Table 2. *Dihedral angles*

	L-Leucine molecule 1 ($n=0$)	L-Leucine molecule 2 ($n=10$)	L-Leucine in DL-leucine*
$O(n+1)-C(n+1)-C(n+2)-C(n+3)$	92	82	84
$O(n+1)-C(n+1)-C(n+2)-N(n+1)$	−26	−36	−36
$C(n+1)-C(n+2)-C(n+3)-C(n+4)$	68	74	71
$C(n+2)-C(n+3)-C(n+4)-C(n+5)$	−172	−167	−162
$C(n+2)-C(n+3)-C(n+4)-C(n+6)$	69	63	76

* Values calculated from atom coordinates of Di Blasio *et al.* (1975) after interchanging their O(1) and O(2).

Hydrogen bonds hold the carboxyl and amino groups together in double layers while the non-polar groups lie alongside each other. The whole structure is very similar to L-isoleucine (Torii & Iitaka, 1971). In fact the structures of many amino-acids with non-polar side chains have this same arrangement of a double layer of carboxyl and amino groups; for L-valine (Torii & Iitaka, 1970), L-methionine (Torii & Iitaka, 1973), L-cysteine (Harding & Long, 1968) and L-leucine and L-isoleucine, the atom positions within the double layer are the same, within ~0·25 Å; there are two molecules per asymmetric unit, in space group $P2_1$, with $a=9·6\pm0·1$ Å and $b=5·2\pm0·1$ Å; c and β vary according to the size and packing of the side chains, and are tabulated by Torii & Iitaka (1971). Here we have used the unconventional choice, $\beta<90°$, for L-leucine because this makes the atom coordinates directly comparable with those in the other structures. (In L-cysteine the published a and c must be interchanged.)

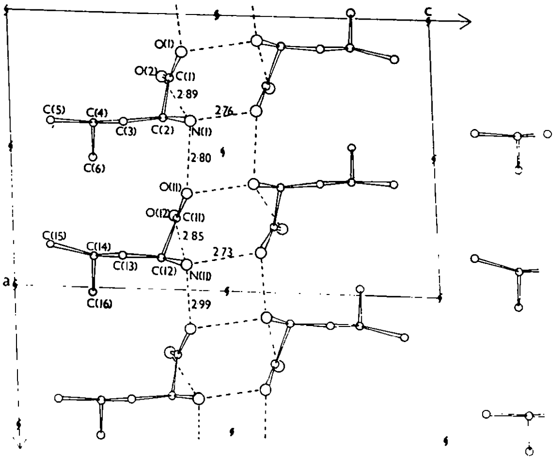

Fig. 1. Projection of the structure looking down the *b* axis. Comparison of this with Fig. 3 of Torii & Iitaka (1971) shows the very close similarity to L-isoleucine.

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References

Di Blasio, B., Pedone, C. & Sirigu, A. (1975). *Acta Cryst.* **B31**, 601–602.

Harding, M. M. & Long, H. A. (1968). *Acta Cryst.* **B24**, 1096–1102.

Main, P., Woolfson, M. M. & Germain, G. (1971). *MULTAN, a Computer Program for the Automatic Solution of Crystal Structures*, Univ. of York (England).

Torii, K. & Iitaka, Y. (1970). *Acta Cryst.* **B26**, 1317–1325.

Torii, K. & Iitaka, Y. (1971). *Acta Cryst.* **B27**, 2237–2246.

Torii, K. & Iitaka, Y. (1973). *Acta Cryst.* **B29**, 2799–2807.

Stewart, J. M., Kruger, G. J., Ammon, H., Dickinson, C. H. & Hall, S. R. (1972). X-RAY 72 system. Tech. Rep. TR72-192, Computer Science Center, Univ. of Maryland, implemented for the I.B.M. 370-155 at Edinburgh Regional Computing Centre.

Acta Cryst. (1976). **B32**, 634

Tetraamminepalladium(II) Chloride Monohydrate: The Location of the Water Molecule

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Abstract. Tetragonal, apparently $P4/mbm$, $a=10·337$ (1), $c=4·2707$ (6) Å, $Pd(NH_3)_4Cl_2.H_2O$, $Z=2$, $D_c=1·917$ g cm^{-3}. The structure is confirmed as previously described, except that the water molecule appears to be disordered over positions in the vicinity of $(0,\frac{1}{2},\pm\frac{1}{4})$.

Introduction. Crystals were grown as colourless tetragonal needles, which quickly discolour on exposure and continue to darken until they have obviously decomposed. They could be stabilized by sealing, either in a capillary or by spraying with varnish. During data collection monitor reflexions showed no change in intensity. Data were collected using a Hilger–Watts automated diffractometer, with Mo $K\alpha$ radiation, from a crystal of dimensions 0·05 × 0·07 × 0·14 mm. The diffraction symmetry was $4/mmm$. Reflexions were scanned for positive h,k,l to $\theta_{\max}$ of 29°, and the 248 unique observed data were corrected for absorption. Systematic absences were in $0kl$ with k odd; space group $P4/mbm$ was initially assumed. The structure was confirmed from heavy-atom phased electron density syntheses as being that described by Dickinson (1934), except that no obvious peak appeared corresponding to the water molecule.

The palladium, chlorine and nitrogen coordinates were refined by full-matrix least squares, minimizing $\sum w(F_o-F_c)^2$ where w was calculated assuming that $\sigma(I)=[\sigma^2(c)+(0{\cdot}04I)^2]^{1/2}$, $\sigma^2(c)$ being the variance based on counting statistics. Anisotropic thermal motion was assumed and real and imaginary dispersion terms for Pd were included; R converged at 0·065. The dominant feature on a difference synthesis at this stage was an extensive diffuse peak, centred near $0,\frac{1}{2},\frac{1}{4}$, with a maximum density of only 2·0 e Å^{-3}. In $P4/mbm$ this position is of twice the multiplicity that would correspond to a monohydrate. A half-weighted oxygen was introduced at this position, and refinement continued assuming an isotropic thermal parameter for this atom. Although the temperature factor assumed the very high value of 19·0 Å^2, the R index reduced to 0·058, the decrease being highly significant ($\alpha<0{\cdot}005$) for 4 additional parameters (Hamilton, 1965).

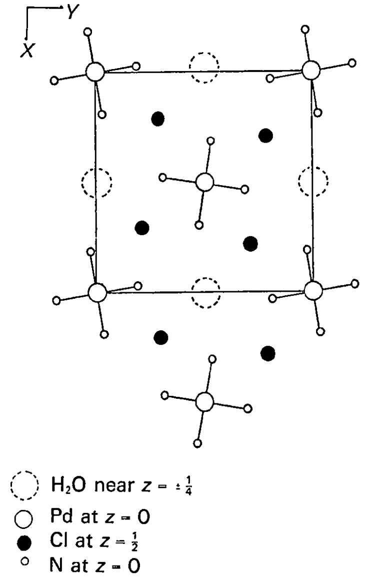

Fig. 1. The structure projected on (001).

It was notable that prior to the inclusion of the water molecule several of the low-θ data had shown discrepancies between the observed and calculated amplitude of up to 8 times the experimental standard deviation; after inclusion no discrepancy was greater than 3σ. Because of the very low peak density, the refinement was repeated allowing the occupancy factor to vary also. It did not decrease but in fact increased by about one standard deviation, the associated reduction in R (0·0577 → 0·0574) being not significant at the α = 0·05 level. In a further refinement assuming the occupancy factor of oxygen to be $\frac{1}{2}$ but the thermal motion anisotropic, R fell to 0·0567, the decrease for the 2 additional thermal parameters being significant for $\alpha<0{\cdot}02$. Atom coordinates and thermal parameters for this latter refinement are listed in Table 1. A projection of the structure is shown in Fig. 1. The Pd–N bond length is 2·06 (1) Å.*

Discussion. This investigation was prompted by a project in which the $hk0$ data were collected for the isomorphous platinum compound, $Pt(NH_3)_4Cl_2.H_2O$, and the (001) electron density projection calculated.

Table 2. *Chemical analyses and density measurements*

Analyses		Calculated (%)		
	Found (%)	Mono-hydrate	An-hydrous	Ref.
$Pd(NH_3)_4Cl_2$	Pd: 40·6	40·45	43·4	(1)
$Pt(NH_3)_4Cl_2$	Pt: 55·1	55·4	58·4	(1)
	55·7			(2)
	55·8			(3)
	Cl: 19·9	20·1	21·2	(2)
	N: 15·8	15·9	16·8	(3)
	H_2O: 4·3	5·1	–	(3)

Density values (g cm^{-3})		D_c		
	D_m	Mono-hydrate	An-hydrous	Ref.
$Pd(NH_3)_4Cl_2$	1·91	1·917	1·786	(4)
	1·93			(5)
	1·94			(1)

References: (1) Cox & Preston (1933); (2) Keller (1946); (3) Kurnakov & Andréeski (1930); (4) *CRC Handbook of Chemistry and Physics* (1973); (5) Dickinson (1934).

Table 1. *Atomic coordinates* (× 10³) *and thermal parameters* (× 10³)

The anisotropic temperature factors are of the form $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}
Pd	0	0	0	5·7 (2)	5·7	40 (1)	
Cl	287·6 (7)	787·6	500	10·6 (7)	10·6	48 (3)	3·0 (4)
N	196·4 (10)	31·4 (9)	0	5·3 (9)	8·9 (13)	71 (7)	1·3 (8)
O	0	500	269 (18)	46 (16)	46	363 (88)	−31 (11)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31418 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Coordinates* ($\times 10^3$) *and geometry of possible oxygen sites*

			Contact distances (Å)		Contact angles (°)		
x	y	z	O···Cl	O···N	N···O···N	Cl···O···Cl	N···O···Cl
470·6	29·4	351	3·20	3·21	76·7	152·2	64·9, 141·3
529·4	−29·4	351					
470·6	29·4	185	2·94	3·41	85·1	131·1	65·0, 131·1
529·4	−29·4	185					

The Pt, Cl and N atoms were revealed as expected, but surprisingly the water molecule was not. In order to minimize the dominance of the heavy atom attention was transferred to the palladium compound, and two independent data sets have been collected, one photographically and the other as herein described. Both led to the same conclusion: after subtracting the Pd, Cl and N atoms a difference synthesis shows no peak with $\varrho_{\max}$ greater than 2 e Å^{-3}, shows no peak at all at the positions $0,\frac{1}{2},0$ and $0,\frac{1}{2},\frac{1}{2}$ which in *P*4/*mbm* are of the expected multiplicity, and the outstanding residual feature is an extensive diffuse region with maximum at $0,\frac{1}{2},\frac{1}{4}$.

Table 2 lists various published chemical analyses and density determinations for these compounds, together with calculated values for the monohydrate and anhydrous compositions. It is apparent that the crystals are indeed hydrated, and the significant improvement in agreement for the X-ray data lends credence to the interpretation of the residual peak as the water molecule, notwithstanding the very low peak density.

Neither of the sites in *P*4/*mbm* consistent with the stoichiometry is in fact appropriate as the location of a structural water molecule, in that no reasonable hydrogen bonding scheme is apparent. At $0,\frac{1}{2},0$ the water would be at the centre of a rectangle of ammine groups, O···N approach 3·15 Å, the nitrogen lone pair electrons being involved in coordination and directed away from the water. At $0,\frac{1}{2},\frac{1}{2}$ there are only two close neighbours, chloride ions at O···Cl of 3·27 Å, the three atoms being collinear. By contrast a water molecule at $0,\frac{1}{2},0·269$ has two chloride neighbours at 3·26 Å with Cl···O···Cl angle 144·7° and four nitrogen neighbours at 3·36 Å, such that for various alternative pairs the N···O···N angle is 140·0, 93·7 or 72·7°, and the N···O···Cl angles 62·5 and 131·9° in each case. This environment could represent the formation of four weak hydrogen bonds although it might well be improved by an appropriate small displacement of the water molecule. If this displacement were random over several possibilities the associated electron density would be diffuse, as is observed.

The major axes of the r.m.s. thermal displacement tensor for the oxygen atom are along the [110], [1$\bar{1}$0], and [001] axes, of length 0·085, 0·430 and 0·352 Å respectively. The latter two are abnormally high, and could well be interpreted as indicating positional disorder. Fractional coordinates for the four sites obtained by combinations of these two displacements from the mean position are listed in Table 3. Each places the oxygen closer to a particular pair of nitrogen atoms, giving 4 distinct near neighbours with geometry as in Table 3. For the sites with $z=0·352$ all 4 hydrogen-bond approaches are shorter than for the mean position, at the expense of a less favourable Cl···O···Cl angle, whereas for those at $z=0·185$ the O···N bonds are considerably shorter, but the O···Cl bonds are a little longer. Presumably the size of the cavity occupied by the water molecule is dictated by the packing requirements of the cation and anion, and is slightly too large for the water molecule, which can attain lower potential energy at one of several more or less equivalent sites. A displacement along [110], which would shorten one O···Cl approach at the expense of the other, is apparently not favoured.

Quite apart from the randomness of displacement about the mean position, the occupancy of the site is only one half with respect to space group *P*4/*mbm*, *i.e.* there is disorder with regard to whether the z coordinate is positive or negative. Because the c axial length is only 4·27 Å, sites in the vicinity of $0,\frac{1}{2},\frac{1}{4}$ and $0,\frac{1}{2},-\frac{1}{4}$ could not both be occupied on any ordered basis, but the separation of successive displaced positions along c can be as great as 3·12 Å, so that order in this respect could well be short range only. The thermal parameters of atoms other than O are quite normal, giving no reason to suppose that a lower symmetry space group should be adopted.

References

CRC Handbook of Chemistry and Physics (1973). 54th ed., p. B-116. Cleveland: Chemical Rubber Co. Press.

Cox, E. G. & Preston, G. H. (1933). *J. Chem. Soc.* pp. 1089–1093.

Dickinson, B. N. (1934). *Z. Kristallogr.* **88**, 281–297.

Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502–510.

Keller, R. N. (1946). *Inorganic Syntheses*, Vol. 2, p. 250. New York: McGraw-Hill.

Kurnakov, N. S. & Andréeski, I. A. (1930). *Z. anorg. Chem.* **189**, 137–144.