Acta Cryst. (1983). C**39**, 1173–1174

Disilver(I) Decachlorodioxotetraaluminate(III), $Ag_2[Al_4Cl_{10}O_2]$

By Dieter Jentsch, Peter G. Jones,* Einhard Schwarzmann and George M. Sheldrick

Institut für Anorganische Chemie der Universität, Tammannstrasse 4, *D*–3400 *Göttingen, Federal Republic of Germany*

(*Received* 6 *April* 1983; *accepted* 20 *June* 1983)

Abstract. $M_r = 710{\cdot}20$, orthorhombic, *Pbca*, $a = 11{\cdot}240\,(2)$, $b = 12{\cdot}278\,(4)$, $c = 12{\cdot}955\,(3)$ Å, $U = 1788$ Å^3, $Z = 4$, $D_x = 2{\cdot}64$ g cm^{-3}, Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å, $\mu = 39$ cm^{-1}), $F(000) = 1328$, $R = 0{\cdot}045$ for 1802 unique observed reflections. The compound is formed in the system $AgCl/AlCl_3$ when traces of water are present; the deliberate use of the theoretical amount of $AlCl_3.6H_2O$ gives a quantitative yield of polycrystalline material. The structure contains $[Al_4Cl_{10}O_2]^{2-}$ ions with crystallographic $\bar{1}$ symmetry. The Ag^+ ions are coordinated by five chlorines in a distorted trigonal-bipyramidal arrangement (the first observation of such coordination of Ag^I). The extended structure is a three-dimensional polymer.

Introduction. In the course of studies of systems MCl–$AlCl_3$ we have already reported the structure of $CuAlCl_4$ (Hildebrandt, Jones, Schwarzmann & Sheldrick, 1982). For M = Ag we obtained colourless, extremely moisture-sensitive crystals; these were sealed into glass capillaries in a dry-box. It was impossible to avoid some surface decomposition, but the crystal quality was still suitable for an X-ray structure determination of the nature of the product.

Experimental. D_m not measured. 6281 profile-fitted reflections (Clegg, 1981) measured on a Stoe four-circle diffractometer with monochromated Mo $K\alpha$ radiation ($2\theta_{\max} = 55°$). Three standard reflections: no variation. After Lp and semi-empirical absorption corrections (crystal size 0·4 × 0·3 × 0·2 mm), merging equivalents gave 2054 independent reflections, of which 1802 with $F > 4\sigma(F)$ were used for all calculations; $R_{\text{int}} = 0{\cdot}026$. Cell constants refined from 2θ values of 40 reflections in the range $20° < 2\theta < 24°$. Systematic absences indicated space group *Pbca*. Ag-atom coordinates obtained from the Patterson function; all other atoms located in subsequent difference syntheses. After anisotropic refinement (on F) of all atoms, the final R value was 0·045 [R_w 0·043, weighting scheme $w^{-1} = \sigma^2(F) + 0{\cdot}0001F^2$]. $(\Delta/\sigma)_{\max} = 0{\cdot}02$; max. and min. heights in final $\Delta\rho$ map +1 and −1·5 e Å^{-3}; no correction for secondary extinction. Calculations performed with *SHELXTL* (Sheldrick, 1978).

Table 1. *Atomic coordinates* (× 10^4) *and temperature factors* (Å^2 × 10^3)

$U_{\text{eq}} = \frac{1}{3}$ of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Ag	4843 (1)	6489 (1)	1912 (1)	56 (1)
Al(1)	2098 (1)	4563 (1)	1352 (1)	25 (1)
Al(2)	5168 (1)	6059 (1)	4978 (1)	25 (1)
Cl(1)	3712 (1)	5131 (1)	685 (1)	45 (1)
Cl(2)	6831 (1)	5286 (1)	2168 (1)	46 (1)
Cl(3)	4457 (1)	7113 (1)	3855 (1)	45 (1)
Cl(4)	6197 (1)	8112 (1)	1092 (1)	44 (1)
Cl(5)	2155 (1)	2832 (1)	1431 (1)	40 (1)
O	885 (3)	4873 (2)	546 (2)	27 (1)

Table 2. *Bond lengths* (Å) *and angles* (°)

Ag–Cl(1)	2·631 (1)	Ag–Cl(2)	2·700 (1)
Ag–Cl(3)	2·666 (1)	Ag–Cl(4)	2·723 (1)
Ag–Cl(5$^{\text{vii}}$)	2·855 (1)	Al(1)–Cl(1)	2·127 (2)
Al(1)–Cl(5)	2·128 (2)	Al(1)–O	1·759 (3)
Al(1)–Cl(2$^{\text{v}}$)	2·134 (2)	Al(2)–Cl(3)	2·105 (2)
Al(2)–Cl(4$^{\text{vi}}$)	2·110 (2)	Al(2)–O$^{\text{viii}}$	1·804 (3)
Al(2)–O$^{\text{ii}}$	1·798 (3)		
Cl(1)–Ag–Cl(2)	97·3 (1)	Cl(1)–Ag–Cl(3)	132·4 (1)
Cl(2)–Ag–Cl(3)	100·1 (1)	Cl(1)–Ag–Cl(4)	119·9 (1)
Cl(2)–Ag–Cl(4)	89·2 (1)	Cl(3)–Ag–Cl(4)	104·4 (1)
Cl(1)–Ag–Cl(5$^{\text{vii}}$)	81·6 (1)	Cl(2)–Ag–Cl(5$^{\text{vii}}$)	173·8 (1)
Cl(3)–Ag–Cl(5$^{\text{vii}}$)	85·0 (1)	Cl(4)–Ag–Cl(5$^{\text{vii}}$)	86·1 (1)
Cl(1)–Al(1)–Cl(5)	108·7 (1)	Cl(1)–Al(1)–O	110·4 (1)
Cl(5)–Al(1)–O	105·6 (1)	Cl(1)–Al(1)–Cl(2$^{\text{v}}$)	110·4 (1)
Cl(5)–Al(1)–Cl(2$^{\text{v}}$)	112·1 (1)	O–Al(1)–Cl(2$^{\text{v}}$)	109·6 (1)
Cl(3)–Al(2)–Cl(4$^{\text{vi}}$)	112·6 (1)	Cl(3)–Al(2)–O$^{\text{viii}}$	115·0 (1)
Cl(3)–Al(2)–O$^{\text{ii}}$	114·0 (1)	Ag–Cl(1)–Al(1)	112·0 (1)
Ag–Cl(2)–Al(1$^{\text{ii}}$)	117·0 (1)	Ag–Cl(3)–Al(2)	114·5 (1)
Ag–Cl(4)–Al(2$^{\text{iii}}$)	108·2 (1)	Al(1)–Cl(5)–Ag$^{\text{i}}$	124·3 (1)
Al(1)–O–Al(2$^{\text{iv}}$)	127·8 (2)	Al(1)–O–Al(2$^{\text{v}}$)	138·3 (2)
Al(2$^{\text{iv}}$)–O–Al(2$^{\text{v}}$)	93·8 (1)		

Symmetry operators

(i)	$0{\cdot}5-x,\ -0{\cdot}5+y,\ z$	(v)	$-0{\cdot}5+x,\ y,\ 0{\cdot}5-z$
(ii)	$0{\cdot}5+x,\ y,\ 0{\cdot}5-z$	(vi)	$x,\ 1{\cdot}5-y,\ 0{\cdot}5+z$
(iii)	$x,\ 1{\cdot}5-y,\ -0{\cdot}5+z$	(vii)	$0{\cdot}5-x,\ 0{\cdot}5+y,\ z$
(iv)	$0{\cdot}5-x,\ 1{\cdot}0-y,\ -0{\cdot}5+z$	(viii)	$0{\cdot}5+x,\ y,\ 0{\cdot}5-z$

Discussion. Final atomic coordinates and derived parameters are given in Tables 1 and 2.† The structure

---

* To whom correspondence should be addressed.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38672 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/83/091173-02$01.50

solution shows that the product is $AgAl_2Cl_5O$ (empirical formula), rather than the expected $AgAlCl_4$. This may perhaps be attributed to the extremely low water content of the $AlCl_3$ (anhydrous. '*puriss.*', Fluka) used in the synthesis; the formation of HCl was observed. Quantitative yields could be obtained by heating AgCl (powder, 99·9%, Ventron), $AlCl_3$ (freshly sublimed) and $AlCl_3.6H_2O$ ('*krist. reinst*', Merck) to 443 K in molar ratio 6:11:1 in an evacuated quartz ampoule. On cooling the melt, polycrystalline $AgAl_2Cl_5O$ forms, with evolution of HCl.

The structure contains the centrosymmetric $[Al_4Cl_{10}O_2]^{2-}$ ion (Fig. 1). This ion has recently been reported by Thewalt & Stollmaier (1982), although with only moderately accurate dimensions (probably due to the presence of two heavy Nb atoms and two dichloromethane molecules); it has also been prepared independently in this laboratory during investigations of aluminium/silicon compounds (Graalmann, Hesse, Klingebiel, Clegg, Haase & Sheldrick, 1983).

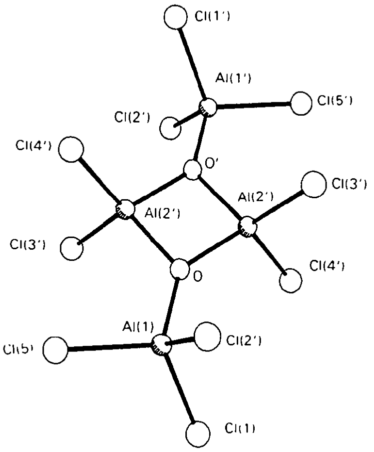

Fig. 1. The centrosymmetric $[Al_2Cl_{10}O_2]^{2-}$ ion, showing the atom numbering. Primes indicate symmetry-equivalent atoms (see Table 2).

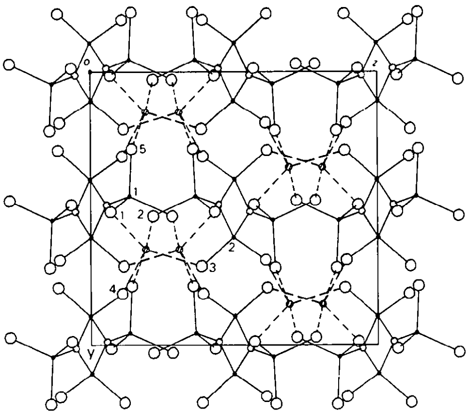

Fig. 2. Projection of the polymeric structure along **a**. Ag—Cl bonds are indicated by dashed lines. Atom key: black dots Al, hatched circles Ag, small open circles O, large open circles Cl. The numbering scheme of Al and Cl is shown.

The Ag^+ ions are coordinated by five chlorines in a somewhat distorted trigonal-biypyramidal arrangement (see packing plot, Fig. 2). To the best of our knowledge this is the first time that such a coordination geometry has been observed for Ag^I. The Ag—Cl bond lengths lie in the range 2·631—2·855 Å; there are no other Ag···Cl contacts < 3·8 Å. The extended structure forms a three-dimensional polymer (Fig. 2).

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

References

Clegg, W. (1981). *Acta Cryst.* A**37**, 22–28.

Graalmann, O., Hesse, M., Klingebiel, U., Clegg, W., Haase, M. & Sheldrick, G. M. (1983). *Angew. Chem.* Submitted.

Hildebrandt, K., Jones, P. G., Schwarzmann, E. & Sheldrick, G. M. (1982). *Z. Naturforsch. Teil B*, **37**, 1129–1131.

Sheldrick, G. M. (1978). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*. Univ. of Göttingen.

Thewalt, U. & Stollmaier, F. (1982). *Angew. Chem.* **94**, 137–138.