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Formation and crystal structure of an unexpected inclusion complex of a metal-free phthalocyanine and oxalic acid†

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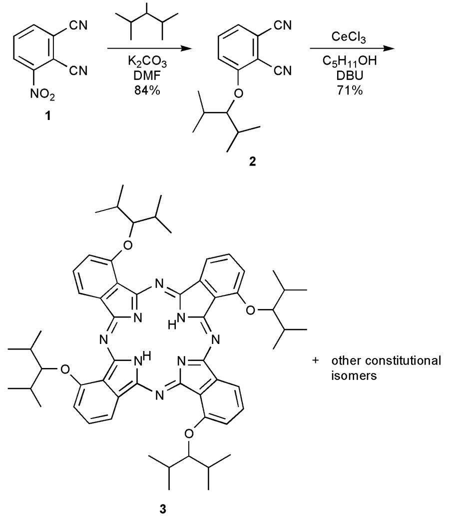
Treatment of 3-(2,4-dimethyl-3-pentyloxy)phthalonitrile (2) with $CeCl_3$ in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in *n*-pentanol gives the corresponding metal-free phthalocyanine 3, which unexpectedly traps the oxalic acid in the crystal lattice forming a 1 : 1 inclusion complex.

Phthalocyanines, which were first developed as industrial pigments, have been actively exploited in various technological applications such as optical recording, photovoltaics, photocopying, gas sensing and photodynamic therapy.[1] The performance of these materials depends not only on the molecular composition including the metal centre and the number, position and nature of the substituents, but also on the molecular architecture. The molecular arrangement in the condensed phase is a determining factor controlling many of the physical properties of the macrocycles including electrical and photo-conductivity, magnetic susceptibility and optical nonlinearity.[2] Although synthetic methodologies to a wide range of phthalocyanines have been well-established, structural data remain relatively scarce, in particular for the substituted analogues,[3] and crystal engineering of these materials is still in its infancy.[4] We report herein the crystal structure of a novel 1 : 1 inclusion complex of metal-free 1,8,15,22-tetrakis(2,4-dimethyl-3-pentyloxy)phthalocyanine (**3**) and oxalic acid, which is generated serendipitously in a cerium-promoted cyclisation reaction.

In attempts to prepare cerium phthalocyanines with a half-sandwich or sandwich structure,[5] 3-(2,4-dimethyl-3-pentyloxy-)phthalonitrile (**2**),[6] which was prepared by treating 3-nitrophthalonitrile (**1**) with 2,4-dimethyl-3-pentanol in the presence of K_2CO_3, was treated with anhydrous $CeCl_3$ and DBU in *n*-pentanol. Unexpectedly, the reaction gave a significant amount of the metal-free phthalocyanine **3** (Scheme 1). Under optimum conditions (ESI†), compound **3** together with its constitutional isomers were isolated in 71% yield.[7] The major isomer **3** could be purified readily by chromatography followed by recrystallisation.



Scheme 1

The C_{4h} symmetry of compound **3** (assuming that there is a rapid NH proton exchange) was confirmed by ^{1}H NMR spectroscopy. The spectrum displayed two doublets for the methyl protons showing that there is a restricted rotation for the bulky 2,4-dimethyl-3-pentyloxy group. The internal NH protons resonated at $\delta -0.06$ as a broad signal, which disappeared upon addition of CD_3OD. Leznoff and coworkers have studied the effects of aggregation on the ^{1}H NMR data of a series of metal-free octalkynylphthalocyanines.[8] It has been found that the signal for the internal NH protons shifts downfield by almost 2 ppm (from *ca.* $\delta -2.5$) as the aggregation tendency decreases. The downfield position of this signal for **3** ($\delta -0.06$), which appears to be concentration independent, suggests that the compound is relatively free from aggregation. This is in accord with the UV–Vis spectra in $CHCl_3$, which strictly obey the Lambert–Beer law from 10^{-7} to 10^{-5} mol dm^{-3}.

Layering MeOH onto a $CHCl_3$ solution of **3** afforded a green powder together with a few pieces of green transparent plates which were suitable for X-ray diffraction analysis. The compound crystallises in the monoclinic system with two molecules per unit cell.[9] The molecular structure, which contains an inversion centre relating the two halves of the molecule is given in Fig. 1, while the packing of molecules in the lattice is shown in Fig. 2. The phthalocyanine rings are stacked in a herringbone fashion[3] along the crystallographic *b* axis with a stacking angle of 55.0° and an interplanar distance of 7.22 Å. This arrangement is similar to that of the unsubstituted phthalocyanine (both α and β forms),[10] but the interplanar distance is much larger for **3** (7.22 *vs.* 3.31 Å), probably due to the bulky 2,4-dimethyl-3-pentyloxy sub-

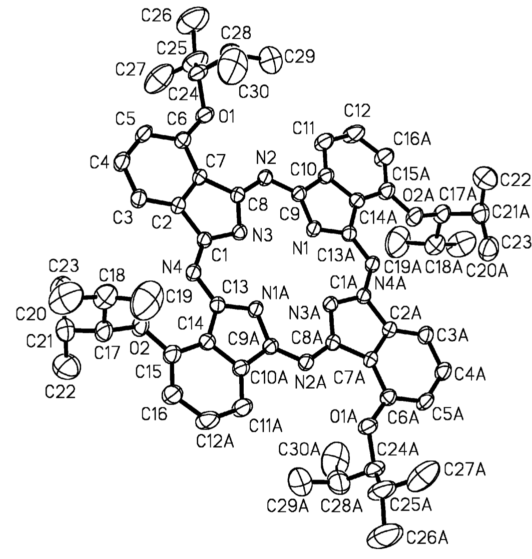


Fig. 1 Molecular structure of **3** showing the 30% probability thermal ellipsoids for all non-hydrogen atoms.

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† Electronic supplementary information (ESI) available: experimental procedure to prepare compound **3** and its characterising data. See http://www.rsc.org/suppdata/cc/b1/b111133g/

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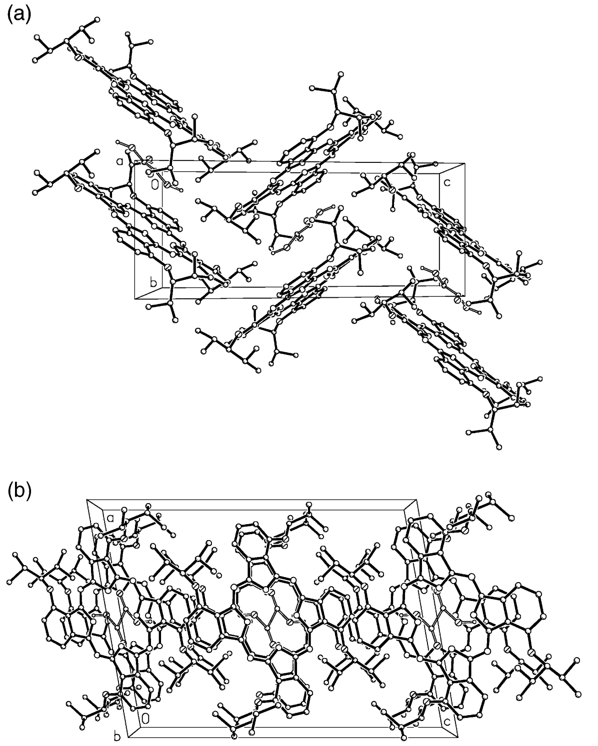

Fig. 2 Crystal structure of $\mathbf{3}\cdot C_2H_2O_4$: (a) view along the *a* axis, (b) view along the *b* axis. All hydrogen atoms are omitted for clarity.

stituents, which act as the spacers. The crystal structure of **3**, however, is significantly different from those of 1,4,8,11,15,18,22,25-octasubstituted phthalocyanines H_2PcR_8 (R = *n*-C_6H_{13}, *iso*-OC_5H_{11}),[11] which adopt a brickstone arrangement[3] in which the inter-ring spacing within a stack is slightly larger (*ca.* 8.5 Å).

The most remarkable feature of the crystal structure is the presence of oxalic acid molecules intercalated between the phthalocyanine rings (Fig. 3). On the basis of the separation between the phthalocyanine core and the oxalic acid molecule, it seems that hydrogen bonding is not significant between these species. The inclusion phenomenon may be simply due to the polar nature of oxalic acid, which preferentially resides in the more polar cavity between the phthalocyanine rings rather than in bulk $CHCl_3$.

The presence of oxalic acid in the crystal lattice was corroborated with the analytical[12] and IR data of **3** in a crystal form. The IR spectrum showed strong bands at 3425 and 1693 cm^{-1} which can be ascribed to the O–H and C=O stretches of the oxalic acid, respectively. These bands were not observed in the IR spectrum of the green powder of **3**, showing that oxalic acid is not present in this batch of sample. It has been found that in the presence of some lanthanide complexes, oxalate anion can be produced by reductive coupling of carbon dioxide.[13] We suggest that a small amount of oxalic acid is generated similarly in this cerium-promoted cyclisation reaction. The guest molecules co-crystallise with a small portion of **3** forming the green transparent plates, while the major portion in green solid form is free from oxalic acid. Attempts to recrystallise this sample by the layering method ($CHCl_3$/MeOH) always led to precipitation. However, by the addition of one equiv. of oxalic acid in the MeOH layer, a substantial amount of green plates were obtained for which the IR spectrum and the X-ray structure were found to be identical with those of $\mathbf{3}\cdot C_2H_2O_4$.

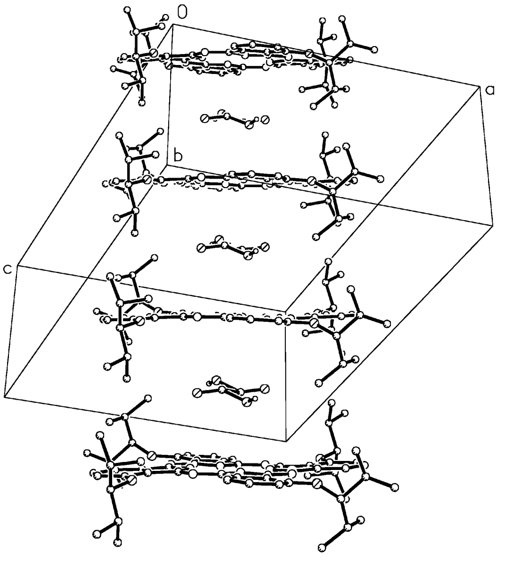

Fig. 3 Packing of $\mathbf{3}\cdot C_2H_2O_4$: view nearly parallel to the phthalocyanine planes. All hydrogen atoms are omitted for clarity.

In summary, we have reported a new cerium-promoted method to prepare the metal-free phthalocyanine **3**, which forms a novel 1 : 1 inclusion complex with oxalic acid generated serendipitously in the reaction.

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