

Molecular Structure Corporation (1989). *TEXSAN*. Single-crystal structure analysis software. MSC, 3200A Research Forest Drive, The Woodlands, TX 77381, USA.  
 NARUKE, H., OZEKI, T. & YAMASE, T. (1991). *Acta Cryst.* C47, 489–492.  
 OZEKI, T. & YAMASE, T. (1991). *Acta Cryst.* C47, 693–696.

SHANNON, R. D. (1976). *Acta Cryst.* A32, 751–767.  
 STILLMAN, M. J. & THOMSON, A. J. (1976). *J. Chem. Soc. Dalton Trans.* pp. 1138–1144.  
 YAMASE, T. & NARUKE, H. (1991). *J. Chem. Soc. Dalton Trans.* pp. 285–292.  
 YAMASE, T., NARUKE, H. & SASAKI, Y. (1990). *J. Chem. Soc. Dalton Trans.* pp. 1687–1696.

*Acta Cryst.* (1992). C48, 1374–1376

## Structure of 2RbCl·CuCl<sub>2</sub>·2H<sub>2</sub>O

BY KENJI WAIZUMI, HIDEKI MASUDA AND HITOSHI OHTAKI\*

*Coordination Chemistry Laboratories, Institute for Molecular Science, Myodaiji, Okazaki 444, Japan*

AND KIM A. BURKOV AND LUDMILA CHERNYKH

*Department of Inorganic Chemistry, Leningrad University, Leningrad, Russia*

(Received 28 September 1991; accepted 6 January 1992)

**Abstract.** Copper(II) dirubidium tetrachloride dihydrate,  $M_r = 412.32$ , tetragonal,  $P4_2/mnm$ ,  $a = 7.596$  (2),  $c = 8.027$  (3) Å,  $V = 463.1$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.957$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 13.63$  mm<sup>-1</sup>,  $F(000) = 382$ ,  $T = 293$  K,  $R(F) = 0.039$  for 277 independent reflections with  $|F_o| > 3\sigma|F_o|$ . The Cu<sup>2+</sup> ion has a distorted octahedral coordination consisting of two Cl(1) ions at 3.000 (3) Å, two Cl(2) ions at 2.257 (3) Å and two water molecules at 1.969 (8) Å at the equatorial positions of the square plane. Each of the water molecules is trigonally coordinated and forms two equivalent O—H···Cl(1) hydrogen bonds with an O···Cl(1) length of 3.130 (7) Å. Four Cl(1) and four Cl(2) ions form a distorted cube around the Rb<sup>+</sup> ion with Rb—Cl(1) and Rb—Cl(2) lengths of 3.367 (2) and 3.380 (2) Å, respectively.

**Introduction.** An approximate structure of the 2RbCl·CuCl<sub>2</sub>·2H<sub>2</sub>O crystal was first determined by Hendricks & Dickinson (1927), together with crystallographically isomorphic 2KCl·CuCl<sub>2</sub>·2H<sub>2</sub>O and 2NH<sub>4</sub>Cl·CuCl<sub>2</sub>·2H<sub>2</sub>O crystals using the X-ray diffraction method. The three crystals were tetragonal with space group  $P4_2/mnm$ , and the Cu<sup>2+</sup> ion in the complex showed distorted octahedral coordination consisting of two elongated Cu—Cl(1) bonds, two Cu—Cl(2) and two Cu—H<sub>2</sub>O bonds, the order of the interatomic distances being reported as Cu—Cl(1) > Cu—O > Cu—Cl(2). For 2KCl·CuCl<sub>2</sub>·2H<sub>2</sub>O and 2NH<sub>4</sub>Cl·CuCl<sub>2</sub>·2H<sub>2</sub>O crystals, detailed structural analyses have been carried out by X-ray and neutron

diffraction methods (Chrobak, 1934; Matković, Peterson & Willett, 1969; Chidambaram, Navarro, Garcia, Linggoatmodjo, Lin Shi-Chien, Il-Hwan Suh, Sequeira & Srikanta, 1970; Bhakay-Tamhane, Sequeira & Chidambaram, 1980). These results showed that the order of the bond lengths should be Cu—Cl(1) > Cu—Cl(2) > Cu—O for 2KCl·CuCl<sub>2</sub>·2H<sub>2</sub>O and 2NH<sub>4</sub>Cl·CuCl<sub>2</sub>·2H<sub>2</sub>O, which is different from that reported by Hendricks & Dickinson (1927).

The crystal structure of 2RbCl·CuCl<sub>2</sub>·2H<sub>2</sub>O, however, has not been redetermined except for the lattice parameters (Swanson, McMurdie, Morris, Evans, Paretzkin, Degroot & Carmel, 1972; Stepin, Iskharova, Serebrennikova, Starikova & Trunov, 1976). Thus, the crystal structure of 2RbCl·CuCl<sub>2</sub>·2H<sub>2</sub>O is reinvestigated here to refine the bond lengths between the Cu<sup>2+</sup> ion and ligands in order to compare the results with those of 2KCl·CuCl<sub>2</sub>·2H<sub>2</sub>O and 2NH<sub>4</sub>Cl·CuCl<sub>2</sub>·2H<sub>2</sub>O.

**Experimental.** A crystal suitable for the X-ray analysis was prepared from an RbCl—CuCl<sub>2</sub>—H<sub>2</sub>O ternary solution by slow evaporation. A blue lumpy crystal with dimensions 0.3 × 0.3 × 0.4 mm was used for data collection at 293 K. Diffraction intensities were measured on a Rigaku AFC-5S automatic four-circle diffractometer with graphite-monochromated Mo K $\alpha$  radiation. The unit-cell parameters were determined from the setting angles ( $23.07 \leq 2\theta \leq 30.66^\circ$ ) of 25 reflections. Intensities of 453 reflections ( $0 \leq h \leq 11$ ,  $0 \leq k \leq 11$ ,  $0 \leq l \leq 11$ ) within the range  $\theta < 30^\circ$  were measured using an  $\omega$ - $2\theta$  scan mode

\* To whom correspondence should be addressed.

with a scan width of  $(1.40 + 0.50 \tan \theta)^\circ$ .  $R_{\text{int}} = 0.0273$ . Reflections were monitored every 100 reflections by three standard reflections, and the result showed no significant variation in the intensities during the measurement. All the reflections were corrected for Lorentz and polarization effects. An empirical absorption correction using *DIFABS* (Walker & Stuart, 1983) was applied after an isotropic refinement, with corrections in the range 0.97–1.02. The corrected intensities did not definitely show whether the crystal had the tetragonal space group  $P4_2/mnm$ ,  $P\bar{4}n2$  or  $P4_2nm$ . The structure was successfully solved in the centrosymmetric space group  $P4_2/mnm$ . The standard deviations,  $\sigma(F_o)$ , were estimated from counting statistics, and 277 independent reflections with  $|F_o| > 3\sigma|F_o|$  were used for the structure determination and refinement. The heavy-atom method was applied and the structure was refined by the full-matrix least-squares method. Several cycles of refinement (on  $F$ ) for the atomic positions, including anisotropic thermal parameters of ions, were carried out with the weighting scheme  $w = [(\sigma|F_o|)^2 + (0.020|F_o|)^2]^{-1}$ . The electron density associated with H atoms could be discerned at the expected locations in the difference map, and H atoms were refined isotropically. The final values were:  $R = 0.039$ ,  $wR = 0.055$ ,  $S = 0.99$ ,  $(\Delta/\sigma)_{\text{max}} = 0.08$  for positional parameters and 0.24 for thermal parameters. Difference Fourier maps calculated using the final parameters showed maximum and minimum electron-density peaks of 0.7 and  $-1.3 \text{ e } \text{Å}^{-3}$ , located around the  $\text{Rb}^+$  ions. Scattering factors and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed on a MicroVAX II computer at the Institute for Molecular Science by using the Enraf-Nonius *SDP* program system (Frenz, 1985).

**Discussion.** The final positional parameters are listed in Table 1.\* Selected interatomic distances and angles are given in Table 2. An *ORTEP* (Johnson, 1965) drawing of the crystal structure, together with the atomic numbering, is shown in Fig. 1. The distorted octahedral coordination around  $\text{Cu}^{2+}$  consists of two Cl(1) and two Cl(2) ions, and two water molecules. The order of the bond lengths is  $\text{Cu—Cl(1)} > \text{Cu—Cl(2)} > \text{Cu—O}$ , which is consistent with the bond-length order in the  $2\text{KCl}\cdot\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  (Chrobak, 1934; Chidambaram *et al.*, 1970) and  $2\text{NH}_4\text{Cl}\cdot\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  (Chrobak, 1934; Matković *et*

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55007 (4 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0559]

Table 1. *Coordinates and equivalent isotropic thermal parameters* ( $\text{Å}^2$ )

$$B_{\text{eq}} = (4/3) \sum_i \beta_{ii} \mathbf{a}_i \cdot \mathbf{a}_i$$

	x	y	z	$B_{\text{eq}}$
Rb	0	0.5	0.25	2.0
Cu	0	0	0	1.6
Cl(1)	0.7207 (4)	-x	0	1.8
Cl(2)	0.2101 (4)	x	0	1.6
O	0	0	0.2454 (9)	2.4
H	0.070 (16)	x	0.308 (20)	9.5 (61)

Table 2. *Bond lengths* ( $\text{Å}$ ) *and angles* ( $^\circ$ )

Cu octahedron			
Cu—O	1.969 (8) × 2	Cl(1)—Cu—O	90
Cu—Cl(1)	3.000 (3) × 2	Cl(2)—Cu—O	90
Cu—Cl(2)	2.257 (3) × 2	Cl(1)—Cu—Cl(2)	90
Rb polyhedron (cube)			
Rb—Cl(1)	3.367 (2) × 4		
Rb—Cl(2)	3.380 (2) × 4		
Water molecule and hydrogen bond			
O—H	0.91 (15)	Cu—O—H	124 (12)
O—Cl(1)	3.130 (7)	H—O—H	113 (14)
Cl(1)—H	2.24 (15)	Cl(1)—H—O	170 (14)

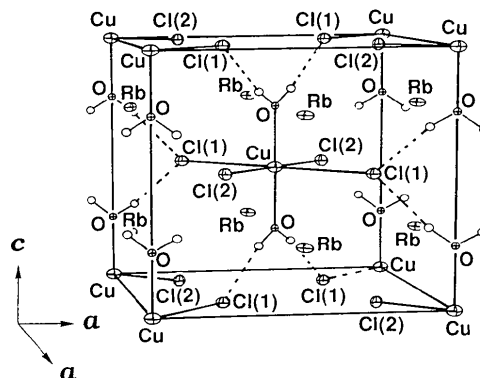


Fig. 1. An *ORTEP* drawing (Johnson, 1965) of  $2\text{RbCl}\cdot\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  with the thermal ellipsoids scaled at 30% probability level. H atoms and hydrogen bonds are represented by small circles with 0.1  $\text{Å}$  radius and by dotted lines, respectively.

*et al.*, 1969) crystals. The length of the  $\text{Cu—Cl(1)}$  bond varies from 2.895  $\text{Å}$  for  $2\text{KCl}\cdot\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  (Chidambaram *et al.*, 1970) to 3.000  $\text{Å}$  for  $2\text{RbCl}\cdot\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  (Bhakay-Tamhane *et al.*, 1980), although the lengths of the  $\text{Cu—Cl(2)}$  and  $\text{Cu—O}$  bonds are not very different in the three compounds.

The O atoms of the water molecules are situated above and below the  $\text{Cu}^{2+}$  ion along the  $c$  axis, forming two equivalent hydrogen bonds with the Cl(1) ions belonging to the nearest-neighbour Cu octahedra. The  $\text{Cl}\cdots\text{O}$  distance of the  $\text{Cl(1)}\cdots\text{H—O}$  hydrogen bonds of 3.130 (7)  $\text{Å}$  is comparable with 3.116 (5)  $\text{Å}$  for  $2\text{KCl}\cdot\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  (Chidambaram *et al.*, 1970) and 3.146 (2)  $\text{Å}$  for  $2\text{NH}_4\text{Cl}\cdot\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  (Bhakay-Tamhane *et al.*, 1980).

Four Cl(1) and four Cl(2) ions form a distorted cube around the Rb<sup>+</sup> ion located on the  $\bar{4}$  axes as shown in Fig. 2. The average distance between the Rb<sup>+</sup> and Cl<sup>-</sup> ions, 3.374 Å, is similar to that between the NH<sub>4</sub><sup>+</sup> and Cl<sup>-</sup> ions in 2NH<sub>4</sub>Cl·CuCl<sub>2</sub>·2H<sub>2</sub>O, 3.364 Å (Bhakay-Tamhane *et al.*, 1980). The average distance between the K<sup>+</sup> and Cl<sup>-</sup> ions in 2KCl·CuCl<sub>2</sub>·2H<sub>2</sub>O, 3.320 Å (Chidambaram *et al.*, 1970), is shorter than those between the monovalent cation and Cl<sup>-</sup> ion in the 2RbCl·CuCl<sub>2</sub>·2H<sub>2</sub>O and 2NH<sub>4</sub>Cl·CuCl<sub>2</sub>·2H<sub>2</sub>O crystals. Since the ionic radii reported for the ions with eight coordination are 1.51, 1.61 (Shannon, 1976) and 1.66 Å (Khan & Baur, 1972) for K<sup>+</sup>, Rb<sup>+</sup> and NH<sub>4</sub><sup>+</sup>, respectively, the interionic distances estimated by using 1.81 Å for the ionic radius of Cl<sup>-</sup> (Shannon, 1976) become 3.32, 3.42 and 3.47 Å for the K<sup>+</sup>—Cl<sup>-</sup>, Rb<sup>+</sup>—Cl<sup>-</sup> and NH<sub>4</sub><sup>+</sup>—Cl<sup>-</sup> pairs, respectively. For 2KCl·CuCl<sub>2</sub>·2H<sub>2</sub>O, the average K<sup>+</sup>—Cl<sup>-</sup> distance measured is comparable to the sum of the ionic radii thus calculated, although the average distances between the

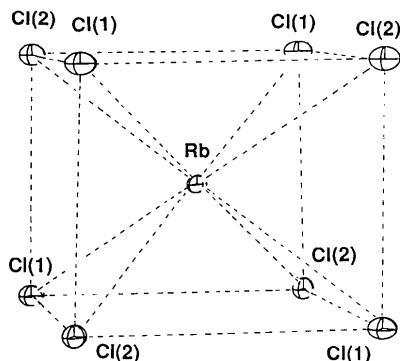


Fig. 2. An ORTEP drawing (Johnson, 1965) of the surroundings of the Rb<sup>+</sup> ion with the thermal ellipsoids scaled at the 30% probability level.

monovalent cation and Cl<sup>-</sup> ion for 2RbCl·CuCl<sub>2</sub>·2H<sub>2</sub>O and 2NH<sub>4</sub>Cl·CuCl<sub>2</sub>·2H<sub>2</sub>O are significantly shorter than the sum of the relevant ionic radii. Judging from the above M<sup>+</sup>—Cl<sup>-</sup> distances, the ionic radius of the K<sup>+</sup> ion may be most suitable to occupy the space of the three-dimensional network consisting of [CuCl<sub>4</sub>·2H<sub>2</sub>O] octahedra and the hydrogen bonds.

The present work has been financially supported by the Grant-in-Aid for Scientific Research on Priority Area of 'Molecular Approaches to Non-equilibrium Processes in Solutions' (No. 02245106) from the Ministry of Education, Science and Culture, Japan.

#### References

- BHAKAY-TAMHANE, S. N., SEQUEIRA, A. & CHIDAMBARAM, R. (1980). *Acta Cryst.* B36, 2925–2929.  
 CHIDAMBARAM, R., NAVARRO, Q. O., GARCIA, A., LINGGOAT-MODJO, K., LIN SHI-CHEN, IL-HWAN SUH, SEQUEIRA, A. & SRIKANTA, S. (1970). *Acta Cryst.* B26, 827–830.  
 CHROBAK, L. (1934). *Z. Kristallogr.* 88, 35–47.  
 FRENZ, B. A. (1985). *Enraf-Nonius Structure Determination Package; SDP User's Guide*. Version 4. Enraf-Nonius, Delft, The Netherlands.  
 HENDRICKS, S. B. & DICKINSON, R. G. (1927). *J. Am. Chem. Soc.* 49, 2149–2162.  
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.  
 KHAN, A. A. & BAUR, W. H. (1972). *Acta Cryst.* B28, 683–693.  
 MATKOVIĆ, B., PETERSON, S. W. & WILLETT, R. D. (1969). *Croat. Chem. Acta*, 41, 65–72.  
 SHANNON, R. D. (1976). *Acta Cryst.* A32, 751–767.  
 STEPIN, B. D., ISKHAKOVA, L. D., SEREBRENNIKOVA, G. M., STARIKOVA, Z. A. & TRUNOV, V. K. (1976). *Zh. Neorg. Khim.* 21, 2783–2786.  
 SWANSON, H. E., MCMURDIE, H. F., MORRIS, M. C., EVANS, E. H., PARETZKIN, B., DEGROOT, J. H. & CARMEL, S. J. (1972). *Natl Bur. Stand. US Monogr.* 25, 47.  
 WALKER, N. & STUART, D. (1983). *Acta Cryst.* A39, 158–166.

*Acta Cryst.* (1992). C48, 1376–1380

## Structures of SrV<sub>6</sub>O<sub>11</sub> and NaV<sub>6</sub>O<sub>11</sub>

BY YASUSHI KANKE, KATSUO KATO, EIJI TAKAYAMA-MUROMACHI AND MITSUMASA ISOBE

National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba, Ibaraki 305, Japan

(Received 30 November 1990; accepted 14 January 1992)

**Abstract.** Strontium hexavanadate, SrV<sub>6</sub>O<sub>11</sub>,  $M_r = 569.26$ , hexagonal,  $P6_3/mmc$ ,  $a = 5.7716$  (1),  $c = 13.0793$  (5) Å,  $V = 377.32$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 5.010$  g cm<sup>-3</sup>,  $\mu = 137.58$  cm<sup>-1</sup>,  $F(000) = 528.0$ , final  $R = 0.060$  for 488 unique observed reflections;

sodium hexavanadate, NaV<sub>6</sub>O<sub>11</sub>,  $M_r = 504.63$ , hexagonal,  $P6_3/mmc$ ,  $a = 5.7123$  (1),  $c = 13.0974$  (4) Å,  $V = 370.12$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 4.50$ ,  $D_x = 4.528$  g cm<sup>-3</sup>,  $\mu = 71.64$  cm<sup>-1</sup>,  $F(000) = 474.0$ , final  $R = 0.017$  for 580 unique observed reflections.

0108-2701/92/081376-05\$06.00

© 1992 International Union of Crystallography