

## Supplementary information

# Host-guest influence on metallo-supramolecular assemblies with a cyclotriveratrylene-type ligand

Christopher Carruthers, Julie Fisher, Lindsay P. Harding and Michael J. Hardie

### 1. Synthesis

All chemicals were obtained from Sigma-Aldrich Chemical Company or Alfa Aesar and were used without further purification. Tris(4-pyridylmethylamino)cyclotriguaiacylene **1** was synthesised by literature methods.<sup>1</sup> Microanalyses were obtained on a Carlo Erba Elemental Analyser MOD 1106 instrument. Infrared spectra were recorded on a Perkin-Elmer FTIR spectrometer and samples analysed as solids. Mass spectra of organic compounds were obtained using a micrOTOF spectrometer using time-of-flight electrospray analysis.

#### Complex [Cd(**1**)(OAc)<sub>2</sub>(*o*-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>)]·2(H<sub>2</sub>O) **2**

Tris(4-pyridylmethylamino)cyclotriguaiacylene (10mg, 15μmol) and *o*-carborane (13mg, 90μmol, 6 equiv.) were dissolved in a solution of Cd(OAc)<sub>2</sub> (11.8mg, 45μmol, 3 equiv.) in methanol. The mixture was left to slowly evaporate to give crystals of complex **2** (6mg, 38 %). IR (Solid State)  $\nu$  (cm<sup>-1</sup>) 671, 797, 936, 1015, 1067, 1149, 1267, 1519, 2029, 2159, 2566, 3041, 3400. Elemental analysis calcd. (%) for C<sub>48</sub>H<sub>60</sub>B<sub>10</sub>CdN<sub>6</sub>O<sub>7</sub>·5H<sub>2</sub>O: C 50.41, H 6.17, N 7.35; found: C 50.30, H 5.65, N 7.05.

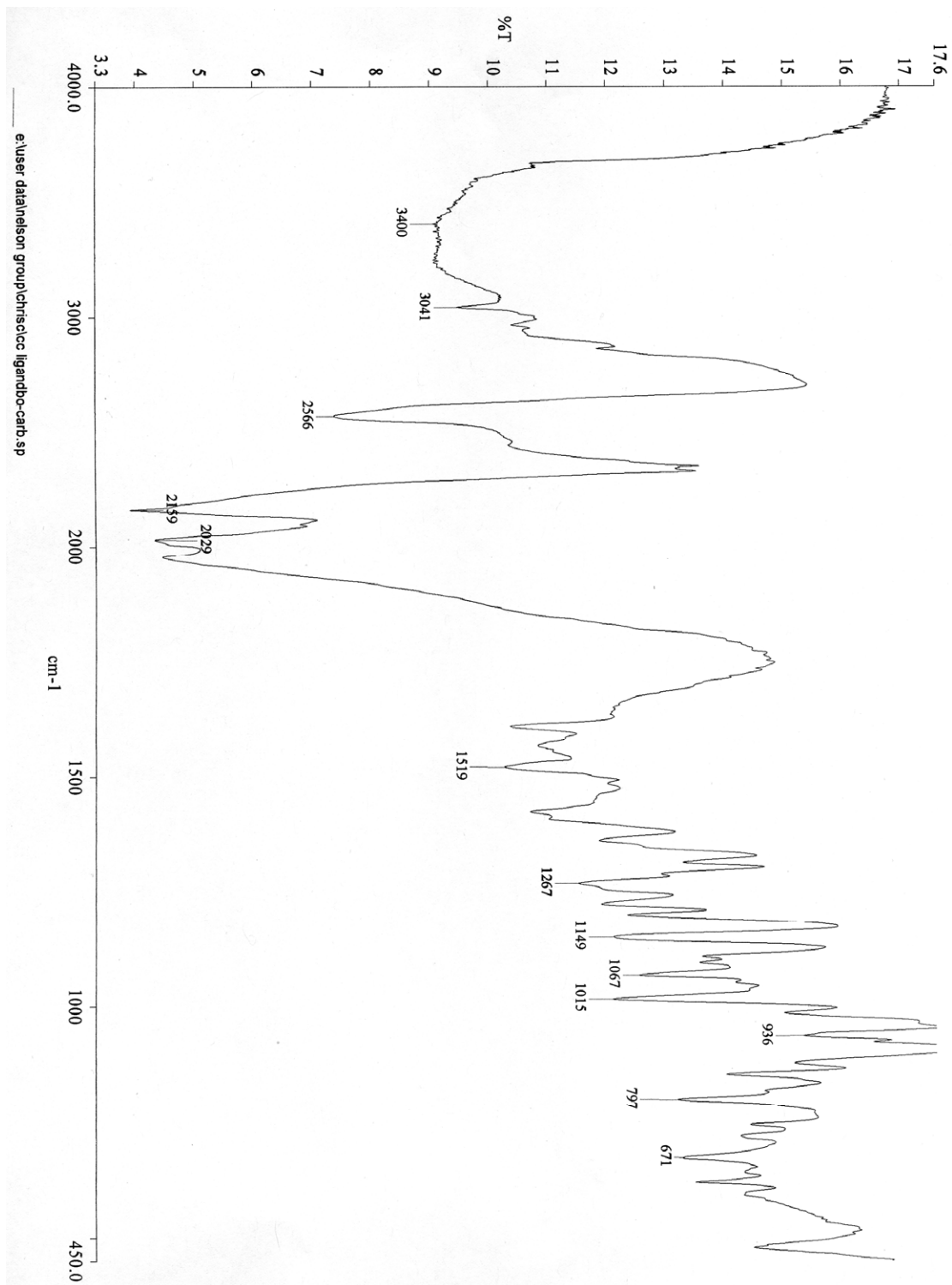
#### Complex [Cd<sub>3</sub>(**1**)(OAc)<sub>6</sub>]

Tris(4-pyridylmethylamino)cyclotriguaiacylene (10mg, 15μmol) was dissolved a methanol solution of Cd(OAc)<sub>2</sub> (11.8mg, 45μmol, 3 equiv.). The mixture was left to slowly evaporate during which time 12 mg of crystals appeared. IR (Solid State)  $\nu$  (cm<sup>-1</sup>) 533, 616, 668, 753, 824, 941, 1019, 1149, 1526 (broad), 3341 (broad). Satisfactory microanalysis could not be obtained presumably due to high levels of solvation of the crystals. ES-MS:  $m/z$ : 2683.83 {[Cd<sub>6</sub>(**1**)<sub>2</sub>(OAc)<sub>11</sub>]<sup>+</sup>}, 2451.33 {[Cd<sub>5</sub>(**1**)<sub>2</sub>(OAc)<sub>9</sub>]<sup>+</sup>}, 2220.39 {[Cd<sub>4</sub>(**1**)<sub>2</sub>(OAc)<sub>7</sub>]<sup>+</sup>}, 1989.46 {[Cd<sub>3</sub>(**1**)<sub>2</sub>(OAc)<sub>5</sub>]<sup>+</sup>}, 1773.55

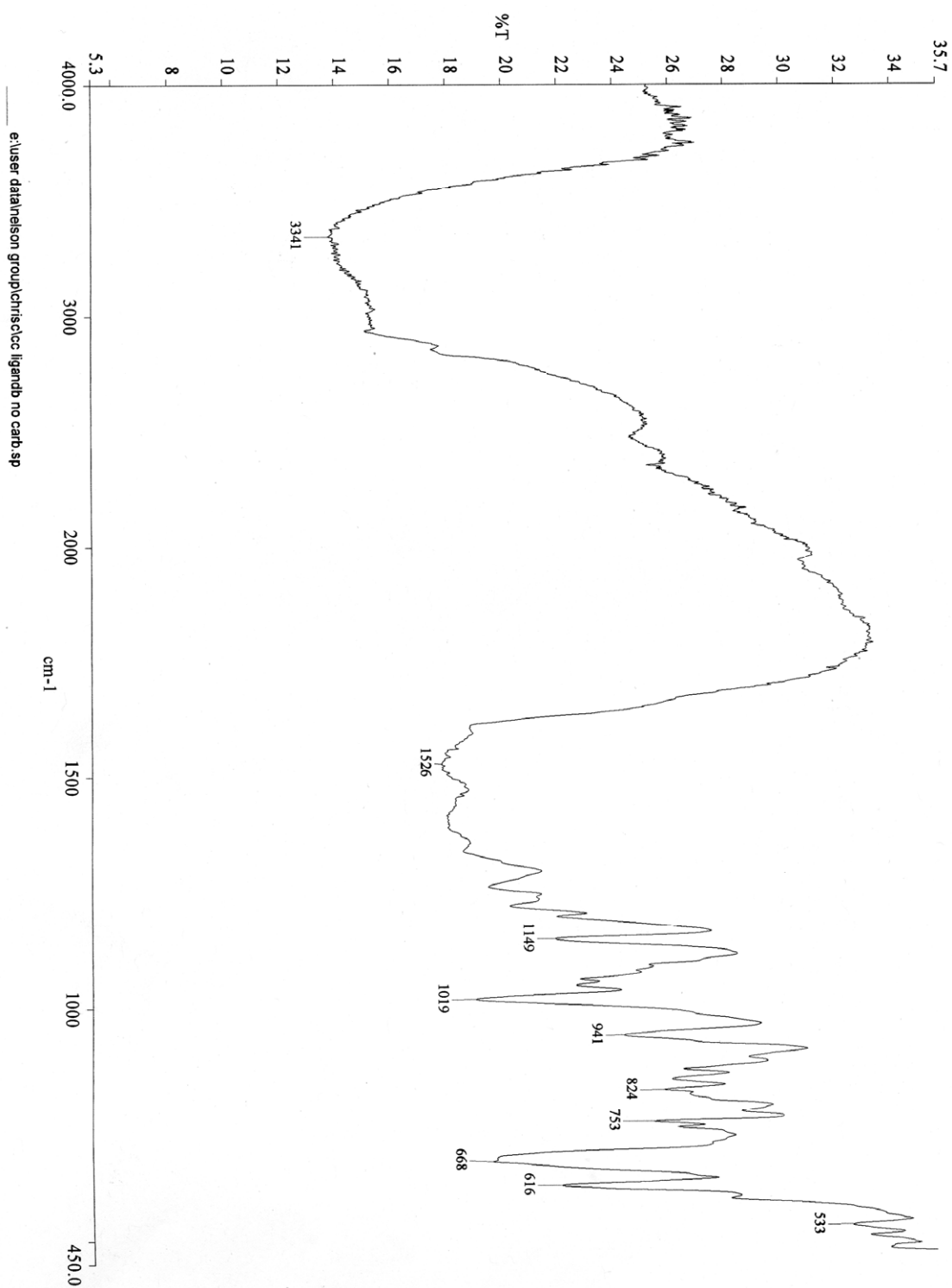
$\{[\text{Cd}_5(\mathbf{1})_1(\text{OAc})_9]^+\}$ , 1759.52  $\{[\text{Cd}_2(\mathbf{1})_2(\text{OAc})_3]^+\}$ , 1529.59  $\{[\text{Cd}_1(\mathbf{1})_2(\text{OAc})_1]^+\}$ , 1311.12  
 $\{[\text{Cd}_3(\mathbf{1})_1(\text{OAc})_5]^+\}$ , 851.26  $\{[\text{Cd}_1(\mathbf{1})_1(\text{OAc})_1]^+\}$ .

### Infrared Spectra:

#### Complex 2

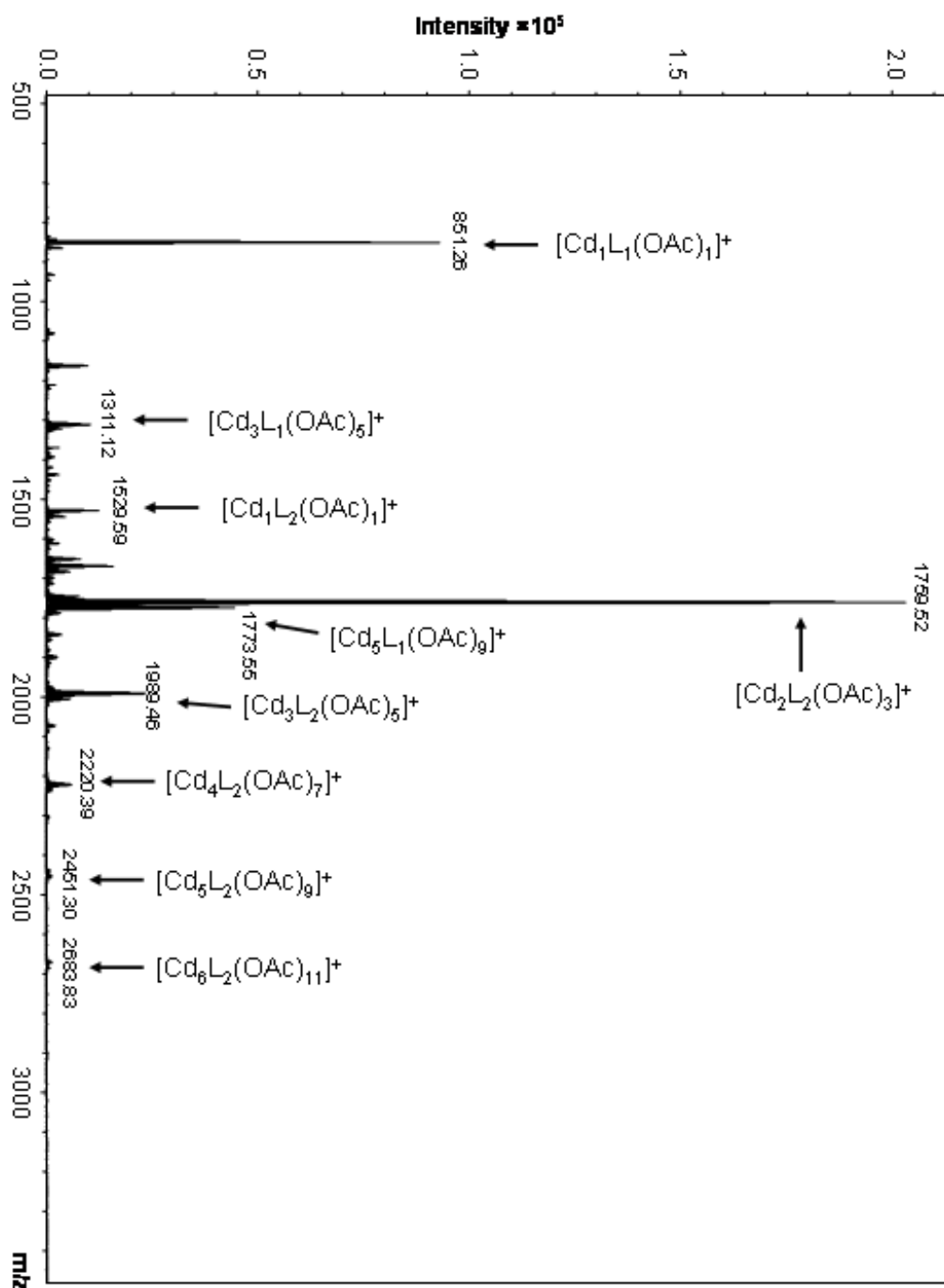


**Infrared of crystals from  $[\text{Cd}_3(1)(\text{OAc})_6]$  solution:**





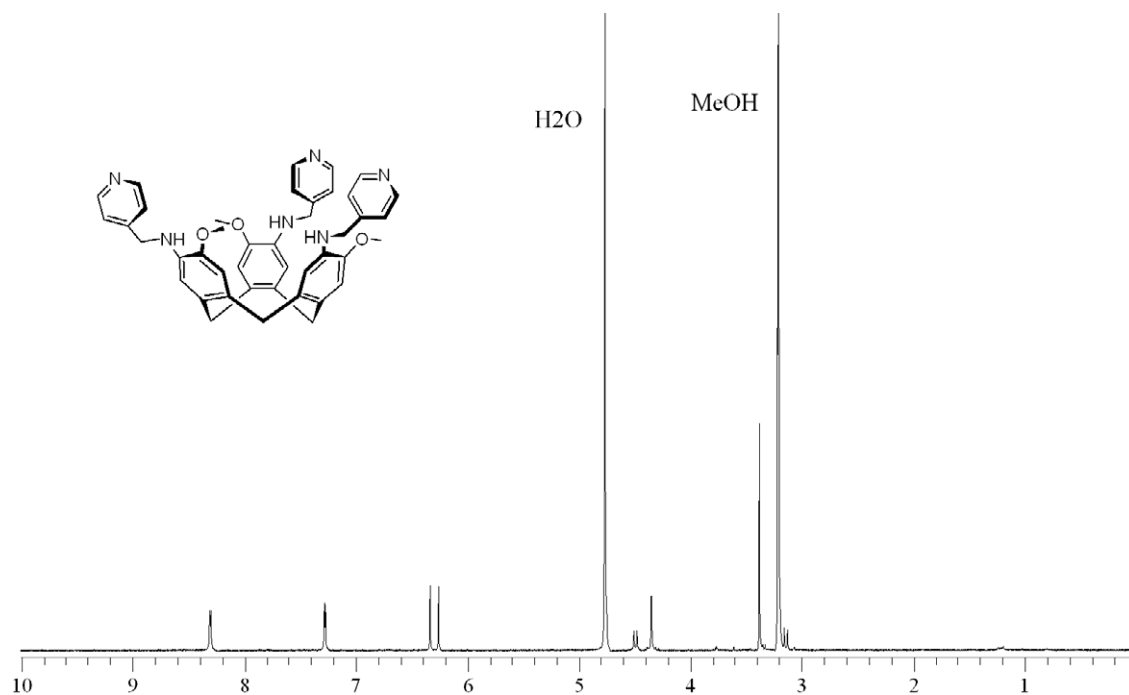
**ES-MS of Cd(OAc)<sub>2</sub>:1 solution:**



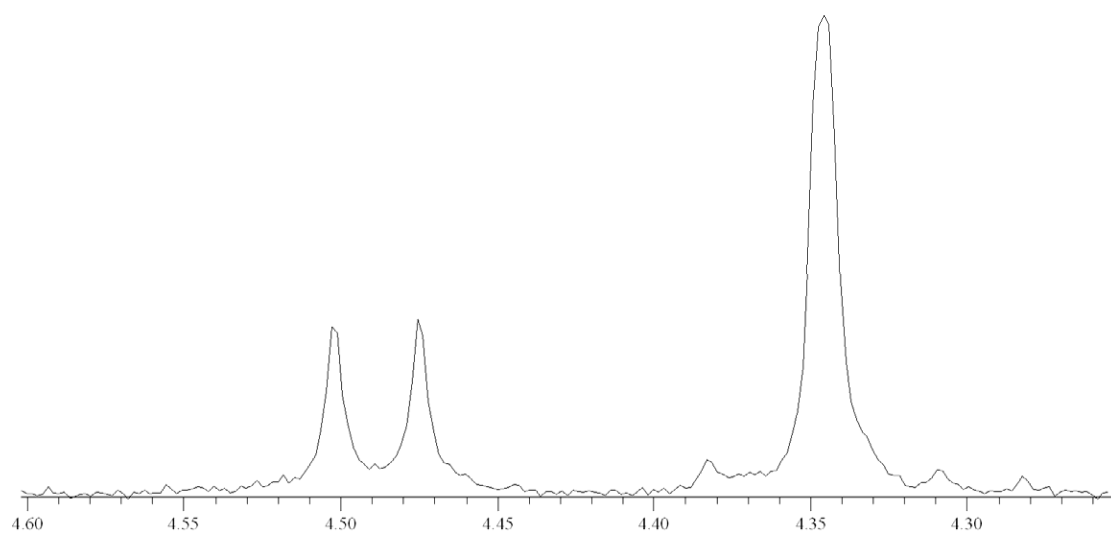
**2. NMR studies**

<sup>1</sup>H Nuclear Magnetic Resonance spectra were recorded using a Bruker Advance 500 instrument and run in d<sub>4</sub>-MeOH and spectra are shown below:

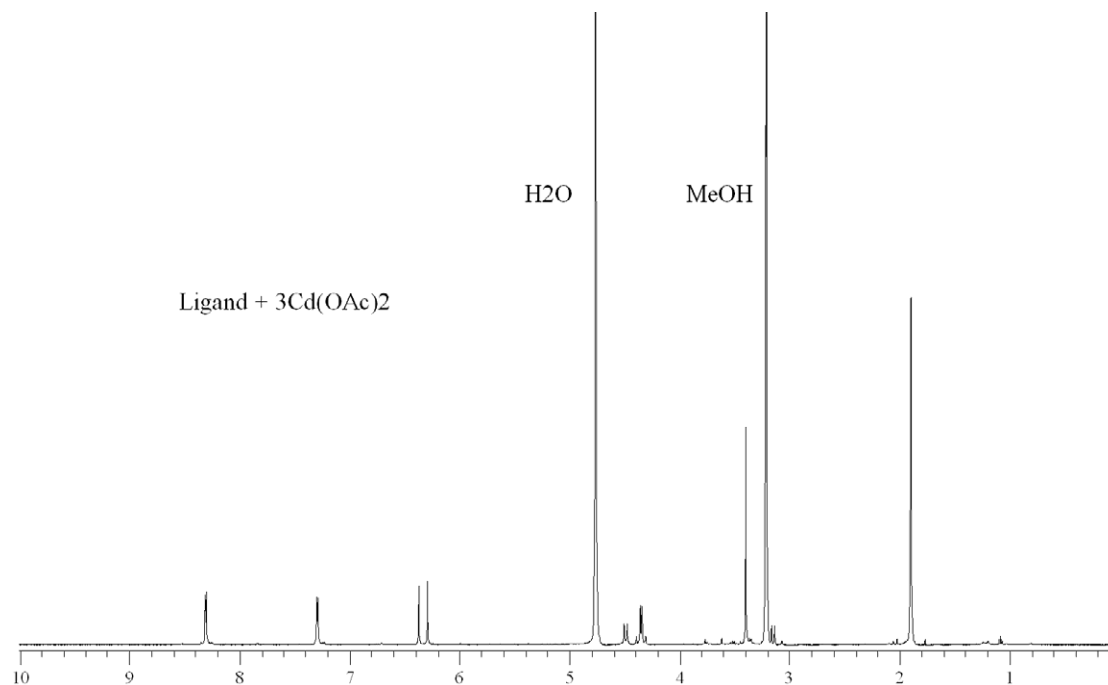
### <sup>1</sup>H NMR Ligand 1



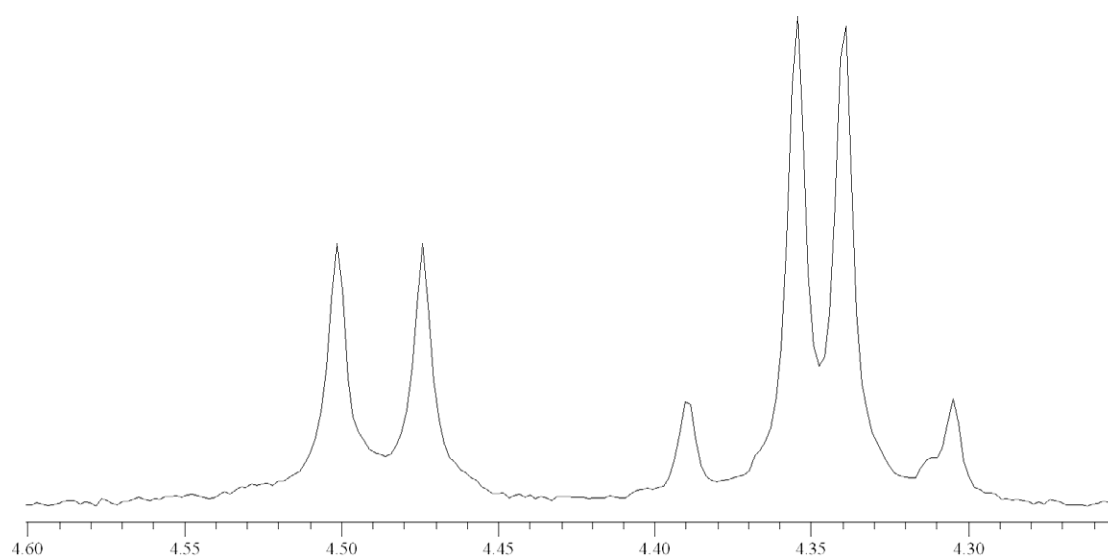
### Expansion in region 4.25-4.6 ppm



**$^1\text{H}$  NMR of mixture of  $\text{Cd}(\text{OAc})_2:1$  in 3:1 ratio**

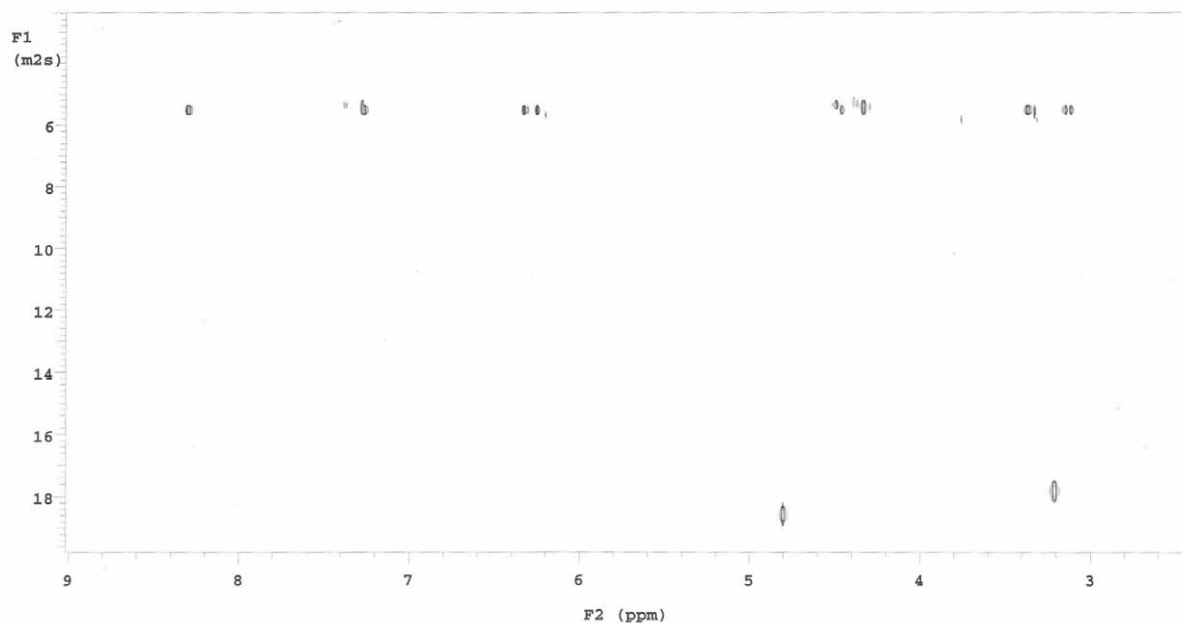


**Expansion in region 4.25-4.6 ppm**



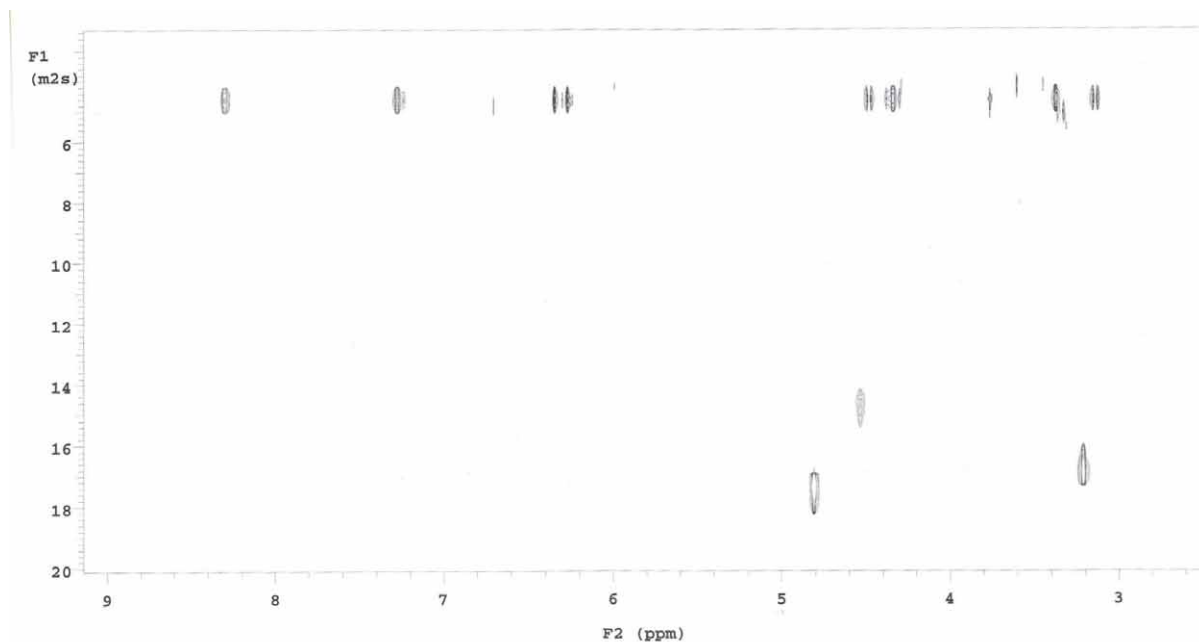
**DOSY NMR measurements:** Diffusion data were recorded for samples with concentrations of 4 mM of ligand **1** and 3 equivalents of Cd(OAc)<sub>2</sub>. DOSY NMR measurements were made on a Varian Inova 500 MHz spectrometer operating under regulated temperature conditions (20 °C), with a 5 mm probe. The pulse sequence employed was a bipolar pulse pair simulated echo (BPPSTE) operating in the ONESHOT experiment. Experiments included a number of transients ranging from 16-32, diffusion delays ranged from 0.02 – 0.04s, gradient length 0.002 -0.0025 s, collected in 32k of complex points and Fourier transformed into 64k following application of a 1Hz line broadening. Spectra were phased and baseline corrected prior to generation of the DOSY plots.

Diffusion coefficient for ligand **1** averaged across all signals =  $5.5 \times 10^{-10} \text{m}^2 \cdot \text{s}^{-1}$ . DOSY spectrum for ligand **1** shown below:



Diffusion coefficient for ligand **1** and 3 equivalents Cd(OAc)<sub>2</sub> averaged across all signals =  $4.6 \times 10^{-10} \text{m}^2 \cdot \text{s}^{-1}$ . DOSY spectrum shown below:



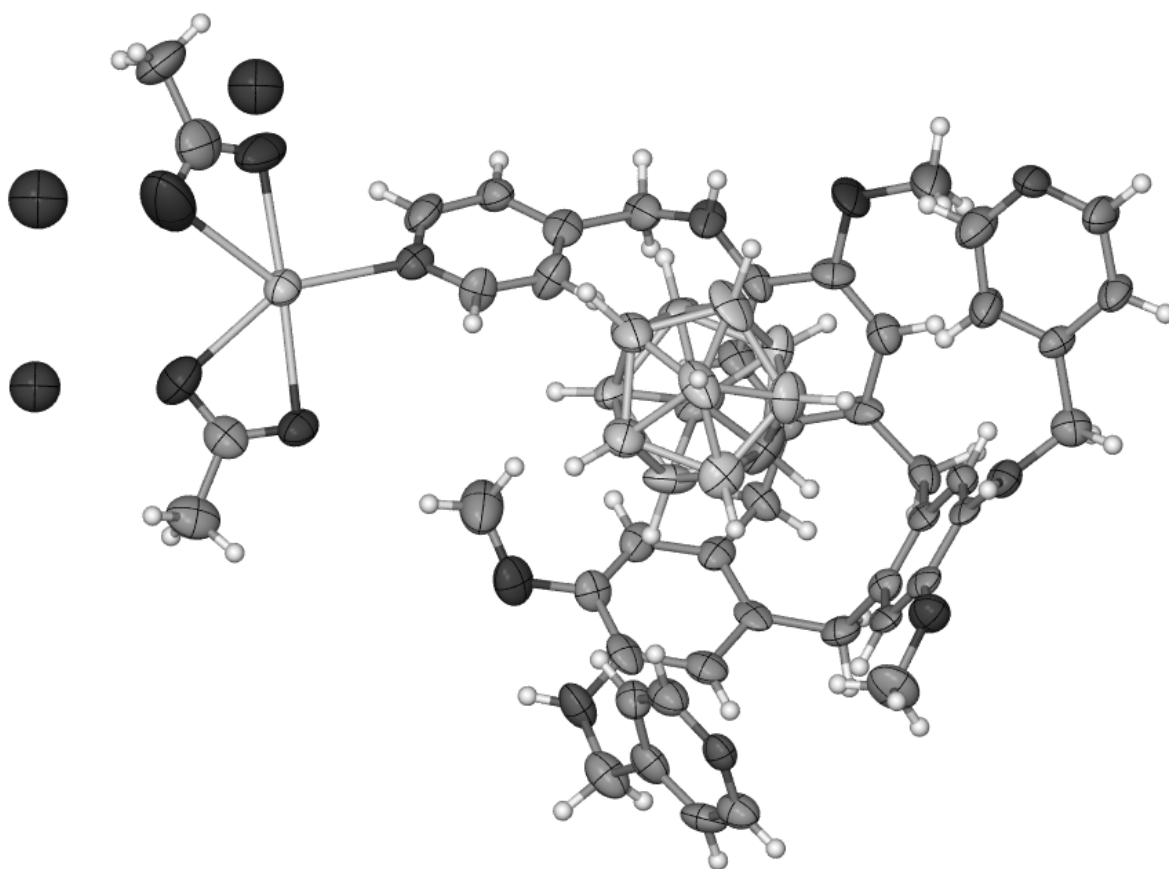


Acetate has a diffusion coefficient of 7.0 in the complex and  $23.8 \times 10^{-10} \text{m}^2 \cdot \text{s}^{-1}$  free in methanol, which is a clear indication that the acetate is complexed. The diffusion coefficient is an average of that for the free and bound acetate and thus suggests that there is slightly more metal acetate in solution than the 1:3 ratio quoted.

### 3. X-Ray crystallography

A single crystal of complex **2** was mounted on a glass fibre under oil and X-ray diffraction data were collected at 150(1) K on a Bruker X8 diffractometer fitted with an APEX II detector using a rotating anode Mo source ( $\lambda = 0.71073 \text{ \AA}$ ). Data were corrected for Lorentz and polarization effects and absorption corrections were applied using multi-scan methods. The structures were solved by direct methods using *SHELXS-97*<sup>2</sup> and refined by full-matrix least-squares on  $F^2$  using *SHELXL-97*,<sup>3</sup> using the *X-Seed* GUI.<sup>4</sup> Crystals were only weakly diffracting and did not give any high angle data and the data was cut off at a  $2\theta$  of  $45^\circ$  during refinement. All non-hydrogen atoms were refined anisotropically aside from waters of hydration and hydrogen atoms were included at geometrically estimated positions, aside from those of water molecules which were excluded from the refinement. C positions within the carborane were assigned by an analysis of bond lengths and anisotropic thermal parameters.

An ORTEP diagram of the asymmetric unit with ellipsoids shown at 50% probability levels is shown below:



1. C. J. Sumby, J. Fisher, T. J. Prior and M. J. Hardie, *Chem. Eur. J.*, **2006**, *12*, 2945.
2. G. M. Sheldrick, SHELXS-97, University of Göttingen, Germany, **1990**.
3. G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany, **1997**.
4. L. J. Barbour, *J. Supramol. Chem.* **2001**, *1*, 189.