

The pseudosymmetric structure of bis(diisopropylammonium) hexachloroiridate(IV) and its relationship to potassium hexachloroiridate(III)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(C-C)$ = 0.009 Å
R factor = 0.034
wR factor = 0.094
Data-to-parameter ratio = 19.2

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

Bis(diisopropylammonium) hexachloroiridate(IV), $[(H_3C)_2CH)_2NH_2]_2[IrCl_6]$, crystallizes in the monoclinic centrosymmetric space group $P2_1/c$ with two crystallographically independent $[IrCl_6]^{2-}$ anions, each located on a center of symmetry, and two crystallographically independent diisopropylammonium cations in general positions. Weak hydrogen bonding occurs between the cations and anions to form layers parallel to the bc plane. Each layer is built by annealed 24-membered rings that can be classified according to Etter's nomenclature as $R^8_8(24)$. The structural relationship between $K_3[IrCl_6]$ and the title compound shows that a replacement of three potassium cations by two diisopropylammonium cations leads to a layered structure. The hydrophilic layers that are dominated by hexachloroiridate(IV) anions are separated by lipophilic regions in the planes at $x = 1/4$ and $x = 3/4$.

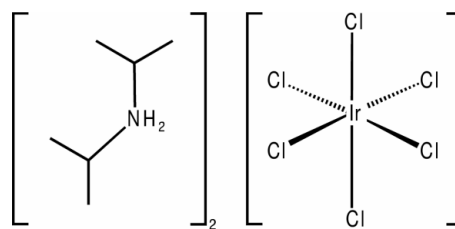
Received 16 November 2001

Accepted 8 January 2002

Online 18 January 2002

Comment

Diisopropylammonium cations (dip) are known as stabilizing counter-ions for various anionic systems (Reiss, 1998, and references therein). A preliminary communication of a systematic study on the structural chemistry of diisopropylammonium halogenides (Reiss, 2000) and of analogous hydrogen difluorides (Reiss, 2001) showed that all known structures of diisopropylammonium halogenides are isostructural and form hydrogen-bonded chains. By contrast, bis-(diisopropylammonium) hexafluorosilicate, $(dip)_2SiF_6$ (Reiss, 1998), has been shown to be constructed about quasi-molecular ion pairs of one hexafluorosilicate anion and two diisopropylammonium cations held together by two strong N—H...F hydrogen bonds with only weak contacts to the neighboring units.



(I)

The structure of the title compound, (I) (Fig. 1 and Table 1), comprises hexachloroiridate(IV) dianions located on centers of inversion (Wyckoff sites $2a$ and $2d$) and two crystallographically independent diisopropylammonium cations in general positions connected *via* weak N—H...Cl hydrogen bonds (Table 2).

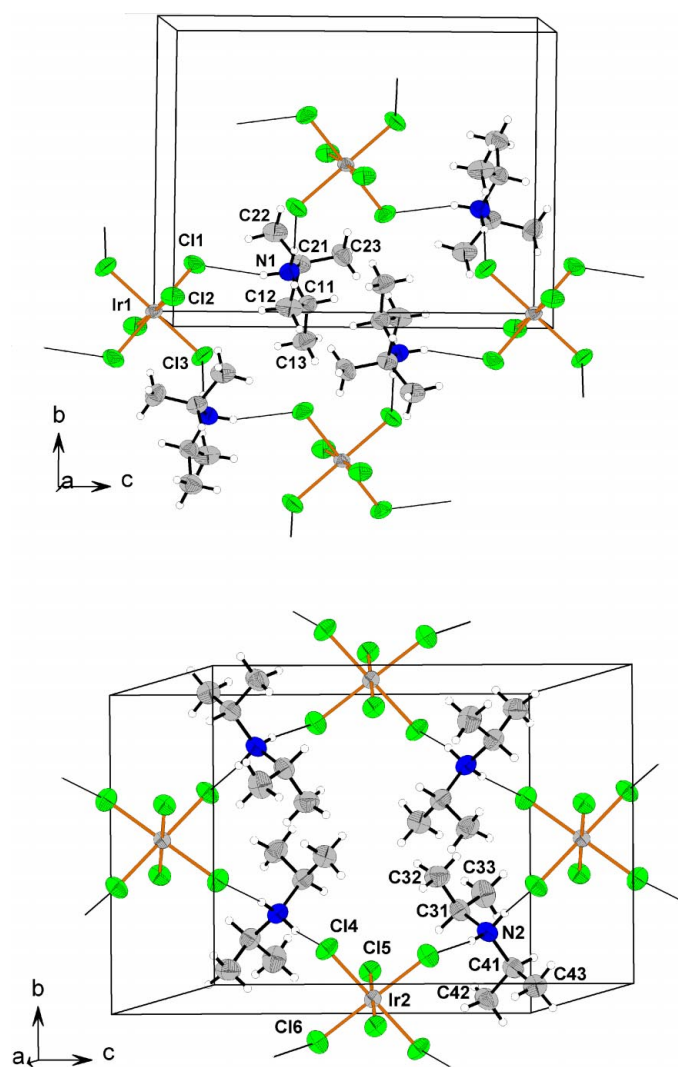


Figure 1
Diagrams showing the primary hydrogen-bonding motifs. Displacement ellipsoids are drawn at the 40% probability level.

The C—C and N—C bond lengths in both crystallographically independent diisopropylammonium cations are as expected. The conformations of the crystallographically independent cations are very similar (Table 1). The almost exactly octahedral geometry found in the title structure is consistent with the results of other structure determinations of hexachloroiridates (Coll *et al.*, 1987).

Taking into account only the shortest H···Cl contacts, each of the two crystallographically independent hexachloroiridate(IV) anions and each of the dip cations in the asymmetric unit form two crystallographically independent layers parallel to the *bc* plane, each of which shows the same hydrogen-bonding motif. The hydrogen-bonded layers are comprised of annealed 24-membered rings, as shown in Fig. 1. The rings can be classified in Etter's nomenclature (Etter *et al.*, 1990; Bernstein *et al.*, 1995) as $R_8^s(24)$.

It is known from the literature that potassium hexachloroiridate(III) crystallizes with similar lattice constants and in the

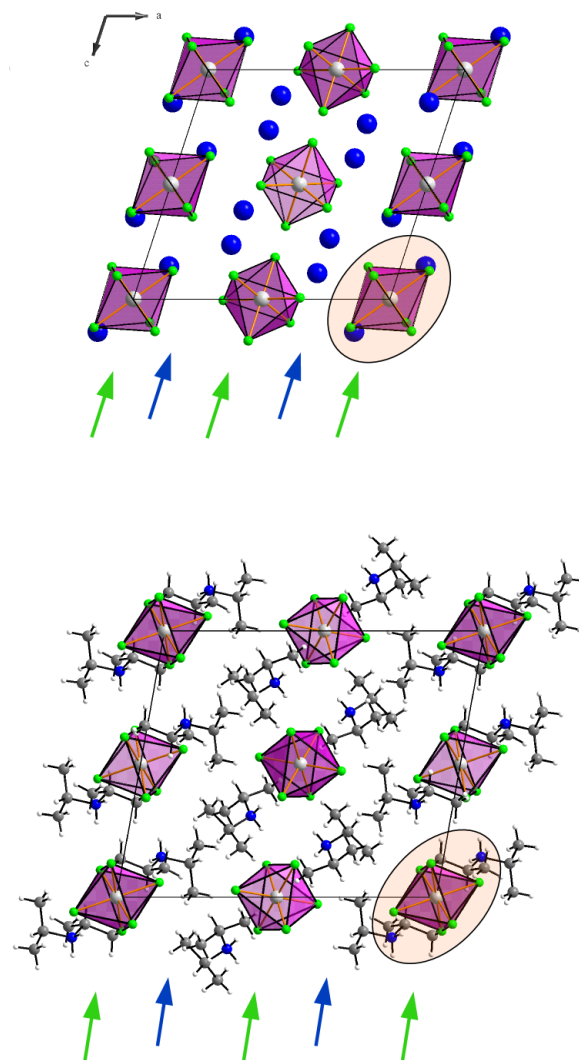


Figure 2
Packing, with view along *b*, for $\text{dip}_2[\text{IrCl}_6]$ (bottom) and $\text{K}_3[\text{IrCl}_6]$ (top)

same space group (*i.e.* $P2_1/c$). In addition, the hexachloroiridate(III) anions occupy the same sites as in the title compound (Fig. 2). A detailed investigation of the similarities between the two structures was undertaken. The structure of the title compound and that of potassium hexachloroiridate(III) can be separated into layers comprised of hexachloroiridate(IV) anions and cations in the planes at $x = 0$ and $x = 1/2$, and layers defined by the some of the cations separating them.

Reducing the dip cations to their centers of gravity (blue N atom), the two structures are very similar concerning the layers at $x = 0$ (Fig. 2, green arrows). The orientation of the octahedral anions is similar and the ammonium cations in this layer occupy approximately the same gaps as in the potassium salt (Fig. 2, orange ellipses). For the layer at $x = 1/2$ this is not true. The octahedra are tilted with respect to the cell edges, whilst in the potassium salt, four of the six chlorides lie exactly within the *ab* and *bc* planes, respectively (Fig. 2). One of the

two remaining potassium sites is substituted by one of the dip cations. Substitution of potassium by diisopropylammonium cations leads to a significant change of the principal structural feature, *i.e.* from a three-dimensional inorganic compound, $K_3[IrCl_6]$, with Ir···Ir distances of 6.98 and 7.27 Å, to a layered compound, $dip_2[IrCl_6]$, with lipophilic regions in the planes at $x = 1/4$ and $x = 3/4$ (Ir···Ir distances 6.82 and 8.05 Å) (Fig. 2).

The fact that structures with different compositions crystallize with one part of the structure unchanged is well known from host–guest systems such as zeolites or clathrates. For systems in which the subsystems are interconnected *via* hydrogen bonds, this seems to be rarer (Mootz & Schilling, 1992). The present example of an alkylammonium hexachloroiridate(IV) salt shows that some features of the inorganic parent structure are retained. Other features, such as the generation of layers, can be incorporated within the original framework.

Finally, it should be mentioned that the ammonium hexachloroiridate(IV) salt (Bokii & Ussikov, 1940), caesium hexachloroiridate(IV) (Coll *et al.*, 1990) and the potassium/ammonium mixed crystals $[K_{0.3},(NH_4)_{0.7}]_2[IrCl_6]$, (Reiss, unpublished results) form, by contrast to the above-mentioned structures, highly symmetric arrangements having cubic symmetry ($Fm\bar{3}m$).

Experimental

The title compound was synthesized by the reaction of diisopropylamine with $IrCl_3$ dissolved in a concentrated hydrochloric acid solution. Recrystallization of the microcrystalline powder at room temperature yielded dark-red platelets.

Crystal data

$(C_6H_{16}N)_2[IrCl_6]$	$D_x = 1.802 \text{ Mg m}^{-3}$
$M_r = 609.30$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 693 reflections
$a = 16.0939 (14) \text{ \AA}$	$\theta = 5\text{--}20^\circ$
$b = 10.3961 (12) \text{ \AA}$	$\mu = 6.66 \text{ mm}^{-1}$
$c = 13.6382 (13) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 100.196 (9)^\circ$	Plate, dark red
$V = 2245.8 (4) \text{ \AA}^3$	$0.20 \times 0.10 \times 0.05 \text{ mm}$
$Z = 4$	

Data collection

Stoe CCD diffractometer	2977 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.073$
Absorption correction: numerical (XRED; Stoe & Cie, 1999)	$\theta_{max} = 25.0^\circ$
$T_{min} = 0.294$, $T_{max} = 0.712$	$h = -19 \rightarrow 19$
25279 measured reflections	$k = -12 \rightarrow 12$
3932 independent reflections	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.04P)^2 + 4P]$
$R[F^2 > 2\sigma(F^2)] = 0.034$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.094$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.03$	$\Delta\rho_{max} = 0.89 \text{ e \AA}^{-3}$
3932 reflections	$\Delta\rho_{min} = -0.83 \text{ e \AA}^{-3}$
205 parameters	
H-atom parameters constrained	

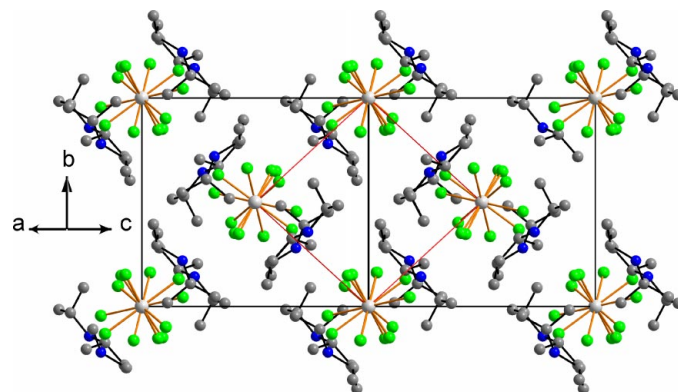


Figure 3

Diagram showing the packing with a view along [101]. The approximate twofold motifs that are tetragonally packed, responsible for the pseudosymmetry effects (see *Experimental*), are highlighted.

Table 1

Selected geometric parameters (Å, °).

Ir1—Cl3	2.3133 (14)	Ir2—Cl6	2.3319 (14)
Ir1—Cl1	2.3221 (13)	N1—C11	1.501 (7)
Ir1—Cl2	2.3194 (15)	N1—C21	1.510 (7)
Ir2—Cl4	2.3212 (13)	N2—C41	1.517 (7)
Ir2—Cl5	2.3232 (12)	N2—C31	1.510 (7)
Cl1—Ir1—Cl2	89.30 (6)	Cl4—Ir2—Cl6	89.34 (6)
Cl1—Ir1—Cl3	90.72 (6)	Cl5—Ir2—Cl6	89.45 (5)
Cl2—Ir1—Cl3	90.40 (6)	C11—N1—C21	119.2 (5)
Cl4—Ir2—Cl5	90.52 (5)	C41—N2—C31	119.0 (4)

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1···Cl3 ⁱ	0.90	2.50	3.346 (5)	158
N1—H2···Cl1	0.90	2.46	3.329 (5)	164
N2—H3···Cl6	0.90	2.54	3.434 (4)	172
N2—H4···Cl4 ⁱⁱ	0.90	2.66	3.414 (5)	142

Symmetry codes: (i) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$.

The intensity weighted reciprocal lattice shows, beside strong reflections with the cell constants $a = 9.56$, $b = 10.40$, $c = 11.43$ Å and $\gamma = 99.8^\circ$, also weak superstructure reflections doubling the volume of this sublattice. The transformation of this cell ($\bar{1}01,010,\bar{1}0\bar{1}$) leads to the true cell. After a crystal-faces-based numerical absorption correction had been performed, the Laue class was clearly identified to be $2/m$. The analysis of the systematic absences identifies, uniquely, the centrosymmetric space group $P2_1/c$. The structure refinement is complicated by correlation effects that can be reduced by increasing the weight of the weak reflections, accepting the disadvantage of higher R values. Fig. 3 shows a packing plot, viewed along the [101] direction. The reasons for the pseudosymmetry effects are apparent from this figure. There is an approximate twofold motif that is tetragonally packed along the view direction (red square).

As discussed above, weak hydrogen bonding occurs between the ammonium groups and the hexachloroiridate(IV) anions. These weak interactions do not appear to affect the N—H distances within the dip cations.

The atomic coordinates of the H atoms belonging to NH_2 and CH groups have therefore been refined using a riding model, while their

U_{iso} values were refined freely. H atoms belonging to methyl groups were included in the refinement, riding on their attached C atoms, and were allowed to rotate about the C–C bond, with one common U_{iso} value for each group.

Data collection: *CrysAlis* (Kuma, 2000); cell refinement: *CrysAlis RED* (Kuma, 2000); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

The author thanks J. Graf for reading the manuscript and for useful discussions.

References

- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1584.
- Bokii, G. B. & Ussikov, P. I. (1940). *Dokl. Akad. Nauk SSSR*, **26**, 782–784.
- Brandenburg, K. (1998). *DIAMOND*. Version 2.0. Crystal Impact GbR, Bonn, Germany.
- Coll, R. K., Fergusson, J. E., Penfold, B. R., Rankin, D. A. & Robinson, W. T. (1987). *Aust. J. Chem.* **40**, 2115–2122.
- Coll, R. K., Fergusson, J. E., Penfold, B. R., Rankin, D. A. & Robinson, W. T. (1990). *Inorg. Chim. Acta*, **177**, 107–114.
- Etter, M. C., McDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* **B46**, 256–262.
- Kuma (2000). *CrysAlis* (Version 1.166) and *CrysAlis RED* (Version 1.166). Kuma Diffraction Instruments, Wroclaw, Poland.
- Mootz, D. & Schilling, M. (1992). *J. Am. Chem. Soc.* **114**, 7435–7439.
- Reiss, G. J. (1998). *Acta Cryst.* **C54**, 1489–1491.
- Reiss, G. J. (2000). *Z. Kristallogr. Suppl.* **17**, 184.
- Reiss, G. J. (2001). *Acta Cryst.* **C57**, 994–995.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Stoe & Cie (1999). *XRED*. Version 1.10. Stoe and Cie, Darmstadt, Germany.