

temperature factors (0.020–0.042 Å²) equal to those of their parent atoms. Anisotropic temperature factors assigned to all non-H atoms in final cycles of refinement. Final $R = 0.068$ and $wR = 0.050$ using 2991 'observed' reflections for 289 refined parameters. $\sum w(|F_o| - |F_c|)^2$ minimized with $w = 1/\sigma^2(F_o)$ where $\sigma^2(F_o) = \sigma_c^2 + 0.000054 |F_o|^2$ with σ_c from counting statistics. $(\Delta/\sigma)_{\max} = 0.01$. A final difference map showed residual fluctuations of -1.7 to $1.6 \text{ e } \text{Å}^{-3}$ (especially close to the I atoms). Scattering factors from *International Tables for X-ray Crystallography* (1974). *SHELX* (Sheldrick, 1976) used for structure determination and refinement, *PLUTO* (Motherwell & Clegg, 1976) for figures.

Discussion. Final atom parameters are listed in Table 1, distances and angles in Table 2.* The structure is built up from $[\text{Cu}(\text{HIO}_6)_2]^{5-}$, K^+ , Na^+ and crystal water. Two distorted $\text{IO}_5(\text{OH})$ octahedra are joined to a central CuO_4 square by edge sharing (see Fig. 1), forming a planar $\text{O}_2\text{—I—O}_2\text{—Cu—O}_2\text{—I—O}_2$ network. According to Hathaway & Hodgson (1973) a normal short Cu—O distance is about 2.00 Å but Cu—O distances of 1.90 Å are frequent in square-coplanar Cu complexes. In the present structure containing trivalent copper the average Cu—O distance is as short as 1.84 (2) Å. Inspection of the difference map indicated that the anion contains hydrogen bonds to O(5) and O(11) although the I(1)—O(5) bond, 1.826 (10) Å, is significantly shorter than the I(1)—O(6) bond, 1.993 (9) Å, in the opposite direction. Chains of anions

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a list of interatomic distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44529 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Refinement of the Crystal Structure of $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$

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Abstract. Cobalt(II) sulfate hexahydrate, $M_r = 263.08$, monoclinic, $C2/c$, $Z = 8$, $a = 10.022$ (3), $b = 7.217$ (2), $c = 24.224$ (3) Å, $\beta = 98.42$ (2)°, $V = 1733.2$ Å³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $D_x = 2.02 \text{ Mg m}^{-3}$, $\mu(\text{Mo } K\alpha) = 2.3 \text{ mm}^{-1}$, 629 independent single-crystal diffractometer data up to $(\sin\theta)/\lambda = 0.55 \text{ Å}^{-1}$, $F(000) = 1080$, $T = 297$ (1) K, $R = 0.032$,

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are linked together by hydrogen bonds $\text{O}(5)\text{—H}\cdots\text{O}(6)$ and $\text{O}(11)\text{—H}\cdots\text{O}(12)$ in the direction of the a axis. The position of the H in the $\text{O}(5)\cdots\text{O}(6)$ bond may be considered, however, as somewhat uncertain from the above discussion. All 26 H atoms are involved in hydrogen bonding. The observed H-atom positions confirm this conclusion although in some cases alternative hydrogen bonds may be proposed. Furthermore, all 12 crystal waters and seven of the 12 oxygen atoms in the anion are coordinated to alkali ions. The four Na^+ ions are coordinated by six oxygens, and the K^+ ion is coordinated by seven oxygens. The crystal packing, as viewed down a , is shown in Fig. 2.

The stability, shape, hydrogen-bonding capability and charge of the $[\text{Cu}(\text{HIO}_6)_2]^{5-}$ ion make it potentially useful for preparation of heavy-atom derivatives of protein structures.

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$wR = 0.028$. The structure consists of alternate layers of $\text{Co}(\text{H}_2\text{O})_6$ octahedra and SO_4 tetrahedra. Each water molecule is a donor for two hydrogen bonds with $\text{O}\cdots\text{O}$ distances between 2.663 (4) and 2.984 Å.

Introduction. The crystal structure of $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ has been solved by Zalkin, Ruben & Templeton (1962).

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The positions of the heavy atoms were determined and the structure refined to $R = 0.13$. The hydrogen-atom positions were not located in this study. The present investigation has been performed in order to obtain more precise data on the hydrogen-bonding scheme.

Experimental. Crystals were grown from a saturated aqueous solution at 323 K. A prismatic crystal, $0.2 \times 0.2 \times 0.1$ mm, was used for data collection. The lattice parameters were refined from 15 centred reflections on a Syntex $P2_1$ diffractometer ($5.65 < \theta < 19.79^\circ$) up to $h_{\max} = 10$, $k_{\max} = 7$ and $l_{\max} = \pm 26$. A data set of 4858 reflections up to $(\sin\theta)/\lambda = 0.55 \text{ \AA}^{-1}$ was registered by ω - 2θ scans. All reflections were used in subsequent refinements. Three standard reflections measured after every 50 observations did not show noticeable intensity fluctuations. The internal consistency of the diffraction data is $R(I) = \sum I - \langle I \rangle / \sum I = 0.026$. An absorption correction was applied with $\mu = 2.3 \text{ mm}^{-1}$; the transmission factor ranged from 0.698 to 0.804. A profile-analysis technique (Blessing, Coppens & Becker, 1974) was applied for background corrections. A data set of 629 reflections resulted after weighted averaging of equivalent values and was used in subsequent calculations with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The positional parameters of the Co, S and O atoms were obtained using Patterson and Fourier techniques. These parameters are in good agreement with the values reported by Zalkin *et al.* (1962). The structure was refined with individual weights given to the structure factors with $w = 1/\sigma^2(F_o)$ where $\sigma^2(F_o) = \sigma^2(\text{count}) + 0.02F_o^2$; shift to e.s.d. in last cycle, $(\Delta/\sigma)_{\max} = 0.03$. Maximum and minimum heights in the final difference Fourier synthesis were 0.80 and -0.30 e \AA^{-3} . Scattering factors were from *International Tables for X-ray Crystallography* (1974) except for H (Stewart, Davidson & Simpson, 1965). Refinement of anisotropic temperature factors and of an isotropic extinction parameter ($g = 2.55 \times 10^{-6}$) yielded $R(F) = 0.050$ and $wR(F) = 0.040$. H atoms were localized by difference Fourier syntheses and refined with isotropic temperature factors to a final $R(F) = 0.032$, $wR(F) = 0.028$ and $S = 1.98$. The positional parameters are summarized in Table 1.*

Discussion. The crystal structure of CoSO₄·6H₂O may be described by successive layers of Co(H₂O)₆²⁺ octahedra and SO₄²⁻ tetrahedra (Fig. 1). The environment of cobalt is a slightly distorted octahedron with Co—O distances ranging from 2.048 (5) to 2.112 (4) Å

Table 1. Positional parameters (with e.s.d.'s in parentheses) and equivalent isotropic thermal parameters (Å²)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$U_{\text{eq}}/U_{\text{iso}}$
Co(1)	0.0	0.0	0.0	0.0208 (6)
Co(2)	0.0	0.9481 (1)	0.25	0.0179 (6)
S(1)	0.8685 (1)	0.4520 (1)	0.1245 (1)	0.0219 (8)
O(1)	0.7742 (3)	0.6030 (5)	0.1349 (1)	0.0286 (9)
O(2)	0.9821 (3)	0.4462 (2)	0.1696 (2)	0.0428 (11)
O(3)	0.9164 (2)	0.4977 (4)	0.0704 (1)	0.0370 (9)
O(4)	0.7988 (3)	0.2729 (5)	0.1191 (1)	0.0306 (9)
O(5)	0.5965 (3)	0.7234 (5)	0.0452 (1)	0.0305 (9)
O(6)	0.5348 (4)	0.3295 (7)	0.0682 (2)	0.0429 (11)
O(7)	0.3080 (4)	0.5540 (5)	0.0215 (1)	0.0420 (11)
O(8)	0.8841 (3)	0.1575 (5)	0.2812 (1)	0.0301 (9)
O(9)	0.8870 (3)	0.7445 (5)	0.2820 (3)	0.0380 (10)
O(10)	0.8589 (3)	0.9506 (4)	0.1786 (2)	0.0377 (10)
H(51)	0.641 (4)	0.697 (6)	0.076 (2)	0.024 (10)
H(52)	0.564 (3)	0.795 (5)	0.053 (2)	0.025 (11)
H(61)	0.487 (4)	0.210 (6)	0.064 (2)	0.023 (10)
H(62)	0.586 (4)	0.322 (4)	0.090 (2)	0.051 (10)
H(71)	0.267 (4)	0.502 (6)	0.001 (3)	0.042 (11)
H(72)	0.300 (5)	0.623 (5)	0.046 (2)	0.034 (9)
H(81)	0.815 (4)	0.150 (4)	0.270 (2)	0.071 (10)
H(82)	0.904 (4)	0.285 (5)	0.288 (2)	0.041 (11)
H(91)	0.812 (4)	0.718 (4)	0.284 (2)	0.057 (10)
H(92)	0.907 (5)	0.850 (4)	0.296 (2)	0.041 (10)
H(101)	0.845 (4)	0.069 (5)	0.172 (3)	0.023 (11)
H(102)	0.790 (4)	0.930 (4)	0.201 (3)	0.056 (9)

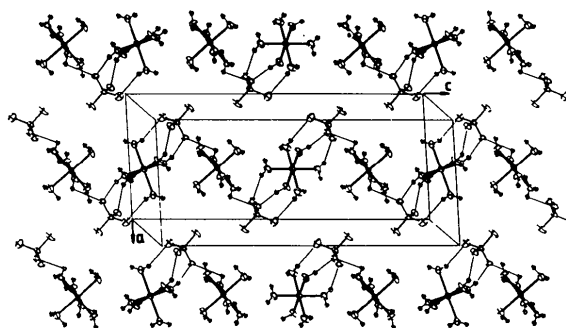


Fig. 1. Crystal structure of CoSO₄·6H₂O. Hydrogen bonds are indicated by light connections.

and angles between 88.0 (1) and 95.5 (1)°. The distance Co(2)—O(8) is significantly longer than the mean value of the remaining five Co—O distances. This particular oxygen atom belongs to the only water molecule which acts as an acceptor to a hydrogen bond. The mean Co—O value of 2.086 Å is considerably longer than in Co(NO₃)₂·2H₂O (Ribar, Milinski, Herak, Kirstanovic & Djuric, 1976) where a mean of 2.038 Å was observed.

S—O distances in the sulfate group spread from 1.458 (4) to 1.497 (3) Å with a mean length of 1.477, in good agreement with previously reported values. The mean value for the O—S—O angle of 109.5° is very near to the ideal tetrahedral configuration. S—O distances found in other sulfates spread from 1.458 (4) to 1.497 (3) Å. They were found to be between 1.460 (3) and 1.482 (2) Å in MgSO₄·6H₂O (Zalkin,

* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44618 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å) and angles (°) for $\text{Co}(\text{H}_2\text{O})_6^{2+}$ octahedra, SO_4^{2-} tetrahedra and hydrogen bonds

Water octahedron for Co(1)			
Co(1)—O(5)	2.103 (3)	O(5)—Co(1)—O(6)	91.7 (2)
—O(6)	2.048 (5)	O(5)—Co(1)—O(7)	95.5 (1)
—O(7)	2.102 (4)	O(6)—Co(1)—O(7)	88.0 (1)
Mean	2.084 (4)	Mean	91.7 (1)
Water octahedron for Co(2)			
Co(2)—O(8)	2.112 (4)	O(8)—Co(2)—O(9)	90.8 (1)
—O(9)	2.074 (4)	O(8)—Co(2)—O(10)	87.0 (1)
—O(10)	2.079 (4)	O(9)—Co(2)—O(10)	88.6 (2)
Mean	2.088 (4)	Mean	88.8 (1)
SO_4 tetrahedron			
S(1)—O(1)	1.488 (4)	O(1)—S(1)—O(2)	109.0 (2)
—O(2)	1.458 (4)	O(1)—S(1)—O(3)	106.2 (2)
—O(3)	1.497 (3)	O(1)—S(1)—O(4)	110.8 (2)
—O(4)	1.466 (4)	O(2)—S(1)—O(3)	110.3 (2)
Mean	1.477 (4)	O(2)—S(1)—O(4)	110.5 (3)
		O(3)—S(1)—O(4)	109.0 (2)
		Mean	109.3 (2)
Hydrogen bonds			
O(5)...O(1 ⁱ)	2.742 (4)	O(8)...O(1 ⁱⁱ)	2.783 (4)
O(5)...O(3 ⁱ)	2.806 (4)	O(8)...O(2 ⁱⁱ)	2.663 (2)
O(6)...O(3 ⁱ)	2.676 (5)	O(9)...O(2 ⁱⁱ)	2.698 (5)
O(6)...O(4 ⁱ)	2.781 (5)	O(9)...O(8 ⁱ)	2.984 (5)
O(7)...O(3 ⁱⁱⁱ)	2.947 (4)	O(10)...O(4 ⁱ)	2.756 (5)
O(7)...O(4 ⁱ)	2.856 (4)	O(10)...O(1 ⁱ)	2.806 (5)
Mean	2.791 (4)		

Symmetry-related positions: (i) x, y, z ; (ii) $-x, y, \frac{1}{2} - z$; (iii) $-x, -y, -z$.

Ruben & Templeton, 1964), between 1.45 (1) and 1.48 (1) Å in $\text{NiSO}_4 \cdot 6\text{D}_2\text{O}$ (O'Connor & Dale, 1966) and between 1.460 (4) and 1.482 (4) Å in $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (Baur, 1964). Bond distances and angles are summarized in Table 2.

The six independent water molecules for two different $\text{Co}(\text{H}_2\text{O})_6$ octahedra around the Co(1) and Co(2) atoms are involved in hydrogen bonds in which the oxygen atoms of the sulfate group and an O(8) oxygen atom of water act as acceptors (Table 2). The

hydrogen-bonding scheme confirms the results of Zalkin *et al.* (1962). The average O...O hydrogen-bonding distance is 2.791 Å. The individual values range from 2.663 (4) to 2.984 (5) Å. They are shorter than the sum of the van der Waals radii which is given by Bondi (1964) as $r_{\text{O}} + r_{\text{O}} = 3.04$ Å. They were found by O'Connor & Dale (1966) to be between 2.69 (2) and 2.84 (2) Å and by Baur (1964) to be between 2.70 and 2.98 Å, in $\text{NiSO}_4 \cdot \text{D}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ respectively.

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Structure of the Tetrakis(acetato)bis(triphenylphosphine)dicopper(II) Complex $\text{Cu}_2\text{Ac}_4(\text{PPh}_3)_2$

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Abstract. $[\text{Cu}_2(\text{C}_2\text{H}_3\text{O}_2)_4(\text{C}_{18}\text{H}_{15}\text{P})_2]$, $M_r = 887.84$, triclinic, $P\bar{1}$, $a = 9.149$ (7), $b = 9.559$ (3), $c = 14.709$ (3) Å, $\alpha = 61.00$ (2), $\beta = 72.67$ (5), $\gamma = 90.34$ (5)°, $V = 1056.3$ (2.1) Å³, $Z = 1$, $D_m = 1.40$, $D_x = 1.395$ g cm⁻³, $\text{Mo K}\alpha$, $\lambda = 0.71069$ Å, $\mu = 11.7$ cm⁻¹, $F(000) = 428$, $T = 293$ K, $R = 5.22\%$ for

1065 reflections. The crystal structure of $\text{Cu}_2\text{Ac}_4(\text{PPh}_3)_2$ comprises centrosymmetrical molecules each consisting of a dimeric unit Cu_2Ac_4 , similar to that found in the structure of copper(II) acetate monohydrate, with the PPh_3 molecules bonded to the Cu^{II} atoms. The interatomic distance Cu—Cu in the dimeric