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The crystal structure of anhydrous potassium tetrachloroaurate(III).

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$KAuCl_4$ crystallizes from ethanol as monoclinic crystals, space group *Pc* with $a=8{\cdot}671$ (10), $b=6{\cdot}386$ (5), $c=12{\cdot}243$ (10) Å, $\beta=95{\cdot}37$ (8)°; $Z=4$, $D_x=3{\cdot}72$. The anhydrous complex was obtained from the dihydrate as described by Cox & Webster [*J. Chem. Soc.* (1936). pp. 1635–1637]. Two crystallographically independent tetrachloroaurate ions are present in the cell, each having the gold atoms in an essentially square planar coordination.

Introduction

Recrystallization of the dihydrate from absolute ethanol gave golden yellow prisms of the anhydrous complex which rapidly decomposed in air under the influence of X-rays. Because of this, measurements were taken on samples previously dipped in Nujol and sealed in Lindemann glass capillaries. The size of the crystal used was approximately 0·07 mm across, μ(Cu $K\alpha$) = 606 cm^{-1}. Cell constants were determined by a modified version of Christ's method (Mazzone, Vaciago & Bonamico, 1963) from zero-layer Weissenberg films taken about the *a* and *b* axes (Cu $K\alpha$ radiation, $\lambda=1{\cdot}5418$ Å). Space group *Pc* was deduced from systematic absences and confirmed by the structure determination. Unsystematic 0*k*0 absences lead to simulation of the centrosymmetric space group $P2_1/c$, which accounts for the report by Cox & Webster (1936), as previously pointed out by the present authors (Bonamico, Dessy & Vaciago, 1965). The intensities of 704 independent reflexions above film background (*ca.* 48% of those possible with Cu $K\alpha$ radiation) were estimated visually from sets of multiple-film equi-inclination Weissenberg photographs. Corrections for Lorentz and polarization effects and for spot extension and cylindrical absorption, were applied. The structure was solved by conventional Patterson and Fourier methods.

Full matrix least-squares refinement with anisotropic thermal parameters yielded a final *R* value of 0·063 and the parameters listed in Tables 1 and 2.*

Bond lengths and angles are given in Table 3.

Table 1. *Final coordinates with standard deviations* ($\times 10^4$)

	x/a	*y/b*	*z/c*
Au(1)	0 (13)	2480 (5)	0 (4)
Au(2)	4983 (13)	2446 (7)	28 (4)
K(1)	7985 (27)	2042 (29)	3204 (18)
K(2)	2286 (27)	7041 (27)	1838 (18)
Cl(1,1)	−1068 (27)	5406 (27)	517 (18)
Cl(1,2)	1453 (29)	−484 (28)	−466 (19)
Cl(1,3)	1105 (33)	1950 (31)	1788 (18)
Cl(1,4)	−825 (33)	2936 (30)	−1784 (21)
Cl(2,1)	5197 (35)	4023 (38)	1777 (19)
Cl(2,2)	5101 (35)	1017 (40)	−1593 (20)
Cl(2,3)	6774 (29)	−104 (28)	762 (18)
Cl(2,4)	3516 (36)	5059 (34)	−618 (22)

Table 3. *Bond distances and angles and their estimated standard deviations in* $KAuCl_4$

Au(1)–Cl(1,1)	2·20 (2) Å	Cl(1,1)–Au(1)–Cl(1,3)	90 (1)°
Au(1)–Cl(1,2)	2·37 (2)	Cl(1,1)–Au(1)–Cl(1,4)	94 (1)
Au(1)–Cl(1,3)	2·33 (2)	Cl(1,2)–Au(1)–Cl(1,3)	86 (1)
Au(1)–Cl(1,4)	2·25 (3)	Cl(1,2)–Au(1)–Cl(1,4)	90 (1)
Au(2)–Cl(2,1)	2·36 (2)	Cl(2,1)–Au(2)–Cl(2,3)	87 (1)
Au(2)–Cl(2,2)	2·20 (3)	Cl(2,1)–Au(2)–Cl(2,4)	90 (1)
Au(2)–Cl(2,3)	2·37 (2)	Cl(2,2)–Au(2)–Cl(2,3)	88 (1)
Au(2)–Cl(2,4)	2·20 (3)	Cl(2,2)–Au(2)–Cl(2,4)	94 (1)

Discussion

Since $Z=4$ there are two crystallographically independent molecules in the cell. The two independent gold atoms are

* The table of structure factors has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30099. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Thermal parameters (with* e.s.d.'*s*)

b_{ij} is defined by: $T=\exp[-10^{-4}(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)]$.

	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Au(1)	112 (6)	−23 (7)	11 (3)	128 (4)	−2 (4)	33 (1)
Au(2)	97 (6)	−3 (8)	39 (3)	144 (4)	9 (5)	46 (2)
K(1)	117 (26)	70 (72)	−32 (30)	274 (42)	−156 (41)	65 (13)
K(2)	116 (27)	−129 (66)	5 (32)	221 (37)	145 (39)	81 (16)
Cl(1,1)	87 (25)	100 (59)	2 (28)	223 (43)	−117 (33)	53 (11)
Cl(1,2)	102 (29)	60 (59)	49 (31)	203 (41)	10 (34)	68 (13)
Cl(1,3)	173 (39)	6 (76)	36 (31)	208 (38)	−6 (36)	35 (11)
Cl(1,4)	119 (29)	49 (72)	−20 (32)	181 (38)	32 (40)	66 (13)
Cl(2,1)	156 (39)	322 (91)	−24 (33)	371 (62)	−71 (44)	49 (11)
Cl(2,2)	107 (29)	77 (81)	−14 (30)	358 (54)	−89 (44)	54 (11)
Cl(2,3)	113 (28)	240 (66)	17 (31)	211 (41)	−3 (35)	55 (12)
Cl(2,4)	148 (35)	14 (91)	4 (42)	274 (52)	97 (51)	88 (19)

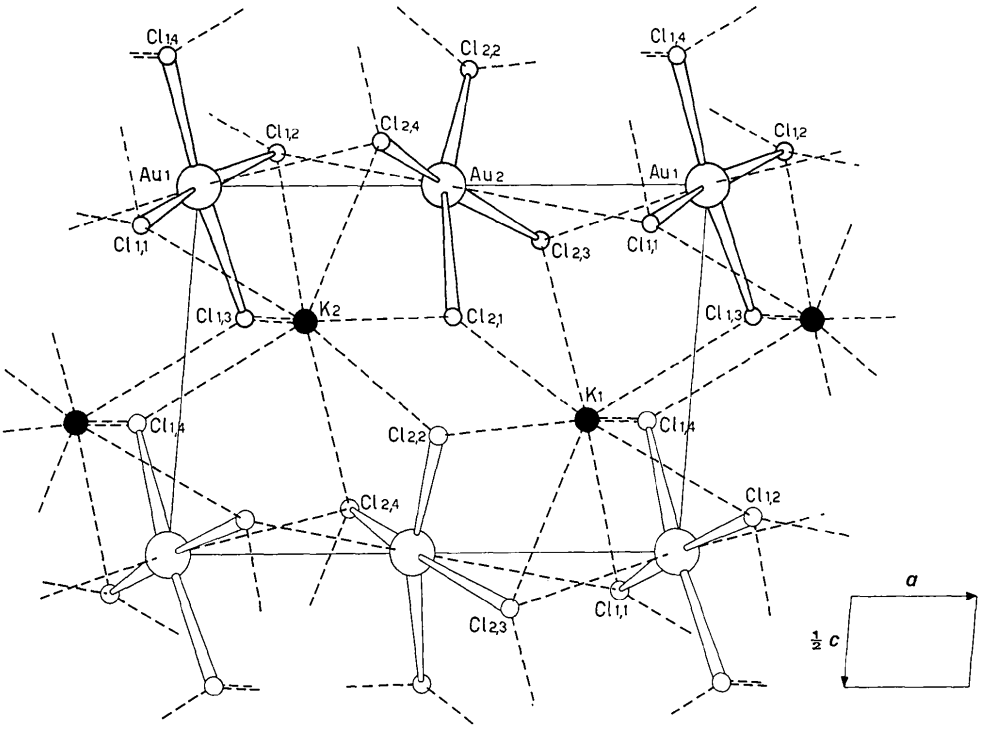

Fig. 1. [010] Projection, showing environment of the potassium atoms.

K(1) environment is:		Cl(2,3)	x, y, z
Cl(1,3)	$1+x$, y, z	Cl(1,4)	$1+x$, $-y$, $\frac{1}{2}+z$
Cl(1,4)	$1+x$, $1-y$, $\frac{1}{2}+z$	Cl(1,2)	$1+x$, $-y$, $\frac{1}{2}+z$
Cl(1,1)	$1+x$, $1-y$, $\frac{1}{2}+z$	Cl(2,3)	x, $-y$, $\frac{1}{2}+z$
Cl(2,2)	x, $-y$, $\frac{1}{2}+z$	Cl(2,1)	x, y, z.
K(2) environment is:		Cl(1,2)	x, $1+y$, z
Cl(2,4)	x, y, z	Cl(2,1)	x, y, z
Cl(2,2)	x, $1-y$, $\frac{1}{2}+z$	Cl(2,4)	x, $1-y$, $\frac{1}{2}+z$
Cl(1,4)	x, $1-y$, $\frac{1}{2}+z$	Cl(1,3)	x, y, z
Cl(1,3)	x, $1+y$, z	Cl(1,1)	x, y, z.

at 0, $\frac{1}{4}$, 0 and near $\frac{1}{2}$, $\frac{1}{4}$, 0, while there is a pseudo-centre of symmetry at $\frac{1}{4}$, $\frac{1}{4}$, 0 in the crystal structure. As was pointed out by Srinivasan (1961), in non-centrosymmetric structures containing a partial centre of symmetry, 'inverse overlap' between the atoms related by inversion through the centre occurs. The problem of the refinement of structures affected by 'inverse overlap' has been examined by Rae & Maslen (1963) who concluded that accurate refinement of the atomic parameters is not possible, even using different refinement techniques.

As described above, the present structure was refined using a full-matrix least-squares method and the presence of 'inverse overlap' is evident on examination of the standard deviations in atomic parameters. These are much larger than those found for sodium tetrachloroaurate (Bonamico, Dessy & Vaciago, 1965). In view of these relatively large standard deviations in atomic parameters, it is not possible to give a detailed discussion of individual bond angles and distances. Nevertheless, it is seen that the average Au–Cl distances are in agreement with those found in the sodium salt. Coordination about the gold atoms is essentially square planar.

The planes of the two independent $[AuCl_4]^-$ ions are nearly parallel (to *ca.* 2°). Each gold atom interacts (contacts of *ca.* 3·6 Å) with two chlorine atoms from neighbouring ions to form polymeric infinite chains of $[AuCl_4]^-$ ions along the *a* axis (see Fig. 1). Adjacent tetrachloroaurate chains are held together by coordination of chlorine atoms to potassium ions. This occurs so as to give ninefold coordination about both potassium ions, the shortest K–Cl distance being 3·1 Å and the longest 3·6 Å.

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