First example of a di-cadmium tris-phthalocyanine triple-decker sandwich complex†

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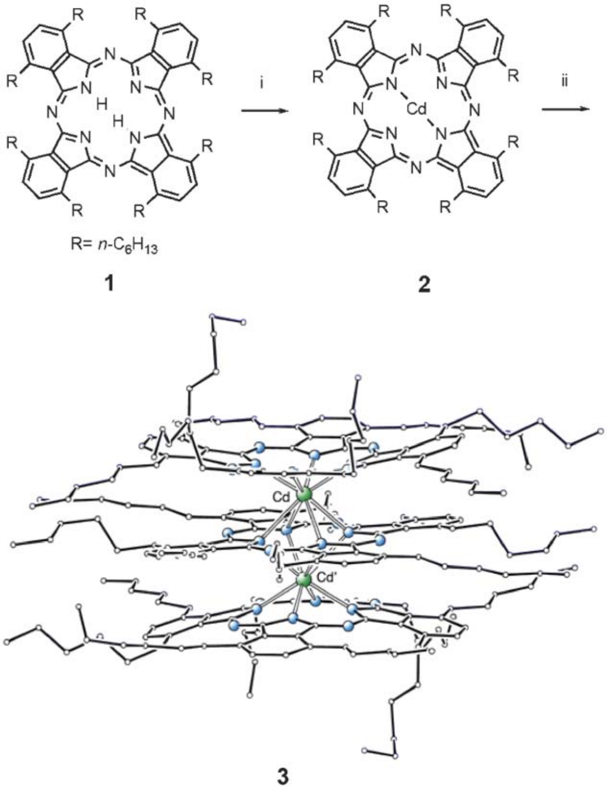
An unprecedented $M^{(II)}_2Pc_3$ (M = Cd) triple-decker sandwich complex has been synthesized and characterised by single crystal X-ray crystallography; cyclic voltammetry shows an unusually large range of redox states and EPR spectroscopy indicates that the material exists in at least two redox states, one having spin ½.

Phthalocyanines (Pcs) exhibit a remarkable range of photophysical, semiconduction and charge carrier properties that lend themselves to applications in, for example, electrophotography, CD-Rs, laser/LED printing, sensors, optical limiters, solar cells, and photodynamic therapy.[1] These complement their long established use as commercial blue/green colorants. Pc sandwich complexes are a sub-class in which a metal ion is coordinated to, and located between, two Pc^{2-} ligands. Lanthanide bisphthalocyanines, especially $LuPc_2$, have attracted much attention because the normal formal charge on the metal centre, *e.g.* Lu^{III}, does not counterbalance the charges on the two ligands.[2] This leads to interesting redox and electrochromic behaviour. For $LuPc_2$ the most familiar states are the 'green' form, a free radical species that exhibits semiconductivity properties,[3] and the 'blue' form obtained by one-electron reduction. The blue form requires the presence of an 'extra hydrogen' to achieve charge neutrality although the location of the latter is unclear.[2] Triple-decker sandwich compounds of the type $M^{III}_2Pc_3$ where M^{III} is a lanthanide,[2] indium[4] or bismuth[5] are also known. Here the total formal positive charges on the two metals balance those on the three ligands. In this paper we report the discovery of the first $M^{II}_2Pc_3$ complex, where M = Cd^{II}, a compound that provides a conundrum with regard to the charge imbalance and which further enhances the already impressive portfolio of Pc derivatives.

The new material was obtained during work-up of a reaction to metallate 1,4,8,11,15,18,22,25-octakis(hexyl)phthalocyanine **1**[6] with Cd^{II} to form the green cadmium derivative **2**. The reaction, Scheme 1, is based on a standard procedure to form $M^{II}Pc$ derivatives, here using $Cd(OAc)_2$ as the source of the metal ion. During isolation and purification of **2** we became aware of the presence, indeed generation, of a blue compound. Indeed, a solution of **2** in chloroform slowly turned from green to blue on standing. A pure sample of the new blue compound, designated **3**, was obtained upon slow recrystallization of **2** from MeOH/THF. Structural elucidation of **3** was hindered by a ^{1}H-NMR spectrum (benzene-d_6) that showed no signals for aromatic and benzylic protons. That this was due to the presence of a paramagnetic species was confirmed by EPR spectroscopy. Maldi MS showed signals for ions of higher mass than **2** and elemental analysis was consistent with a 2 : 3 ratio of Cd ions to Pc ligands.

X-ray crystallography revealed that **3** indeed comprises three Pc ligands linked by coordination through two Cd ions, Scheme 1 and Fig. 1. The molecule lies about a centre of symmetry. The Cd ions are unevenly spaced between their two coordinating ligands, displaced 1.222(2) Å from the N_4 mean plane of the outer ligands and 1.742(2) Å from the N_4 mean plane of the inner. Accordingly the mean of the Cd–N distances to the outer ligand is 2.340(3) Å and 2.62(3) Å to the central ligand. Coordination to the Cd ions is eightfold in a pattern closer to square-antiprism than square-prism; the mean acute torsion angle of the type N–X1–X2–N is 34.1(2)°,



Scheme 1 Synthesis of **2** and **3**. *Reagents and conditions*: (i) $Cd(OAc)_2$, pentanol, reflux; (ii) slow recrystallisation of **2** from THF/MeOH.

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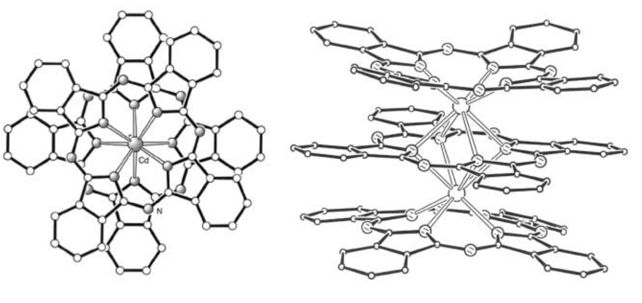

Fig. 1 X-ray structure of **3** viewed from above and from the side with alkyl chains removed for clarity. The top ring, left hand side, effectively eclipses the bottom ring whereas the central ring is staggered.

Fig. 1, where X1 is the centroid of the four coordinated atoms of the outer ring and X2 is the centre of symmetry.[7,10] (See Supporting Information).‡ Previous reports of Pc derivatives linked by M^{II} ions appear to be limited to polymeric structures in which the rings are linked by Hg^{II} ions.[8] In these materials the ends of the polymer complex were capped, for example by Hg^{II} monoacetate groups, effectively satisfying the valence requirements of the ligands and metals.

Fig. 2 compares the UV-vis spectra of solutions of **2** and **3** in hexane. That of **2** shows a spectrum characteristic of M^{II}Pc derivatives (UV absorptions and a Q-band at *ca.* 700 nm). In contrast, the spectrum of **3** is more complex, particularly in the 550–650 region; there is also a very weak absorption at *ca.* 870 nm. Pc derivatives that show bands in the 550–650 nm region include the 'green' free radical form of Ln^{III}Pc$_2$ compounds. Fig. 3 shows the UV-vis spectral changes upon oxidation of **3** in CH_2Cl_2 with up to 2 mole equivalents of iodine. Oxidation by iodine reduces the Q-band absorbance and intensifies the band to lower wavelength. A new band appears at 776 nm with added iodine.

Further EPR studies of **3** in *n*-hexane (295 K) showed a signal at 1.9965 with a bandwidth of 7 Gauss. The signal was integrated (MTSL as standard) and showed that the mole fraction of radical was 0.37. This rose to 0.62 in CH_2Cl_2. Thus we conclude that solutions of **3** contain the complex in more than one redox state, one of which has a spin of ½.

Pcs with redox inactive metals in the cavity show two ring-based one-electron oxidations and four ring-based one-electron reductions.[9] Thus the triple-decker complex **3** can in principle show six one-electron oxidation and 12 one-electron reduction processes. CV, Osteryoung square wave voltammetry (SWV) and linear sweep voltammetry were undertaken on **3** in a solution of CH_2Cl_2 (0.5 mM) in the presence of 50 mM $NBu_4{\cdot}B[C_6H_3(CF_3)_2]_4$ at −40 °C. LSV current flow data show that the species at zero current flow undergoes six one-electron oxidations giving rise to the three peaks A, B, and C in Fig. 4. Peaks I, II and III each represent a one-electron reduction process whereas those labelled IV and V are both associated with three one-electron transfer processes. The observation that **3** in the rest state can undergo six one-electron ring-based oxidations strongly indicates that each ligand in **3** is in the Pc^{2-} state and thus to achieve neutrality the species must contain two extra protons, in at present undefined positions. Such a species which can be denoted as $[2H]{\cdot}[Cd_2Pc_3]$ would have spin 0. The electrochemical data show that the first one-electron oxidation of the complex, contributing to the unresolved band A, occurs at $E^{\circ\prime} = 0.162$ V. This is a much lower potential than that typical for the first one-electron oxidation of simple MPc rings ($E^{\circ\prime}$ *ca.* 0.5–0.7 V)[9] and could account for the presence of amounts of the oxidized species with spin ½ that are evident in the EPR experiment.

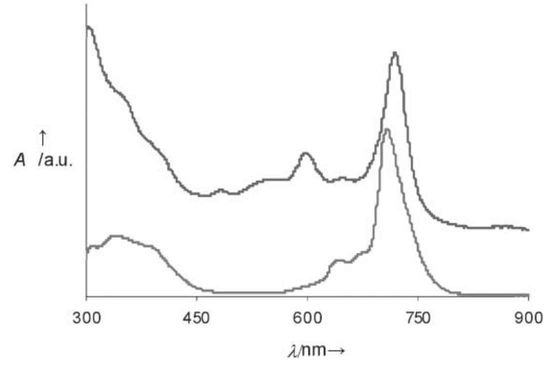

Fig. 2 UV-vis spectra of **2** (below) and **3** (above) in hexane. The spectra are offset for clarity.

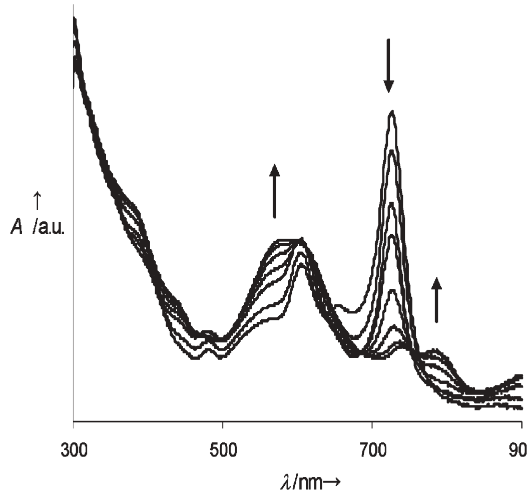

Fig. 3 UV-vis spectra of a solution of **3** in CH_2Cl_2 upon successive addition of aliquots of iodine solution in the same solvent (0.3 eq. per aliquot). The arrows indicate the changes in absorption.

Demonstrating the presence of one or more 'extra protons' in the proposed $[2H]{\cdot}[Cd_2Pc_3]$ redox state of **3** is likely to prove as

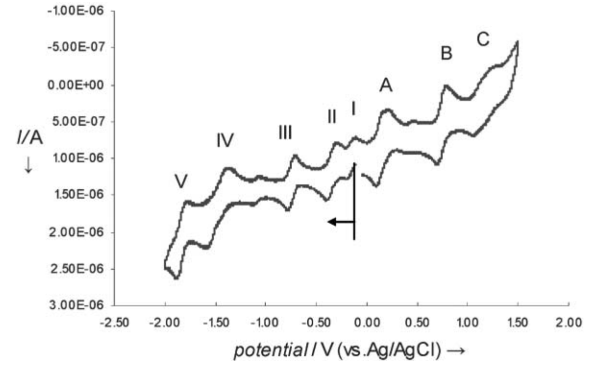

Fig. 4 CV of **3** in CH_2Cl_2 (0.5 mM) at a scan rate of 100 mV s^{-1} and −40 °C. The arrow indicates the initial potential and scan direction. Under our conditions the Fc/Fc^{+}couple is at 0.464 mV.

challenging as the detection of the extra proton in the blue form of lanthanide bisphthalocyanines referred to above. The Maldi MS of **3** was unhelpful, showing only fragmentation ions, while careful analysis of the X-ray diffraction data failed to support or preclude the presence of such protons.

In conclusion a new and unexpected type of triple-decker phthalocyanine sandwich compound has been characterized by X-ray crystallography. The combination of accessible redox states leading to free radical character suggests that the complex may have interesting materials chemistry properties. A more detailed discussion of the CV results will be reported elsewhere as will results of studies of the scope for developing further analogues.

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7 Crystal structure determination of **3**: black, needle prisms; $C_{240}H_{336}N_{24}Cd_2$; M = 3782.1; triclinic; space group P-1 (no. 2); a = 13.081(3), b = 20.240(4), c = 22.548(5) Å, α = 108.83(3), β = 105.91(3), γ = 101.51(3)°; V = 5154.7(18) Å^3; Z = 1; D_c = 1.218 g cm^{-3}; F(000) = 2040; Abs. coeff. = 0.268 mm^{-1}; T = 140(1) K; μ(Mo-Kα) = 2.7 cm^{-1}; λ(Mo-Kα) = 0.71069 Å; crystal dimensions: 0.7 × 0.12 × 0.12 mm; θ range = 1.7–25.4°, total no. reflections = 24748; no. unique reflections = 15926 (R_{int} = 0.076); no. 'observed' reflections = 9586 ($I > 2\sigma(I)$). Direct methods in SHELXS and refinement (against F^2) with SHELXL[10] data = 15926, restraints = 0, parameters = 1198; S = 0.903; 'observed' data R_1 = 0.052. wR_2 = 0.111; all data R_1 = 0.099(2B), wR_2 = 0.120; reflections weighted $w = [\sigma^2(F_0^2) + (0.0436P)^2]^{-1}$ with $P = (F_0^2 + 2F_c^2)/3$.

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