

## Supplementary X-ray Crystallographic Information For Dalton

### B711879A

#### [*Fac*-(Me)<sub>5</sub>-D<sub>3h</sub>tricosaneN<sub>6</sub>-2H](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>

A colourless crystal with dimensions 0.20 x 0.24 x 0.21 mm was mounted on a Philips PW-1100/20 diffractometer for data collection at T = 298 K using graphite monochromated Cu-K $\alpha$  radiation,  $\lambda = 1.5418 \text{ \AA}$ . Lattice parameters were obtained by least-squares refinement of the setting angles of 25 reflections with  $60 < 2\theta < 72^\circ$ .

#### *Crystal data and data collection*

C<sub>24</sub>H<sub>50</sub>F<sub>6</sub>N<sub>6</sub>O<sub>6</sub>S<sub>2</sub>,  $M = 696.81$ . Monoclinic, space group  $P2_1/n$ ,  $a = 10.713(1)$ ,  $b = 13.768(1)$ ,  $c = 23.554(1) \text{ \AA}$ ,  $U = 3473.4 \text{ \AA}^3$ ,  $Z = 4$ ,  $D_c = 1.332 \text{ g cm}^{-3}$ .  $F(000) = 1480$ ,  $\mu(\text{Cu-K}\alpha) = 20.4 \text{ cm}^{-1}$ . Data to  $2\theta = 120^\circ$  were collected using  $\theta$ - $2\theta$  scans of width  $(0.9 + 0.142 \tan\theta)^\circ$  in  $\theta$  at a rate of  $2^\circ \text{ min}^{-1}$  in  $\theta$  with 7s background counts on each side. The data consisted of 5165 unique reflections of the type  $-12 \leq h \leq 12$ ,  $-15 \leq k \leq 0$ ,  $0 \leq l \leq 26$ , 3448 with  $I > 3\sigma(I)$ . Three check reflections measured every 120 min showed an 11% intensity decrease over the total data collection and a decomposition correction was applied to all data,<sup>16</sup> which were also corrected for absorption (transmission factors 0.68 – 0.74).

#### *Structure solution and refinement*

The structure was solved by direct methods<sup>17</sup> and  $\Delta F$  techniques, and refined on  $F$  by full-matrix least-squares, using anisotropic displacement factors for all non-hydrogen atoms except those in the disordered parts of one CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> anion. Hydrogen atoms attached to carbon atoms were included at calculated positions, and 7 of the 8 amine hydrogen atoms were located in an electron density difference map, but their parameters were not refined. The refinement involved 385 variables and converged at  $R = 0.092$ ,  $R_w = 0.131$ , GOF = 3.23 (see footnote<sup>||</sup> for definitions), with maximum  $\Delta/\sigma$

= 0.07 and maximum  $\Delta\rho = 0.68 \text{ e}\text{\AA}^{-3}$  in the disordered  $\text{CF}_3\text{SO}_3^-$  region. The final weighting scheme was  $w^{-1} = \sigma^2(F) + 0.0009F^2$ . Atomic scattering factors for neutral atoms, as well as  $f$  and  $f'$ , were taken from International Tables for X-ray crystallography.<sup>18</sup> Data reduction and refinement computations were performed with XTAL 3.0.<sup>19</sup> Tables of final atomic coordinates, anisotropic displacement parameters, interatomic distances and angles, torsion angles and least-squares planes have been deposited as supplementary material.

***[Cd(fac-(Me)<sub>5</sub>-D<sub>3h</sub>tricosaneN<sub>6</sub>)](PF<sub>6</sub>)<sub>2</sub>.3H<sub>2</sub>O***

A cross section with dimensions 0.26 x 0.17 x 0.18 mm was cleaved from a large colourless needle in a representative sample of  $[\text{CdL}^2](\text{PF}_6)_2 \cdot (2-3 \text{ H}_2\text{O})$  crystals. It was mounted on a quartz fibre attached to a Phillips PW-1100/20 diffractometer equipped with a graphite monochromator, and data were collected using Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at  $T = 293 \text{ K}$ . Lattice parameters were determined by least-squares refinement on the  $2\theta$  values of 25 centred reflections with  $76 < 2\theta < 84^\circ$ .

*Crystal data and data collection.*

$\text{C}_{22}\text{H}_{54}\text{CdF}_{12}\text{N}_6\text{O}_3\text{P}_2$ ,  $M = 853.05$ . Orthorhombic, space group  $Pnma$ ,  $a = 19.692(2)$ ,  $b = 16.616(2)$ ,  $c = 11.137(1) \text{ \AA}$ ,  $U = 3644.1(7) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_c = 1.555 \text{ g cm}^{-3}$ .  $F(000) = 1752$ ,  $\mu(\text{Cu-K}\alpha) = 66.5 \text{ cm}^{-1}$ . Intensity data for 3135 unique  $h.k.l$  reflections ( $0 \leq h \leq 22$ ,  $0 \leq k \leq 19$ ,  $-12 \leq l \leq 0$ ), 2592 with  $I > 3\sigma(I)$ , were collected using  $\theta$ - $2\theta$  scans in the range  $4 < 2\theta < 128^\circ$ . Scan widths were  $(1.0 + 0.142 \tan \theta)^\circ$  in  $\theta$  and the scan rate was  $1.5^\circ \text{ min}^{-1}$  in  $\theta$  with 10 s background counts on each side of a scan. Three standard reflections measured every 90 min showed an 18% decrease in intensity over the data collection period, and a decomposition correction<sup>16</sup> was applied to all data. Intensities were also corrected for absorption (transmission factors 0.449 – 0.352).

Unit cell dimensions changed significantly during the data acquisition and the values quoted are those found for the crystal at commencement.

*Structure solution and refinement.*

The structure was solved in space group *Pnma* by Patterson and difference Fourier techniques.<sup>17</sup> All non-hydrogen atoms in the cation were clearly defined, with a crystallographic mirror plane passing horizontally through the metal atom. Examination of an electron density map implied that the disordered PF<sub>6</sub><sup>-</sup> anion could assume either of two orientations, each of population *ca.* 0.5. Also a water molecule of population *ca.* 0.5 was located just 1.7 Å from a fluorine atom site (F(13)) in one orientation of the PF<sub>6</sub><sup>-</sup> ion. It is therefore likely that PF<sub>6</sub><sup>-</sup> has the second orientation when this water molecule is present, but adopts the first orientation when it is absent. Waser-type restraints<sup>20,21</sup> were imposed on bonds and angles within each orientation of the PF<sub>6</sub><sup>-</sup> group in least-squares refinement. Most of the cation hydrogen atoms were observed in an electron density difference map, but were included at calculated positions (C-H 0.95, N-H 0.85 Å, methyl H atoms staggered relative to vicinal groups) and not refined. A possibility remains that the true space group is *Pn2<sub>1</sub>a* (non-standard setting of *Pna2<sub>1</sub>*) with removal of the crystallographic mirror plane at *y* = 0.25, which potentially allows ordering of the anions and the water oxygen atom (O(2)). However, the cation was successfully refined in *Pnma* to give reasonable displacement parameters, bond lengths and angles for all non-hydrogen atoms and the present procedure has also allowed the observation of the hydrogen atoms. Therefore any refinement in the non-centrosymmetric space group would be highly correlated and the centro-symmetric *Pnma* space group has been retained as the better model for the present data set.

The structure (212 variables) was refined on  $F$  by full-matrix least-squares methods,<sup>19</sup> using anisotropic displacement parameters for all cation non-hydrogen atoms and 2592 data with  $I > 3\sigma(I)$ . Convergence occurred at  $R = 0.071$ ,  $R_w = 0.101$ . GOF = 3.64 with maximum  $\Delta/\sigma < 0.08$ , maximum  $\Delta\rho = 0.8 \text{ e}\text{\AA}^{-3}$  near the orientationally disordered anion and  $w^{-1} = \sigma^2(F) + 0.0004F^2$ . International Tables for X-ray crystallography<sup>18</sup> was the source of all atomic scattering factors (including  $f'$ ,  $f''$ ). Deposited material comprises tables of final atomic coordinates (including calculated hydrogen atom coordinates), anisotropic displacement parameters, interatomic distances and angles, dihedral angles and least-squares planes data.

***[Hg(fac-(Me)<sub>5</sub>-D<sub>3h</sub>tricosaneN<sub>6</sub>)](PF<sub>6</sub>)<sub>2</sub>.2.8H<sub>2</sub>O***

A colourless crystal with dimensions 0.30 x 0.22 x 0.13 mm was chosen for data collection at  $T = 293 \text{ K}$  on a Phillips PW-1100/20 diffractometer using graphite monochromated Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) from a rotating anode source. The setting angles of 25 centred reflections ( $29 < 2\theta < 38^\circ$ ) were used to determine the unit cell dimensions by least-squares refinement. As with the isomorphous cadmium(II) structure these parameters changed significantly during data collection but more rapidly. In order to improve the accuracy of structural results (at the cost of some precision), the data for the [HgL<sup>2</sup>](PF<sub>6</sub>)<sub>2</sub>.2.8H<sub>2</sub>O crystal were obtained using much higher scan rates and the lattice parameters used in the structure analysis are the averaged values over the data acquisition period of less than 5 hours. The e.s.d.s therefore reflect the spread on this time scale rather than the precision of the individual measurements.

*Crystal data and data collection.*

$\text{C}_{22}\text{H}_{53.6}\text{F}_{12}\text{HgN}_6\text{O}_{2.8}\text{P}_2$ ,  $M = 937.62$ . Orthorhombic, space group  $Pnma$ ,  $a = 19.76(5)$ ,  $b = 16.50(3)$ ,  $c = 11.03(2) \text{ \AA}$ ,  $U = 3595(13) \text{ \AA}^3$  (initial values),  $Z = 4$ ,  $D_c = 1.732 \text{ g}$

$\text{cm}^{-3}$ .  $F(000) = 1872$ ,  $\mu(\text{Cu-K}\alpha) = 89.3 \text{ cm}^{-1}$ . Intensity data were collected using  $\omega$ - $2\theta$  scans to  $2\theta = 100^\circ$  for 1925 unique  $h.k.l$  reflections ( $0 \leq h \leq 19$ ,  $0 \leq k \leq 16$ ,  $0 \leq l \leq 10$ ), 1492 with  $I > 3\sigma(I)$ . Scan widths were  $(1.0 + 0.34 \tan \theta)^\circ$  in  $\omega$  and the scan rate was  $20^\circ \text{ min}^{-1}$  in  $\omega$  (with 2 s background counts on each side of a scan), which is more than 12 fold faster than the corresponding rate for the isomorphous  $[\text{CdL}^2](\text{PF}_6)_2 \cdot 3\text{H}_2\text{O}$  crystal. Of the three standard reflections measured every 45 min, two showed an 11% decrease in intensity, but the third increased by 10% during the data collection period. It seemed likely that these variations arose from the slower early stages of a major phase change that occurred after about 10 h. No decay correction was applied but lattice parameters were re-determined 12 times during the data acquisition ( $< 5$  h.). The averaged lattice parameters ( $a = 19.76(5)$ ,  $b = 16.50(3)$ ,  $c = 11.03(2) \text{ \AA}$ ,  $U = 3595 \text{ \AA}^3$ ) were used in the structure solution and refinement computations. The intensity data were corrected for absorption effects (transmission factors 0.288 – 0.471).

#### *Structure solution and refinement*

The structure was isomorphous with that of the analogous cadmium(II) compound, and was also solved and refined in space group  $Pnma$  by similar methods.<sup>17,19</sup> In particular, the least-squares refinement of the two site disordered  $\text{PF}_6^-$  anion and the water molecule with partial occupancy was carried out in a similar manner. Cation hydrogen atoms were sited at periodically recalculated positions (assuming pseudo-tetrahedral carbon and nitrogen atoms), and their parameters were not refined. In this structure, the mercury, nitrogen, methyl carbon and full occupancy oxygen atoms were all refined using anisotropic displacement parameters, whereas isotropic parameters were used for the remaining atoms. The refinement involved 157 variables and 1492 data with  $I > 3\sigma(I)$ , and converged at  $R = 0.067$ ,  $R_w =$

0.090, GOF = 2.06 with maximum  $\Delta/\sigma = 0.09$ , maximum  $\Delta\rho = 1.82(5) \text{ e}\text{\AA}^{-3}$  (near Hg) and weighting scheme  $w^{-1} = \sigma^2(F) + 0.0009F^2$ . The need to refine the  $D_{3h}$ tricosaneN<sub>6</sub> core carbon atoms isotropically was most likely due to the relatively poor precision of the lighter atom parameters in this structure. Several factors may contribute, including the dominance of the Hg scattering centre, the rapid scan rate and the small but observable lattice changes which occurred during the data collection. Data collection at a lower temperature using a slower scan rate may help to reduce contributions from the latter two effects, but not the first. However, the data obtained here were adequate to establish the configuration of the  $[\text{Hg}(\text{fac}-(\text{Me})_5\text{-}D_{3h}\text{tricosaneN}_6)]^{2+}$  ion in the crystal, and to gauge the Hg<sup>II</sup>-N(amine) bond distance relative to those found in other reported Hg<sup>II</sup>N<sub>6</sub>(amine) type structures.<sup>14,22</sup> Tables of final atomic coordinates, anisotropic displacement parameters and bond lengths and angles have been deposited as supplementary information.

**Table 1** Bond lengths (Å) and angles (°) for [CdL<sup>2</sup>] in [CdL<sup>2</sup>](PF<sub>6</sub>)<sub>2</sub>·3H<sub>2</sub>O<sup>a</sup>

Cd-N(12)	2.386(7)	N(12)-C(13)	1.46(1)
Cd-N(22)	2.400(7)	N(22)-C(23)	1.48(1)
Cd-N(32)	2.397(7)	N(32)-C(33)	1.47(1)
C(1)-C(2)	1.55(1)	C(13)-C(14)	1.52(1)
C(2)-C(11)	1.52(2)	C(23)-C(24)	1.51(1)
C(2)-C(21)	1.54(1)	C(33)-C(34)	1.52(2)
C(2)-C(31)	1.53(1)	C(14)-C(14A)	1.54(3)
C(11)-N(12)	1.47(1)	C(24)-C(24A)	1.53(2)
C(21)-N(22)	1.50(1)	C(34)-C(34A)	1.54(2)
C(31)-N(32)	1.50(1)		
N(12)-Cd-N(12)'	82.8(2)	Cd-N(12)-C(11)	115.0(6)
N(22)-Cd-N(22)'	81.6(2)	Cd-N(22)-C(21)	115.0(5)
N(32)-Cd-N(32)'	82.8(3)	Cd-N(32)-C(31)	114.2(6)
N(12)-Cd-N(22)	83.1(2)	Cd-N(12)-C(13)	121.2(6)
N(12)-Cd-N(32)	80.9(3)	Cd-N(22)-C(23)	121.1(5)
N(22)-Cd-N(32)	79.9(2)	Cd-N(32)-C(33)	121.0(6)
N(12)-Cd-N(22)'	138.1(3)	C(11)-N(12)-C(13)	108.3(8)
N(12)-Cd-N(32)'	135.7(2)	C(21)-N(22)-C(23)	108.2(7)
N(22)-Cd-N(32)'	133.6(2)	C(31)-N(32)-C(33)	108.6(8)
C(1)-C(2)-C(11)	108.2(9)	N(12)-C(13)-C(14)	115.5(10)
C(1)-C(2)-C(21)	106.2(8)	N(22)-C(23)-C(24)	114.9(8)
C(1)-C(2)-C(31)	104.5(9)	N(32)-C(33)-C(34)	115.1(9)
C(11)-C(2)-C(21)	113.2(8)	C(13)-C(14)-	106.8(9)
C(11)-C(2)-C(31)	112.4(9)	C(23)-C(24)-	109.0(7)
C(21)-C(2)-C(31)	111.8(9)	C(33)-C(34)-	108.7(8)
C(2)-C(11)-N(12)	115.6(8)	C(13)-C(14)-	111.7(12)
C(2)-C(21)-N(22)	116.1(8)	C(23)-C(24)-	113.3(9)
C(2)-C(31)-N(32)	115.5(8)	C(33)-C(34)-	112.9(11)

<sup>a</sup> Primes indicate atoms generated by the symmetry operation (x, 0.5-y, z).

**Table 2** Bond lengths (Å) and angles (°) for [HgL<sup>2</sup>] in [HgL<sup>2</sup>](PF<sub>6</sub>)<sub>2</sub>.3H<sub>2</sub>O<sup>a</sup>

Hg-N(12)	2.39(2)	N(12)-C(13)	1.46(3)
Hg-N(22)	2.41(1)	N(22)-C(23)	1.46(2)
Hg-N(32)	2.43(1)	N(32)-C(33)	1.49(3)
C(1)-C(2)	1.57(1)	C(13)-C(14)	1.52(3)
C(2)-C(11)	1.52(3)	C(23)-C(24)	1.49(2)
C(2)-C(21)	1.52(3)	C(33)-C(34)	1.48(3)
C(2)-C(31)	1.55(3)	C(14)-C(14A)	1.57(5)
C(11)-N(12)	1.47(3)	C(24)-C(24A)	1.52(4)
C(21)-N(22)	1.49(2)	C(34)-C(34A)	1.55(5)
C(31)-N(32)	1.53(3)		
N(12)-Hg-N(12)'	83.7(5)	Hg-N(12)-C(11)	115(1)
N(22)-Hg-N(22)'	81.8(5)	Hg-N(22)-C(21)	115(1)
N(32)-Hg-N(32)'	81.5(5)	Hg-N(32)-C(31)	111(1)
N(12)-Hg-N(22)	83.0(5)	Hg-N(12)-C(13)	120(1)
N(12)-Hg-N(32)	81.4(5)	Hg-N(22)-C(23)	120(1)
N(22)-Hg-N(32)	79.6(5)	Hg-N(32)-C(33)	120(1)
N(12)-Hg-N(22)'	138.7(5)	C(11)-N(12)-C(13)	108(1)
N(12)-Hg-N(32)'	136.1(5)	C(21)-N(22)-C(23)	108(1)
N(22)-Hg-N(32)'	132.4(5)	C(31)-N(32)-C(33)	109(1)
C(1)-C(2)-C(11)	107(2)	N(12)-C(13)-C(14)	116(2)
C(1)-C(2)-C(21)	108(2)	N(22)-C(23)-C(24)	115(2)
C(1)-C(2)-C(31)	104(2)	N(32)-C(33)-C(34)	113(2)
C(11)-C(2)-C(21)	114(2)	C(13)-C(14)-	107(2)
C(11)-C(2)-C(31)	111(2)	C(23)-C(24)-	108(1)
C(21)-C(2)-C(31)	112(1)	C(33)-C(34)-	108(2)
C(2)-C(11)-N(12)	115(2)	C(13)-C(14)-	110(2)
C(2)-C(21)-N(22)	116(2)	C(23)-C(24)-	115(2)
C(2)-C(31)-N(32)	116(2)	C(33)-C(34)-	116(2)

<sup>a</sup> Primes indicate atoms generated by the symmetry operation ( $x, 0.5-y, z$ ).