Crystal structure of dicopper(I) octa- μ_3 -chlorohexachloro-octahedro-hexatungstate(2-), $\text{Cu}_2[(\text{W}_6\text{Cl}_8)\text{Cl}_6]$

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Source of material: A silica tube ($\varnothing_{\text{outer}} = 15$ mm, $D = 1$ mm, $L = 90$ mm) charged with 500 mg (1.54 mmol) WCl_4 (Aldrich, 97%) and 17 mg (0.17 mmol) CuCl (Merck, p.a.) was heated in the temperature gradient 925 K / 915 K for one week. Greenish yellow crystals grew in the low temperature zone.

$\text{Cu}_2[(\text{W}_6\text{Cl}_8)\text{Cl}_6]$ is isostructural with cubic $\text{Cu}_2[\text{W}_6\text{Br}_{14}]$ (see ref. 1). The $[(\text{W}_6\text{Cl}_8)\text{Cl}_6]^{2-}$ cluster anions deviate slightly from $m\bar{3}m$ symmetry: $d(\text{W}-\text{W}) = 2.609$ Å, $d(\text{W}-\text{Cl}^1) = 2.493$ Å, $d(\text{W}-\text{Cl}^2) = 2.468$ Å, $d(\text{Cl}^1-\text{Cl}^1) = 3.525$ Å, $d(\text{Cl}^1-\text{Cl}^2) = 3.565$ Å, $\text{W}-\text{Cl}^1-\text{W} = 62.8^\circ$. The W atoms are shifted outside the Cl_6 cube by $\Delta = 0.082$ Å. Two Cu^+ cations center two opposite faces of a slightly compressed trigonal antiprism Cl_6 with $d(\text{Cu}-\text{Cu}) = 2.238$ Å (3x). The Cu-Cu distance (2.93 Å) is significantly shorter than that in $\text{Cu}_2[\text{W}_6\text{Br}_{14}]$ (3.066 Å) corresponding to the ratio $d(\text{Cu}-\text{Cl}^1) / d(\text{Cu}-\text{Br}^3) = 0.94$ (see ref. 1).

$\text{Cl}_{14}\text{Cu}_2\text{W}_6$, cubic, $Pn\bar{3}$ (No. 201), $a = 12.8052(5)$ Å, $V = 2099.7$ Å³, $Z = 4$, $R(F) = 0.078$, $R_w(F^2) = 0.115$.

Table 1. Parameters used for the X-ray data collection

Crystal:	greenish yellow block, size 0.06 x 0.12 x 0.16 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	364.7 cm ⁻¹
Diffractometer:	Stoe STADI4
Scan mode:	$\omega/2\theta$
$T_{\text{measurement}}$:	293 K
$2\theta_{\text{max}}$:	49.78°
$N(hkl)_{\text{unique}}$:	622
Criterion for I_0 :	$I_0 > 2 \sigma(I_0)$
$N(\text{param})_{\text{refined}}$:	35
Programs:	SHELXS-86, SHELXL-93

References

1. Zheng, Y.-Q.; Grin, Yu.; Peters, K.; von Schnering, H. G.: Two modifications of copper(I) octahedro-hexatungsten(II) tetradekabromide, $\text{Cu}_2[\text{W}_6\text{Br}_{14}]$. Z. Anorg. Allg. Chem. In press.
2. Sheldrick, G. M.: Phase Annealing in SHELX-90: Direct Methods for Large Structures. Acta Crystallogr. A 46 (1990) 467-473.
3. Sheldrick, G. M.: SHELXL-93. Program for refining crystal structures. University of Göttingen, Germany 1993.

Table 2. Final atomic coordinates and displacement parameters (in Å²)

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W	24h	0.1376(1)	-0.0265(1)	0.0335(1)	0.0136(9)	0.0163(9)	0.0153(9)	-0.0021(7)	-0.0028(7)	-0.0029(7)
Cl(1)	8e	0.1393(7)	x	x	0.028(4)	U_{11}	U_{11}	-0.010(5)	U_{12}	U_{12}
Cl(2)	24h	0.1873(7)	0.0748(8)	-0.1252(8)	0.022(5)	0.025(5)	0.025(5)	-0.014(4)	0.003(5)	-0.008(5)
Cl(3)	24h	0.3197(7)	-0.0652(8)	0.0832(8)	0.013(5)	0.033(6)	0.029(6)	0.004(5)	0.001(5)	-0.002(5)
Cu	8e	0.4339(4)	x	x	0.035(2)	U_{11}	U_{11}	-0.002(3)	U_{11}	U_{11}