The Crystal and Molecular Structure of $Cu(AlCl_4)_2$

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The structure of copper(II) tetrachloroaluminum $Cu(AlCl_4)_2$ was determined by the single-crystal X-ray diffraction technique. The crystal is triclinic: $a=6.582(6)$, $b=7.362(5)$, and $c=12.265(5)$ Å; $\alpha=89.99(5)$, $\beta=85.97(6)$, and $\gamma=89.77°$; space group $P\bar{1}$ and $Z=2$. The structure was solved by the heavy-atom method and refined by applying the block-diagonal matrix least-squares technique on 2628 independent reflections up to a final R value of 0.110. The structure consists of closely-packed centrosymmetric $Cu(AlCl_4)_2$ molecules with copper atoms tetragonally coordinated. Structural difference between $Cu(AlCl_4)_2$ and $Co(AlCl_4)_2$ is described.

Aluminium halides form complexes with various halides in gas phase, and their structures and thermal properties have been extensively studied.[1–5] However, no attempt has been made to isolate crystals of such complexes and determine their crystal structures by single-crystal X-ray analysis, except for $Co(AlCl_4)_2$.[6]

We have reported that aluminium chloride and copper(II) chloride form a 2:1 complex, $2AlCl_3 \cdot CuCl_2$, when heated together.[7] The complex is a very active catalyst for isomerization of pentane at room temperature.[8,9] Studies on the structure of this complex by ESR and Raman spectroscopy have suggested that the complex contains $(AlCl_4)^-$ units and that the coordination environment of Cu(II) ions is of distorted octahedron, though the structure of $CuCl(Al_2Cl_7)$ was proposed for the complex in gas phase.[10,11]

Though the structure of $Co(AlCl_4)_2$ has been determined by Ibers,[6] the powder X-ray pattern of the present complex[8] is different from that of $Co(AlCl_4)_2$.

In the present work, the structure of $2AlCl_3 \cdot CuCl_2$ is determined in order to obtain the structural basis for the catalytic activity of this compound.

Experimental

Suitable crystals for diffraction measurements were prepared by the chemical transport method. A mixture of $AlCl_3$ and $CuCl_2$ (0.5 g each) was sealed under vacuum in a Pyrex glass tube of about 15 cm length with a diameter of 1.5 cm. Then, the tube was partitioned into three parts, which were heated in an electronic furnance at 170, 190, and 230 °C, respectively. Fine yellow prismatic crystals were deposited on the glass wall at the middle part. The density of the crystal was determined by flotation in a mixture of CCl_4 and CH_2Br_2. Since the compound is hygroscopic, a crystal of approximately $0.2 \times 0.3 \times 0.55$ mm^3 was sealed in a thin-walled glass capillary filled with nitrogen. Cell constants were obtained from the least-squares treatment on angular settings of 25 high angle reflections. Data collection was carried out on a Rigaku computer-controlled four-circle diffractometer, using the graphite-monochromated Mo $K\alpha$ radiation. The crystal data and the details of experimental conditions are summarized in Table 1. Attenuators were automatically inserted to keep the counting rate below 8000 cps. Backgrounds were counted for 10 s at each end of scan range. Intensities were corrected for the Lorentz and polarization factors but not for the absorption. Four standard reflections measured after every 100 reflections indicated no significant intensity variation throughout the experiment.

Structure Determination

The structure was solved by the heavy-atom method and atomic parameters were refined by the block-diagonal least-squares technique. The quantity minimized was $\Sigma w(|F_o| - k|F_c|)^2$ with $w=1/\sigma^2(F_o)$. Zero reflections were included in the least-squares calculation by assuming $|F_o| = F_{lim}$ ($=1.86$) where F_{lim} is the observed threshold value, but they were omitted when $|F_c|—F_{lim}$. The final R value was 0.110 for non-zero reflections. Final atomic parameters are listed in Table 2.[12] Atomic scattering factors were taken from the International Table for X-ray Crystallography.[13] Computations were done on a HITAC M-170 computer in Tokyo Institute of Technology by use of the program system XSEN.[14] The programs

TABLE 1. CRYSTAL DATA AND DETAIL OF EXPERIMENTAL CONDITIONS

Formula	$CuAl_2Cl_8$
Formula weight	401.1
Crystal system	$P\bar{1}$
a/Å	6.582(6)
b/Å	7.362(5)
c/Å	12.265(5)
α	89.99(5)°
β	85.97(6)°
γ	89.77(6)°
V/Å^3	592.8
Z	2
D_m/g cm^{-3}	2.25
D_x/g cm^{-3}	2.25
μ(for Mo $K\alpha$)/cm^{-1}	37.9
Crystal size/mm	$0.20 \times 0.30 \times 0.55$
Scan technique	ω-2θ scan
Scan range (ω)	$1.0° + 0.35° \tan\theta$
Scan speed (ω)/min^{-1}	2°
Maximum 2θ	54°
No. of reflections measured	2628
No. of non-zero reflections ($|F_o| > 3\sigma(F)$)	2594

Table 2. Final atomic coordinates and e.s.d.'s

Atom	$10^4 x$	$10^4 y$	$10^4 z$	$10B_{eq}/Å^2$
Cu(1)	0	0	0	33
Cu(2)	0	5000	5000	32
Al(1)	−1915(7)	2752(5)	1812(3)	28
Al(2)	1910(7)	7654(5)	3192(3)	28
Cl(1)	1109(6)	2442(4)	941(3)	34
Cl(2)	−2993(6)	130(5)	1082(3)	36
Cl(3)	−1650(7)	2333(5)	3502(3)	42
Cl(4)	−3589(7)	4868(6)	1368(4)	49
Cl(5)	−1123(6)	7441(5)	4053(3)	33
Cl(6)	3003(6)	5141(5)	3916(3)	35
Cl(7)	1666(7)	7332(5)	1500(3)	41
Cl(8)	3555(7)	9871(6)	3637(3)	50

a) B_{eq} is the equivalent isotropic temperature factor, defined by $B_{eq}=8\pi^2(U_1+U_2+U_3)/3$ where U_1, U_2, and U_3 are the principal components of U matrix.

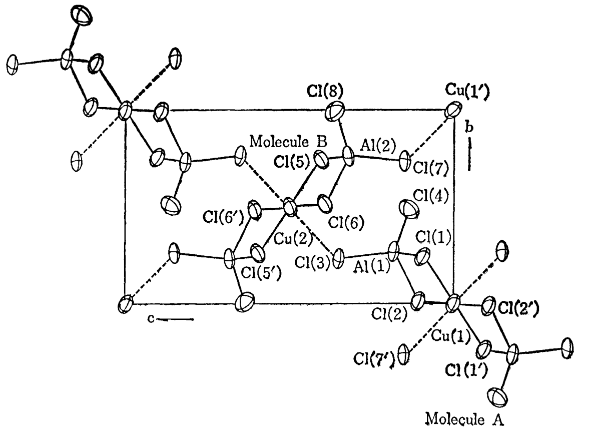


Fig. 1. Atomic numbering and thermal ellipsolids at the 50% probability level.

DCMS for plotting thermal ellipsolids[15] and DCMSGD for drawing crystal structures[16] were also used.

Results and Discussion

The crystal structure of the complex $2AlCl_3\cdot CuCl_2$ consists of two crystallographically independent molecules of $Cu(AlCl_4)_2$ as shown in Fig. 1. Each molecule has a crystallographic center of symmetry; molecule A is on the origin while molecule B resides at (0, 1/2, 1/2). Both molecules are approximately related by a twofold screw axis at $x=0$, $z=1/4$ or by a c glide plane at $y=1/4$, indicating a pseudo $P2_1/c$ symmetry, which was inferred from the systematically weak intensities of $0k0$ and $h0l$ reflections.

Table 3. Interatomic distances and angles

(a) Bond distances (l/Å)			
Cu(1)-Cl(1)	2.286(4)	Cu(2)-Cl(5)	2.288(4)
Cu(1)-Cl(2)	2.298(4)	Cu(2)-Cl(6)	2.306(4)
Cu(1)-Cl(7')	2.951(4)	Cu(2)-Cl(3)	2.951(4)
Cl(7')-Cl(1)	3.844(5)	Cl(3)-Cl(5)	3.842(5)
Cl(7')-Cl(2)	3.752(5)	Cl(3)-Cl(6)	3.766(5)
Cl(7')-Cl(1')	3.618(5)	Cl(3)-Cl(5')	3.624(5)
Cl(7')-Cl(2')	3.729(5)	Cl(3)-Cl(6')	3.725(5)
Cl(1)-Cl(2)	3.192(5)	Cl(5)-Cl(6)	3.189(5)
Cl(1)-Cl(2')	3.291(5)	Cl(5)-Cl(6')	3.307(5)
Al(1)-Cl(1)	2.197(5)	Al(2)-Cl(5)	2.198(5)
Al(1)-Cl(2)	2.203(5)	Al(2)-Cl(6)	2.193(5)
Al(1)-Cl(3)	2.105(6)	Al(2)-Cl(7)	2.106(6)
Al(1)-Cl(4)	2.060(6)	Al(2)-Cl(8)	2.057(6)
Cl(1)-Cl(3)	3.517(5)	Cl(5)-Cl(7)	3.517(5)
Cl(1)-Cl(4)	3.571(6)	Cl(5)-Cl(8)	3.573(6)
Cl(2)-Cl(3)	3.550(5)	Cl(6)-Cl(7)	3.538(5)
Cl(2)-Cl(4)	3.523(6)	Cl(6)-Cl(8)	3.517(6)
Cl(3)-Cl(4)	3.523(6)	Cl(7)-Cl(8)	3.520(6)
Al(1)-Cu(1)	3.150(4)	Al(2)-Cu(2)	3.153(4)
(b) Bond angles (ϕ/°)			
Cl(1)-Cu(1)-Cl(2)	88.3(1)	Cl(5)-Cu(2)-Cl(6)	87.9(1)
Cl(7')-Cu(1)-Cl(2)	90.4(1)	Cl(3)-Cu(2)-Cl(6)	90.7(1)
Cl(7')-Cu(1)-Cl(1)	93.6(1)	Cl(3)-Cu(2)-Cl(5)	93.5(1)
Cl(1)-Al(1)-Cl(2)	93.0(2)	Cl(5)-Al(2)-Cl(6)	93.2(2)
Cl(1)-Al(1)-Cl(3)	109.7(2)	Cl(5)-Al(2)-Cl(7)	109.6(2)
Cl(1)-Al(1)-Cl(4)	114.1(2)	Cl(5)-Al(2)-Cl(8)	114.2(2)
Cl(2)-Al(1)-Cl(3)	111.0(2)	Cl(6)-Al(2)-Cl(7)	110.7(2)
Cl(2)-Al(1)-Cl(4)	111.5(2)	Cl(6)-Al(2)-Cl(8)	111.7(2)
Cl(3)-Al(1)-Cl(4)	115.5(3)	Cl(7)-Al(2)-Cl(8)	115.4(3)
Cu(1)-Cl(2)-Al(1)	88.8(2)	Cu(2)-Cl(6)-Al(2)	89.0(2)
Cu(1)-Cl(1)-Al(1)	89.3(2)	Cu(2)-Cl(5)-Al(2)	89.3(2)
Cu(2)-Cl(3)-Al(1)	126.8(2)	Cu(1')-Cl(7)-Al(2)	126.6(2)

The interatomic distances and angles are listed in Table 3. There are no significant structural differences between the two molecules. Each copper atom is tetragonally coordinated by chlorine atoms with a mean Cu–Cl distance of 2.295 Å, slightly shorter than the sum of the tetrahedral covalent radii.[17] The next nearest neighboring chlorine atoms are located above and below the plane of this group at a distance of 2.951 Å as indicated with the broken lines in Fig. 1. This distance corresponds to a bond number of about 0.1,[18] implying very weak interaction. Similar situations are usually observed with many copper (II) complexes.[19] The Cu(1)→Cl(7') and Cu(2)→Cl(3) vectors make angles of 86.4° and 86.5° with the corresponding basal planes, respectively.

Each aluminium atom is tetrahedrally coordinated by chlorine atoms, and the more strongly the chlorine atom is coordinated to the copper atom, the longer the Al–Cl distance becomes as in the case of $Co(AlCl_4)_2$.[6] The uncoordinated chlorine atoms have the shortest Al–Cl distances of 2.057 and 2.060 Å. These values are smaller than those obtained for $Co(AlCl_4)_2$ (2.105 Å),[6] $C_6H_6CuAlCl_4$ (2.078 Å),[20] $(C_6H_6PdAlCl_4)_2$ (2.10 Å),[21] and $NaAlCl_4$ (2.11 Å),[22] indicating that the $AlCl_4$ tetrahedra in the present complex are the most distorted among these chloroaluminate complexes.

The interplanar angle between the Cu(1), Cl(1), Cl(2), and Cl(1), Cl(2), Al(1) planes and that between the Cu(2), Cl(5), Cl(6), and Cl(5), Cl(6), Al(2) planes are 8.3° and 8.7°, respectively. The Cu–Al distances are long and the bridging Cu–Cl–Al angles are not highly acute, implying that there is no direct metel-metel interaction.[23]

The networks composed of $AlCl_4$ tetrahedra and $CuCl_6$ distorted octahedra lie parallel to the bc plane of the unit cell, forming a layer structure. The closest distance between the layers is about 3.60 Å for Cl(7) Cl(4) at $(1+x, y, z)$. It is equal to twice the van der Waals radius of chlorine (1.80 Å).

The crystal structures of $Co(AlCl_4)_2$[6] and $Cu(AlCl_4)_2$ are compared in Figs. 2(a) and 2(b). In both structures $AlCl_4$ groups play a dual role as monocoordinate as well as bicoordinate ligands. An important difference is the fact that the cobalt atom resides on the crystallographic two-fold axis and has *cis* configuration, 1, whereas the copper atom sits on the center of symmetry and possesses *trans* configuration, 2, as far as the monocoordinate ligands are concerned.

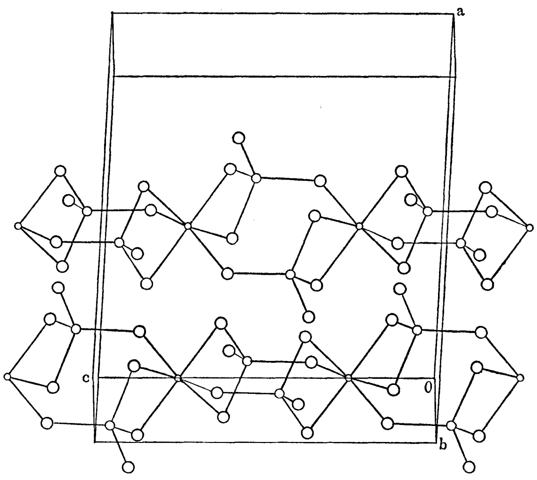


Fig. 2(a). Crystal structure of $Co(AlCl_4)_2$.

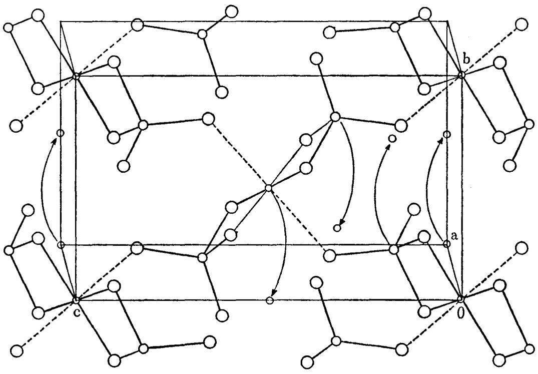


Fig. 2(b). Crystal structure of $Cu(AlCl_4)_2$.
If the copper and aluminum atoms would be transfered as indicated with arrows, the hypothetical structure could be derived as shown in Fig. 2(c).

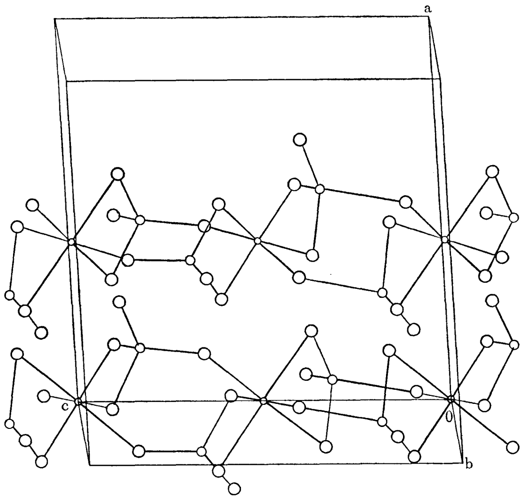
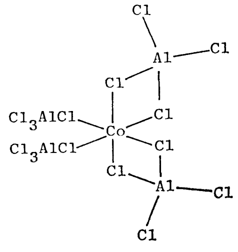
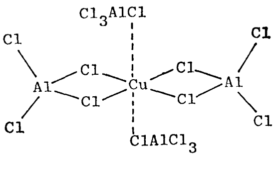


Fig. 2(c). Hypothetical crystal structure of $Cu(AlCl_4)_2$.



(1)



(2)

The crystal structure of the present compound, like that of $Co(AlCl_4)_2$,[6] consists of layers parallel to the (001) plane, each containing atoms of one kind. The layers repeat in the sequence Cu–Cl–Al–Al–Cl. As shown in Fig. 3, the chlorine atoms are arranged in the unit cell in approximately hexagonal close-packed arrays like those observed with $Co(AlCl_4)_2$,[6] with copper and aluminium atoms occupying a part of the available octahedral and tetrahedral interstices, respectively. The volume per chlorine atom is 37.1 Å^3, which is slightly larger than the volume for $Co(AlCl_4)_2$,[6] 35 Å^3.

The essential difference between the two structures originates from the different intralayer arrangement of cobalt and copper atoms, and from the interlayer displacement of aluminium atoms in two successive layers. Thus, the hypothetical structure of $Co(AlCl_4)_2$ type could be generated from the observed structure of $Cu(AlCl_4)_2$ by simply translating metal atoms along the b axis in the way given in Fig. 2(b), though the obtained structure (Fig. 2(c)) as it is, has abnormalities in some of interatomic distances and bond angles. On the other hand, if cobalt atoms in $Co(AlCl_4)_2$ were replaced by copper atoms, these atoms would inevitably be in an octahedral geometry with nearly equal Cu–Cl distances. The structural difference between $Cu(AlCl_4)_2$ and $Co(AlCl_4)_2$[6] may result from the difference in preferred coordination geometries of the transition metals in this system.

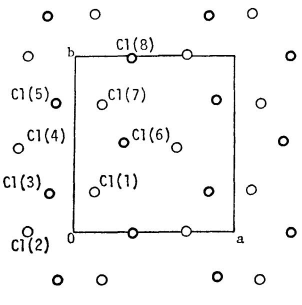


Fig. 3. Projection of chlorine layers.
The atoms drawn with thicker circles are nearer to the viewer.

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References

1) A. Dell'Anna and F. P. Emmenegger, *Helv. Chim. Acta*, **58**, 1145 (1975).
2) A. Anundskas and H. A. Øye, *J. Inorg. Nucl. Chem.*, **37**, 1609 (1975).
3) W. C. Laughlln and N. W. Gregory, *J. Phys. Chem.*, **80**, 127 (1976).
4) G. N. Papatheodorou and G. H. Kucera, *Inorg. Chem.*, **16**, 1006 (1977).
5) H. Schafer, *Angew. Chem., Int. Ed. Engl.*, **15**, 713 (1976).
6) J. A. Ibers, *Acta Crystallogr.*, **15**, 967 (1962).
7) N. Kitajima and Y. Ono, *J. Mol. Catal.*, **10**, 121 (1981).
8) Y. Ono, N. Kitajima, T. Nakajima, and T. Keii, *Proc. 7th Int. Congr. Catal., Tokyo*, p. 1006 (1980).
9) Y. Ono, T. Tanabe, and N. Kitajima, *J. Catal.*, **56**, 47 (1979).
10) F. P. Emmenengger, C. Rohrbasser, and C. W. Schlapfer, *Inorg. Nucl. Chem. Lett.*, **12**, 127 (1976).
11) C. W. Schlapfer and C. Rohrbasser, *Inorg. Chem.*, **17**, 1623 (1978).
12) The anisotropic thermal parameters and the list of the observed and calculated structure factors are kept at the Chemical Society Japan as Document No. 8239.
13) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV, p. 71.
14) A. Takenaka, XSEN, The crystallographic Computing System, Laboratory of Chemistry for Natural Products, Tokyo Institute of Technology (1980).
15) A. Takenaka, Program DCMS, Schematic Drawing of Crystal and Molecular Structures Containing Atomic Thermal Motions, Laboratory of Chemistry for Natural Products, Tokyo Institute of Technology (1974).
16) K. Harata, Program DCMSGD, A Computer Program for Drawing Crystal and Molecular Structures on Graphic Display or X-Y Plotter, Research Institute for Polymers and Textiles, Yatabemachi Higashi, Tsukuba-gun, Ibaraki 305 (1978).
17) L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y. (1960), p. 246.
18) L. Pauling, "Nature of the Chemical Bond," 3rd ed Cornell University Press, Ithaca, N. Y. (1960), p. 255.
19) B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970).
20) R. W. Turner and E. L. Amma, *J. Am. Chem. Soc.*, **88**, 1877 (1966).
21) G. Allegra, G. T. Casagrande, A. Immirzi, L. Porri, and G. Vitulli, *J. Am. Chem. Soc.*, **92**, 289 (1970).
22) N. C. Baenziger, *Acta Crystallogr.*, **4**, 216 (1951).
23) L. F. Dahl, E. R. de Gil, and R. D. Feltham, *J. Am. Chem. Soc.*, **91**, 1653 (1969).