Electronic Supplementary Material for CrystEngComm


Supplementary Information

# "Flattened trigonal bipyramidal coordination assembly with *trans* geometry"

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## General Experimental

Ligand N,N',N''-tris(6-methyl-2-pyridyl)benzene-1,3,5-tricarboxamide was synthesised by literature methods.[1] Other chemicals were obtained from commercial sources and used without further purification. Infra-red spectra were recorded as solid phase samples on a Perkin-Elmer Spectrometer. Microanalyses were performed by the University of Leeds microanalytical service.

## NMR studies

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. Additional parameters: number of different gradient levels, 15; gradient stabilisation delay, 0.002 s; gradient length, 0.002 s; diffusion delay, 0.03 s; relaxation delay, 5 s; Kappa (unbalancing factor), 0.2. An exponential function with 1 Hz line broadening was applied prior to Fourier transformation. The resulting array was phased and baseline corrected using a macro provided by Prof. Gareth Morris (Department of Chemistry, University of Manchester, UK). Standard $^{1}$H NMR spectra recorded on the same instrument were generally acquired with spectral width of 8500 Hz, in 16,384 complex data points and a relaxtion delay of 3 s. Nuclear Overhauser spectra were recorded on a Bruker DRX 500 using the noemul sequence. Sample temperature was maintained at -20 $^{0}$C throughout; this was to slow down the conversion from asymmetric to symmetric entity (this was before it was discovered that conversion occurred over a period of days at room temperature). Typically a spectral width of 7500 Hz was used in 8192 data points. The total nOe build-up time of 6 s was employed.

Sections of the standard NMR spectra of the ligand L1 and a $CDCl_3$ solution of L1 and $Pd(O_2CCH_3)_2$ are shown in Figure S1.

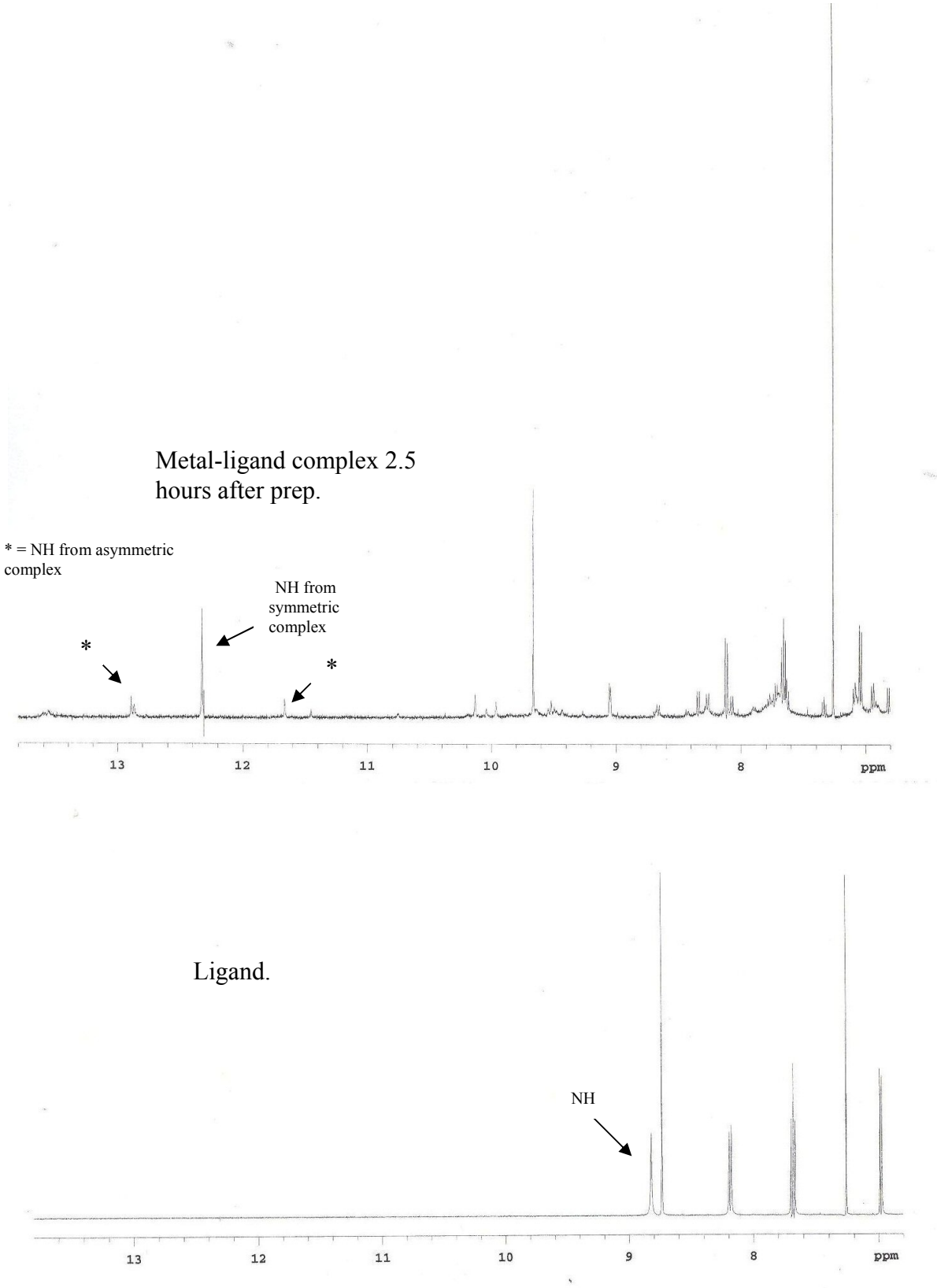



*Figure S1:Section of the $CDCl_3$ $^1H$ NMR spectra of a 2:3 mixture of ligand L1 and Pd($O_2CCH_3$)$_2$ 2.5hrs after mixing (top), and ligand L1 (bottom).*

*DOSY calibration*
Spectra were acquired in a similar manner to that described above, with diffusion delay and gradient length optimised for each sample. Solution concentrations were all 5 mM.

| Name | Molecular weight | Diffusion coefficient (x $10^{10}$)$m^2s^{-1}$ |
|---|---|---|
| Hexakis(2-pyridylmethyl)cyclotriveratrylene | 913.11 | 8.703 |
| Tris(4-[2-pyridyl]benzyloxy) cyclotriguaiacylene | 910.14 | 9.037 |
| Tris(4-[2,2',6',2"-terpyridyl]benzyl)cyclotriguaiacylene | 323.4 | 10.197 |
| Benzene-1, 3, 5-tricarboxylic acid tris(6-methyl-2-pyridinyl) amide | 480.0 | 11.503 |
| Dipyridyl | 184.24 | 13.573 |
| 4-aminopyrimidine | 95.11 | 17.821 |

**Diffusion coefficients (x $10^{10}$)$m^2s^{-1}$ of;**

Ligand L1 – 11.5

Asymmetric species – 7.0

Symmetric species – 7.5

**Mass spectrometry studies**

Electrospray (ES) mass spectra were measured on a Bruker MicroTOF-Q instrument in positive ion mode. The spectra obtained for $CHCl_3$ solutions of ligand L1 and $Pd(O_2CCH_3)_2$ in 2:3 and 1:5 proportions are shown in Figures S2 and S3 respectively.

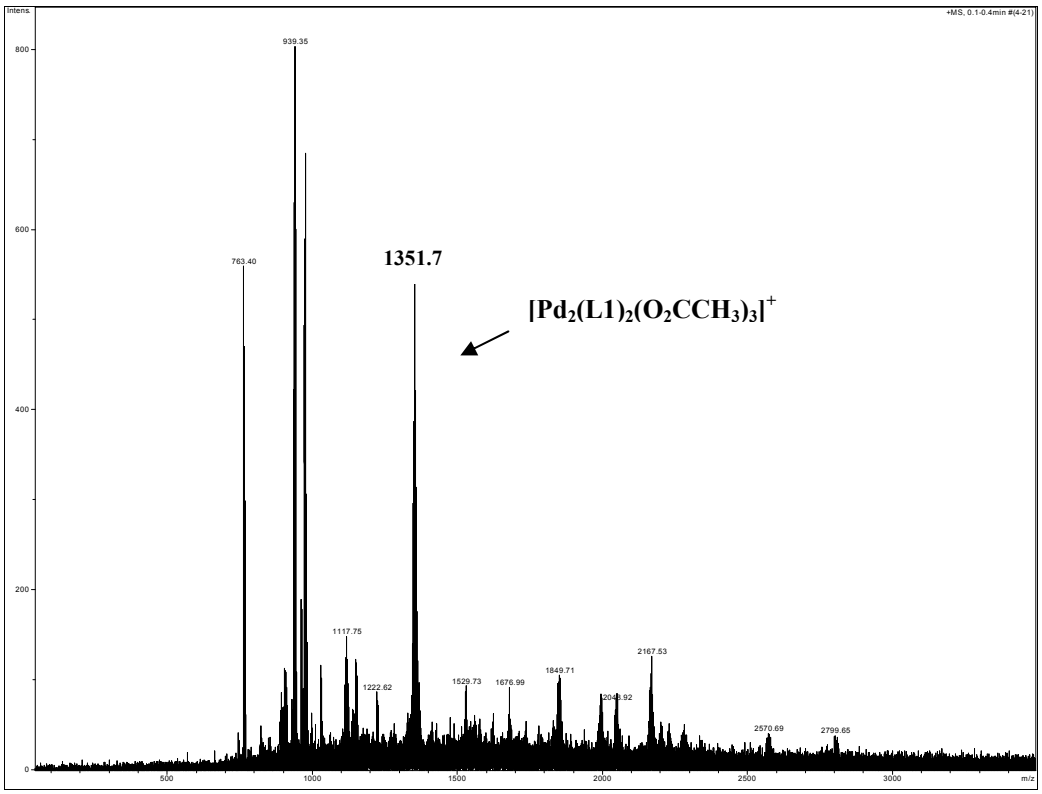



*Figure S2: Mass spectrum of a $CHCl_3$ solution of ligand L1 and $Pd(O_2CCH_3)_2$ in 2:3 proportions.*

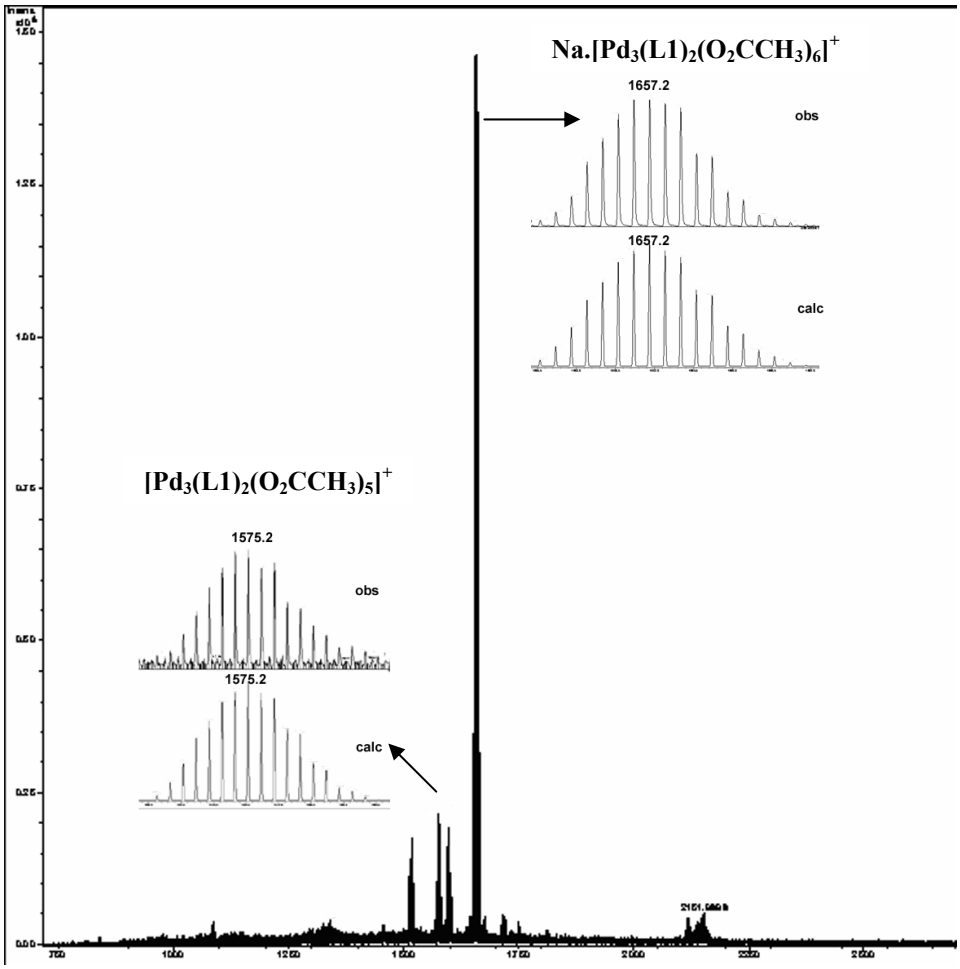


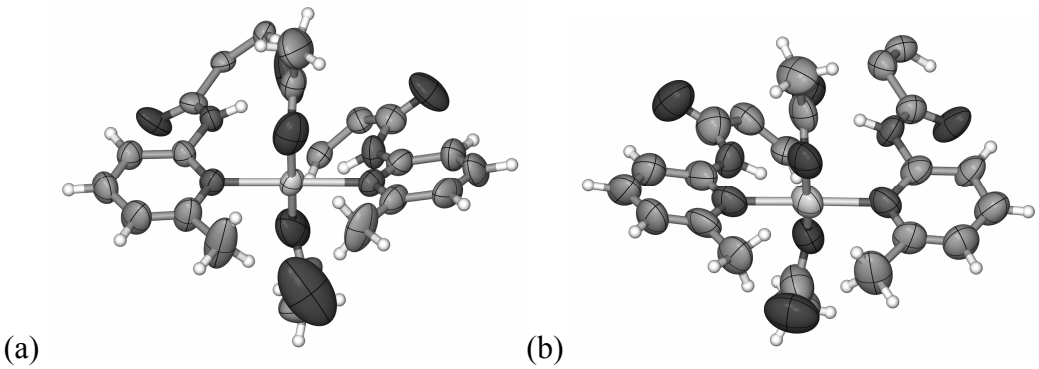

*Figure S3: Mass spectrum of a $CHCl_3$ solution of ligand L1 and $Pd(O_2CCH_3)_2$ in 1:5 proportions.*

**Synthesis of single crystals of [$Pd_3$(N,N',N''-tris(6-methyl-2-pyridyl)benzene-1,3,5-tricarboxamide)$_2$($O_2CCH_3$)$_6$] 1** A solution of benzene-1,3,5-tricarboxylic acid tris-[(6-methyl-pyridin-2-yl)-amide] (10 mg, 21 μmol) in trifluoroethanol (6 mL) was added to a solution of $Pd(OAc)_2$ (4.7 mg, 21μmol) in methanol (1 mL) in a glass vial giving a pale yellow suspension. The solution was allowed to evaporate slowly through pin holes in the cap of the vial, and gave crystals suitable for X-ray structure determination after eight months. Yield: 8.26 mg, 24 %; CHN Anal. With sample dried under vacuum prior to analysis: (Found: C, 46.75; H, 3.80; N, 10.05. Calc. for $Pd_3C_{54}H_{48}O_6N_{12}.2.5H_2O(O_2CCH_3)_6$: C, 47.19; H, 4.27; N, 10.01 %); IR (solid state): $\upsilon_{max}$ = 622, 695, 792, 949, 1049, 1109, 1152, 1175, 1238, 1258, 1305, 1393, 1471, 1526, 1592, 1694, 1899, 2001, 2022, 2136, 2148, 2331, 2353, 3324 $cm^{-1}$.

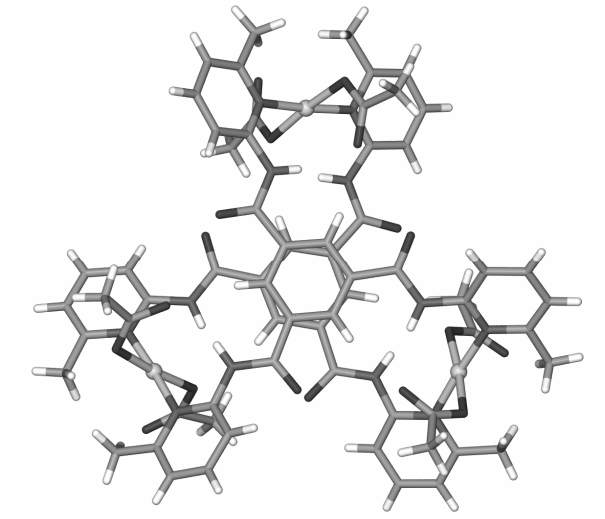
**Crystallographic procedures:**

Crystals were mounted under oil or grease onto a glass fibre and X-ray data collected at low temperature on a Bruker X8 Apex II diffractometer with Mo-$K\alpha$ radiation ($\lambda$ = 0.71073 Å). A crystal of **1** was mounted directly from the mother liquor, whereas **1a** were dried under vacuum at 100 ºC for 24 hours before being cooled and exposed to the atmosphere prior to mounting. Data were corrected for Lorentz and polarisation effects, and absorption corrections applied using a multi-scan method (SADABS). Structures were solved by direct methods using SHELXS-97 [2] and refined by full-matrix least squares on $F^2$ by SHELXL-97 [3] via the X-Seed GUI.[4] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as invariants at geometrically estimated positions. The asymmetric unit for both structure determinations and molecular species for **1a** are shown in Figure S4.

**Crystal data for complex 1a**: $C_{66}H_{66}N_{12}O_{18}Pd_3$, $Mr$ = 1634.51, trigonal, $a$ = 22.6400(11), $c$ = 19.219(3) Å, $V$ = 8531.2(15) Å$^3$, space group $P$-31c, $Z$ = 4, $\rho_{calc}$ = 1.273 g.cm$^{-3}$, $\mu$ = 0.689 mm$^{-1}$, $\theta_{max}$ = 23.25 º, 62587 data collected, 4080 unique, $R_{int}$ = 0.1100, 302 parameters, $R_1$ = 0.1046 (for 2224 data $I > 2\sigma(I)$), $wR_2$ = 0.3427 (all data), $S$ = 1.142, max. residual e-density = 1.192 e Å$^3$ .



(a) (b)



(c)

*Figure S4. Asymmetric units of the crystal structures of (a) complex **1**; (b) complex **1a**. Ellipsoids are shown at 50% probability levels. (c) [$Pd_3(L1)_2(OAc)_6$] complex **1a**.*

[1] B. Koenig, O. Moeller, P. Bubenitschek and P. G. Jones, *J. Org. Chem.*, 1995, **60**, 4291

[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.

[5] A. Spek, P. can der Sluis, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1990**, 46, 194.