

## Structure and spectra character of cobalt nickel sulfate twelvehydrate (CNSH) single crystal

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The title compound  $\text{CoNi}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  has been prepared and its crystal structure determined by single crystal X-ray diffraction at room temperature. The CNSH crystal structure belongs to the monoclinic space group  $C2/c$ ,  $a=9.966(2)\text{\AA}$ ,  $b=7.2265(14)\text{\AA}$ ,  $c=24.218(5)\text{\AA}$ ,  $\beta=98.32(3)^\circ$ ,  $V=1725.9(6)\text{\AA}^3$ ,  $z=4$ ,  $D_c=2.024\text{gcm}^{-3}$ . The optical transmission character of CNSH crystal in aqueous solution is discontinuous in the range from ultraviolet to near IR wavelengths. The relationship between the structure and the optical transmission property is further discussed.

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### 1 Introduction

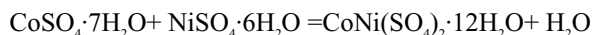
Inorganic compounds such as  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  (NSH) aqueous solution with commercially available filters to give high transmission, wide bandwidth filters for the visible region [1]. For most optical crystal materials, their optical transmission spectra are continuous in the range from UV to near IR wavelengths, only a few of hydrate salts of transition metals such as that of NSH [2] is discontinuous, since these hydrated transition metal ions  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  and  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  and so on known to be selectively absorbing in the visible wavelengths. The crystal and aqueous solution of nickel sulfate hexahydrate (NSH) have the same spectra character with high transmission efficiency and narrow spectrum bandwidth at 250 and 500nm. The ultraviolet light filters and UV sensors made of NSH crystals are already commercially available. Recently, we have reported the structure and optical transmission character of some hydrated nickel sulfates [3].

In this paper, we synthesized and grew a new crystal of the title compound. Its structure, optical transmission spectrum in the range from UV to near IR wavelength and thermal properties are reported and compared with NSH and FNSH (iron nickel sulfate twelvehydrate) crystals.

### 2 Experiment

#### 2.1 Preparation and crystal growth

Single crystal of the title compound was prepared by equal molar proportion  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  (A.R.) and  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  (A.R.) dissolving in hot double distilled water and the reaction can be expressed as:

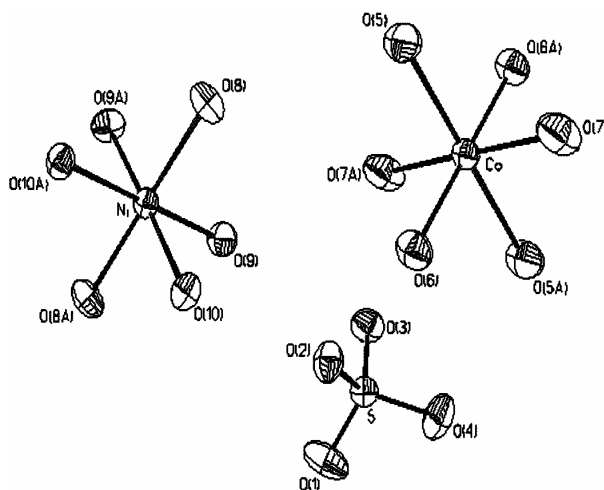


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Small crystals appeared in the beginning due to slow evaporation at 45°C and grew larger in considerable finite time. The brown, transparent and well formed crystal of X-ray quality were selected from this and used for the measurement of crystal structure. A brown rhombic tabular crystal with size about 10×10mm<sup>2</sup> has been grown (shown in Fig.1).



**Fig. 1** Photograph of CNSH crystal.



**Fig. 2** The molecule structure.

**Table 1** Crystal data and structure refinement.

Empirical formula	Co Ni (SO <sub>4</sub> ) <sub>2</sub> · 12(H <sub>2</sub> O)
Formula weight	525.95
Temperature	293(2) K
Wavelength	0.71073
Crystal system, space group	Monoclinic, C 2/c
Unit cell dimensions	a = 9.966(2) Å, α = 90° b = 7.2265(14) Å, β = 98.32(3)° c = 24.218(5) Å, γ = 90°
Volume	1725.9(6) Å <sup>3</sup>
Z, Calculated density	4, 2.024 Mg/m <sup>3</sup>
Absorption coefficient	2.389 mm <sup>-1</sup>
F(000)	1084
Theta range for data collection	1.70 to 25.99 deg.
Crystal size	1.50 x 1.00 x 1.00 mm
Limiting indices	0 ≤ h ≤ 12, 0 ≤ k ≤ 8, -29 ≤ l ≤ 29
Reflections collected / unique	1758 / 1656 [R(int) = 0.0885]
Completeness to theta = 25.99	97.5 %
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	1656 / 12 / 160
Goodness-of-fit on F <sup>2</sup>	1.110
Final R indices [I > 2σ(I)]	R1 = 0.0329, wR2 = 0.0876
R indices (all data)	R1 = 0.0334, wR2 = 0.0879
Extinction coefficient	0.0135(8)
Largest diff. peak and hole	0.567 and -0.761 e.Å <sup>-3</sup>

**Table 2** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ). U(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	U(eq)
Co	5000	5000	5000	23(1)
Ni	5000	4491(1)	2500	22(1)
S	1296(1)	4517(1)	3757(1)	25(1)
O(1)	172(3)	4469(3)	3301(1)	49(1)
O(2)	2253(2)	5997(3)	3658(1)	34(1)
O(3)	1991(2)	2713(3)	3811(1)	36(1)
O(4)	809(3)	4911(3)	4291(1)	42(1)
O(5)	6905(2)	5568(4)	4788(1)	48(1)
O(6)	4064(2)	7233(3)	4559(1)	35(1)
O(7)	5322(3)	6655(4)	5695(1)	48(1)
O(8)	6435(2)	4501(3)	3203(1)	36(1)
O(9)	3855(2)	2507(3)	2824(1)	35(1)
O(10)	3833(2)	6532(3)	2811(1)	28(1)

**Table 3** Bond lengths [ $\text{\AA}$ ] and angles [deg.].

Co-O(7)	2.051(2)	O(7)-Co-O(7)#1	80.000(1)	O(9)-Ni-O(8)	92.51(9)
Co-O(7)#1	2.051(2)	O(7)-Co-O(5)	92.74(12)	O(9)#2-Ni-O(8)	87.76(9)
Co-O(5)	2.079(2)	O(7)#1-Co-O(5)	87.26(12)	O(9)-Ni-O(8)#2	87.76(9)
Co-O(5)#1	2.079(2)	O(7)-Co-O(5)#1	87.26(12)	O(9)#2-Ni-O(8)#2	92.51(9)
Co-O(6)	2.080(2)	O(7)#1-Co-O(5)#1	92.74(12)	O(8)-Ni-O(8)#2	179.60(13)
Co-O(6)#1	2.080(2)	O(5)-Co-O(5)#1	180.000(1)	O(9)-Ni-O(10)#2	178.68(9)
Ni-O(9)	2.058(2)	O(7)-Co-O(6)	88.53(10)	O(9)#2-Ni-O(10)#2	89.20(9)
Ni-O(9)#2	2.058(2)	O(7)#1-Co-O(6)	91.47(10)	O(8)-Ni-O(10)#2	86.51(9)
Ni-O(8)	2.059(2)	O(5)-Co-O(6)	94.44(9)	O(8)#2-Ni-O(10)#2	93.20(9)
Ni-O(8)#2	2.059(2)	O(5)#1-Co-O(6)	85.56(9)	O(10)#2-Ni-O(10)	89.96(11)
Ni-O(10)#2	2.086(2)	O(7)-Co-O(6)#1	91.47(10)	O(1)-S-O(3)	110.33(14)
Ni-O(10)	2.086(2)	O(7)#1-Co-O(6)#1	88.53(10)	O(1)-S-O(4)	110.87(19)
S-O(1)	1.455(2)	O(5)-Co-O(6)#1	85.56(9)	O(3)-S-O(4)	107.65(14)
S-O(3)	1.473(2)	O(5)#1-Co-O(6)#1	94.44(9)	O(1)-S-O(2)	109.73(15)
S-O(4)	1.474(2)	O(6)-Co-O(6)#1	180.00(11)	O(3)-S-O(2)	110.43(14)
S-O(2)	1.476(2)	O(9)-Ni-O(9)#2	91.66(13)	O(4)-S-O(2)	107.78(14)

**Table 4** Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ).

	x	y	z	U(eq)
H(5A)	7040(40)	6480(50)	4523(15)	60(13)
H(5B)	7650(40)	5190(70)	5047(18)	66(15)
H(6A)	4630(50)	8190(60)	4470(20)	76(15)
H(6B)	3430(30)	6930(60)	4255(12)	41(10)
H(7A)	6220(20)	6760(60)	5888(15)	44(10)
H(7B)	4970(40)	7870(40)	5657(18)	59(13)
H(8A)	6580(60)	5630(50)	3410(20)	78(17)
H(8B)	6640(40)	3390(40)	3386(18)	59(13)
H(9A)	4250(40)	1370(40)	2945(18)	60(13)
H(9B)	2940(30)	2260(80)	2680(20)	75(15)
H(10A)	4340(40)	7550(40)	2952(18)	59(13)
H(10B)	3320(40)	6110(70)	3084(14)	59(13)

**Table 5** Hydrogen bonds [ $\text{\AA}$  and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
O(10)-H(10B)...O(2)	0.94(2)	1.87(2)	2.787(3)	164(5)
O(6)-H(6B)...O(2)	0.925(19)	1.85(2)	2.771(3)	172(4)
O(9)-H(9A)...O(1)#3	0.94(2)	1.80(2)	2.727(3)	168(4)
O(8)-H(8B)...O(2)#3	0.93(2)	1.92(2)	2.833(3)	170(4)
O(5)-H(5A)...O(3)#4	0.94(2)	1.94(2)	2.840(3)	160(4)
O(10)-H(10A)...O(1)#4	0.93(2)	1.77(2)	2.690(3)	172(4)
O(8)-H(8A)...O(3)#4	0.95(2)	1.81(2)	2.762(3)	175(5)
O(6)-H(6A)...O(4)#4	0.94(2)	1.81(2)	2.742(3)	176(5)
O(7)-H(7B)...O(4)#5	0.94(2)	1.79(2)	2.728(4)	169(4)
O(7)-H(7A)...O(3)#1	0.947(19)	1.87(2)	2.808(3)	170(4)
O(5)-H(5B)...O(4)#1	0.94(2)	2.05(2)	2.968(4)	164(5)
O(9)-H(9B)...O(10)#6	0.95(2)	2.05(2)	2.974(3)	165(5)

**Table 6** Lattice parameters of NSH,CNSH and FNSH crystal.

Crystal	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	$\text{CoNiSO}_4 \cdot 12\text{H}_2\text{O}$	$\text{FeNiSO}_4 \cdot 12\text{H}_2\text{O}$
Space Group		C2/c	
$\beta$ ( $^\circ$ )	98.35(3)	98.32(3)	98.83(3)
a ( $\text{\AA}$ )	9.889(2)	9.962(2)	9.994(2)
b ( $\text{\AA}$ )	7.1903(14)	7.2265(14)	7.2444(14)
c ( $\text{\AA}$ )	24.243(15)	24.218(15)	24.257(15)
V ( $\text{\AA}^3$ )	1707.3(6)	1725.9(6)	1735.9(6)
Dc ( $\text{gcm}^{-3}$ )	2.045	2.024	2.001

## 2.2 Crystal structure determination

The crystal structure of title compound was determined for the first time by X-ray single crystal diffraction method. The determination of the unit cell and diffraction data collection were performed on an Enraf-Nonius CAD4 diffractometer. The structure was solved by direct methods and refined by full matrix least-squares method with the SHELXTL-97 program package [5]. Table 1 shows the crystal data and structure refinement. Atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, hydrogen bonds are listed in the table 2,3,4 and 5, respectively. Fig.2 and Fig.3 are the molecule structure and packing of the molecules in unit cell. In the CNSH crystal structure, each  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  ions is coordinated with six  $\text{H}_2\text{O}$  molecules forming a distorted octahedral  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  and  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  units. The  $\text{SO}_4^{2-}$  units assume regular tetrahedral geometry which are bridged with the  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  or  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  units through O-H...O hydrogen bonds. The whole structure has alternative octahedral and tetrahedral layered packing arrangement.

## 2.3 Optical transmission spectra

In order to investigate the optical transmission properties of CNSH crystal and compared with NSH and FNSH crystal in water, three samples of 0.25mol crystal aqueous solution were prepared by dissolving the single crystals of NSH, CNSH and FNSH in double distilled water, respectively. The optical transmission spectra were recorded on a PE-lambda 900 spectrometer with performing wavelength the ranged from 200 to 1600nm and as depicted in Fig.4 (a, b, c). The thickness of solution is 10mm.

## 2.4 Thermo-gravimetric analysis (TGA)

We preformed the thermo-gravimetric analysis on freshly grown CNSH crystal by using a DELTA SERIES TGA7 apparatus. The TGA curve as shown in Fig.5, showed that the dehydration temperature of CNSH crystal is above  $84.74^\circ\text{C}$ , which is higher than that of NSH crystal ( $73.03^\circ\text{C}$ ) and FNSH crystal ( $80.05^\circ\text{C}$ ).

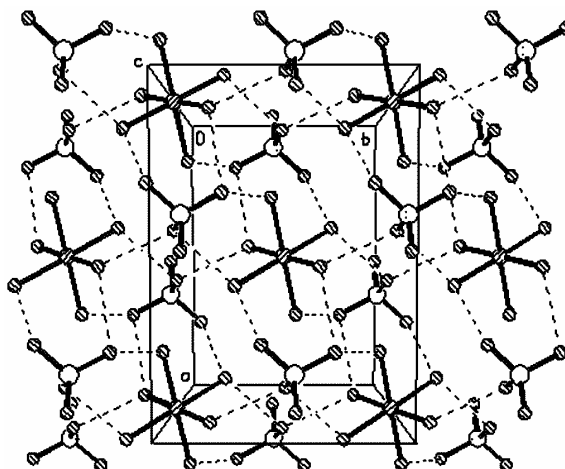


Fig. 3 The packing of the molecule structure in unite cells.

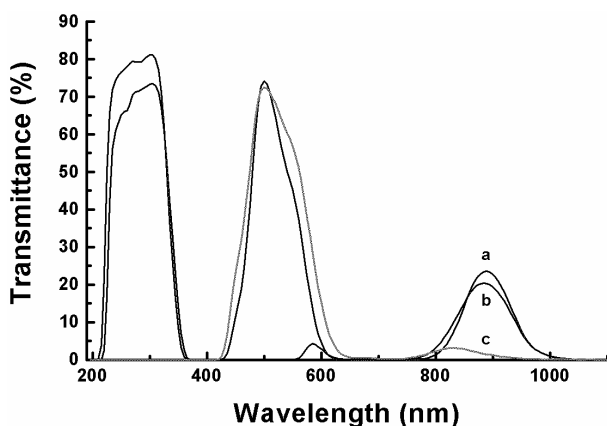


Fig. 4 The optical transmission spectra (a) NSH; (b) CNSH; (c) FNSH.

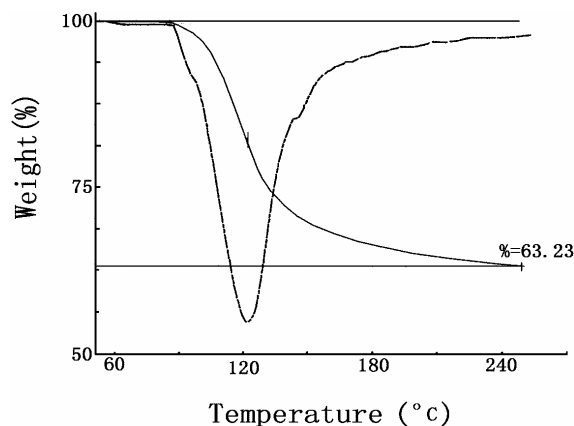


Fig. 5 The thermo-gravimetric curve of CNSH crystal.

### 3 Result and discussions

The empirical formula of the title compound is  $\text{CoNi}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  with the formula weight 525.95. Its structure belongs to the monoclinic space group  $C2/c$ ,  $a=9.966(2)\text{\AA}$ ,  $b=7.2265(14)\text{\AA}$ ,  $c=24.218(5)\text{\AA}$ ,  $\beta=98.32(3)^\circ$ ,  $V=1725.9(6)\text{\AA}^3$ ,  $z=4$ ,  $D_c=2.024\text{gcm}^{-3}$  and is isomorphous with  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{FeNi}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  crystals. Their lattice parameters are much the same as listed in table 6 and the cell volume of CNSH is larger than that of NSH and less than that of FNSH. The bond lengths of Co-O are 2.051(2)-2.089(2)  $\text{\AA}$ , less than that of Fe-O 2.076(3) - 2.101(3)  $\text{\AA}$  since the radius of  $\text{Fe}^{2+}$  (0.76  $\text{\AA}$ ) is slightly larger than that of  $\text{Co}^{2+}$  (0.74  $\text{\AA}$ ). The NSH (Fig.4a) has several characteristic optical transmission bands centred at 300,500 and 900 nm. It agrees with that the hydrated nickel ion,  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  in aqueous solution has three main absorption bands at  $8500\text{cm}^{-1}$  and  $14000\text{cm}^{-1}$  and  $26000\text{cm}^{-1}$  [6]. This unique optical transmission property mainly arise from the hydrated transition metal ions  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ . In the CNSH (Fig.4b), the transmission bands centred at 500 nm was disappeared and kept two high transmission peaks at 500 and 880 nm, since the hydrated cobalt ion  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  in aqueous solution has a broad absorption band from about  $15000\text{cm}^{-1}$  to about  $28000\text{cm}^{-1}$  [7]. For the FNSH (Fig.4c), due to the  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  ion in aqueous solution has strong absorption at near 300 and 900nm, there is only a transmission peak at about 500nm.

The high optical transmission efficiency with narrow band width at the 300nm, higher thermo-stability, and the large single crystal can be grown by the cooling solution method. It's possible that the CNSH crystal as a crystalline material of band pass filters for the near UV band.

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