Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2008, **18**, 82–83
Mendeleev Communications

Synthesis and properties of [4′-(*p*-triphenylmethylphenoxy)-7,8:12,13:17,18-tribenzoporphyrazinato]nickel(II)

Yulia V. Romanenko, Elena A. Danilova, Olga G. Khelevina and Mikhail K. Islyaikin*

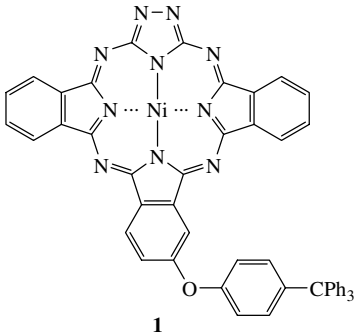
Ivanovo State University of Chemistry and Technology, 153000 Ivanovo, Russian Federation. Fax: +7 4932 41 7742; e-mail: islyaikin@isuct.ru

DOI: 10.1016/j.mencom.2008.03.009

A new noncentrosymmetric structural analogue of phthalocyanine, [4′-(*p*-triphenylmethylphenoxy)-7,8:12,13:17,18-tribenzoporphyrazinato]nickel(II), was obtained by the condensation of 3,5-bis(1-imino-3-isoindolinylidenamino)-1,2,4-triazole in the presence of $Ni(OAc)_2·4H_2O$ or a Ni complex of 3,5-bis(1-imino-3-isoindolinylidenamino)-1,2,4-triazole with 4-(*p*-triphenylmethylphenoxy)phthalonitrile.

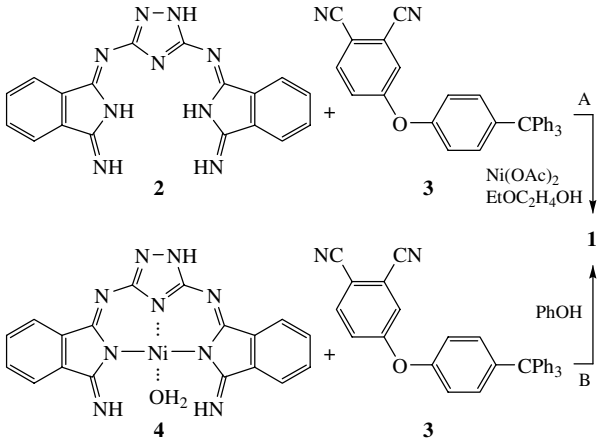
Noncentrosymmetrical structural phthalocyanine analogues are of interest[1] because they can form Langmuir–Blodgett layers[2] and reveal interesting coordination[3] and nonlinear optical properties.[4]

We synthesised a Ni complex of triazolephthalocyanine, [4′-(*p*-triphenylmethylphenoxy)-7,8:12,13:17,18-tribenzoporphyrazinato]nickel(II) **1**,† which is a structural analogue of phthalocyanine.



1

The synthesis of **1** was carried out by (A) the condensation of 3,5-bis(1-imino-3-isoindolinylidenamino)-1,2,4-triazole[5] **2** with 4-(*p*-triphenylmethylphenoxy)phthalonitrile[6] **3** in the presence of $Ni(OAc)_2·4H_2O$ in ethoxyethanol and (B) the interaction of Ni complex **4** with **3** in phenol (Scheme 1).†



Scheme 1

Taking into account the low stability of the products[7] under the reaction conditions, the synthesis was carried out at 50 °C for 100 h (method A). The use of Ni complex **4** allows us to increase the temperature and to reduce the duration of synthesis (method B). Phenol used as a solvent in this case transforms phthalonitrile into more reactive phenoxy derivatives[8] and prevents phthalocyanine formation.

The dark brown compounds obtained after extraction and column chromatography were slightly soluble in $CHCl_3$ and DMF and almost insoluble in pyridine.

The mass spectrum (MALDI-TOF) of compound **1** contains a signal (*m*/*z* 858), which corresponds to a molecular ion

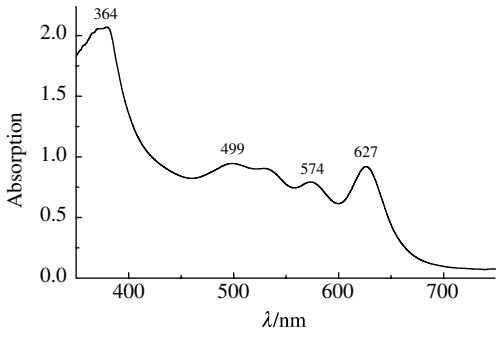


Figure 1 UV-VIS spectrum of a solution of **1** in $CHCl_3$ (c = 0.136 mmol dm^{-3}).

† *Synthesis of [4′-(*p*-triphenylmethylphenoxy)-7,8:12,13:17,18-tribenzoporphyrazinato]nickel(II)* **1**.

(A) A mixture of 3,5-bis(1-imino-3-isoindolinylidenamino)-1,2,4-triazole **2** (0.33 g, 0.92 mmol), 4-(*p*-triphenylmethylphenoxy)phthalonitrile[6] **3** (0.42 g, 0.92 mmol) and nickel(II) acetate tetrahydrate (0.23 g, 0.92 mmol) in 2-ethoxyethanol (40 ml) was stirred at 50 °C for 100 h. The solvent was removed in a vacuum, and the crude product was washed with hot MeOH and then extracted with $CHCl_3$ in a Soxhlet apparatus. After solvent evaporation, the product was purified by column chromatography on silica gel ($CHCl_3$–MeOH, 25:1). The solvents were removed and the brown solid was dried in a vacuum. Yield, 0.060 g (7.7%).

(B) A mixture of compound **4** (0.38 g, 0.92 mmol), 4-(*p*-triphenylmethylphenoxy)phthalonitrile **3** (0.42 g, 0.92 mmol) and phenol (3 g) was stirred at 140 °C for 8 h. The reaction mass was heated to 160 °C, stirred at this temperature for 2 h and then poured into water. The residue was filtered and washed with water and acetone to remove phenol. A crude product was purified as described above. Yield, 0.063 g (8.0%).

MS (MALDI-TOF, dithranol), *m*/*z*: 858 $(M + H)^+$. UV-VIS [$CHCl_3$, λ_{max}/nm (log ε)]: 364 (4.25), 627 (3.83). IR (KBr, ν/cm^{-1}): 3084, 3055, 3029, 1664, 1612, 1594, 1471, 1444, 1400, 1323, 1088, 1048, 839, 753, 701, 653, 512. Found (%): C, 70.73; H, 3.80; N, 16.75; O, 2.04; Ni, 6.68. Calc. for $C_{51}H_{30}N_{10}ONi$ (%): C, 71.43; H, 3.53; N, 16.33; O, 1.87; Ni, 6.84.

$[(M + H)^+]$. A series of bands due to the molecular core and functional group vibrations can be observed in the IR spectrum of compound **3**. The bands at 1612–1471 and 1323 cm^{-1} correspond to the stretching vibrations of C=C and C=N bonds in aromatic systems; a band at 1255 cm^{-1} is due to the stretching vibrations of the C–O–C bond, and absorption bands at 1088 and 1048 cm^{-1} can be assigned to deformation vibrations of bezene rings.

The intense band at 364 nm dominating in the electron absorption spectrum of **1** can be interpreted as a Soret band (Figure 1). The Q-band position at 627 nm suggests that an aromatic macrosystem similar to that of phthalocyanine is at the heart of this compound.

References

1 M. S. Rodríguez-Morgade, G. de la Torre and T. Torres, in *Porphyrin Handbook*, eds. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, Amsterdam, Boston, London, New York, Oxford, Paris, San Diego, San Francisco, Singapore, Sydney, Tokyo, 2003, vol. 15, ch. 99, p. 125.

2 F. Armand, B. Cabezón, M. V. Martínez-Díaz, A. Ruaudel-Teixier and T. Torres, *J. Mater. Chem*., 1997, **7**, 1741.

3 O. G. Khelevina, V. R. Ferro, M. K. Islyaikin, E. A. Veselkova, M. G. Stryapan and J. M. García de la Vega, *J. Phys. Org. Chem*., 2005, **18**, 329.

4 G. de la Torre, P. Vázquez, F. Agulló-López and T. Torres, *Chem. Rev*., 2004, **104**, 3723.

5 F. Fernández-Lásaro, S. Rodrígues-Morgade and T. Torres, *Synth. Met*., 1994, **62**, 281.

6 I. A. Yelkin, *Ph.D. Thesis*, Ivanovo, 2002, p. 134.

7 M. E. Baguley and J. A. Elvidge, *J. Chem. Soc*., 1957, 709.

8 R. K. Bartlett, L. V. Renny and K. K. Chan, *J. Chem. Soc. C*, 1969, 129.

Received: 4th October 2007; Com. 07/3021