

Electrocrystallization and X-Ray Structure of a New Porphycene-based Material, $[\text{Ni}(\text{OMPc})]_{2.5}(\text{BF}_4)_2 \cdot \text{C}_{10}\text{H}_7\text{Cl}$

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Electrochemical oxidation of Ni(OMP) (OMP = 2,3,6,7,12,13,16,17-octamethylporphycene) produces single crystals of the $[\text{Ni}(\text{OMP})]_{2.5}(\text{BF}_4)_2 \cdot \text{C}_{10}\text{H}_7\text{Cl}$ material; the X-ray crystallographic study, IR and ESR results, and conductivity measurements are reported, and show that the material behaves as a conductive molecular crystal.

Considerable interest has been devoted to the access to polymeric materials starting from phthalocyanines and porphyrins.¹⁻⁷ Numerous examples of such species have been reported, *e.g.* Ni(Pc)I.^{1,8-10} The striking features of this latter material are its electrical properties, and especially its high room-temperature conductivity.^{1,8-10} Recently, new porphyrin-like macrocycles named porphycenes have been synthesized by Vogel *et al.*¹¹⁻¹⁴ These compounds, which are isomers of porphyrins, present a relatively flat structure and a suitable solubility in most organic solvents. In the light of these findings, we focused our work on the synthesis of the non-bulky 2,3,6,7,12,13,16,17-octamethylporphycene, H₂(OMPc).¹⁵ After metallation with nickel acetate, the resulting Ni(OMPc) complex was used as a starting material in electrochemical doping experiments.

We report here the electrosynthesis and X-ray crystallographic study of $[\text{Ni}(\text{OMPc})]_{2.5}(\text{BF}_4)_2 \cdot \text{C}_{10}\text{H}_7\text{Cl}$.† Single crystals of this compound were grown at the anode of a two-compartment electrochemical cell by constant current electrolysis ($I = 5 \mu\text{A}$).‡¹⁶

The asymmetric unit contains formally: $[\text{Ni}(\text{OMPc})]_{2.5} \cdot \text{C}_{10}\text{H}_7\text{Cl}$, corresponding to 10 metallomacrocycles, 8 BF_4^- , and 4 $\text{C}_{10}\text{H}_7\text{Cl}$ in the unit cell. The structure of the electrocrystallized material consists of the stacking of Ni(OMPc) units along the *b* [0,1,0] direction. The stacks of oxidized porphycene molecules induce the formation of free

surrounding tunnels which are occupied by BF_4^- anions and solvent molecules (1-chloronaphthalene). More precisely, each columnar arrangement of Ni(OMPc) consists of the stacking of groups of five metallomacrocycles (hereinafter referred to as 'pentamers') (see Fig. 1). Each pentamer contains five Ni(OMPc) planar molecules which are cofacially piled up with a metal-over-metal arrangement with the Ni(3) nickel atom of the central molecule lying on an inversion centre [0,0,1/2]. The angle between the spine axis of each pentamer and the *b* direction is 5.7°. The inter-ring distances within the pentamer range from 3.33 to 3.38 Å and between two consecutive pentamers is 3.40 Å. Surprisingly, two adjacent Ni(OMPc) molecules within the pentamer are staggered by 90° (Fig. 2). Such a rotation is generally observed for oxidized metalloporphyrins (*ca.* 25–30°)⁵ and metallophthalocyanines (*ca.* 40°)⁹ to relieve steric repulsion between macrocycles, whereas for the corresponding neutral species this steric repulsion is not minimized by the rotation but by the slippage of the macrocycles with respect to each other. For the oxidized forms, the partial emptying of the 'valence' band induces bonding interactions between the macrocycles leading to metal-over-metal stacking, the minimization of the steric repulsion being achieved by a simple rotation of the macrocycle.¹⁷ The material described in the present study is elaborated from Ni(OMPc) which presents a D_{2h} symmetry, and therefore 90° rotation leads to the least steric repulsion.

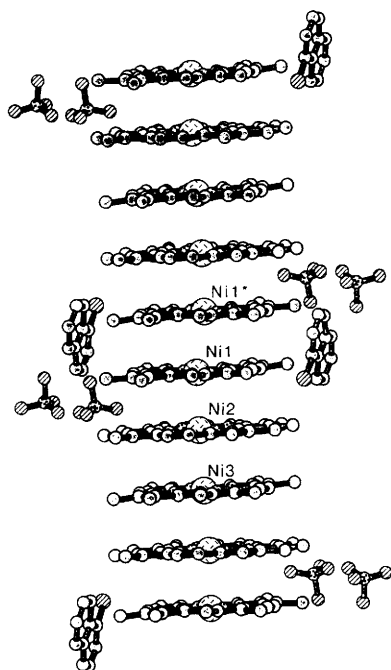


Fig. 1 View of the stacking of two consecutive pentamers along the *b* direction. Ni(1)–Ni(2) 3.327(2) Å; Ni(2)–Ni(3) 3.387(2) Å; Ni(1)–Ni(1)* 3.818(2) Å [Ni(1)* is related to Ni(1) by an inversion centre].

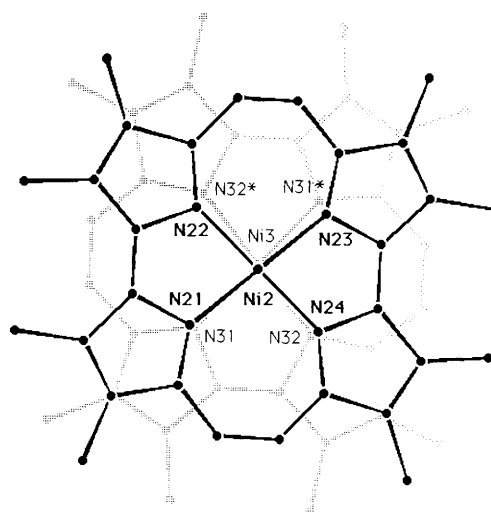


Fig. 2 View of the stacking of 'Ni(2)' and 'Ni(3)' molecules exhibiting a staggering angle of 90° [the stacking of 'Ni(1)' and 'Ni(2)' molecules being identical except for Ni–Ni distance]. Following are selected bond distances (Å) and angles (°). 'Ni(3)' molecule: Ni(3)–N(31): 1.93(1), Ni(3)–N(32): 1.92(1), N(31)–Ni(3)–N(32): 83.5(5), N(32)–Ni(3)–N(31)*: 96.5(5). 'Ni(2)' molecule: Ni(2)–N(21): 1.90(1), Ni(2)–N(22): 1.91(1), Ni(2)–N(23): 1.89(1), Ni(2)–N(24): 1.91(1), N(21)–Ni(2)–N(22): 82.8(5), N(21)–Ni(2)–N(24): 96.7(4), N(22)–Ni(2)–N(23): 97.1(5), N(23)–Ni(2)–N(24): 83.3(5).

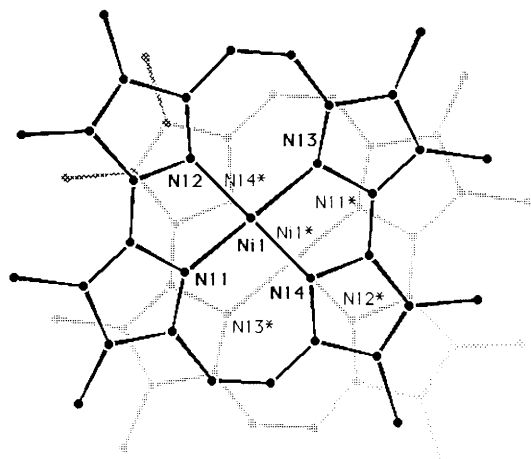


Fig. 3 View of the stacking of 'Ni(1)' and 'Ni(1)*' molecules. These two molecules are consecutive and belong to two adjacent pentamers. They are related by an inversion centre. The staggering angle is equal to 0° . The lateral shift of Ni(1)* with respect to Ni(1) is equal to 1.62 Å. Following are selected bond distances (Å) and angles ($^\circ$). Ni(1)–N(11): 1.92(1), Ni(1)–N(12): 1.91(1), Ni(1)–N(13): 1.90(1), Ni(1)–N(14): 1.90(1), N(11)–Ni(1)–N(12): 83.1(5), N(11)–Ni(1)–N(14): 96.8(5), N(12)–Ni(1)–N(13): 97.3(5), N(13)–Ni(1)–N(14): 82.8(5).

The interplanar spacing (<3.40 Å) which compares to $[M(\text{TMP})_2(\text{ReO}_4)]$ ($M = \text{Ni, Cu, Pt}$; TMP = 5,10,15,20-tetramethylporphyrin) shows that an overlap occurs between π orbitals.⁵ Two consecutive pentamers did not rotate but are shifted with respect to each other by 1.62 Å (Fig. 3).§ Two 1-chloronaphthalene solvent molecules are located near the pentamers junction.

The presence of four BF_4^- anions located around the columnar stacking suggests four oxidation sites per pentamer. The ESR spectrum recorded at room temp. in a magnesium sulfate matrix (10% compound concentration) presents a single line at $g = 2.002$. Since this value is nearly the same as the free-electron g value (2.0023), the electrochemical doping induces a ligand-centred oxidation. As a consequence from these previous remarks, a 60% occupation of the valence band occurs which is rather less than that observed for oxidized Ni(Pc)^{1,8–10} (oxidation level: 1/3; 83% conduction band occupation) and Ni porphyrins^{2–4,18} (oxidation level: 1/2 or 2/3; 75 or 66% conduction band occupation). The IR spectrum of the material exhibits a strong and very broad absorption at ca. 3000 cm^{-1} , which is in accordance with an intermolecular electron transfer.

Microwave conductivity measurements were performed at 10 GHz using the cavity perturbation method.¹⁹ With this technique, the conducting regime of the system is determined by the temperature dependence of the frequency shift of the cavity due to the presence of the perturbing system. As the frequency shift is not temperature-independent, a metallic character of the material can be ruled out.²⁰ A thermally activated conductivity has been found ($\sigma = \sigma_0 e^{-\Delta E/kT}$) with a room temperature conductivity of $\sigma(300\text{ K}) \approx 0.06\ \Omega^{-1}\text{ cm}^{-1}$ of $\Delta E = 0.120\text{ eV}$. This conducting behaviour is in agreement with the observed Curie law of the spin system and a hopping process between localized states may be inferred.

Other substituted nickel porphyrines are currently electrocrystallized and especially 9,10,19,20-alkyl substituted porphyrines which exhibit a rather planar structure without steric hindrance induced by the alkyl groups, and a good solubility in organic solvents.¹³

Received, 22nd September 1994; Com. 4/05781C

Footnotes

† Only very few of the collected crystals were suitable for an X-ray study. The size of the selected one was $0.18\text{ mm} \times 0.08\text{ mm} \times 0.09\text{ mm}$. Owing to the small size of the crystal the data collection was performed at low temperature (105 K). *Crystal data* for $[\text{Ni}(\text{OMPc})]_{2.5}(\text{BF}_4)_2 \cdot \text{C}_{10}\text{H}_7\text{Cl}$: $M = 1389.7$, monoclinic, space group $P2_1/n$, $a = 14.500(3)$, $b = 16.922(3)$, $c = 26.447(7)$ Å, $\beta = 96.51(2)^\circ$, $V = 6447\text{ Å}^3$, $Z = 4$, $D_c = 1.43\text{ g cm}^{-3}$, $F(000) = 2904$. Data were collected at 105 K using a CAD 4 Enraf-Nonius diffractometer with Mo-K α radiation ($\lambda = 0.71073\text{ Å}$). The structure was solved by the mean of a Patterson search program²¹ and refined on 3897 unique reflections with $I > 3\sigma I$.²² As the atoms number is large compared to the data number, only Ni, B, F and Cl atoms were refined anisotropically ($N = 488$) leading to final residual $R = 0.080$, $R_w = 0.087$, and $\text{GOF} = 1.12$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ The concentration of the solution was $6 \times 10^{-3}\text{ Ni}(\text{OMPc})$, and $0.1\text{ mol dm}^{-3} [\text{N}(\text{Bu})_4](\text{BF}_4)$.

§ This contrasts with the recently published Ni(TPrPc)_{1.67} material which presents a slipped stacking of the macrocycles [slipping distance: $3.73(2)\text{ Å}$] and a rather large Ni–Ni distance [$4.982(1)\text{ Å}$].²³

References

- C. J. Schramm, R. P. Scaringe, D. R. Stojakovic, B. M. Hoffman, J. A. Ibers and T. J. Marks, *J. Am. Chem. Soc.*, 1980, **102**, 6702.
- T. E. Phillips, R. P. Scaringe, B. M. Hoffman and J. A. Ibers, *J. Am. Chem. Soc.*, 1980, **102**, 3435.
- J. Martinsen, L. J. Pace, T. E. Phillips, B. M. Hoffman and J. A. Ibers, *J. Am. Chem. Soc.*, 1982, **104**, 83.
- L. J. Pace, J. Martinsen, A. Ulman, B. M. Hoffman and J. A. Ibers, *J. Am. Chem. Soc.*, 1983, **105**, 2612.
- E. M. McGhee, B. M. Hoffman and J. A. Ibers, *Inorg. Chem.*, 1991, **30**, 2162 and references therein.
- K. Y. Liou, T. P. Newcomb, M. D. Heagy, J. A. Thompson, W. B. Heuer, R. L. Musselman, C. S. Jacobsen, B. M. Hoffman and J. A. Ibers, *Inorg. Chem.*, 1992, **31**, 4517 and references therein.
- M. R. Godfrey, T. P. Newcomb, B. M. Hoffman and J. A. Ibers, *J. Am. Chem. Soc.*, 1990, **112**, 7260.
- J. Martinsen, R. L. Greene, S. M. Palmer and B. M. Hoffman, *J. Am. Chem. Soc.*, 1983, **105**, 677.
- J. Martinsen, S. M. Palmer, J. Tanaka, R. C. Greene and B. M. Hoffman, *Phys. Rev. B*, 1984, **30**, 6269.
- J. Martinsen, J. L. Stanton, R. L. Greene, J. Tanaka, B. M. Hoffman and J. A. Ibers, *J. Am. Chem. Soc.*, 1985, **107**, 6915.
- E. Vogel, M. Köcher, H. Schmickler and J. Lex, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 257.
- E. Vogel, M. Balci, K. Pramod, P. Koch, J. Lex and O. Ermer, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 928.
- E. Vogel, M. Köcher, J. Lex and O. Ermer, *Isr. J. Chem.*, 1989, **29**, 257.
- E. Vogel, P. Koch, X.-L. Hou, J. Lex, M. Lausman, M. Kisters, M. A. Aukauloo, P. Richard and R. Guillard, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1600.
- R. Guillard, unpublished results.
- R. Guillard, J.-M. Barbe, P. Richard, P. Petit, J. J. André, C. Comte and K. M. Kadish, *J. Am. Chem. Soc.*, 1989, **111**, 4684.
- A. Rosa and E. J. Baerends, *Inorg. Chem.*, 1992, **31**, 4717.
- E. M. McGhee, M. R. Godfrey, B. M. Hoffman and J. A. Ibers, *Inorg. Chem.*, 1991, **30**, 803.
- L. I. Buranov and I. F. Shchegolev, *Prib. Tek. Eksp.*, 1971, **2**, 171.
- W. Bauhofer, *J. Phys. E. Sci. Instrum.*, 1981, **14**, 934.
- G. M. Sheldrick, SHELX86, Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1985.
- G. M. Sheldrick, SHELX76, Program for Crystal Structure Determination, University of Cambridge, England, 1976.
- D. C. Miller, J. C. Bollinger, B. M. Hoffman and J. A. Ibers, *Inorg. Chem.*, 1994, **33**, 3354.