

Table 2. Geometric parameters (Å, °)

|                |           |                   |           |
|----------------|-----------|-------------------|-----------|
| Cd—C(1)        | 2.109 (3) | C(1)—C(2)         | 1.377 (4) |
| Cd—C(7)        | 2.111 (3) | C(1)—C(6)         | 1.369 (4) |
| C(2)—F(1)      | 1.361 (3) | C(2)—C(3)         | 1.374 (4) |
| C(3)—F(2)      | 1.345 (3) | C(3)—C(4)         | 1.376 (4) |
| C(4)—F(3)      | 1.344 (3) | C(4)—C(5)         | 1.374 (4) |
| C(5)—F(4)      | 1.340 (3) | C(5)—C(6)         | 1.377 (4) |
| C(6)—F(5)      | 1.352 (3) | C(7)—C(8)         | 1.370 (4) |
| C(8)—F(6)      | 1.353 (3) | C(7)—C(12)        | 1.376 (4) |
| C(9)—F(7)      | 1.343 (3) | C(8)—C(9)         | 1.375 (4) |
| C(10)—F(8)     | 1.342 (3) | C(9)—C(10)        | 1.373 (5) |
| C(11)—F(9)     | 1.346 (3) | C(10)—C(11)       | 1.371 (4) |
| C(12)—F(10)    | 1.353 (3) | C(11)—C(12)       | 1.374 (4) |
| C(1)—Cd—C(7)   | 173.9 (1) | Cd—C(7)—C(8)      | 121.0 (2) |
| Cd—C(1)—C(2)   | 125.1 (2) | Cd—C(7)—C(12)     | 123.0 (2) |
| Cd—C(1)—C(6)   | 119.1 (2) | C(8)—C(7)—C(12)   | 115.9 (3) |
| C(2)—C(1)—C(6) | 115.7 (3) | C(7)—C(8)—F(6)    | 119.5 (3) |
| C(1)—C(2)—F(1) | 120.2 (3) | C(9)—C(8)—F(6)    | 117.1 (3) |
| C(3)—C(2)—F(1) | 116.5 (3) | C(7)—C(8)—C(9)    | 123.4 (3) |
| C(1)—C(2)—C(3) | 123.3 (3) | C(8)—C(9)—F(7)    | 121.3 (3) |
| C(2)—C(3)—F(2) | 122.1 (3) | C(10)—C(9)—F(7)   | 120.1 (3) |
| C(4)—C(3)—F(2) | 119.3 (3) | C(8)—C(9)—C(10)   | 118.6 (3) |
| C(2)—C(3)—C(4) | 118.6 (3) | C(9)—C(10)—F(8)   | 119.5 (3) |
| C(3)—C(4)—F(3) | 119.9 (3) | C(11)—C(10)—F(8)  | 120.2 (3) |
| C(5)—C(4)—F(3) | 119.8 (3) | C(9)—C(10)—C(11)  | 120.3 (3) |
| C(3)—C(4)—C(5) | 120.3 (3) | C(10)—C(11)—F(9)  | 119.4 (3) |
| C(4)—C(5)—F(4) | 119.8 (3) | C(12)—C(11)—F(9)  | 121.6 (3) |
| C(6)—C(5)—F(4) | 121.6 (3) | C(10)—C(11)—C(12) | 119.0 (3) |
| C(4)—C(5)—C(6) | 118.6 (3) | C(7)—C(12)—F(10)  | 119.8 (3) |
| C(1)—C(6)—F(5) | 119.7 (3) | C(11)—C(12)—F(10) | 117.3 (3) |
| C(5)—C(6)—F(5) | 116.7 (3) | C(7)—C(12)—C(11)  | 122.9 (3) |
| C(1)—C(6)—C(5) | 123.5 (3) |                   |           |

Data collection and cell refinement: *DIF4* (Stoe, 1985a). Data reduction: *REDU4* (Stoe, 1985b). Structure solution: *SHELXS86* (Sheldrick, 1986). Structure refinement: *SHELXL76* (Sheldrick, 1976). Molecular graphics: *XP (SHELXTL-Plus)*; Sheldrick, 1990).

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Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55621 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SE1005]

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## Structure of Bis[pentaamminechloro-iridium(III)] Hexachloroplatinate(IV) Dichloride

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## Abstract

The crystal is built up from octahedral  $\text{PtCl}_6^{2-}$  and nearly octahedral  $\text{Ir}(\text{NH}_3)_5\text{Cl}^{2+}$  ions; the electro-neutrality is assumed by the  $\text{Cl}^-$  ions. The structure can be described as comprising layers of  $\text{PtCl}_6^{2-}$  and layers containing  $\text{Ir}(\text{NH}_3)_5\text{Cl}^{2+}$  and  $\text{Cl}^-$ , parallel to (001). The layers are stabilized by electrostatic interactions, and numerous  $\text{N—H}\cdots\text{Cl}$  hydrogen bonds possibly take part in the packing of the ions.

## Comment

The title compound is one of a series of inorganic Pt–Ir complexes which are reforming-catalyst precursors. The reaction of  $\text{Ir}(\text{NH}_3)_5\text{Cl}_2$  and  $\text{K}_2\text{PtCl}_6$  leads to  $\text{Ir}(\text{NH}_3)_5\text{ClPtCl}_6$  (Michelot, Ouali, Blais,

Guérin & Kappenstein, 1988) and also to the title compound.

The structure is constituted of  $\text{Cl}^-$  and  $\text{PtCl}_6^{2-}$  anions and  $\text{Ir}(\text{NH}_3)_5\text{Cl}^{2+}$  cations. It may be regarded as comprising ion layers parallel to (001): successively one  $\text{PtCl}_6^{2-}$  layer and two other layers, each containing  $\text{Cl}^-$  and  $\text{Ir}(\text{NH}_3)_5\text{Cl}^{2+}$ .

The Pt—Cl bond lengths in related structures containing the  $\text{PtCl}_6^{2-}$  anion are in the range 2.310 (4)–2.314 (1) Å (Bisi-Castellani, Manotti-Lanfredi, Tiripicchio, Maresca & Natile, 1984; Ohba & Saito, 1984; Terzis & Mentzafos, 1983; Delafontaine, Toffoli, Khodadad & Rodier, 1987) which compare favourably with our average value of 2.319 (12) Å, since  $\text{PtCl}_6$  is subject to only  $2/m$  symmetry. The Ir atom exhibits a more distorted octahedral surrounding than that in  $\text{Ir}(\text{NH}_3)_5\text{Cl}_2$  (Hambley & Lay, 1986). Of interest, are the distances  $\text{Cl}(3)\cdots\text{Cl}(3^i) = 3.288$  (2) Å and the possible N—H $\cdots$ Cl bonds: N(1)—H(13) $\cdots$ Cl(4<sup>ii</sup>) = 3.436 (5) Å, 158 (4)°; N(2)—H(22) $\cdots$ Cl(4<sup>ii</sup>) = 3.381 (4) Å, 155 (3)°; N(3)—H(32) $\cdots$ Cl(3<sup>ii</sup>) = 3.293 (6) Å, 151 (4)°; N(1)—H(11) $\cdots$ Cl(4<sup>iii</sup>) = 3.396 (4) Å, 158 (3)°; N(3)—H(31) $\cdots$ Cl(4<sup>iv</sup>) = 3.200 (7) Å, 159 (6)° [symmetry code: (i)  $x, -y, z$ ; (ii)  $x, y, z$ ; (iii)  $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 2$ ; (iv)  $x - \frac{1}{2}, y - \frac{1}{2}, z$ ].

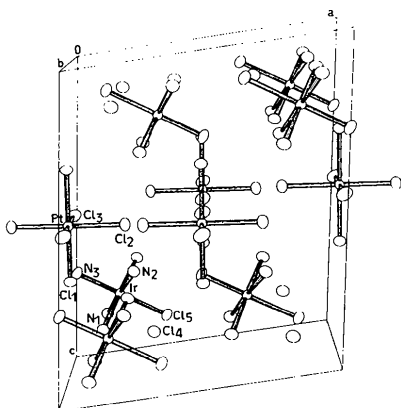
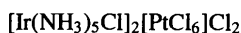


Fig. 1. A MACORTEP view of the title compound.

## Experimental

### Crystal data



$M_r = 1104.35$

Monoclinic

$C2/m$

$a = 11.2428$  (21) Å

$b = 7.8935$  (16) Å

$c = 13.4055$  (24) Å

$\beta = 99.435$  (15)°

$V = 1173.6$  (4) Å<sup>3</sup>

$Z = 2$

Mo  $K\alpha$  radiation

$\lambda = 0.71069$  Å

Cell parameters from 25 reflections

$\theta = 6.65$ – $17.54$ °

$\mu = 18.43$  mm<sup>-1</sup>

$T = 294$  K

Prismatic

$0.117 \times 0.116 \times 0.081$  mm

Red

$D_x = 3.127$  Mg m<sup>-3</sup>

$D_m = 3.13$  Mg m<sup>-3</sup>

Density measured by flotation

### Data collection

CAD-4L diffractometer

$\omega/2\theta$  scans [width

$(1.0 + 0.35 \tan \theta)^\circ$ ]

Absorption correction:

empirical [ABSORB

(Ugozzoli, 1987); DIFABS

(Walker & Stuart, 1983)]

$T_{\min} = \varphi 0.866, \theta 0.905,$

$T_{\max} = \varphi 1.203, \theta 1.037$

3962 measured reflections

3822 independent reflections

### Refinement

Refinement on  $F$

Final  $R = 0.0290$

$wR = 0.0354$

$S = 1.171$

2489 reflections

88 parameters

Only H-atom  $U$ 's refined

$w = 1.0939/[\sigma^2(F) +$

$0.000075(F^2)]$

Crystal source: diffusion of  $\text{Ir}(\text{NH}_3)_5\text{Cl}_2$  and  $\text{K}_2\text{PtCl}_6$  in a gel of tetramethoxysilane

2489 observed reflections  
[ $F > 6.0\sigma(F)$ ]

$\theta_{\max} = 40^\circ$

$h = 0 \rightarrow 20$

$k = 0 \rightarrow 14$

$l = -24 \rightarrow 24$

3 standard reflections

monitored every 100

reflections

intensity variation:

$< 2\sigma(I)$

$(\Delta/\sigma)_{\max} = 0.0001$

$\Delta\rho_{\max} = 3.17$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -2.10$  e Å<sup>-3</sup>

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1986). Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976). Program(s) used for complete geometry: *PARST* (Nardelli, 1983). Molecular graphics: *MACORTEP* (Michalowicz & André, 1991).

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>) with their *e.s.d.*'s (Schomaker & Marsh, 1983) in parentheses

|       | $B_{\text{eq}} = \frac{8\pi^2}{3} [U_{22} + 1/\sin^2\beta(U_{11} + U_{33} + 2U_{13}\cos\beta)]$ |              |              |                 |
|-------|---|--------------|--------------|-----------------|
|       | $x$   | $y$          | $z$          | $B_{\text{eq}}$ |
| Pt    | 0.0   | 0.5          | 0.5          | 1.202 (4)       |
| Ir    | 0.17222 (2)   | 0.0          | 0.80063 (2)  | 1.310 (3)       |
| Cl(1) | 0.00786 (15)  | 0.5          | 0.67468 (11) | 2.060 (27)      |
| Cl(2) | 0.20937 (15)  | 0.5          | 0.52188 (13) | 2.363 (23)      |
| Cl(3) | 0.0   | 0.20824 (21) | 0.5          | 2.344 (26)      |
| Cl(4) | 0.32403 (17)  | 0.5          | 0.87643 (13) | 2.188 (23)      |
| Cl(5) | 0.36508 (15)  | 0.0          | 0.90065 (13) | 2.284 (24)      |
| N(1)  | 0.11538 (39)  | 0.18738 (57) | 0.89274 (30) | 2.123 (59)      |
| N(2)  | 0.22306 (38)  | 0.18497 (54) | 0.71048 (29) | 1.938 (54)      |
| N(3)  | 0.00210 (55)  | 0.0          | 0.71310 (48) | 2.357 (95)      |

Table 2. Geometric parameters (Å, °)

|                |            |               |             |
|----------------|------------|---------------|-------------|
| Pt—Cl(1)       | 2.329 (2)  | Ir—N(1)       | 2.093 (5)   |
| Pt—Cl(2)       | 2.324 (2)  | Ir—N(2)       | 2.081 (4)   |
| Pt—Cl(3)       | 2.303 (2)  | Ir—N(3)       | 2.073 (6)   |
| Ir—Cl(5)       | 2.355 (2)  |               |             |
| Cl(1)—Pt—Cl(2) | 90.14 (6)  | N(3)—Ir—Cl(5) | 179.77 (18) |
| N(1)—Ir—Cl(5)  | 90.33 (11) | N(3)—Ir—N(1)  | 89.50 (12)  |
| N(2)—Ir—Cl(5)  | 88.34 (12) | N(3)—Ir—N(2)  | 91.83 (12)  |
| N(2)—Ir—N(1)   | 90.46 (17) |               |             |

Chemical analysis found Ir/Pt = 2 (quantitative electron microprobe). Criterion for measured reflections was  $h + k = 2n$ , which also applied to unique reflections; thus there is no value of  $R_{\text{int}}$ . H atoms were refined isotropically with a common  $B_{\text{iso}}$  value and

constrained geometry (*DFIX* parameter in *SHELX76*: N—H = 1.01 Å). Considering the values of  $\Delta\rho_{\max}$  and  $\Delta\rho_{\min}$  no attempt was made to refine the H-atom positional parameters.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55553 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1021]

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## Structure of Potassium Theobrominium Tetrakis(thiocyanato)palladate(II) Monohydrate

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## Abstract

The main structural features are columns of alternating theobrominium cations, protonated at N(9), and

tetrakis(thiocyanato)palladate(II) anions. The anions are in the shape of a gammadion, with small but significant deviations from  $C_{4h}$  symmetry. Average stereochemical data for the  $[\text{Pd}(\text{SCN})_4]^{2-}$  anion are given.

## Comment

Potassium theobrominium tetrakis(thiocyanato)palladate(II) monohydrate was prepared in the course of our research into the metal complexes of purine bases (Colacio *et al.*, 1989, and references therein; Skipworth *et al.*, 1992). Although there is no bond between the Pd atom and the base in this structure, it has some interesting features.

The tetrakis(thiocyanato)palladate(II) anions are in the shape of a gammadion,\* but with some significant deviations from  $C_{4h}$  symmetry (Fig. 1). The thiocyanato ligands are linear and the four S atoms are coplanar to within experimental error, with the Pd atom displaced by 0.013(1) Å from the  $S_4$  least-squares plane. The thiocyanato ligands (1', 2', 3', 4') lie at angles of 88.48(4), 76.22(4), 89.08(4) and 84.26(4)°, respectively, to the normals to this plane. Average stereochemical data for the anion are: Pd—S 2.338(1), S—C 1.673(5), C—N, 1.138(6) Å and Pd—S—C 107.6(2)°. A search of the literature, including the Cambridge Structural Database (Allen *et al.*, 1991), revealed only one other example of the  $[\text{Pd}(\text{SCN})_4]^{2-}$  anion [in  $\text{K}_2\text{Pd}(\text{SCN})_4$  (Mawby & Pringle, 1972), a structure that was determined from limited film data]. The details of the  $[\text{Pd}(\text{SCN})_4]^{2-}$  anion reported here therefore represent the best available stereochemical data for this anion. There is an example of the  $[\text{Pt}(\text{SCN})_4]^{2-}$  analogue (Gysling & Luss, 1984), but the anion is disordered.

The theobrominium cations are protonated at N9. The C8—N7 and C8—N9 bond lengths are not significantly

\* A gammadion is a pattern formed of combinations of the Greek letter gamma and is suggested here as a name to cover all species of this shape.

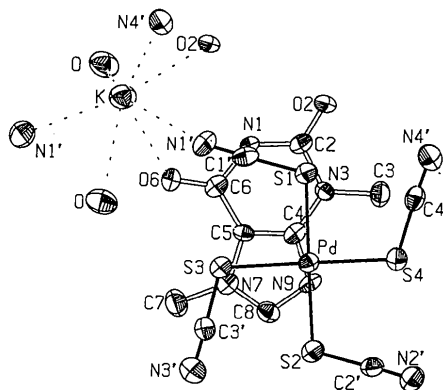


Fig. 1. The complex cation and anion viewed perpendicular to their planes and including the environment of the potassium ion. Thermal ellipsoids are represented at the 50% probability level and H atoms are omitted for clarity.