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Tetraammineplatinum(II) Aquapentachloroiridate(III) Dihydrate, $[Pt(NH_3)_4][IrCl_5(H_2O)].2H_2O$

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Abstract

The crystal is built up from planar $Pt(NH_3)_4^{2+}$ cations, octahedral $IrCl_5(H_2O)^{2-}$ anions and two H_2O molecules. The coordination of these ions is 6/6, thus leading to a NaCl crystal structure. Electrostatic interactions and N···Cl, N···O and N···N short contacts (possible hydrogen bonds) take part in the packing of the structure and form a three-dimensional network.

Comment

The title compound is one of a series of inorganic platinum–iridium complexes (Garnier, 1993) which are reforming-catalyst precursors. The diffusion of K_3IrCl_6 and $Pt(NH_3)_4Cl_2$ in a tetramethoxysilane gel led to $[Pt(NH_3)_4][IrCl_6]_2$ (Michelot, 1986) as well as the title compound.

The complex crystallizes with nearly octahedral $Ir(H_2O)Cl_5^{2-}$ anions, planar $Pt(NH_3)_4^{2+}$ cations and two H_2O molecules. The coordination of these ions is 6/6 with distances of 5.41–6.16 Å between Pt and Ir. The structure may also be regarded as comprising layers parallel to (001) with the two hydration H_2O molecules (O2, O3) located between and inside these layers.

The Pt—N bond lengths in related structures containing the $Pt(NH_3)_4^{2+}$ ion are in the range 2.01 (2)–2.08 (1) Å (Endres, Keller, Moroni, Nöthe & Dong, 1978; Khodadad & Rodier, 1987, 1989; Rochon & Melanson, 1980; Tanaka, Tsujikawa, Toriumi & Ito, 1986; Toffoli, Khodadad, Rodier & Viossat, 1987), which compare favourably with our average value of 2.04 (1) Å. The Ir atom has a more distorted octahedral environment with an Ir—Cl mean distance of 2.36 (2) Å. The Ir—Cl distances in related structures containing the octahedral $IrCl_6^{3-}$ anion are in the range 2.335 (8)–2.359 (4) Å (Gray, Gulliver, Levason & Webster, 1982; Williams, Flack & Vincent, 1980). Of interest are the N···N, N···O and N···Cl short contacts (possible hydrogen bonds) which form a three-dimensional network.

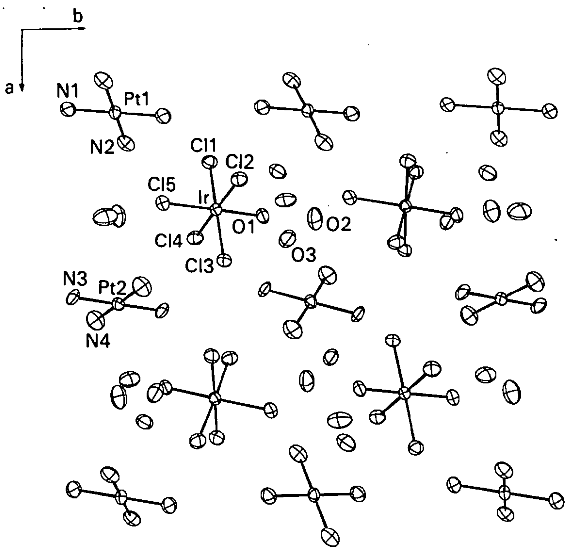

Fig. 1. A *MACORTEP* (Michalowicz & Andre, 1991) view of the packing of the ions in the *ab* plane of the title compound.

Experimental

Crystals were grown by diffusion of K_3IrCl_6 and $Pt(NH_3)_4Cl_2$ in tetramethoxysilane gel. Chemical analysis: Ir/Pt = 1 (quantitative electron microprobe).

Crystal data

$[Pt(NH_3)_4][IrCl_5(H_2O)]$.-
$2H_2O$
M_r = 686.74
Tetragonal
$I4_1/a$
a = 15.655 (2) Å
c = 23.554 (3) Å
V = 5773 (1) Å^3
Z = 16
D_x = 3.161 Mg m^{-3}
D_m = 3.14 Mg m^{-3}
D_m measured by flotation

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 11.62–21.53°
μ = 19.89 mm^{-1}
T = 294 K
Parallelepiped
0.164 × 0.114 × 0.100 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: by integration from crystal shape
$T_{\min} = 0.069$, $T_{\max} = 0.214$
6686 measured reflections
3778 independent reflections
2035 observed reflections [$F > 6.0\sigma(F)$]
$\theta_{\max} = 35°$
$h = 0 \rightarrow 25$
$k = 0 \rightarrow 25$
$l = 0 \rightarrow 38$
3 standard reflections monitored every 100 reflections
intensity variation: <3%

Refinement

Refinement on F
$R = 0.0404$
$wR = 0.0441$
$S = 0.808$
2035 reflections
168 parameters
Only H-atom U's refined
$w = 0.7325/[\sigma^2(F) + 0.0001F^2]$
$(\Delta/\sigma)_{\max} = 0.022$
$\Delta\rho_{\max} = 1.50$ e Å^{-3}
$\Delta\rho_{\min} = -1.83$ e Å^{-3}
Extinction correction: empirical
$F_c = F(0.0001xF^2/\sin\theta)$
Extinction coefficient: $x = 5.0(1) \times 10^{-5}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Pt1	1/4	1/4	1/4	2.15 (2)
Pt2	0	0	1/2	2.22 (2)
Ir	0.25601 (4)	0.25585 (4)	0.01126 (2)	2.05 (1)
Cl1	0.1342 (2)	0.2465 (3)	−0.0475 (1)	2.87 (6)
Cl2	0.1714 (2)	0.3080 (3)	0.0859 (3)	2.91 (6)
Cl3	0.3802 (2)	0.2682 (3)	0.0678 (1)	2.91 (6)
Cl4	0.3397 (3)	0.2069 (3)	−0.0662 (1)	3.21 (7)
Cl5	0.2339 (3)	0.1169 (2)	0.0441 (1)	3.00 (7)
O1	0.2777 (7)	0.3807 (6)	−0.0174 (4)	2.7 (2)
O2	0.2774 (9)	0.5024 (7)	0.0613 (5)	4.8 (3)
O3	0.3149 (7)	0.4144 (7)	0.1583 (4)	3.8 (2)
N1	0.3725 (8)	0.2395 (9)	0.2794 (5)	3.3 (3)
N2	0.2776 (9)	0.1671 (9)	0.1845 (4)	3.3 (3)
N3	0.0260 (9)	0.1142 (8)	0.5370 (5)	3.3 (3)
N4	0.0556 (10)	−0.0601 (10)	0.5669 (5)	4.1 (3)

Table 2. *Selected geometric parameters* (Å, °)

Pt1—N1	2.05 (1)	Ir—Cl4	2.373 (4)
Pt1—N2	206 (1)	Ir—Cl5	2.334 (4)
Pt2—N3	2.03 (1)	Ir—O1	2.10 (1)
Pt2—N4	2.03 (1)	O1—O2	2.66 (2)
Ir—Cl1	2.361 (4)	O2—O3	2.73 (2)
Ir—Cl2	2.347 (4)	O1—O3$^{\rm i}$	2.63 (1)
Ir—Cl3	2.364 (4)		
N1—Pt1—N2	90.4 (5)	Cl2—Ir—Cl5	89.6 (1)
N3—Pt2—N4	89.4 (5)	Cl2—Ir—Cl4	178.0 (1)
Cl5—Ir—O1	179.1 (3)	Cl2—Ir—Cl3	90.8 (1)
Cl4—Ir—O1	87.9 (3)	Cl1—Ir—O1	90.0 (3)
Cl4—Ir—Cl5	92.1 (1)	Cl1—Ir—Cl5	91.0 (1)
Cl3—Ir—O1	88.4 (3)	Cl1—Ir—Cl4	88.6 (1)
Cl3—Ir—Cl5	90.7 (1)	Cl1—Ir—Cl3	178.1 (1)
Cl3—Ir—Cl4	90.3 (1)	Cl1—Ir—Cl2	90.3 (1)
Cl2—Ir—O1	90.5 (3)		

Symmetry code: (i) $y - \frac{1}{4}, \frac{3}{4} - x, z - \frac{1}{4}$.

Table 3. *Hydrogen-bonding geometry* (Å, °)

D	H	A	H···A	D···A	D—H···A
N2	H21	Cl5	2.9 (1)	3.47 (1)	116 (9)
N1	H11	Cl2$^{\rm i}$	2.5 (1)	3.33 (1)	141 (8)
N3	H31	Cl3$^{\rm ii}$	2.5 (1)	3.41 (1)	150 (12)
N3	H33	Cl4$^{\rm iii}$	2.5 (1)	3.33 (1)	139 (9)
N4	H41	Cl3$^{\rm iv}$	2.6 (1)	3.41 (2)	139 (7)
N4	H43	Cl5$^{\rm iv}$	2.55 (9)	3.46 (2)	149 (9)
N4	H42	Cl1$^{\rm v}$	2.7 (1)	3.41 (1)	127 (9)
N1	H11	N2$^{\rm ii}$	2.6 (2)	2.90 (2)	97 (7)
N4	H41	N3$^{\rm vi}$	2.7 (2)	2.89 (2)	90 (3)
N3	H32	O1$^{\rm ii}$	2.4 (1)	3.11 (2)	127 (9)
N2	H22	O2$^{\rm vii}$	2.3 (1)	3.07 (2)	134 (12)

Symmetry codes: (i) $\frac{3}{4} - y, \frac{1}{4} + x, \frac{1}{4} + z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$; (iii) $x - \frac{1}{2}, y, \frac{1}{2} - z$; (iv) $\frac{1}{2} - x, -y, \frac{1}{2} + z$; (v) $\frac{1}{4} - y, x - \frac{1}{4}, \frac{3}{4} + z$; (vi) $-x, -y, 1 - z$; (vii) $y - \frac{1}{4}, \frac{1}{4} - x, \frac{1}{4} - z$.

The criterion for measured reflections, $h + k + l = 2n$, was also applied to unique reflections and thus there is no value of $R_{\rm int}$. H atoms were refined isotropically with a common $B_{\rm iso}$ and constrained geometry (N—H = 1.01 Å). Considering $\Delta\rho_{\min}$ and $\Delta\rho_{\max}$, no attempt was made to refine the H-atom positional parameters and no H-atom parameters were found for the H_2O molecules (O2, O3). *MULTAN*80 (Main *et al.*, 1980) and *SHELXS*86 (Sheldrick, 1985) were used to solve the structure. Refinement was performed with *SHELX*76 (Sheldrick, 1976). Molecular graphics were produced using *MACORTEP* (Michalowicz & Andre, 1991). Geometrical calculations were made with *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71798 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1068]

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A Revised Structure for α-Dicalcium Silicate Hydrate

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Abstract

The structure of α-dicalcium silicate hydrate, Ca$_2$(SiO$_3$OH)(OH), has recently been described and refined [Yano, Urabe, Ikawa, Teraushi, Ishizawa & Udagawa (1993). *Acta Cryst.* C**49**, 1555–1559] in space group $P2_12_12_1$ (orthorhombic; $a = 9.487$ (4), $b = 9.179$ (4), $c = 10.666$ (7) Å, $Z = 8$). It is better described in *Pbca*. Revised coordinates are given.

Comment

In their report of the structure of Ca$_2$(SiO$_3$OH)(OH), Yano, Urabe, Ikawa, Teraushi, Ishizawa & Udagawa (1993) noted that 'most of the reflections matched the extinction rules consistent with (space group) *Pbca*', but that some 'very weak' violations were detected. They further noted that least-squares refinement in *Pbca*, with isotropic B values, led to $R = 0.073$, after which 'the space group was altered to $P2_12_12_1$'; no mention is made as to how the inherent singularities were avoided. The resulting structure, although generally reasonable, showed relatively large e.s.d.'s for so hard a crystal (0.01–0.02 Å in the positions for the O atoms) and surprisingly large variations in presumably equivalent bond lengths and angles. Perhaps even more disturbing were the large discrepancies between the U_{ij} values of equivalent atoms; for example, Ca(3) showed $U_{\rm eq} = 0.0020$ (9) Å^2 while the structurally equivalent atom Ca(4) showed $U_{\rm eq} = 0.0131$ (7) Å^2. Since such manifestations are typical of attempts to refine a centrosymmetric structure in a non-centrosymmetric space group, a further consideration of space group *Pbca* seemed appropriate.

A listing of 1677 F_o and $\sigma(F_o)$ values was obtained from SUP 71140. Included were six reflections – 0,17,6, 10,0,7, 16,0,9, 10,0,11, 15,2,0 and 7,11,0 – forbidden in *Pbca*. The largest of these had $F_o/\sigma(F_o) = 4.2$, which corresponds to $I/\sigma(I) = 2.1$ – a truly marginal observation. [The authors reported that the 1677 'non-zero' reflections had $I > 3\sigma(I)$, but apparently the cutoff was lower, at $F_o > 3\sigma(F_o)$]. In the face of the approximately 200 other space-group violators that lay within the sphere of reflection and were indeed unobserved, the apparent presence of these six very weak violations – which could well have resulted from double reflection – seemed an inadequate reason to reject *Pbca*.

Full-matrix refinement in *Pbca* proceeded routinely to $R = 0.056$ for 1671 reflections and 81 parameters, slightly higher than the 0.054 reported by Yano *et al.* (1993) (and reproduced by me) for 95 parameters in $P2_12_12_1$. Presumably of greater significance is the goodness-of-fit value, which was 0.97 (according to my calculations) for the $P2_12_12_1$ model and 0.90 for the revised, *Pbca* model. (I have no idea as to how the value could be less than 1.0.) The O atoms were modeled as anisotropic in *Pbca*, but isotropic in $P2_12_12_1$ (where, presumably, the correlations would have been intolerable). Late in the refinement, a difference map based on the low-order reflections – out to $\sin^2\theta/\lambda^2 = 0.1$ Å^{-2} – indicated H atoms bonded to O(2) and O(5), as suggested by Yano *et al.* (1993); these atoms were included in the final refinements. In the last cycle, the maximum shift was 0.02σ.

Final *Pbca* coordinates are given in Table 1. They are more precise, by an average factor of about 5, than those reported by Yano *et al.* (1993), due to the removal of near-singularities; they are surely more *accurate* as well. Bond lengths and angles within the SiO$_4$ and the O—H···O groups are given in Table 2. Two items may warrant comment: (1) the shortness of the Si—O(4) bond relative to Si—O(1) and Si—O(3) correlates with its environment, since O(4) is coordinated to only two Ca atoms, and accepts a very weak hydrogen bond [O(5)···O(4$^{\rm ii}$) 3.093 (4) Å; symmetry code: (ii) $\frac{1}{2}+x, y, \frac{1}{2}-z$], whereas O(1) is coordinated to three Ca atoms, and O(3) is coordinated to two Ca atoms and accepts a strong hydrogen bond [O(2)···O(3$^{\rm i}$) 2.679 (4) Å; symmetry code: (i) $\frac{1}{2}-x, \frac{1}{2}+y, z$]; (2) the nonlinearity of the O(5)—H(5)···O(4$^{\rm ii}$) grouping reflects not only the weakness of the interaction but also the wish of H(5) to complete an approximate tetrahedron about O(5), which is also coordinated to three Ca atoms. Other details of the structure are approximately as described by Yano *et al.* (1993).

In deciding upon space group $P2_12_12_1$, Yano *et al.* (1993) were undoubtedly influenced by Heller (1952), who had also rejected *Pbca* on the basis of apparent

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† Contribution No. 8896.