00 Å). R = 0.084. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

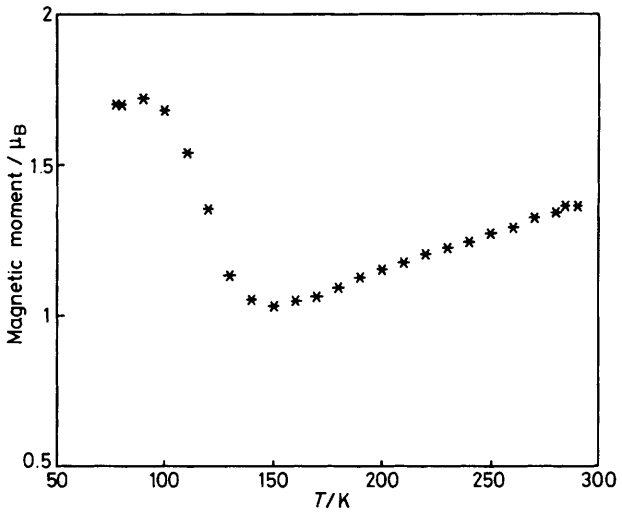

Figure 2. Variation of magnetic moment of lithium complex of phthalocyanine radical with temperature.

The magnetic susceptibility of a powder sample of Li(pc$^{\cdot-}$) was measured by the Faraday method using a Shimadzu MB-2 torsion magnetometer. As shown in Figure 2, the magnetic moment decreased with decrease in temperature to about 150 K. Below this temperature, however, it increased again to approach the free radical value (1.73 μ_B). The approximately constant subnormal susceptibility of 7~8 × 10^{-4} e.m.u. observed above 150 K seems to suggest considerable interaction between the electron spins, and may be related to the marked approach of the α-pyrrole carbon atoms to the adjacent radical molecules (3.0—3.5 Å). A concrete explanation for the reincrease at lower temperatures seems to be difficult; possible candidates include low-temperature transition to a structure which is less favourable to antiferromagnetic interaction, or a co-operative phenomenon of electric conduction and magnetism. A closer approach to the relation between the structure and physicochemical properties including electric conductivity is being studied and will be reported elsewhere.

Received, 10th February 1986; Com. 184

References

1 B. M. Hoffman and J. A. Ibers, *Acc. Chem. Res.*, 1983, **16**, 15, and references therein; T. J. Marks, *Ann. N.Y. Acad. Sci.*, 1978, **313**, 594; C. W. Dirk, E. A. Mintz, K. F. Schoch, Jr., and T. J. Marks, *J. Macromol. Sci., Chem.*, 1981, **A16**, 275; Y. Yamamoto, K. Yoshino, and Y. Inuishi, *J. Phys. Soc. Jpn.*, 1979, **47**, 1887.
2 H. Sugimoto, T. Higashi, and M. Mori, *J. Chem. Soc., Chem. Commun.*, 1983, 622.
3 D. Dolphin, J. R. Sams, and T. B. Tsin, *Inorg. Synth.*, 1980, **20**, 155.
4 A. W. Moore, in 'Chemistry and Physics of Carbon,' vol. 11, eds. P. L. Walker and P. A. Thrower, Dekker, New York, 1973.
5 J. Martinsen, J. L. Stanton, R. L. Greene, J. Tanaka, B. M. Hoffman, and J. A. Ibers, *J. Am. Chem. Soc.*, 1985, **107**, 6915.