Refinement

Refinement on F
$R = 0.032$
$wR = 0.040$
$S = 0.46$
501 reflections
43 parameters
H-atom parameters not refined
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{\max} = 0.0049$
$\Delta\rho_{\max} = 1.52$ e Å^{-3}
$\Delta\rho_{\min} = -3.82$ e Å^{-3}
Extinction correction: Zachariasen (1963)
Extinction coefficient: $5.82\,(6) \times 10^{-7}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.3.1 and 2.2B)

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Pb	0	0.2513 (1)	1/4	0.0036 (1)
Se	0.1492 (1)	0.1796 (2)	0.7378 (2)	0.0026 (1)
O1	0.1018 (6)	0.3781 (18)	0.5993 (18)	0.004 (1)
O2	0.0749 (6)	0.0821 (18)	0.9086 (17)	0.004 (1)
O3	0.2039 (6)	0.3335 (20)	0.9309 (20)	0.005 (1)

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

Pb—O1	2.760 (11)	Pb—O2$^{\rm vi}$	2.573 (10)
Pb—O1$^{\rm i}$	2.949 (11)	Pb—O2$^{\rm vii}$	2.555 (10)
Pb—O1$^{\rm ii}$	2.760 (11)	Se—O1	1.655 (11)
Pb—O1$^{\rm iii}$	2.949 (11)	Se—O2	1.688 (10)
Pb—O2$^{\rm iv}$	2.573 (10)	Se—O3	1.727 (11)
Pb—O2$^{\rm v}$	2.555 (10)		
O1—Se—O2	102.4 (5)	O2—Se—O3	99.9 (5)
O1—Se—O3	99.7 (5)		

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

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1127). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Re-Examination Shows that Copper(II) Tetrachloroaluminium, Cu(AlCl$_4$)$_2$, is Monoclinic and not Triclinic as Originally Stated

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Abstract

Analysis of the published diffraction data for copper(II) tetrachloroaluminium, Cu(AlCl$_4$)$_2$ [Kitajima, Shimanouchi, Ono & Sasada (1982). *Bull. Chem. Soc. Jpn*, **55**, 2064–2067], shows that the crystals are monoclinic (space group $P2_1/c$, $Z = 2$) and not triclinic ($P\bar{1}$, $Z = 2$) as originally stated. Refinement on this basis gives $R = 0.0883$ for all 1218 data compared with 0.1191 for the triclinic cell. Revised coordinates are given. The changes in the structure are small.

Comment

The crystal structure of copper(II) tetrachloroaluminium, Cu(AlCl$_4$)$_2$, was determined from four-circle diffractometer measurements using graphite-monochromated Mo $K\alpha$ radiation (Kitajima, Shimanouchi, Ono & Sasada, 1982; hereinafter KSOS82) and reported to be triclinic with $a = 6.582\,(6)$, $b = 7.362\,(5)$, $c = 12.265\,(5)$ Å, $\alpha = 89.99\,(5)$, $\beta = 85.97\,(6)$, $\gamma = 89.76\,(6)°$, space group $P\bar{1}$, $Z = 2$. Some 2600 reflections were used in a block-diagonal least-squares refinement, giving $R_F = 0.110$ for 2594 non-zero [$|F_o| > 3\sigma(F_o)$] reflections. The structure was stated to have pseudo $P2_1/c$ symmetry 'inferred from the systematically weak intensities of $0k0$ and $h0l$ reflections'. We show that the true

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space group is $P2_1/c$ and refine the structure on the basis of F_o values (the subscript '*o*' is used both for 'observed' and 'original') taken from Document No. 8239 of the Chemical Society of Japan; the experimental data given are from KSOS82.

The following lines of evidence show that the crystals have space group $P2_1/c$ and not $P\bar{1}$:

(1) We have refined the structure in the triclinic cell (on F_o^2) with *SHELXL*93 (Sheldrick, 1993) and obtained coordinates for the two purportedly independent formula units (I, II) related by $x(\text{I}) = x(\text{II})$; $y(\text{I}) = y(\text{II}) - 1/2$; $z(\text{I}) = 1/2 - z(\text{II})$; the displacement factors are related by $U_{ij}(\text{I}) \simeq \pm U_{ij}(\text{II})$, where the positive sign applies except for ij = 23 and 12. The r.m.s. values of (Δ/σ), U_{eq} and U_{ii} for the coordinate pairs are 1.3, 0.68 and 1.38, respectively, suggesting that the departures from $P2_1/c$ symmetry are less than twice the least-squares e.s.d.'s.

(2) KSOS82 gave $F_{\text{lim}} = 1.86$ as their observed threshold value. Of the nine $0k0$ reflections in Document No. 8239, five have k odd of which three are given as $F = 0$, $F(010) = 2.6$ and $F(090) = 3.7$. There are 193 $h0l$ reflections, of which 102 have l odd and 80 are given as zero; the largest of the remaining 22 is $F(0,0,13) = 4.6$ $(2.5 \times F_{\text{lim}})$. In the triclinic structure, none of the $|F_{\text{calc}}|$ values for the $0k0$ (k odd) and $h0l$ (l odd) reflections is larger than 3.1, and all are smaller than the parallel F_o values except when the reflections are unobserved. We have not been able to identify the reasons for the these violations; the Renninger effect is one of many possibilities.

(3) The F_o values of 1056 pairs of hkl, $h\bar{k}l$ reflections ($h0l$ excluded) were plotted pairwise and fitted by the linear equation $F_o(h\bar{k}l) = 0.9721F_o(hkl) + 0.8109$ (the linear correlation coefficient $r = 0.9778$). R_F(merge) = 14.8%, which is appreciably higher than the values usually cited for symmetry-related reflections. Analysis of the differences $[F_o(hkl) - F_o(h\bar{k}l)]$ following the method of Abrahams & Keve (1971) would have been desirable but could not be carried out because the $\sigma^2(F_o)$ values were not deposited although they were used in the original structure determination. The small systematic differences between $F_o(hkl)$ and $F_o(h\bar{k}l)$ are possibly the result of absorption corrections not being performed.

(4) The deviation of γ from 90° ($\delta = 3.8\sigma$) is ascribed to systematic error or underestimation of σ (Taylor & Kennard, 1986).

Before refining the structure in space group $P2_1/c$, the $F_o(h\bar{k}l)$ were corrected by multiplying by 1.0288 and subtracting 0.8. When the corrected F_o pairs were plotted, the best straight line through them (Fig. 1) had the equation $F_{\text{corr}}(h\bar{k}l) = 1.00004F_o(hkl) + 0.034$ ($r = 0.9778$); R_F(merge) = 15.1% after correction. The set of original $F_o(hkl)$ and corrected $F_{\text{corr}}(h\bar{k}l)$ values were then averaged in accordance with monoclinic symmetry, the space-group absences applied and the structure refined with *SHELXL*93 (on F^2 with β set to 94.03° and the monoclinic cell lengths related to those of the triclinic cell by $a_m = -a_t$, $b_m = -b_t$, $c_m = c_t$). The revised parameters are given in Table 1 and interatomic distances and angles in Table 2. The differences from the KSOS82 values are small; this also holds for the structural description and diagrams, which are not repeated (however, the change in β from acute to obtuse should not be forgotten).

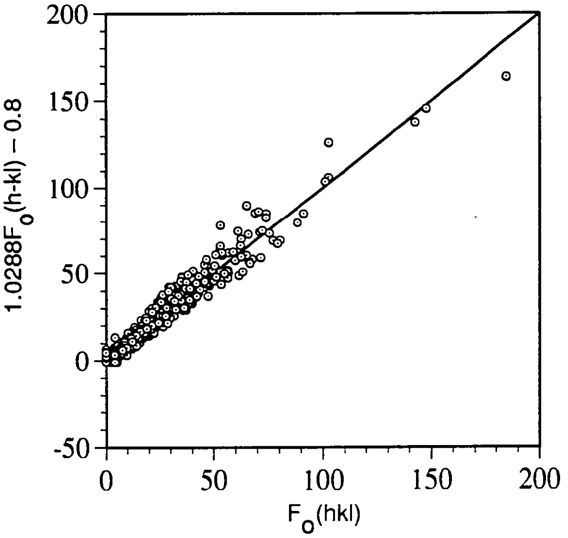

Fig. 1. $F_{\text{corr}}(h\bar{k}l) = 1.0288F_o(h\bar{k}l) - 0.8$ plotted against $F_o(hkl)$. The straight line has the equation $F_{\text{corr}}(h\bar{k}l) = 1.00004F_o(hkl) + 0.034$ ($r = 0.9778$). 1056 points are plotted.

The rather large value of R is probably the result of systematic errors in the intensity measurements and the neglect of absorption and, perhaps, extinction effects. The program output lists the twenty 'most disagreeable' reflections which have $\{[2(|F_o - F_{\text{calc}}|)]/(F_o + F_{\text{calc}})\}$ values between 0.298 and 0.180; we have deliberately not suppressed these reflections during refinement. The principal mean-square atomic displacement ellipsoids are appreciably anisotropic, all in the same sense $[\langle U_{11}\rangle > \langle U_{22}\rangle > \langle U_{33}\rangle$; $\langle U_1\rangle = 0.072\,(15)$, $\langle U_2\rangle = 0.044\,(7)$, $\langle U_3\rangle = 0.024\,(7)$ Å^2].

The structure of $Co(AlCl_4)_2$ has been reported (Ibers, 1962). Although KSOS82 state that $Cu(AlCl_4)_2$ and $Co(AlCl_4)_2$ have different powder patterns, they have compared the reported structures. Dr R. E. Marsh has drawn our attention to intriguing relationships between the atomic coordinates of corresponding atoms in the two structures. Reinvestigation of both structures appears desirable but we do not intend to do this.

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

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cu	0	0	0	0.0425 (5)
Al1	0.1918 (3)	−0.2649 (3)	0.1812 (2)	0.0360 (6)

Cl1	−0.1115 (3)	−0.2444 (3)	0.0944 (2)	0.0429 (6)
Cl2	0.2992 (3)	−0.0131 (3)	0.1086 (2)	0.0453 (6)
Cl3	0.1665 (4)	−0.2331 (3)	0.3503 (1)	0.0517 (6)
Cl4	0.3576 (4)	−0.4876 (3)	0.1365 (2)	0.0626 (7)

Table 2. *Geometric parameters* (Å, °)

Cu—Cl1	2.288 (2)	Al1—Cl4	2.065 (3)
Cu—Cl1^{i}	2.288 (2)	Al1—Cl3	2.105 (3)
Cu—Cl2	2.300 (3)	Al1—Cl2	2.195 (3)
Cu—Cl2^{i}	2.300 (3)	Al1—Cl1	2.201 (3)
Cl1—Cu—Cl1^{i}	180.0	Cl4—Al1—Cl2	111.82 (15)
Cl1—Cu—Cl2	88.06 (7)	Cl3—Al1—Cl2	110.85 (13)
Cl1^{i}—Cu—Cl2	91.94 (7)	Cl4—Al1—Cl1	113.83 (14)
Cl1—Cu—Cl2^{i}	91.94 (7)	Cl3—Al1—Cl1	109.70 (14)
Cl1^{i}—Cu—Cl2^{i}	88.06 (7)	Cl2—Al1—Cl1	93.01 (11)
Cl2—Cu—Cl2^{i}	180.0	Al1—Cl1—Cu	89.23 (9)
Cl4—Al1—Cl3	115.46 (15)	Al1—Cl2—Cu	89.06 (9)

Symmetry code: (i) $-x$, $-y$, $-z$.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: MD1003). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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