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The isomorphism between $CuSeO_4 \cdot 5H_2O$ and $CuSO_4 \cdot 5H_2O$

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Solid solution / Crystal structure / **$Cu(SO_4)_x\,Cu(SeO_4)_{1-x} \cdot 5H_2O$**

Abstract. The solid solution between $CuSeO_4 \cdot 5H_2O$ and $CuSO_4 \cdot 5H_2O$ has been studied by solubility triangular diagram, powder X-ray diffraction and spectroscopic techniques. The cell parameters alter from $a = 6.132(4)$, $b = 10.755(7)$, $c = 5.979(3)$ Å, $\alpha = 97.78(5)$, $\beta = 107.13(5)$, $\gamma = 77.21(5)^\circ$ in $CuSO_4 \cdot 5H_2O$ to $a = 6.213(3)$, $b = 10.877(4)$, $c = 6.092(3)$ Å, $\alpha = 97.67(4)$, $\beta = 107.00(3)$. $\gamma = 77.14(4)^\circ$ in $CuSeO_4 \cdot 5H_2O$. The crystal structure of a mixed crystal with 37 mol% $CuSO_4 \cdot 5H_2O$ has been refined, yielding cell parameters equal to $a = 6.160(2)$, $b = 10.774(3)$, $c = 6.045(2)$ Å, $\alpha = 97.60(2)$, $\beta = 107.30(2)$, $\gamma = 77.22(2)^\circ$, $V = 409.0(4)$ Å^3, space group $P\bar{1}$, $D_x = 6.841$ g cm^{-3}, $Z = 2$, $F(000) = 834$. The final R value was 0.068 for 1446 observed reflections.

Introduction

The isostructurality of hydrated sulphate and selenate metal complexes is well known from the literature. In a preceding paper by Mestres et al. (1985) it was shown that crystals of $CoSeO_4 \cdot 5H_2O$ are isostructural to $CuSO_4 \cdot 5H_2O$. In order to determine the possible isomorphism between the hydrated sulphate and selenate different compounds with the formula $Cu(SO_4)_x(SeO_4)_{1-x} \cdot 5H_2O$ have been prepared and studied by different techniques. The crystal structure of one of them was refined in order to determine a possible ordering in this substitution.

Table 1. Composition of samples. Composition of saturated solutions and solid phase (g per 100 g solution). Theoretical values from the triangular diagram.

Sample	x	Saturated solution		Solid (dry)		Solid, theoretical	
		$CuSeO_4$	$CuSO_4$	$CuSeO_4$	$CuSO_4$	$CuSeO_4$	$CuSO_4$
0	1.0	0.0	36.7				
1	0.85	3.2	30.0	11.9	53.2	12.0	53.3
2	0.8	4.7	27.7	15.9	49.5	16.0	49.3
3	0.75	6.5	21.0	19.5	46.0	20.0	46.0
4	0.65	8.5	16.4	27.0	39.3	27.3	39.3
5	0.5	11.8	12.7	37.7	29.6	38.0	29.3
6	0.4	14.7	9.9	44.4	23.2	44.7	23.3
7	0.3	15.3	9.2	51.0	17.5	51.3	17.0
8	0.25	16.3	8.7	54.4	14.3	54.0	14.7
9	0.1	19.3	6.5	63.3	5.8	63.3	6.0
10	0	27.3	0.0				

Experimental

Crystals of $Cu(SO_4)_x(SeO_4)_{1-x} \cdot 5H_2O$ were obtained from an aqueous solution of $CuSO_4 \cdot 5H_2O$ and $CuSeO_4 \cdot 5H_2O$ in the quantities given in Table 1. Crystals were obtained by slow evaporation at 30°C, they were separated from the solution and dried at room temperature. The results of analyses of dry crystals and saturated solutions are shown in Table 1. The analyses of copper and selenium were made by atomic absorption (Pye-UNICAM, S.P. 1900 and Varaian 875, respectively), while the sulphur analyses were from gravimetry.

The IR spectra were measured on a Beckman IR-20 spectrophotometer. The X-ray powder diffraction was made in an automatic Siemens D500-DA-COMP diffractometer, using Cu$K\alpha$ radiation, Ni-filtered, with a scan speed equal to 1/20 min^{-1} and a θ range between 5 and 30°.

An equidimensional mixed crystal ($0.1 \times 0.1 \times 0.1$ mm) was selected and mounted on a Philips PW-1100 four-circle diffractometer. Unit-cell parameters were determined from 25 reflections ($4 \leqslant \theta \leqslant 12°$) and refined by least-squares. Intensities were collected with graphite monochromatized Mo$K\alpha$ radiation, using the ω-scan technique, with scan width of 0.8°, and scan speed of 0.03° s^{-1}. 1532 reflections were measured in the range $2 \leqslant \theta \leqslant 25°$; 1446 of which were assumed as observed applying the condition $I \geqslant 2.5\ \sigma(I)$. Three intensities were measured every 2 h as orientation and intensity control. A significant intensity decay was not observed. Lorentz-polarization and absorption corrections were made.

The structure was solved by isomorphous replacement from the atomic coordinates of $CoSeO_4 \cdot 5H_2O$ crystal structure and refined by full-matrix least-squares procedures using the SHELX76 computer program

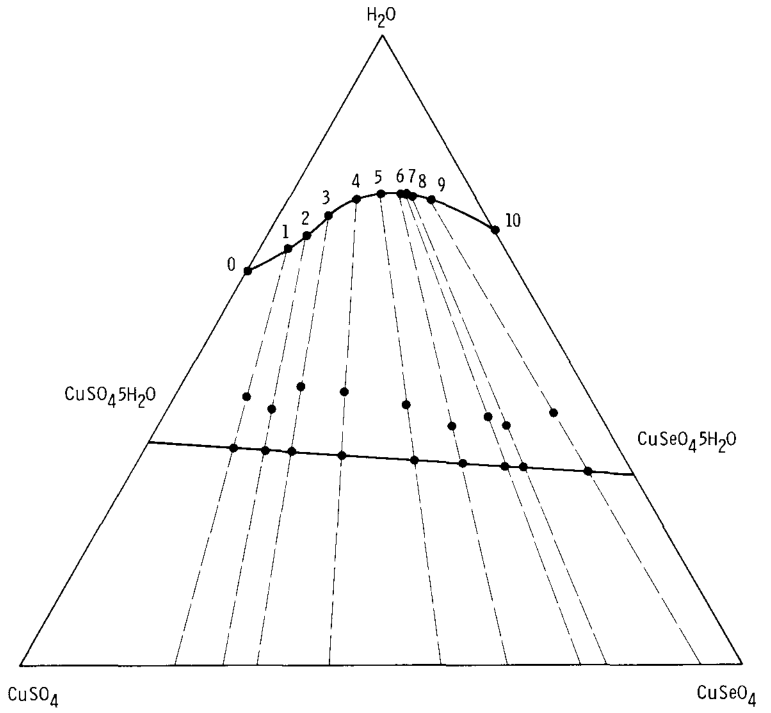

Fig. 1. System $CuSO_4 - CuSeO_4 - H_2O$ at 30°C.

(Sheldrick, 1976). The function minimized was $\Sigma w||F_o| - |F_c||^2$, where $w = (\sigma^2(F_o) + 0.0099\ |F_o|^2)^{-1}$. Nine hydrogen atoms were obtained from a difference synthesis and refined with an overall isotropic temperature factor. The remaining atoms were refined anisotropically. Occupancy factors of S and Se atoms were refined, obtaining the final values of 0.37(1) and 0.63(1), respectively. The final R factor was 0.068 ($wR = 0.086$), for all observed reflections Weissenberg photographs of the crystal used in the crystal structure determination were carried out on a Enraf-Nonius camera. The photographs do not show extra diffraction peaks.

Study of the $CuSO_4 - CuSeO_4 - H_2O$ system

Figure 1 presents the triangular diagram. Figure 2 shows the variation of IR spectra, where the variation of $\nu(S-O)$ and $\nu(Se-O)$ for each sample can be observed.

The identification of the obtained solid phases was performed by X-ray powder analyses. The indexing was carried out from the results of $CoSeO_4$

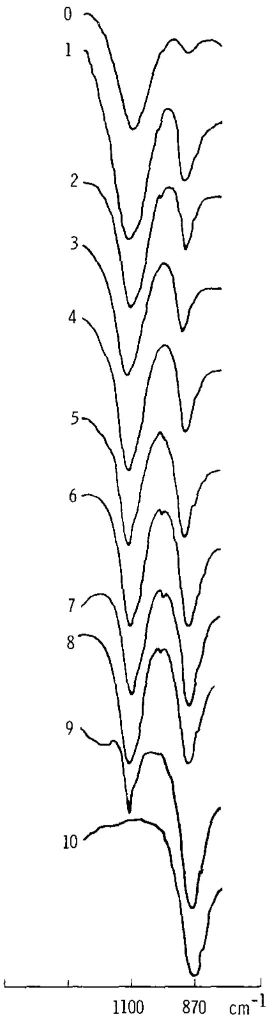

Fig. 2. IR spectra of the samples.

$\cdot 5H_2O$. Cell parameters for each phase were refined by full-matrix least-squares methods from the cell parameters of $CoSeO_4 \cdot 5H_2O$. The computer program used was AFFMAIL (Stewart, 1970). The function minimized was $|d_o - d_c|^2$. Overlapped peaks were omitted in the refinement. The obtained cell parameters are listed in Table 2. They agree with the IR spectroscopic data.

In order to determine the homogeneity of the substitution between the SO_4^{2-} and SeO_4^{2-} ions a linear regression of cell parameters and cell volume

Table 2. Cell parameters and volume for each member of solid solution (NP = number of peaks used in the cell parameters determination).

X_{CuSO_4}	*a*	*b*	*c*	α	*β*	*γ*	*v*		NP
1.00	6.132(4)	10.755(7)	5.979(3)	97.78(5)	107.13(5)	77.21(5)	366.4(7)	2.7	32
0.85	6.144(3)	10.762(4)	5.996(3)	97.62(4)	107.20(4)	77.38(3)	368.6(4)	2.2	41
0.80	6.158(3)	10.753(3)	6.004(2)	97.61(3)	107.34(3)	77.45(3)	369.4(2)	2.5	45
0.75	6.157(2)	10.760(3)	6.005(3)	97.60(3)	107.08(3)	77.31(2)	370.0(1)	1.9	42
0.65	6.156(2)	10.778(3)	6.015(2)	97.68(3)	107.10(3)	77.31(3)	371.1(1)	2.3	47
0.50	6.177(2)	10.820(3)	6.039(2)	97.66(3)	107.20(3)	77.21(3)	375.0(1)	2.0	45
0.40	6.190(3)	10.826(3)	6.042(3)	97.62(4)	107.16(4)	77.21(3)	376.3(1)	2.5	45
0.30	6.193(2)	10.831(2)	6.056(2)	97.61(3)	107.14(2)	77.17(2)	377.6(1)	1.7	47
0.26	6.209(2)	10.862(3)	6.064(2)	97.70(3)	107.13(3)	77.27(3)	380.2(1)	1.8	50
0.11	6.207(2)	10.878(5)	6.079(2)	97.68(4)	106.98(3)	77.10(3)	381.6(4)	2.5	50
0.00	6.213(3)	10.877(4)	6.092(3)	97.67(4)	107.00(3)	77.14(4)	382.8(4)	2.2	39

Table 3. Regression linear equations, and largest deviation from linearity.

Regression equation	Largest deviation	in x
$a = -0.085\,x + 6.219$	-0.012	0.26
$b = -0.149\,x + 10.885$	-0.018	1.00
$c = -0.112\,x + 6.091$	0.004	0.40
$\alpha = 0.01\ x + 97.65$	-0.12	1.00
$\beta = 0.18\ x + 107.04$	-0.16	0.80
$\gamma = 0.23\ x + 77.14$	0.15	1.00
$V = -17.39\ x + 383.3$	-1.4	1.00

Table 4. S(or Se)—Cu interatomic distance in Å for each member of solid solution, and regression linear equation.

X_{CuSO_4}	d_1 (Se—Cu)	d_2 (S—Cu)
1.00	3.555	3.506
0.85	3.561	3.517
0.80	3.562	3.517
0.75	3.565	3.518
0.65	3.570	3.521
0.50	3.577	3.536
0.40	3.581	3.539
0.30	3.584	3.543
0.26	3.598	3.549
0.11	3.600	3.555
0.00	3.604	3.557

$d_1 = -0.052\,x + 3.604$; $d_2 = -0.053\,x + 3.560$.

Table 5. Atomic coordinates ($\times 10^4$) of $Cu(SO_4)_{0.37}(SeO_4)_{0.63} \cdot 5H_2O$ ($B_{eq} = 8\,\pi^2/3\, u_{ij}\, a_i^* a_j^* a_i a_j$).

	x	y	z	B_{eq}
Cu(1)	10000	0	0	1.47(4)
Cu(2)	5000	5000	0	1.42(5)
Se	9897(2)	2862(1)	3785(2)	1.07(6)
S	9955(26)	2890(10)	3771(26)	8.0(1)
O(1)	11035(7)	1462(4)	3274(8)	2.5(2)
O(2)	9586(7)	3008(4)	6293(7)	2.2(2)
O(3)	11462(9)	3777(5)	3649(8)	2.6(2)
O(4)	7481(8)	3181(4)	1985(8)	2.4(2)
OW(1)	1823(7)	716(4)	−1512(7)	2.0(2)
OW(2)	7135(8)	1176(4)	−1467(8)	2.3(2)
OW(3)	5360(7)	4061(5)	−2912(8)	2.7(2)
OW(4)	2462(9)	4189(6)	−187(8)	2.9(2)
OW(5)	5713(7)	1218(4)	3721(8)	2.4(2)

Table 6. Anisotropic thermal parameters ($\times 10^4$) of $Cu(SO_4)_{0.37}(SeO_4)_{0.63} \cdot 5H_2O$. The temperature factor is in the form $\exp(-2\pi u_{ij}h_ih_ja_i^*a_j^*)$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu(1)	110(6)	59(5)	344(6)	−37(4)	5(4)	−34(4)
Cu(2)	99(6)	104(6)	306(6)	−91(4)	7(4)	−83(4)
Se	46(7)	81(10)	230(7)	−73(6)	−34(4)	−55(5)
S	1232(206)	422(58)	983(154)	−385(55)	60(80)	161(55)
O(1)	195(20)	180(18)	443(23)	−171(16)	−54(16)	−43(15)
O(2)	205(21)	135(19)	432(25)	−185(17)	54(17)	−98(16)
O(3)	341(25)	199(24)	411(25)	−210(19)	69(19)	−189(20)
O(4)	266(24)	157(21)	370(22)	−70(18)	−62(18)	−29(18)
OW(1)	225(21)	90(19)	406(22)	−54(17)	32(16)	−28(15)
OW(2)	235(20)	134(20)	438(23)	−183(17)	81(18)	−63(17)
OW(3)	114(19)	380(29)	412(24)	−255(21)	10(16)	−15(18)
OW(4)	306(25)	519(32)	283(23)	−185(21)	25(18)	−287(24)
OW(5)	150(19)	140(20)	547(27)	−211(19)	29(18)	−68(16)

Table 7. Bond lengths in Å and angles in degrees for $Cu(SO_4)_{0.37}(SeO_4)_{0.63} \cdot 5H_2O$.

O(1)−Cu(1)	2.382(4)	OW(1)−Cu(1)−O(1)	88.5(2)
OW(1)−Cu(1)	1.968(4)	OW(2)−Cu(1)−O(1)	93.2(2)
OW(2)−Cu(1)	1.970(4)	OW(2)−Cu(1)−OW(1)	91.8(2)
O(4)−Cu(2)	2.413(1)	OW(3)−Cu(2)−O(4)	87.6(2)
OW(3)−Cu(2)	1.958(4)	OW(4)−Cu(2)−O(4)	86.4(2)
OW(4)−Cu(2)	1.922(5)	OW(4)−Cu(2)−OW(3)	89.8(2)
O(1)−Se	1.548(4)	O(2)−Se−O(1)	108.7(2)
O(2)−Se	1.567(4)	O(3)−Se−O(1)	110.1(2)
O(3)−Se	1.549(5)	O(3)−Se−O(2)	109.2(2)
O(4)−Se	1.558(4)	O(4)−Se−O(1)	109.1(2)
O(1)−S	1.56(1)	O(4)−Se−O(2)	109.5(2)
O(2)−S	1.59(2)	O(4)−Se−O(3)	110.3(3)
O(3)−S	1.49(2)	O(2)−S−O(1)	106.7(9)
O(4)−S	1.58(2)	O(3)−S−O(1)	112.3(10)
		O(3)−S−O(2)	110.7(8)
		O(4)−S−O(1)	107.4(7)
		O(4)−S−O(2)	107.3(10)
		O(4)−S−O(3)	112.2(9)
		Se−O(1)−Cu(1)	130.6(2)
		S−O(1)−Cu(1)	131.1(6)
		Se−O(4)−Cu(2)	138.3(3)
		S−O(4)−Cu(2)	136.7(5)

has been carried out. The results are given in Table 3. The largest deviation from the linearity are within three times the highest standard deviation, so we assume the substitution to be homogeneous.

The linear variation of the cell parameters produces a linear variation in the Cu−S or Se interionic lengths (Table 4). The two distances corre-

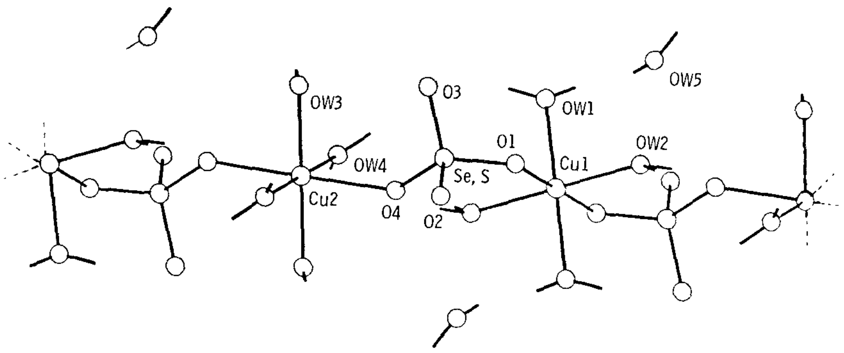

Fig. 3. Crystal structure of $Cu(SO_4)_{0.37}(SeO_4)_{0.63} \cdot 5H_2O$.

Table 8. Hydrogen bond distances (Å) and distance between hydrogen and acceptor atoms.

O(W5)...O(1)	(i)	3.056(6)	
O(W3)–...O(2)	(ii)	2.978(6)	
O(W4)–H(OW4)...O(2)	(iii)	2.814(6)	2.10(2)
O(W3)–...O(3)	(iii)	2.873(6)	
O(W4)–H(OW4)...O(3)	(i)	2.717(6)	2.10(2)
O(W2)–...O(4)	(iv)	2.794(6)	
O(W5)–...O(4)	(iv)	3.063(6)	
O(W1)–H(OW1)...O(W2)	(v)	2.735(6)	2.49(2)
O(W1)–H(OW1)...O(W5)	(v)	2.812(6)	2.44(6)

Symmetry code: (i) $x-1, y, z$; (ii) $x, y, z-1$; (iii) $x-1, y, z-1$; (iv) x, y, z (v) $2-x, -y, -z$.

spond to lengths between the S or Se atoms to non-symmetry-equivalent sites of the Cu atom. The slope of regression distance is the same for both lengths.

The crystal structure of $Cu(SO_4)_{0.37}(SeO_4)_{0.63} \cdot 5H_2O$

In order to corroborate the preceding result, the crystal structure analysis of a sample was carried out as described above. Atomic parameters, anisotropic thermal parameters and bond lengths and angles are listed in Tables 5–7, respectively.

The two crystallographic different Cu atoms are octahedrically coordinated by four water oxygen atoms and two sulfate or selenate oxygen atoms. They share corners with the coordination tetrahedra around the S or Se atoms to form chains of alternating octahedra and tetrahedra extending parallel to $[1\bar{1}0]$. The fifth water molecule is not coordinated to a Cu atom. It is held in the structure by hydrogen bonds in an approximately tetrahedral arrangement (Table 8). The crystal structure determination does not show a special arrangement of the SO_4^{2-} and SeO_4^{2-} ions, which confirms the homogeneity of substitution.

References

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