

of 100–139°. Referring to the results of two electron deformation density studies on NH<sub>4</sub>SCN and NaSCN (Bats & Coppens, 1977; Bats, Coppens & Kvick, 1977), the pronounced bond-direction selectivity of thiocyanate S is attributable to two cooperative effects: (i) by the presence of a larger ring-like region of electron lone-pair density around S lateral to the SCN group, and (ii) by the simultaneous presence of an electron-deficient region protruding from the S atom in the axial direction of the SCN group. Both effects are considered to stem from a thiocyanate S atom which is almost unhybridized and has its electron lone pairs concentrated in 3s and 3p $\pi$  orbitals.

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## Structure of K<sub>3</sub>Na<sub>4</sub>H<sub>2</sub>[TbW<sub>10</sub>O<sub>36</sub>].20H<sub>2</sub>O

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**Abstract.** Tripotassium tetrasodium dihydrogen decatungstotribate icosahydrate, K<sub>3</sub>Na<sub>4</sub>H<sub>2</sub>[TbW<sub>10</sub>O<sub>36</sub>].20H<sub>2</sub>O, *M<sub>r</sub>* = 3209, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 29.772 (8), *b* = 16.164 (2), *c* = 11.443 (1) Å,  $\beta$  = 96.01 (2)°, *V* = 5476 (2) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 3.81 g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha)$  = 0.71069 Å,  $\mu$  = 230 cm<sup>-1</sup>, *F*(000) = 5584, *T* = 298 K, *R* = 0.053 for 8398 unique reflections. The *D*<sub>4d</sub> [TbW<sub>10</sub>O<sub>36</sub>]<sup>9-</sup> anion consists of two [W<sub>5</sub>O<sub>18</sub>]<sup>6-</sup> groups chelating to the central Tb<sup>3+</sup> ion. The Tb<sup>3+</sup> cation exhibits a tetragonal antiprismatic coordination with Tb—O distances of 2.40–2.44 Å. The average Tb—W distance is 3.83 Å. Two K<sup>+</sup>

cations play a prominent role in linking the two highly negatively charged [W<sub>5</sub>O<sub>18</sub>]<sup>6-</sup> units of the polyanion. While the three K<sup>+</sup> cations have direct contacts to the polyanion O atoms, forming bridges to the neighboring polyanions, only one O atom of the polyanion is observed in the coordination spheres of the four Na<sup>+</sup> cations.

**Introduction.** Heteropolyanions containing lanthanoid atoms have been attracting much interest owing to their fluorescent activity. However, the photoluminescent polyanions whose crystal structures

have been determined are limited to red-emissive polyoxometalloeuropates such as  $K_{15}H_3[Eu_3(H_2O)_3(SbW_9O_{33})(W_5O_{18})_3] \cdot 2.5H_2O$  (Yamase, Naruke & Sasaki, 1990),  $Eu_2(H_2O)_{12}[Mo_8O_{27}] \cdot 6H_2O$  (Yamase & Naruke, 1991) and  $(NH_4)_{12}H_2[Eu_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4] \cdot 13H_2O$  (Naruke, Ozeki & Yamase, 1991). On the other hand, the heteropolyanions  $[LnW_{10}O_{36}]^{9-}$ , where Ln is trivalent Eu, Pr or Nd (Stillman & Thomson, 1976) and Sm, Dy, Tb or Eu (Blasse, Dirksen & Zonnevillje, 1981), have been most extensively investigated as they show high quantum efficiency of luminescence. This type of polyanion has been regarded as isostructural with the non-luminescent tetravalent Ce analogue,  $[CeW_{10}O_{36}]^{8-}$  (Iball, Low & Weakley, 1974). This paper deals with the structure of the potassium sodium salt of the green-emissive decatungstotribate,  $K_3Na_4H_2[TbW_{10}O_{36}] \cdot 20H_2O$ .

**Experimental.** 20 ml of an aqueous solution containing 8.3 g of  $Na_2WO_4 \cdot 2H_2O$  was brought to pH 7 by adding  $CH_3COOH$ . 1.02 g of  $Tb(CH_3COO)_3 \cdot 4H_2O$  in 10 ml  $H_2O$  and 1.49 g KCl in 10 ml  $H_2O$  were added. The solution was kept at room temperature and colorless crystals were obtained after a week. A single crystal with dimensions  $0.21 \times 0.25 \times 0.045$  mm, sealed in a glass capillary, was mounted on a Rigaku AFC-5R four-circle diffractometer with graphite-monochromated  $Mo K\alpha$  radiation ( $\lambda = 0.71069$  Å). Cell parameters were obtained from  $2\theta$  values of 16 reflections with  $23 < 2\theta < 30^\circ$ . A total of 16 484 reflections was collected with  $2\theta$  ranging from 5 to  $55^\circ$ , of which 8398 with  $I_{obs} > 3\sigma(I_{obs})$  were used for the structure determination. The  $\omega$ - $2\theta$  scan technique was used for data collection;  $\Delta\omega = (0.85 + 0.14 \tan\theta)^\circ$ , scan speed  $8^\circ \text{ min}^{-1}$  in  $\omega$ . The range of indices was  $-38 \leq h \leq 38$ ,  $0 \leq k \leq 20$ ,  $0 \leq l \leq 14$ ,  $(\sin\theta/\lambda)_{max} = 0.65 \text{ \AA}^{-1}$ . Lp and absorption corrections [transmission factors 0.039–0.359 (de Meulenaar & Tompa, 1965)] were applied. Three standard reflections (400, 020 and 111) monitored every 150 reflections showed intensity variations within  $\pm 1.2\%$  in  $I_{obs}$ .

The positions of the Tb and W atoms were obtained from direct methods using *MITHRIL* (Gilmore, 1984). Succeeding difference Fourier syntheses located the O atoms of the anion. At this point, the three largest peaks in the difference Fourier map were assigned as K atoms. The next four largest peaks showed six contacts to the O atoms with distances 2.3–2.6 Å. These peaks were assigned as Na atoms. Bond-valence calculations (Brown & Altermatt, 1985) supported these assignments. Twenty O atoms of water of crystallization were located. Anisotropic temperature factors were refined for W, Tb, K and Na atoms. The full-matrix least-squares refinement on  $F$  converged to  $R = 0.053$

Table 1. Fractional coordinates ( $\times 10^4$ ;  $\times 10^5$  for W and Tb) and equivalent isotropic or isotropic thermal parameters ( $\text{\AA}^2$ )

W, Tb, K and Na atoms were refined anisotropically;  $B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$ . Atomic label  $w$  denotes O atoms of water of crystallization.

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}/B_{iso}$
W(0)	58746 (3)	20667 (5)	46086 (8)	1.92
W(1)	66450 (3)	8929 (5)	61783 (7)	1.70
W(2)	67210 (3)	28957 (5)	63541 (7)	1.59
W(3)	67224 (3)	30233 (4)	35173 (7)	1.59
W(4)	66519 (3)	10117 (5)	33417 (7)	1.66
W(5)	95601 (3)	17333 (5)	57766 (8)	1.83
W(6)	87246 (3)	17239 (5)	74977 (7)	1.63
W(7)	87277 (3)	3516 (4)	53989 (7)	1.58
W(8)	87694 (3)	18223 (5)	34711 (7)	1.65
W(9)	87710 (3)	32060 (5)	55662 (7)	1.70
Tb	77246 (4)	18420 (5)	51267 (8)	1.41
K(1)	7786 (2)	-39 (3)	7416 (5)	3.3
K(2)	7945 (2)	3758 (3)	2855 (5)	3.2
K(3)	9222 (2)	-688 (3)	2892 (5)	3.1
Na(1)	2598 (4)	2053 (5)	4818 (8)	2.9
Na(2)	6216 (5)	1881 (6)	9076 (10)	4.4
Na(3)	7510 (4)	767 (5)	288 (8)	2.9
Na(4)	9978 (4)	617 (7)	1228 (10)	4.6
O(0)	5299 (6)	2153 (10)	4457 (15)	3.3 (3)
O(1)	6572 (5)	104 (8)	7163 (13)	2.3 (3)
O(2)	6689 (5)	3614 (8)	7464 (12)	2.1 (3)
O(3)	6693 (6)	3817 (8)	2477 (13)	2.5 (3)
O(4)	6594 (6)	297 (9)	2188 (13)	2.5 (3)
O(5)	10137 (6)	1686 (9)	5978 (14)	2.9 (3)
O(6)	8741 (6)	1648 (9)	9019 (14)	2.8 (3)
O(7)	8793 (5)	-715 (8)	5327 (13)	2.3 (3)
O(8)	8850 (6)	1855 (9)	1981 (14)	2.6 (3)
O(9)	8849 (6)	4259 (9)	5646 (14)	3.0 (3)
O(1')	7236 (5)	976 (8)	6170 (12)	1.7 (2)
O(2')	7308 (5)	2713 (7)	6343 (11)	1.5 (2)
O(3')	7311 (5)	2834 (7)	3818 (11)	1.5 (2)
O(4')	7245 (5)	1066 (8)	3673 (12)	1.9 (3)
O(6')	8120 (5)	1723 (7)	7063 (12)	1.7 (2)
O(7')	8125 (5)	520 (7)	5202 (11)	1.5 (2)
O(8')	8168 (5)	1871 (8)	3478 (12)	2.0 (3)
O(9')	8166 (5)	3082 (8)	5354 (12)	2.0 (2)
O(01)	5985 (6)	1182 (8)	5726 (13)	2.3 (3)
O(02)	6049 (5)	2820 (8)	5900 (12)	2.0 (2)
O(03)	6047 (5)	2909 (8)	3585 (12)	2.0 (2)
O(04)	5989 (5)	1276 (8)	3411 (12)	2.1 (3)
O(56)	9389 (5)	1691 (8)	7353 (12)	1.8 (2)
O(57)	9396 (5)	603 (8)	5636 (12)	2.0 (3)
O(58)	9428 (5)	1796 (8)	4087 (13)	2.2 (3)
O(59)	9422 (5)	2902 (8)	5823 (12)	2.0 (2)
O(12)	6629 (5)	1873 (7)	7191 (11)	1.6 (2)
O(23)	6709 (5)	3608 (8)	4977 (12)	1.7 (2)
O(34)	6651 (5)	2059 (8)	2489 (12)	1.9 (2)
O(41)	6588 (5)	307 (8)	4667 (13)	2.1 (3)
O(67)	8743 (5)	552 (7)	7061 (12)	1.7 (2)
O(78)	8797 (5)	664 (8)	3791 (12)	1.9 (2)
O(89)	8827 (5)	2989 (7)	3924 (12)	1.8 (2)
O(96)	8776 (5)	2886 (8)	7200 (12)	2.0 (3)
O(a)	6628 (5)	1971 (7)	4821 (11)	1.3 (2)
O(b)	8791 (5)	1771 (8)	5481 (12)	1.8 (2)
O(1w)	7541 (6)	2045 (8)	1502 (13)	2.4 (3)
O(2w)	7686 (6)	125 (10)	2129 (15)	3.2 (3)
O(3w)	2545 (6)	708 (10)	5461 (15)	3.4 (3)
O(4w)	3364 (9)	1825 (13)	5775 (21)	6.4 (6)
O(5w)	24 (6)	974 (10)	9006 (15)	3.4 (3)
O(6w)	9945 (7)	445 (10)	3254 (16)	3.7 (4)
O(7w)	9202 (7)	362 (10)	952 (16)	3.7 (4)
O(8w)	777 (6)	492 (10)	1208 (15)	3.4 (3)
O(9w)	733 (8)	2105 (13)	3201 (20)	5.6 (5)
O(10w)	5812 (7)	2053 (11)	838 (18)	4.5 (4)
O(11w)	5716 (14)	793 (20)	8164 (31)	11.5 (11)
O(12w)	6685 (7)	765 (11)	9844 (16)	4.0 (4)
O(13w)	2617 (7)	563 (10)	488 (15)	3.5 (3)
O(14w)	8200 (7)	375 (10)	9697 (16)	3.8 (4)
O(15w)	1762 (7)	2110 (11)	4932 (18)	4.6 (4)
O(16w)	7507 (6)	1703 (8)	8671 (13)	2.5 (3)
O(17w)	2857 (6)	1436 (10)	3105 (15)	3.4 (3)
O(18w)	4955 (10)	1992 (14)	8284 (23)	7.1 (6)
O(19w)	4543 (13)	1421 (19)	3356 (29)	10.7 (9)
O(20w)	9747 (14)	2104 (20)	1100 (33)	11.8 (11)

and  $wR = 0.063$  for 387 parameters and 8398 independent reflections. The function minimized was  $\sum w(|F_{obs}| - |F_{calc}|)^2$ . The weighting scheme employed was  $w^{-1} = \sigma^2(F_{obs})$ , where  $\sigma^2(F_{obs}^2) = \sigma^2(I_{obs}) + (0.03I_{obs})^2$ .  $S = \sum w^{1/2} ||F_{obs}| - |F_{calc}| / (n - m) = 1.78$ .  $(\Delta/\sigma)_{max} = 0.03$ . The maximum positive and negative peaks in the final difference Fourier map were 3.4 and  $-3.4 e \text{ \AA}^{-3}$ , respectively. The complex atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were carried out on a MicroVAX II computer using the *TEXSAN* (Molecular Structure Corporation, 1989) software package. The final atomic parameters are given in Table 1.\*

**Discussion.** Fig. 1 shows the structure of the  $[TbW_{10}O_{36}]^{9-}$  anion. Two  $[W_5O_{18}]^{6-}$  groups, derived by removing a  $WO_4^{4-}$  unit from the  $[W_6O_{19}]^{2-}$  anion, chelate to the central Tb atom as quadridentate ligands to form a tetragonal antiprismatic coordination. The eight W atoms adjacent to the Tb atom will be referred to as the 'belt' W atoms and the

\* Lists of structure factors, anisotropic thermal parameters and complete interatomic distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55006 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

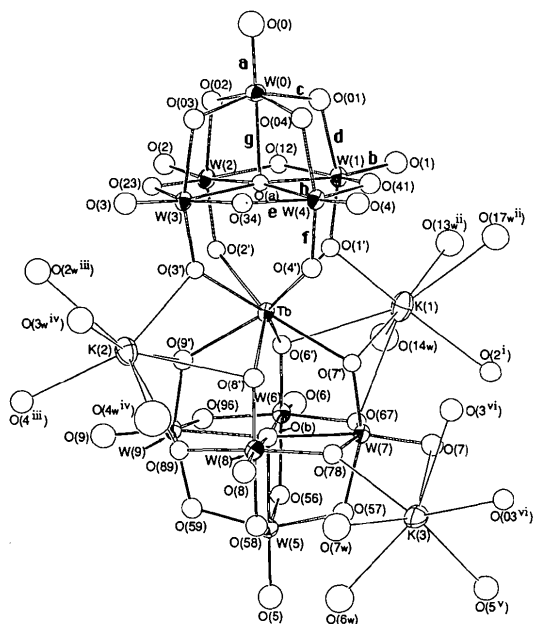


Fig. 1 ORTEP (Johnson, 1976) drawing of the  $[TbW_{10}O_{36}]^{9-}$  anion with the  $K^+$  cations bound to it. Thermal ellipsoids are scaled to enclose the 50% probability level. Letters a-h identify the bond types listed in Table 2. Symmetry code: (i)  $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{3}{2} - z$ ; (ii)  $1 - x, -y, 1 - z$ ; (iii)  $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (iv)  $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$ ; (v)  $2 - x, -y, 1 - z$ ; (vi)  $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$ .

remaining two W atoms as the 'cap' W atoms. O atoms with the primed numerals denote those bridging W and Tb atoms. O atoms shared by five W atoms are named as O(a) and O(b). Fig. 2 shows the packing diagram of the unit cell. In the asymmetric unit there are three  $K^+$  and four  $Na^+$  cations, 20 water molecules of crystallization and a  $[TbW_{10}O_{36}]^{9-}$  anion. Three  $K^+$  cations have seven or eight contacts to O atoms within 3.2 Å, five of each are from the polyanion. K(1) and K(2) bridge two neighboring anions and K(3) coordinates to three anions. On the other hand, only one of the 24 O atoms in the Na coordination spheres belongs to the polyanion; the rest of them are the O atoms of water of crystallization. Each  $Na^+$  cation has six O contacts forming a distorted octahedron. The Na—O distances are 2.3–2.6 Å.

Among the three  $K^+$  cations, K(1) and K(2) play important roles in forming and stabilizing the  $[TbW_{10}O_{36}]^{9-}$  anion. As seen in Fig. 1, they have contacts to one O atom of one  $[W_5O_{18}]^{6-}$  unit and three O atoms of the other  $[W_5O_{18}]^{6-}$  unit of the anion. These interactions are expected to participate in reducing the electrostatic repulsion between the highly negatively charged  $[W_5O_{18}]^{6-}$  groups, which the trivalent  $Tb^{3+}$  cation cannot compensate for as much as the tetravalent  $Ce^{4+}$  cation. In the structure of  $Na_6H_2[CeW_{10}O_{36}] \cdot 30H_2O$  (Iball, Low & Weakley, 1974), none of the  $Na^+$  cations tightly bind to the polyanion. The tetrads of O(1'), O(6'), O(7') and

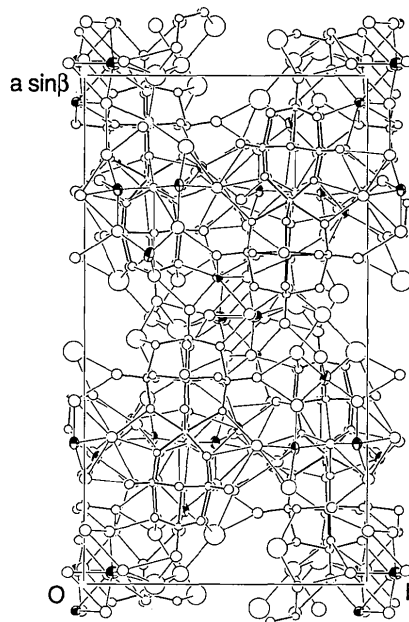


Fig. 2. Packing diagram of the unit cell viewed along the  $c$  axis. Thermal ellipsoids are scaled to enclose the 50% probability level. Na and K atoms are shown as shaded octahedra.

Table 2. Ranges and mean values of the interatomic distances (Å)

Bond type		Range	Mean
W—W*		3.314 (1)–3.350 (1)	3.33 (1)
W—W†		3.250 (1)–3.279 (1)	3.26 (1)
W—W‡		6.265 (2)–6.468 (2)	6.37 (7)
W—Tb		3.807 (2)–3.866 (2)	3.83 (2)
W—O	a§	1.71 (2)–1.71 (2)	1.71 (2)
W—O	b	1.72 (2)–1.75 (2)	1.74 (2)
W—O	c	1.89 (1)–1.94 (1)	1.92 (2)
W—O	d	1.99 (2)–2.03 (2)	2.02 (2)
W—O	e	1.91 (1)–1.97 (1)	1.94 (2)
W—O	f	1.77 (2)–1.82 (1)	1.79 (2)
W—O	g	2.24 (1)–2.28 (1)	2.26 (2)
W—O	h	2.30 (1)–2.34 (1)	2.31 (2)
Tb—O		2.40 (1)–2.44 (1)	2.42 (2)
K—O		2.63 (1)–3.18 (2)	2.91 (15)
Na—O		2.31 (2)–2.63 (2)	2.43 (9)

\* Between the cap and belt W atoms.

† Between the belt W atoms in the same  $[\text{W}_5\text{O}_{18}]^{6-}$  units.‡ Between the belt W atoms in different  $[\text{W}_5\text{O}_{18}]^{6-}$  units.

§ See Fig. 1.

Table 3. Dihedral angles ( $^\circ$ ) among the least-squares planes

Plane	Atoms					
	defining plane	1	2	3	4	5
1	W(1)W(2)W(3)W(4)					
2	W(6)W(7)W(8)W(9)	2.70				
3	TbW(0)W(1)W(3)	89.84	87.52			
4	TbW(0)W(2)W(4)	89.93	89.37	89.95		
5	TbW(5)W(6)W(8)	87.97	89.80	46.35	43.76	
6	TbW(5)W(7)W(9)	88.26	89.78	43.95	46.05	89.81

O(67) and O(3'), O(8'), O(9') and O(89) serve as quadridentate acceptor sites suitable for the binding of  $\text{K}^+$  cations. The attachment of the  $\text{K}^+$  cations to these sites reduces the highly negative charge of the  $[\text{TbW}_{10}\text{O}_{36}]^{9-}$  anion, which may better be formulated as  $[\text{K}_2\text{TbW}_{10}\text{O}_{36}]^{7-}$ . These  $\text{K}^+$  cations may also coordinate to the anion when in solution. This explains the fact that the preparation of single crystals of this complex with only  $\text{Na}^+$  cations was unsuccessful.

Table 2 lists the range and mean values of the interatomic distances and Table 3 lists the dihedral angles among the least-squares planes defined by Tb and W atoms. They show that the  $\text{TbW}_{10}$  skeleton has nearly  $D_{4d}$  symmetry. The average W—W distance between the different  $[\text{W}_5\text{O}_{18}]^{6-}$  units (6.37 Å) is 0.11 Å longer than the corresponding value in  $[\text{CeW}_{10}\text{O}_{36}]^{8-}$ . The average Tb—W distance is 0.04 Å longer than the average Ce—W distance of 3.79 Å (Iball, Low & Weakley, 1974), which shows that the two  $[\text{W}_5\text{O}_{18}]^{6-}$  ligands are not so tightly bonded to the  $\text{Tb}^{3+}$  cation as to the  $\text{Ce}^{4+}$  cation. This implies that the factor for the formation of the  $[\text{LnW}_{10}\text{O}_{36}]^{7-}$  polyanion is the electrostatic attractive force between the two  $[\text{W}_5\text{O}_{18}]^{6-}$  groups and the central lanthanoid atom, which then dominates the Ln—W distance. Therefore, the smaller positive charge of the central lanthanoid atom results in the longer Ln—W distances. On the other hand, the

substitution of the hexavalent W atoms of a Keggin-type polyanion with tetravalent Ti atoms results in shorter Ti—W distances compared with the W—W distances (Ozeki & Yamase, 1991), which implies that the electrostatic repulsive force between the metal atoms dominates the metal—metal distances in this anion. The average W—W distance among the belt W atoms is 3.26 Å and between the cap and belt W atoms is 3.33 Å. The corresponding values are 3.27 and 3.32 Å in the Ce analogue. The average W—W distance in the  $[\text{W}_6\text{O}_{19}]^{2-}$  anion is 3.289 Å (Fuchs, Freiwald & Hartl, 1978). This indicates that the local charge of the W atoms is smaller at the belt sites than at the cap sites. The polarization of the negative charge in the  $[\text{W}_5\text{O}_{18}]^{6-}$  moiety induced by the coordination to the central lanthanoid atom resulted in this asymmetric distribution of the positive charge between the cap and belt W atoms.

The average Tb—O distance of 2.42 Å is longer than the average Ce—O distance of 2.38 Å, because the ionic radius of  $\text{Tb}^{3+}$  is larger (1.04 Å for eight coordination) than that of  $\text{Ce}^{4+}$  [0.97 Å for eight coordination (Shannon, 1976)]. The  $\text{TbO}_8$  square antiprism is elongated along its fourfold axis compared with the  $\text{CeO}_8$  moiety, owing to the weaker bonding of the two  $[\text{W}_5\text{O}_{18}]^{6-}$  groups to the central  $\text{Tb}^{3+}$  atom. The O—O distances in the  $\text{TbO}_8$  square antiprism are 2.82 (2)–2.95 (2) Å [average 2.89 (4) Å] for the O atoms in the same  $[\text{W}_5\text{O}_{18}]^{6-}$  unit and 2.94 (2)–3.12 (2) Å [average 3.02 (6) Å] for those in different  $[\text{W}_5\text{O}_{18}]^{6-}$  units. These values are 2.85–2.90 Å [average 2.87 (2) Å] and 2.89–2.99 Å [average 2.94 (4) Å] in the Ce analogue.

The terminal W—O bond length at the cap W atoms (type *a* in Table 2) is 0.03 Å shorter than that at the belt W atoms (type *b* in Table 2), which shows the opposite tendency compared with the Ce analogue where the type *a* bond is 0.03 Å longer than the type *b* bonds. The distances between the cap W atoms and the five-coordinate O atoms are 2.24 and 2.28 Å, while the corresponding distance in the Ce analogue is 2.29 Å. The other W—O distances are similar to those found in the Ce analogue.

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

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

**Introduction.** An approximate structure of the  $2\text{RbCl}\cdot\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  crystal was first determined by Hendricks & Dickinson (1927), together with crystallographically isomorphic  $2\text{KCl}\cdot\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  and  $2\text{NH}_4\text{Cl}\cdot\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  crystals using the X-ray diffraction method. The three crystals were tetragonal with space group  $P4_2/mnm$ , and the  $\text{Cu}^{2+}$  ion in the complex showed distorted octahedral coordination consisting of two elongated  $\text{Cu}\text{—Cl}(1)$  bonds, two  $\text{Cu}\text{—Cl}(2)$  and two  $\text{Cu}\text{—H}_2\text{O}$  bonds, the order of the interatomic distances being reported as  $\text{Cu}\text{—Cl}(1) > \text{Cu}\text{—O} > \text{Cu}\text{—Cl}(2)$ . For  $2\text{KCl}\cdot\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  and  $2\text{NH}_4\text{Cl}\cdot\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  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  $\text{Cu}\text{—Cl}(1) > \text{Cu}\text{—Cl}(2) > \text{Cu}\text{—O}$  for  $2\text{KCl}\cdot\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  and  $2\text{NH}_4\text{Cl}\cdot\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ , which is different from that reported by Hendricks & Dickinson (1927).

The crystal structure of  $2\text{RbCl}\cdot\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ , 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  $2\text{RbCl}\cdot\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  is reinvestigated here to refine the bond lengths between the  $\text{Cu}^{2+}$  ion and ligands in order to compare the results with those of  $2\text{KCl}\cdot\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  and  $2\text{NH}_4\text{Cl}\cdot\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ .

**Experimental.** A crystal suitable for the X-ray analysis was prepared from an  $\text{RbCl}\text{—CuCl}_2\text{—H}_2\text{O}$  ternary solution by slow evaporation. A blue lumpy crystal with dimensions  $0.3 \times 0.3 \times 0.4 \text{ mm}$  was used for data collection at 293 K. Diffraction intensities were measured on a Rigaku AFC-5S automatic four-circle diffractometer with graphite-monochromated  $\text{Mo K}\alpha$  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  $\omega\text{—}2\theta$  scan mode

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