X-Ray Crystal Structure and ^{113}Cd N.M.R. Spectrum of $\alpha\beta\gamma\delta$-Tetraphenylporphinatocadmium(II)-Bis(dioxan) Solvate

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Summary The ^{113}Cd Fourier transform n m r spectrum of the title compound is characterized by a single resonance at *ca* 422 p p m deshielded from 0 1 M $CdClO_4$ solution, its crystal structure shows an almost planar CdN_4 system with only very weak axial interactions to dioxan molecules

^{113}Cd N m r spectroscopy, with a chemical shift range of *ca* 850 p p m , has been shown in recent years to have considerable potential as a sensitive probe of metal atom sites in a variety of types of compounds [1] The porphyrin ring system offers a unique geometry and electronic environment for a metal atom site Hence, a detailed study of ^{113}Cd n m r spectra of Cd porphyrins could lead to the development of ^{113}Cd n m r spectroscopy as a probe of haemproteins and related metalloproteins We report here the synthesis of $\alpha\beta\gamma\delta$-tetraphenylporphyrinato cadmium(II) 2 dioxan solvate [Cd(TPP)·2 dioxan], its ^{113}Cd n m r spectrum, and its crystal structure to aid the development of ^{113}Cd n m r spectroscopy as a haem probe

A mixture of cadmium acetate dihydrate (1 88 mmol) and tetraphenylporphine (1 66 mmol) was heated in refluxing dimethylformamide (DMF) under nitrogen for 15 min The solid product (yield 71%) was washed with n-hexane and dried, and diffraction-quality crystals of Cd(TPP)-2-dioxan were grown from methanol–methylene chloride–dioxan (1 : 1 : 1)

Crystal data Cadmium tetraphenylporphyrin bis-dioxan, $CdC_{52}H_{44}N_4O_4$, triclinic, space group $P1$, $a = 11\ 327(3)$, $b = 11\ 614(3)$, $c = 9\ 845(3)$ Å, $\alpha = 102\ 59(2)$, $\beta = 114\ 16(1)$, $\gamma = 65\ 50(1)°$, $Z = 1$, $D_c = 1\ 39\ \mathrm{g\ cm^{-3}}$, $D_m = 1\ 10(2)\ \mathrm{g\ cm^{-3}}$ [without dioxan $D_c = 1\ 12$ and since the density was measured in aqueous solution $Cd(NO_3)_2$, the dioxan was no doubt stripped out], Zr-filtered Mo K_α radiation ($\lambda = 0\ 71068$ Å), 3140 independent reflections, $\mu = 4\ 4\ \mathrm{cm^{-1}}$, crystal size 0·36 × 0 23 × 0 39 mm, transmission correction 0 917 maximum, 0 859 minimum

Intensity data were collected on a computer-controlled Picker diffractometer to $2\theta \leqslant 65°$ Absorption and anomalous dispersion corrections were made The structure was solved by standard heavy atom methods and refined by full-matrix least-squares with anisotropic temperature factors for all non-hydrogen atoms to a current conventional $R = 0\ 038$ and a weighted $R = 0\ 043$, based on counting statistics [2] The centric model was tested and it converged to R *ca* 0 16 The centric model would demand that the CdN_4 unit be planar and with equal Cd–O (dioxan) distances No thermal anisotropy or thermal averaging of the Cd or other atoms was sufficient to converge to an agreement index comparable to the non-centric result Further support for the non-centric model or against a thermally averaged Cd model was found from the root-mean-square (r m s) thermal displacement of the Cd atom after the non-centric least-squares refinement The r m s thermal displacement of the Cd atom approximately normal to the N_4 plane (*vide infra*) was found to be 0 32 Å, somewhat high but not abnormally large compare with that of the four nitrogen atoms, 0 21–0 26 Å It is clear that the non-centrosymmetric space group $P1$ is the correct choice †

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† The atomic co-ordinate for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd , Cambridge CB2 1EW Any request should be accompanied by the full literature citation for this communication

The ^{113}Cd n.m.r. spectra of a deuteriochloroform solution of Cd(TPP) in the presence and absence of dioxan were obtained on a Bruker WP-200 spectrometer. The ^{113}Cd spectra of Cd(TPP) in the ternary solvent system (from which crystals were grown) were obtained on a highly modified XL-100 instrument.[3] All measurements were made from 95% isotopically enriched ^{113}Cd samples at 21 °C.

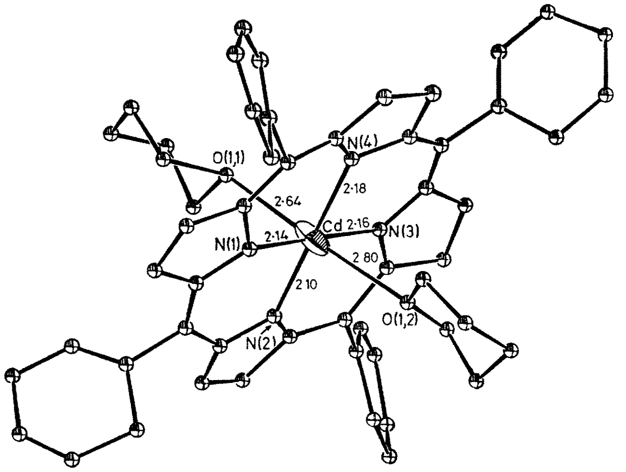

FIGURE. An ORTEP drawing of the $\alpha\beta\gamma\delta$-tetraphenylporphinatocadmium(II) bis(dioxan) solvent unit. Only the Cd–N and Cd–O distances are shown. All other distances have the expected values. The Cd–O and Cd–N e.s.d.s are $\leqslant \pm 0{\cdot}01$ Å. Bond angles N_n–Cd–N_{n+1} ($n = 1$—4) are 90·7, 90·1, 90·8, and 88·5° ± 0·2°, respectively. The O(1,1)–Cd–O(1,2) angle is 177·4 ± 0·2°; however, this O–O vector is tilted from the perpendicular to the N_4 plane towards the N(1)–N(2) bisector by *ca.* 5°.

The resonance observed from Cd(TPP) in the absence of dioxan was found to be concentration-dependent and varied from 454 to 419 p.p.m. with concentrations of Cd(TPP) of 2·7 to 16·2 mM, respectively. This pattern is not unexpected for those systems which can undergo intermolecular stacking interactions. However, there may be other factors which are operational. A 13·6 mM solution of Cd(TPP) in the presence of a 16·1 : 1 mol ratio of dioxan to Cd yielded a ^{113}Cd chemical shift of 429 p.p.m., whereas the ternary solvent (*vide supra*) solution of Cd(TPP) manifested a ^{113}Cd resonance of 413 p.p.m. These values are all deshielded from 0·1M $Cd(ClO_4)_2$ solutions. The resonances were all relatively broad, *ca.* 80 Hz, and independent of ^{1}H decoupling. The observed ^{113}Cd chemical shifts in Cd(TPP) may be contrasted with those obtained for other Cd compounds containing nitrogen and oxygen ligands (70—290 p.p.m.). These differences reflect several factors: differences in metal atom environment symmetry, changes in the degree of covalency of the cadmium–ligand bonds, charge effects, *etc.*

The crystal structure may be described as isolated Cd(TPP)·2 dioxan entities separated by ordinary van der Waals distances. The Cd–N distances are normal compared to what one might expect for Cd–N single bonds, 2·14 Å average. The Cd–O interactions to the 'axial' oxygens are long, 2·65 and 2·80 Å, respectively, and are 0·51 and 0·66 Å longer than what one might expect for Cd–O single bonds. We view this 'axial' situation as only a weak solvent–metal interaction and not that of a covalently bonded species and accordingly describe Cd(TPP)·2dioxan as a four-co-ordinate Cd(TPP). Such weak 'axial' interactions are well known in metalloporphyrin structures.[4] This interpretation is supported by the relatively small variation of the ^{113}Cd resonance under a variety of circumstances (*vide supra*), and also by the fact that Cd(TPP)·X complexes can be identified by changes in absorption spectra arising upon addition of X to Cd(TPP). No such spectral change occurs with the addition of dioxan. In spite of the fact that Cd^{2+} is a post-second row transition metal ion, the amount of ruffling or D_{2d} distortion and doming is small as is the displacement of the Cd^{2+} from the 'plane' of the four pyrrole nitrogens.[5] N(1) and N(3) are $-0{\cdot}016 \pm 0{\cdot}01$ Å and N(2) and N(4) are $+0{\cdot}016 \pm 0{\cdot}01$ Å from the best plane of these atoms, and Cd is $+0{\cdot}028 \pm 0{\cdot}01$ Å displaced from this plane towards O(1).

We now have ^{113}Cd n.m.r. data for four-co-ordinate Cd(TPP) and other Cd porphyrins and a crystal structure of Cd(TPP) as reference points for further ^{113}Cd n.m.r. studies of Cd porphyrins.

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