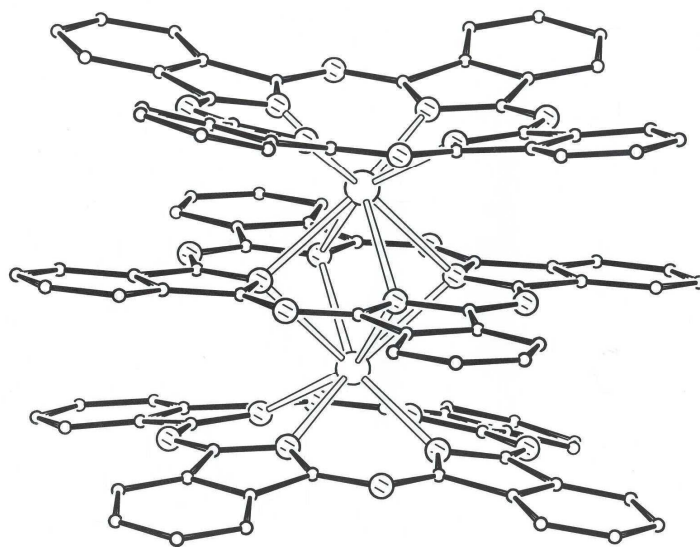


Electrochemical and EPR studies of two substituted *bis*-cadmium *tris*-phthalocyanine complexes: elucidation of unexpectedly different free-radical character

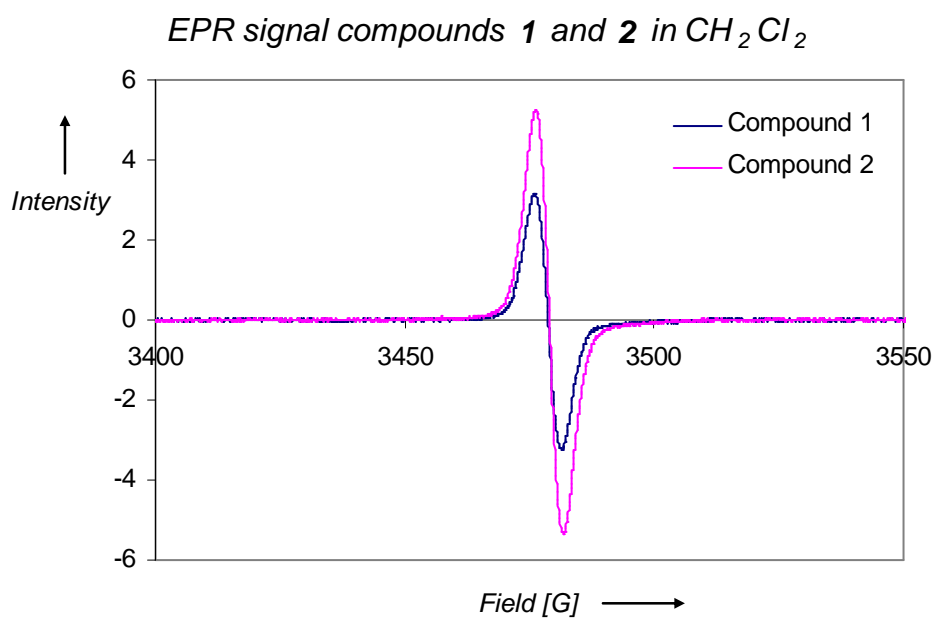
Michael J. Cook, Isabelle Chambrier, Gaye F. White, Eleanor Fourie and Jannie C. Swarts**

1. Detail of X-ray structure

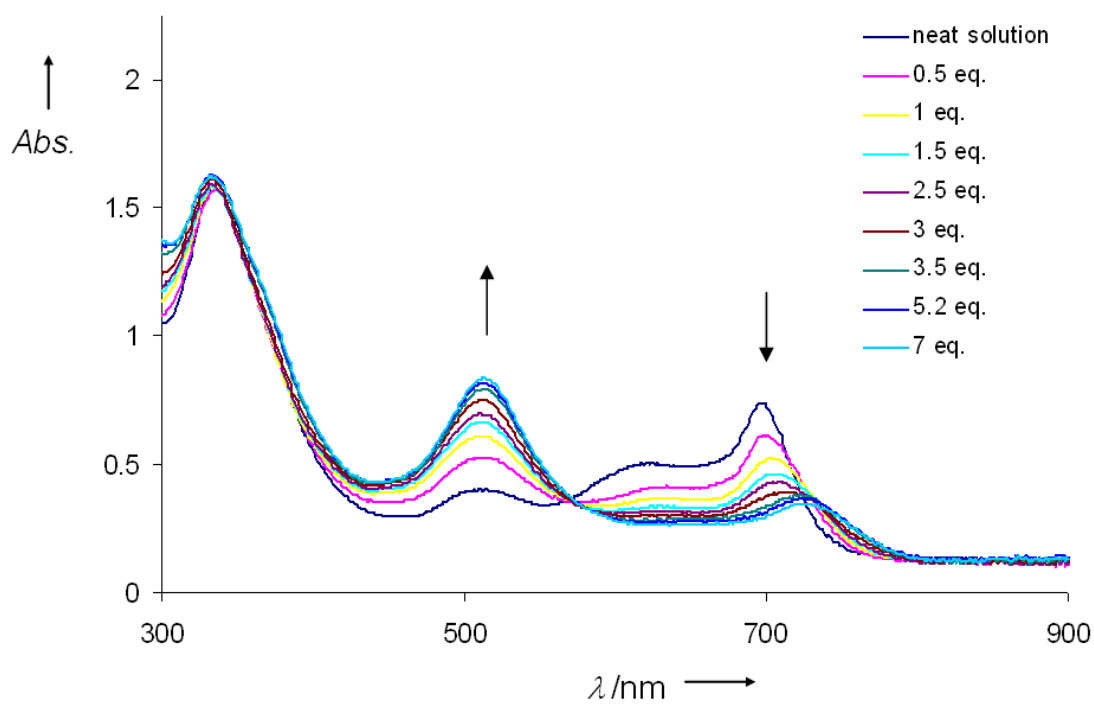
View of compound **1**, the alkyl substituent chains having been removed for clarity: each Cd ion is octa-coordinated to a near planar central Pc^{2-} ligand and an outer saucer shaped ligand. Mean Cd-N (inner ring) length is 2.62 Å, mean Cd-N (outer ring) length 2.34 Å.



2. Examples of EPR spectra obtained for compounds 1 and 2 in dichloromethane



3. Changes in the UV-vis. spectrum of 2 as a solution in CH₂Cl₂ upon addition of aliquots of iodine



5. Electrochemistry of **2** in CH₂Cl₂ and THF

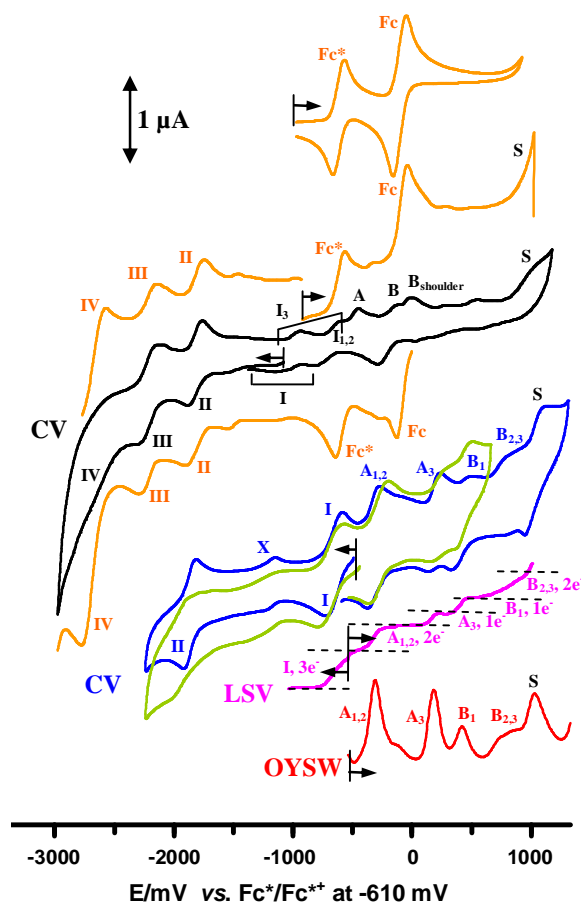


Figure. CV of **2** in CH₂Cl₂ at -40 °C (blue trace) and at 25 °C (green trace). Oxidation peaks are labelled A through C and reduction peaks I through V. Numbering starts from the resting potential to synchronize wave number with sequential redox processes. Peak S is attributed to solvent decomposition or electrode pollution effects. Red: Osteryoung square wave voltammograms (OYSW) at -40 °C. Purple: Linear sweep voltammograms (LSVs) at 2 mV s⁻¹ and -40 °C in CH₂Cl₂. The current has been multiplied by 2 for better display purposes on the scale of the above voltammograms; the broken lines accentuate the electron count associated with each wave. Black: CV of **2** in THF at 25 °C (currents are divided by 2 to get the CV on the same scale as the blue trace). Orange: Addition of Fc and Fc* (decamethylferrocene) allowed proper peak alignment to the reference potential but obscured peaks I, A and B of **2**. The orange CV on top is that of free ferrocene (Fc) in the presence of Fc*. It shows that in THF, when the Fc* peak is aligned to -610 mV, the potential at which it is observed in CH₂Cl₂ when referenced against free ferrocene, then the ferrocene couple is found at -95 mV. For this reason, see experimental section, potentials are referenced against Fc* at -610 mV.

Following the successful identification of the one-electron transfer processes for **1**, attention was focussed on the peripheral substituted complex **2**. For **2**, in dichloromethane at -40 °C (blue trace, see above figure) the anodic sweeps revealed all 6 oxidation steps in three separate oxidative peaks A_{1,2}, A₃B₁ and B_{2,3} each representing two one-electron transfer processes, to generate **2**⁴⁺, much in the manner observed for **1**. This time, however, wave A₃B₁ was clearly observed to split into two equal size components A₃ and B₁ as demonstrated by LSV. The green trace is a CV recorded at 25 °C and shows A₃ and B₁ that are better resolved. The wave labelled S is not part of the electrochemical fingerprint of **2**; it is either solvent decomposition or the result of electrode fouling. OYSW voltammetry more clearly showed that wave B_{2,3} is comprised of two closely overlapping peaks.

Only wave $A_{1,2}$ could not be resolved into two separate one-electron transfer processes, but it does represent the flow of two electrons as estimated by LSV. For **2**, however, only two reduction processes, I and II, each consisting of three highly overlapping one-electron transfer processes, could be observed in CH_2Cl_2 , one less than for **1**. This contrasts with the nine individual reduction steps occurring in three sets of processes that could be observed in CH_2Cl_2 for **1**.

In THF, the last two arrays of reduction waves III and IV could be clearly identified, especially in the presence of ferrocene and decamethylferrocene as internal marker (orange trace, see figure above). LSV was inconclusive to determine if wave IV is associated with 2 electrons or 3 electrons, because electrode deposition by **2** onto the surface of the electrode during the timescale of a LSV led to anomalous current readings below -1000 mV. Wave IV of **2** in THF was observed at $E^{o'} = -2.69$ V and it was $E^{o'}_{2,IV} - E^{o'}_{1,VI} = 0.13$ V more difficult to add electrons 10, 11 and probably also 12 to **2** than to **1**. None of the reducing processes II, III or IV of **2** could be resolved to show any of its three components. In THF, the two separate components $I_{1,2}$ and I_3 of the first reduction process was slow electron transfer processes as indicated by the unusual broadness of these peaks and large ΔE values, Table 2. Overlapping of the peaks of this reduction process with peaks of the first oxidation process, A, was a feature of this complicated region of the CV.

As with **1**, the six-electron oxidation of **2** in THF was achieved in two distinct steps **A** and **B**, each comprising three one-electron transfer steps. Wave **B** resolved partially to show a second component, **B_{shoulder}** that is more clearly on the anodic halfwave (oxidation halfwave, the peak pointing up). Table 2 summarises the electrochemical data that could be extracted from the voltammograms shown above.

Formal reduction potentials, $E^{o'}$, for the oxidation processes of **2** in THF as solvent were much smaller than those observed in CH_2Cl_2 , demonstrating how THF association with oxidised species may change the electrochemical profile of a compound, Table 2. However, on the reducing side, especially at wave II, *i.e.* under strong reducing conditions, formal reduction potentials were essentially the same.

It is important to record that the first oxidation wave - wave A, both in THF and in DCM - was encountered at least at 160 mV lower potential for **2** than for **1**. This implies that **2** is much easier to initially oxidise than **1**. This observation is therefore consistent with the EPR studies described above which showed **2** to have a rest state unpaired electron content of *ca.* 1, compared to the value of 0.62 for **1** in CH_2Cl_2 .