Inorganica Chimica Acta, 53 (1981) L241–L243

Preparation and Characterization of Oxidized and Reduced Forms of Lutetium Diphthalocyanine

ALEXANDER T. CHANG† and JEAN-CLAUDE MARCHON*

Laboratoire d'Electrochimie Organique et Analytique, Département de Recherche Fondamentale, Centre d'Etudes Nucléaires de Grenoble, 85X, 38041 Grenoble Cedex, France

Received January 12, 1981

Although transition-metal phthalocyanides have been intensively studied since the 1930s for their applications in the pigment industry [1, 2] and as model compounds for the naturally occurring metalloporphyrins [3], rare-earth phthalocyanides were first prepared only fifteen years ago [4]. Recent interest in these compounds is due to their peculiar electrochimic properties. Deposited as a thin film on an electrode which is immersed in an electrolyte, lutetium diphthalocyanine exhibits five colors (violet, blue, green, yellow-tan, and red) when the voltage of the cell is varied between –1.5 and +1.5 V [5, 6]. Although its electro-optic properties are well documented, lutetium diphthalocyanine itself has not been satisfactorily characterized due to the lack of a reliable preparative method leading to a single pure compound. Several groups [4, 7–9] have reported two colored compounds (blue and green) as products formed during the preparation of various lanthanide (Ln) phthalocyanine (Pc) complexes. The blue form was identified by Kirin *et al.* [7] as a lanthanide diphthalocyanine complex $LnPc_2H$ (Pc being $C_{32}H_{16}N_8$) by elemental analysis. These authors suggested that the green form was a monophthalocyanine LnPcCl based upon its optical spectrum compared to those of other metal monophthalocyanines, despite the lack of an elemental analysis. MacKay *et al.* [9] reported that both the blue and the green forms are rare earth diphthalocyanines which would interconvert depending upon the nature of the solvent environment, but again no reliable elemental analysis was obtained. Corker *et al.* [10] obtained lutetium diphthalocyanine as a green compound for which they suggested the formula $[LuPc_2H]^+ A^-$, A^- being an unidentified anion; they also showed that blue and violet species could be obtained from the latter by electrochemical reduction, while a yellow-red species was formed by electrochemical oxidation.

In this letter, we report the isolation and characterization of lutetium diphthalocyanine (green form) by elemental analysis, visible spectroscopy, mass spectrometry, magnetic susceptibility measurement and ESR spectroscopy, and we show that the data obtained collectively favor the formula $LuPc_2$ for this compound. Further more, preparative methods for the one-electron oxidized form (yellow-tan) as well as for two reduced forms (blue, violet) are described.

Results and Discussion

Lutetium diphthalocyanine was synthesized by the method of Moskalev and Kirin [11]. Lutetium acetate (Johnson Matthey, 4N purity) and *o*-phthalonitrile (Fluka AG) mixed in the molar ratio 1:10 were slowly heated in a open container. The solid reaction product which formed after 3 hours at 310 °C was washed successively with acetic anhydride, acetone, dimethylformamide, and again with acetone, and dried in air at 110 °C. The resulting product, which gave three spots on a thin-layer chromatogram (silica gel/chloroform–benzene 12%), was chromatographed over silica gel using a 12% chloroform–benzene eluent. The concentrated effluents gave a green microcrystalline powder yielding a single spot on TLC. The elemental analysis of this compound is consistent with a lutetium diphthalocyanine formulation. *Anal.* Calc. for $LuPc_2$ ($C_{32}H_{16}N_8Lu$): C, 64.1; H, 2.7; N, 18.7; Lu, 14.6%. Found: C, 63.3; H, 2.4; N, 17.8; Lu, 13.9%. Mass spectrometric measurements were performed by evaporating the sample at 330–350 °C under 10^{-6} to 10^{-7} torr; m/e values of 1199 and 599.5 were obtained for singly and doubly charged species, in agreement with the formula $LuPc_2$. No peak was observed at 1200 corresponding to the previously proposed formulations $LuPc_2H$ and $[LuPc_2H]^+ A^-$, nor at the values expected for the hypothetical anion A^- (acetate, chloride). Figure 1 shows the visible spectrum of this analytically pure green sample, in good agreement with that of Corker *et al.* [10].

Magnetic susceptibility measurements were made using a vibrating sample magnetometer. Figure 2 shows the uncorrected inverse molar susceptibility *versus* temperature for the green compound. A typical Curie–Weiss behavior is observed with no observable magnetic ordering down to 4.2 K. The effective magnetic moment, independent of temperature, is 1.76 BM indicating a single unpaired spin per molecule. This unpaired electron is also apparent in ESR spectroscopy as an intense signal at $g = 2$ with a band width of *ca.* 2 G, which is typical of a radical species of an extended conjugated ring system [12]. These data are incompatible with the $LuPc_2H$ formu-

---

†Present address: Laboratoire de Recherche Image, Thomson-CSF, 38120 Saint Egrève, France.

*Author to whom correspondence should be addressed.

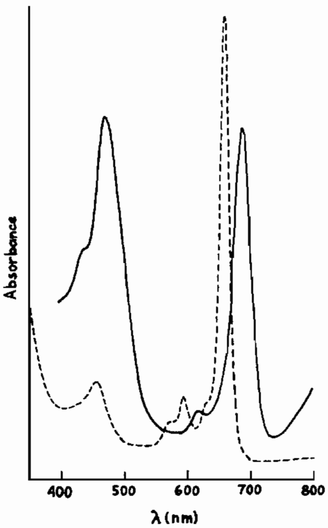

Fig. 1. Optical spectra of $LuPc_2$ (– – – – –) and $(LuPc_2)^+(SbCl_6)^-$ (———) in dichloromethane.

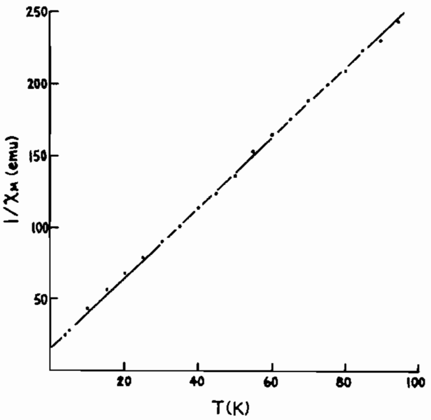

Fig. 2. Inverse molar susceptibility *versus* temperature for $LuPc_2$.

la, which implies a closed-shell f^{14} cation (Lu^{3+}) bound to two diamagnetic phthalocyanine rings (Pc^{2-} and HPc^-), one of them being protonated for charge balance. On the other hand, the above data provide further support to the $LuPc_2$ formulation: the complex can be viewed as a diamagnetic Lu^{3+} cation sandwiched between a phthalocyanine (Pc^{2-}) and a one-electron oxidized phthalocyanine ($Pc^{\bullet -}$), the latter being responsible for the observed paramagnetism. Alternatively, the unpaired electron could be delocalized on both phthalocyanine rings. Interestingly, transition metal complexes of the phthalocyanine radical have been described [12].

Treatment of $LuPc_2$ in dichloromethane with one equivalent of phenoxathiin cation radical-hexachloroantimonate gave the one-electron oxidation product $(LuPc_2)^+(SbCl_6)^-$ which was isolated as a reddish-brown powder. *Anal.* Calcd. for $(LuPc_2)^+(SbCl_6)^-$: C, 50.1; H, 2.1; N, 14.6; Cl, 13.9; Sb, 7.9%. Found: C, 50.2; H, 2.3; N, 14.3; Cl, 13.3; Sb, 9.4%. The visible spectrum of this pure compound is shown in Fig. 1. Its magnetic susceptibility and lack of ESR signal indicate an essentially diamagnetic complex. A similar, but impure, compound was obtained by Corker *et al.* by electrochemical oxidation [10].

Reduction of $LuPc_2$ in dichloromethane with zinc amalgam under argon afforded successively a diamagnetic blue species and a violet species, both of which are readily reoxidized by air to $LuPc_2$, in agreement with the electrochemical studies of Corker *et al.* [10]. Figure 3 shows successive visible spectra recorded during the violet-to-blue conversion by atmospheric oxygen. The spectrum of the blue species is identical to those obtained by other workers for solutions of $LuPc_2$ in dimethylformamide [4, 8–10], indicating that impurities such as dimethylamine in the latter do reduce green $LuPc_2$ to blue $(LuPc_2)^-$.

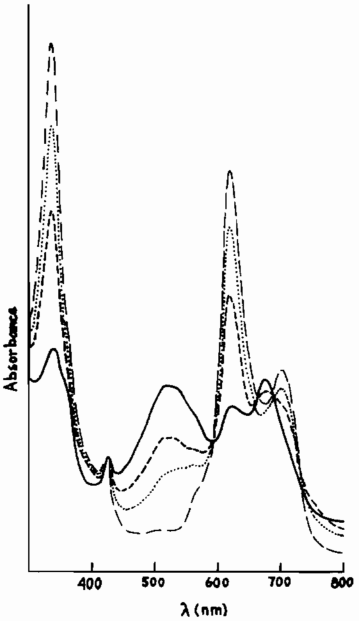

Fig. 3. Optical spectra of reduced lutetium diphthalocyanine upon reoxidation by atmospheric oxygen. Violet species, presumably $LuPc_2^{2-}$ (———); blue species, presumably $LuPc_2^-$ (— —); intermediate spectra (– – – –, ...).

Isosbestic points are observed during interconversion of the violet and blue forms (Fig. 3), and also for the blue-to-green and the gree-to-brown transitions. These observations lend support to the conclusion by Corker *et al.* [10] that all the colored species they obtained electrochemically from green lutetium diphthalocyanine have the same basic structure and differ only by their redox level. However, our isolation and characterization of $LuPc_2$ and $(LuPc_2)^+(SbCl_6)^-$ leads to a different structural assignment: the species responsible for the electrochromic properties would be the following in order of increasing oxidation level: $LuPc_2^{2-}$ (violet, ESR active [10]), $LuPc_2^-$ (blue, diamagnetic), $LuPc_2$ (green, $S = 1/2$), $LuPc_2^+$ (reddish-brown, diamagnetic), $LuPc_2^{2+}$ (red, not characterized). That the phthalocyanine rings are the sites of electron transfers throughout this series, as suggested both by Corker's [10] and our data could be established by further magnetic and structural studies [13, 14].

Acknowledgement

Partial support by the Centre National de la Recherche Scientifique through grant n° ERA 675 is gratefully acknowledged. We wish to thank Dr. Mercier (Groupe des Transitions de Phase, CNRS, Grenoble), for bringing to our attention the present research topic.

References

1 F. H. Moser and A. L. Thomas, 'Phthalocyanine Compounds', Van Nostrand-Reinhold, Princeton, New Jersey (1963).

2 A. B. P. Lever, *Adv. Inorg. Chem. Radiochem.*, *7*, 27 (1965).

3 A. H. Jackson, in 'The Porphyrins' (D. Dolphin, ed.), vol. I, p. 365, Academic Press, New York (1978).

4 I. S. Kirin, P. N. Moskalev and Yu. A. Makashev, *Russ. J. Inorg. Chem.*, *10*, 1065 (1965).

5 P. N. Moskalev and I. S. Kirin, *Russ. J. Phys. Chem.*, *46*, 1019 (1972).

6 M. M. Nicholson and R. V. Galiardi, *U. S. NTIS Report* AD-A039596 (1977).

7 I. S. Kirin, P. N. Moskalev and Yu. A. Makashev, *Russ. J. Inorg. Chem.*, *12*, 369 (1967).

8 S. Misumi and K. Kasuga, *Nippon Kagaku Zasshi*, *92*, 335 (1971).

9 A. G. MacKay, J. F. Boas and G. J. Troup, *Australian J. Chem.*, *27*, 955 (1974).

10 G. A. Corker, B. Grant and N. J. Clecak, *J. Electrochem. Soc.*, *126*, 1339 (1979).

11 P. N. Moskalev and I. S. Kirin, *Russ. J. Inorg. Chem.*, *15*, 7 (1970).

12 J. F. Myers, G. W. Rayner Canham and A. B. P. Lever, *Inorg. Chem.*, *14*, 461 (1975).

13 K. Kasuga and M. Tsutsui, *Coord. Chem. Rev.*, *32*, 67 (1980).

14 K. Kasuga, M. Tsutsui, R. C. Petterson, K. Tatsumi, N. Van Opdenbosch, G. Pepe and E. F. Meyer, Jr., *J. Am. Chem. Soc.*, *102*, 4835 (1980).