In Search of the True Structure of the Sodium Chromium Alum II: Crystal Growth and Structure of the Double Salt $NaCr(SO_4)_2(H_2O)_6$ · $(CH_3OH)_{0.6(2)}$ · $(H_2O)_{1.5(5)}$

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Attempts to crystallize the sodium chromium alum, $NaCr(SO_4)_2(H_2O)_{12}$, from water/methanol solutions at temperatures around 281 K yielded crystals of the title compound instead. Their monoclinic structure can be described as a centered rectangular array of linear ${}^1_\infty[Na(SO_4)_2]^{3-}$ rods aligned parallel to [001] with vicinal rods held together by columns of isolated $[Cr(H_2O)_6]^{3+}$ complexes. The structure forms channels parallel to [001] which are occupied by methanol and water molecules with atomic site occupancy factors of 1/5 and less. Various attempts to crystallize the compound or the sodium chromium alum from purely aqueous solutions remained unsuccessful.

Key words: Chromium Alums, Double Salt, Crystal Growth, Crystal Structure

Introduction

The sodium chromium alum, $NaCr(SO_4)_2(H_2O)_{12}$, has been reported to have a cubic lattice parameter which is by 0.17 Å larger than the one of the isotypic $KCr(SO_4)_2(H_2O)_{12}$ [1]. The task to find an answer to the question whether this is a real "lattice parameter anomaly (LPA)" requires, in the first instance, the determination of the true crystal structure of the sodium chromium alum [1]. Thus, we tried to grow crystals of the compound from water/methanol solutions of mixtures of the two "parent salts". However, crystallization experiments at 293 K yielded platelet-shaped monoclinic crystals of the double salt $NaCr(SO_4)_2(H_2O)_6$ (**1**) instead. Their crystal structure was described in the first article of this series [1].

Results and Discussion

When crystal growth from water/methanol solutions was performed at lower temperatures (*e. g.*, 285 or 278 K) and with additional methanol added after a few days, in most experiments bunches of platelets of **1** grew as well, but prismatic purple monoclinic crys-
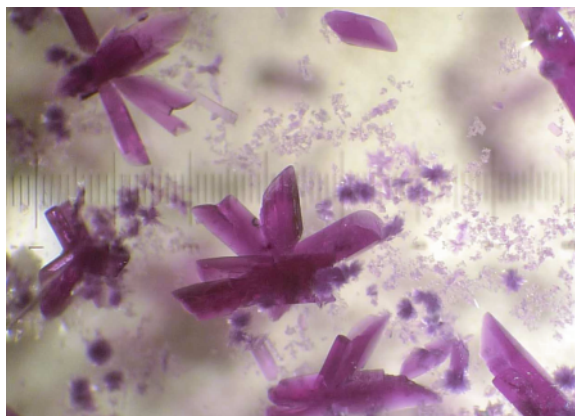

Fig. 1 (color online). Crystals of the title compound (**2**) in their mother liquor, besides bundles of platelets of **1** with isometrical appearance. 10 scale divisions cover a distance of 1 mm.

tals of the title compound **2** with sizes of up to few mm were often obtained as the main product (Fig. 1). Differing from **1**, crystals of **2**, when removed from the mother liquor, dried, and stored on air, change visibly within few days by developing whitish surfaces, while under argon they develop numerous micro-cracks.

Table 1. Crystal structure data for $NaCr(SO_4)_2(H_2O)_6 \cdot (CH_3OH)_{0.6(2)} \cdot (H_2O)_{1.5(5)}$.

Empirical formula	$C_{0.6}H_{17.4}CrNaO_{16.1}S_2$
M_r	421.45
Crystal size, mm^3	$0.25 \times 0.20 \times 0.20$
Temperature, K	170(2)
Crystal system	monoclinic
Space group	$C2/c$
a, Å	15.4466(1)
b, Å	11.0421(1)
c, Å	8.4065(1)
β, deg	92.7666(4)
V, $Å^3$	1432.17(2)
Z	4
$D_{calcd.}$, $g\,cm^{-3}$	1.95
$\mu(Mo\,K_\alpha)$, cm^{-1}	12.0
$F(000)$, e	873
hkl range	$-29 \leq h \leq 30$, $-21 \leq k \leq 21$, $-14 \leq l \leq 15$
$((\sin\theta)/\lambda)_{max}$, $Å^{-1}$	0.9947
Refl. measured/unique/R_{int}	22 083/5746/0.0164
Param. refined	153
$R(F)/wR(F^2)^a$ (all refls.)	0.0279/0.0725
GoF $(F^2)^b$	1.041
$\Delta\rho_{fin}$ (max/min), e $Å^{-3}$	$0.54/-0.80$

^{a} $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w (F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (Max(F_o^2, 0) + 2F_c^2)/3$; ^{b} GoF $= [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

Table 2. Bond lengths (Å) for $NaCr(SO_4)_2(H_2O)_6 \cdot (CH_3OH)_{0.6(2)} \cdot (H_2O)_{1.5(5)}$.

Cr1–O11	1.9754(5)	S1–O1	1.4874(5)
Cr1–O12	1.9548(5)	S1–O2	1.4731(5)
Cr1–O13	1.9571(6)	S1–O3	1.4741(5)
Na1–O1^a	2.6278(6)	S1–O4	1.4702(5)
Na1–O2	2.3186(6)	C20–O20	1.494(14)
Na1–O3	2.9148(6)	C20–O21^b	1.504(13)
Na1–O3^a	2.4119(6)		

Symmetry transformations used to generate equivalent atoms: ^{a} $-x+1, -y, -z+1$; ^{b} $x, -y, z-1/2$.

principle, by the same chemical formula. However, the structure forms flat channels parallel to [001] which are statistically occupied by solvent molecules with atomic site occupancy factors (s. o. f.) of 0.2 or less (Figs. 3 and 4). Due to the low occupancy factors it is difficult to make unambiguous assignments of the corresponding electron density peaks in the Fourier maps to the possible solvent molecules, methanol and water. However, the presence of methanol can be concluded from the fact that we could obtain **2** – in contrast to **1** – only from water/methanol mixtures and never from purely aqueous solutions. Our final chemical assignments are based on geometrical and site occupancy criteria (see Experimental Part). They lead to the chemical formula $NaCr(SO_4)_2(H_2O)_6 \cdot (CH_3OH)_{0.6(2)} \cdot (H_2O)_{1.5(5)}$ for **2**. The additional solvent molecules are real "guests", *i. e.* not coordinated to Na or Cr. Searching the ICSD [2] revealed that methanol and water as concurrent guests

The results of a structure analysis (Tables 1 to 5 and Fig. 2) of a crystal fragment measured at 170 K directly after separation from the mother liquor showed that **2** is closely related to **1** inasmuch as it can be described, in

Atom	x	y	z	U_{eq}	s. o. f.
Cr1	$1/4$	$1/4$	$1/2$	0.015(1)	
O11	0.2850(1)	0.868(1)	0.5749(1)	0.020(1)	
O12	0.2534(1)	0.1917(1)	0.2808(1)	0.024(1)	
O13	0.1283(1)	0.2009(1)	0.5017(1)	0.025(1)	
Na1	0.5000	$-0.200(1)$	0.7500	0.017(1)	
S1	0.4100(1)	$-0.1619(1)$	0.4655(1)	0.012(1)	
O1	0.3600(1)	$-0.688(1)$	0.3720(1)	0.017(1)	
O2	0.3942(1)	$-0.1458(1)$	0.6356(1)	0.018(1)	
O3	0.5029(1)	$-0.1419(1)$	0.4428(1)	0.019(1)	
O4	0.3831(1)	$-0.2836(1)$	0.4122(1)	0.024(1)	
C20	0.662(3)	0.118(5)	0.6440(8)	0.047(2)	0.32(1)
O20	0.911(6)	0.378(9)	0.8146(16)	0.059(3)	0.19(1)
O21	0.829(5)	0.095(4)	0.9715(12)	0.020(2)	0.13(1)
O31	0.1112(5)	0.164(4)	0.8710(7)	0.031(1)	0.21(1)
O32	0.222(7)	0.300(9)	0.7727(14)	0.061(3)	0.128(4)
O33	0.826(8)	0.157(7)	0.8639(14)	0.027(3)	0.12(1)
O34	0.609(12)	0.097(7)	0.9477(14)	0.032(2)	0.11(1)
O35	0.913(8)	0.132(6)	0.9250(20)	0.027(2)	0.11(1)
O36	0.783(10)	0.071(14)	0.5750(30)	0.055(5)	0.089(7)

Table 3. Atomic coordinates and isotropic displacement parameters ($Å^2$) for $NaCr(SO_4)_2(H_2O)_6 \cdot (CH_3OH)_{0.6(2)} \cdot (H_2O)_{1.5(5)}$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cr1	0.015(1)	0.022(1)	0.009(1)	0.002(1)	0.002(1)	0.011(1)
O11	0.022(1)	0.023(1)	0.013(1)	0.001(1)	−0.001(1)	0.012(1)
O12	0.022(1)	0.040(1)	0.011(1)	−0.002(1)	0.001(1)	0.016(1)
O13	0.017(1)	0.029(1)	0.030(1)	0.007(1)	0.003(1)	0.010(1)
Na1	0.015(1)	0.017(1)	0.018(1)	0	−0.003(1)	0
S1	0.011(1)	0.013(1)	0.012(1)	−0.001(1)	−0.001(1)	0.000(1)
O1	0.018(1)	0.017(1)	0.014(1)	−0.001(1)	−0.004(1)	0.005(1)
O2	0.017(1)	0.025(1)	0.012(1)	0.000(1)	0.001(1)	−0.003(1)
O3	0.012(1)	0.021(1)	0.024(1)	0.004(1)	0.003(1)	0.002(1)
O4	0.027(1)	0.015(1)	0.029(1)	−0.005(1)	−0.007(1)	−0.003(1)

Table 4. Anisotropic displacement parameters (Å^2) for NaCr(SO$_4$)$_2$(H$_2$O)$_6$· (CH$_3$OH)$_{0.6(2)}$ · (H$_2$O)$_{1.5(5)}$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12}]$.

Table 5. Hydrogen coordinates and isotropic displacement parameters (Å^2) for NaCr(SO$_4$)$_2$(H$_2$O)$_6$ · (CH$_3$OH)$_{0.6(2)}$· (H$_2$O)$_{1.5(5)}$.

Atom	x	y	z	U_{iso}
H111	0.3091(10)	0.0804(14)	0.6628(19)	0.031(4)
H112	0.3072(10)	0.0411(15)	0.5112(19)	0.035(4)
H121	0.2092(15)	0.1980(20)	0.2250(30)	0.064(6)
H122	0.2969(12)	0.1877(17)	0.2410(20)	0.043(4)
H131	0.0940(12)	0.2468(16)	0.4840(20)	0.035(4)
H132	0.1083(18)	0.1300(30)	0.4780(30)	0.095(9)

have also been reported for some other inorganic or organo-metallic crystal structures (see, for example, refs. [3 – 6] {ICSD collection codes: 170455, 170592, 161161, 180995}).

By neglecting the solvent molecules, the structure of **2** can be seen as a centered rectangular array of linear $\{^1_\infty\}$[Na(SO$_4$)$_2$]$^{3-}$ rods aligned parallel [001] with vicinal rods "glued" together by columns of isolated [Cr(H$_2$O)$_6$]$^{3+}$ complexes (Fig. 3). The same description holds for **1** (with rods aligned parallel to [100]). However, while a rod in the latter consists of a central $\{^1_\infty\}$[Na(SO$_4$)]$^-$ core with SO$_4^{2-}$ "side chains" and with a clear zigzag arrangement of the Na ions (Fig. 5b), a rod in **2** consists of a linear $\{^1_\infty\}$[Na(SO$_4$)$_2$]$^{3-}$ "core" only (with almost linear arrangement of the Na atoms), thus having a much smaller cross section (Fig. 5a).

In **2**, all sulfate ions act as μ_2 bridges, in **1**, the "inner" sulfate ions serve as μ_3 bridges, while the outer ("terminal") ones have no bridging function. In *both* kinds of rods any pair of vicinal Na atoms is bridged by two O$_3$ faces of two sulfate tetrahedra. For any pair in **2** and for any second pair in **1** one of the three O atoms is connecting the two Na atoms directly while the other two are parts of an -O–S–O- bridge. While the Na atoms in **1** are coordinated sixfold by O atoms (like, *e. g.*, in Na$_2$SO$_4$ [7, 8]), they are coordinated eightfold in **2**. The coordination polyhedron is irregular with Na−O bond lengths between 2.32 and 2.91 Å
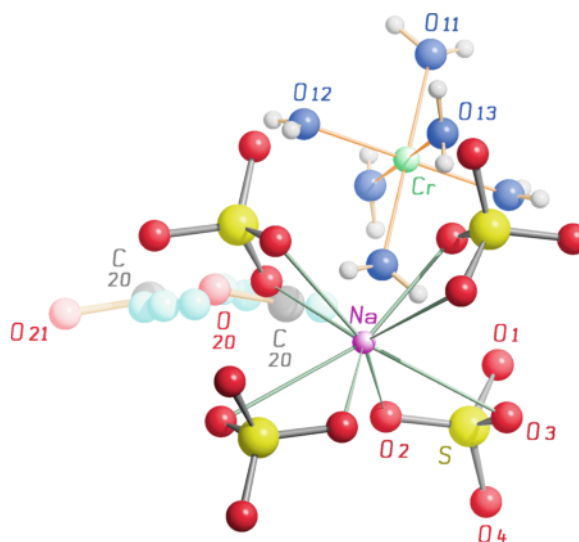

Fig. 2 (color online). The asymmetric unit of **2**, expanded by three additional sulfate ions and three additional H$_2$O ligands plus an additional atom C20. "Isolated" atoms (color cyan) in the background near C20 represent water O atoms with s. o. f's. of 0.2 or lower.

(Table 2). According to SOFTBV [9] the two Na–O3 distances of 2.91 Å correspond to bond valences of 0.06 each (while the valences calculated from the other six distances range from 0.11 to 0.21). This justifies, to our opinion, to assign bonds also to these two Na–O3 distances (*i. e.*, to classify the coordination of Na as eightfold).

To our knowledge there are only two other structurally characterized compounds of the type M(I)M(III)(SO$_4$)$_2$(H$_2$O)$_6$ (M = metal), both with M(I) = Na. Actually, **1** is isotypic to the one with M(III) = Al [10] (a point we regrettably missed in the first paper of this series). The other one with M(III) = Fe [11] adopts a very different structure with both, Na and Fe, coordinated to water as well as to sulfate ions. Among the structurally characterized hydrated
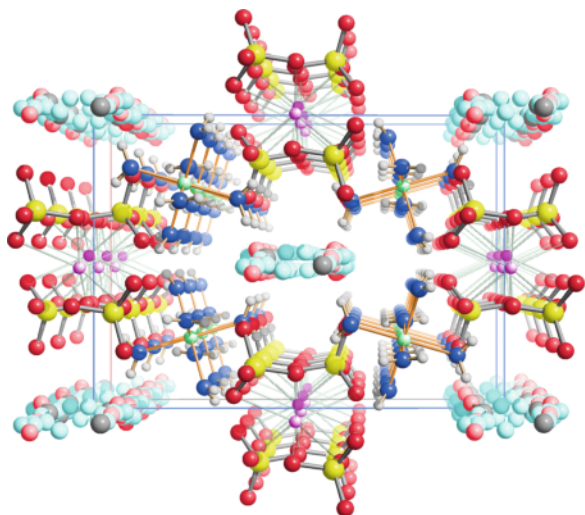
Fig. 3 (color online). The crystal structure of **2** as seen in the [00$\bar{1}$] direction. The *a* axis is pointing to the right, the *b* axis is pointing upwards. Na–O bonds have been drawn comparatively pale for the sake of clarity. Atoms in the "channel" (near 0, 0, *z* and $^1/_2$, $^1/_2$, *z*) have s. o. f's. of 0.3 or less. The channel adjoins four rows of H132 (see Experimental Part).
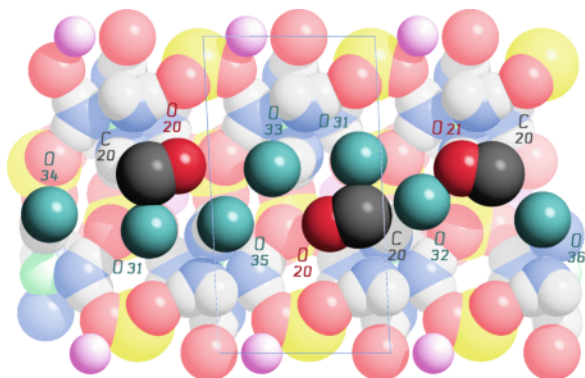

Fig. 4 (color online). A possible configuration of solvent molecules (H atoms omitted) in a channel section of **2** with the *a* axis pointing downwards and the *c* axis pointing to the left. The occurrence of the different solvent atoms corresponds approx. to their s. o. f's.

sodium double sulfates we found no precedents for the $\{^1_\infty\}$[Na(SO$_4$)$_2$]$^{3-}$ rods in **2**. However, eightfold coordination of Na, exclusively to sulfate O atoms, is also a characteristic of the Na*M*(III)(SO$_4$)(H$_2$O) structures (*M* = La and some rare-earth elements) with Na–O bond lengths between 2.4 and 2.9 Å (see, for example, ref. [12]).

Conclusion

As already mentioned above, the formation of **2** was observed only in water/methanol mixtures with **1** usually as a by-product. All crystallization attempts using other solvents like water only (neutral or at pH = 2.5 [13] or lower) led to **1** only or yielded no double salt at all. In no case did we observe the formation of alum crystals, meaning that, under the conditions set up by us, Na$^+$ in the presence of Cr^{3+} clearly seems to prefer sulfate ions to water molecules as coordinative partners, though the exclusive coordination of sodium by water is well known from other sulfate containing structures, *e. g.* Na$_2$SO$_4$(H$_2$O)$_{10}$ [14] or the sodium alum, NaAl(SO$_4$)$_2$(H$_2$O)$_{12}$ [15]. Unsuccessful attempts to synthesize the sodium *chromium* alum have also been reported by others (*e. g.* in refs. [16, 17]), and the compound has been suspected to be principally unstable [18]. Even if the latter actually should not be true, NaCr(SO$_4$)$_2$(H$_2$O)$_{12}$ *did not* show up in our experiments, and therefore its true crystal structure remains unknown.

Experimental Part

Sodium hexaaquachromium disulfate methanol solvate hydrate: NaCr(SO$_4$)$_2$(H$_2$O)$_6$ · (CH$_3$OH)$_{0.6(2)}$ · (H$_2$O)$_{1.5(5)}$

6 mL of H$_2$O is added to 368 mg (0.6 mmol) of Cr$_2$(SO$_4$)$_3$(H$_2$O)$_x$ (Strem Chemicals, $x \approx 12$ [1]) and 168 mg (1.2 mmol) of Na$_2$SO$_4$ (5 N, Strem Chemicals). The rapidly formed solution is separated by means of a pipette from most of a small undissolved residue ($< 1\,\%$) and filled into a flat 50 mL weighing glass with a ground-in lid. The open glass is put into a 250 mL ice bath. During about 5 min, 7.5 mL of methanol (pre-cooled in the ice bath) is added dropwise to the solution while stirring occasionally. The closed weighing glass is stored at 280 K for 4 d, usually leading to the crystallization of some **1**. Then the solution is overlayed with another 3.7 mL of pre-cooled methanol. After another 4 to 10 d, in about one third of the cases purple prismatic crystals of **2** of up to few mm length have grown on a colorless deposit of polycrystalline appearance (but with no other powder diffraction signals than those of **1**), or, (rarely) directly at the bottom of the weighing glass. In both cases, smaller amounts of **1** are usually observed as a by-product (Fig. 1). Additionally, crystals of *anhydrous* Na$_2$SO$_4$ grow in the solution, an effect which is also known from saturated purely aqueous solutions of Na$_2$SO$_4$ at temperatures above 305 K [19].

One of the crystals of **2** obtained this way was separated from the mother liquor, and a fragment of it was transferred

within one hour to a Bruker SMART APEX II diffractometer equipped with a CCD detector and with the measurement temperature set to 170 K. From the measured data the structure was solved and refined with SHELXTL [20]. H atoms on coordinated water O atoms were located from the final difference Fourier maps. As in the structure of **1** [1], free refinement of their positions yielded "too small" O–H bond lengths in the range 0.74 to 0.83 Å. The U_{eq} value for H132 is comparatively large. As revealed by CHECKCIF [21] this H atom is the only one *not* to participate in a hydrogen bond to an acceptor within the "frame" structure. Actually, H132 and its equivalents are forming the border to the "channel" (Fig. 3).

To the difference electron density peaks in the channel we initially assigned water O atoms. Refinement of their occupancy factors led to values of 0.20 or lower. As we postulated the presence of methanol molecules (see Results and Discussion) we then looked for pairs of atoms with suitable distance and s. o. f's. The expected C–O distance for methanol is 1.41 Å [22]. Distances we found for (un-coordinated) methanol in inorganic structures (*e. g.* in refs. [3 – 6, 23 – 31] {ICSD collection codes: 110197, 281114, 281180, 109782, 240363, 249146, 260017, 249853, 174400}) range from 1.23 [24] {281114} to 1.57 Å [29] {260017}. Thus, we decided to treat pairs of atoms with a distance in the range 1.41 ± 0.10 Å and with similar s. o. f's. as methanol molecules. Two such distances (1.49 and 1.50 Å) could be found between one central atom and two others. When the central atom was turned into a C atom (C20) the s. o. f's. of the two others, O20 (0.19) and O21 (0.13), added up to its refined

s. o. f. (0.32). Thus, we see this triplet as a superposition of two disordered methanol molecules with different occupancies. Among other structures with methanol guests we found another example for an O-C-O triplet [25] {281180} as well as one for a C-O-C triplet [30] {249853} and a CO_4 quintuplet [6] {180995}. The distance C20–O32 (1.32 Å) is also in the "critical" range, which means that O21 and O32 (both s. o. f's. = 0.13) could have their roles as methanol/water O atoms exchanged, however with no effect on the unit cell stoichiometry. For another "methanol candidate pair" in **2** (O35 and O36) with distance 1.31 Å the replacement of the weaker O atom by C led to two s. o. f's. differing by a factor of 1.5. Thus, the two were retained as water O atoms. Altogether, these assignments led to 0.64(4) molecules of methanol and 1.5(1) molecules of un-coordinated water per formula unit. To account for a remaining uncertainty regarding the correctness of our assignments the standard deviations (obtained by summing up the atomic s. o. f. standard deviations) have been multiplied by a factor of 5, to result in 0.6(2) [1.5(5)] molecules of methanol [water].

In principle, the composition of the channel contents could have been additionally investigated, *e. g.*, by CHN analysis. However, the calculated C contents is only 1.7%. A positive experimental value in this range could also be caused by mother liquor residing in surface defects of the crystals (forming during growth and when the crystals are detached from their support). A rigorous drying of the crystals would remove these residues but could, on the other hand, lead also to partial loss of the guest molecules (the crystals are not stable after removal from the mother liquor, see Re-
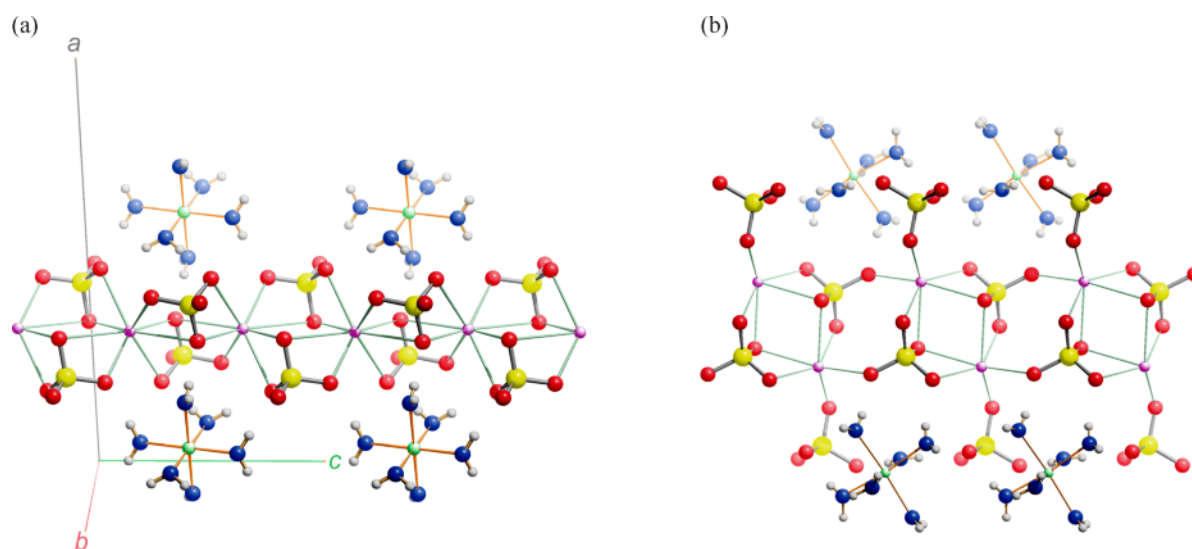
(a)

(b)

Fig. 5 (color online). Section of a $\{^{1}_{\infty}\}[Na(SO_4)_2]^{3-}$ rod plus accompanying $[Cr(H_2O)_6]^{3+}$ complexes in **2** (a) and **1** (b).
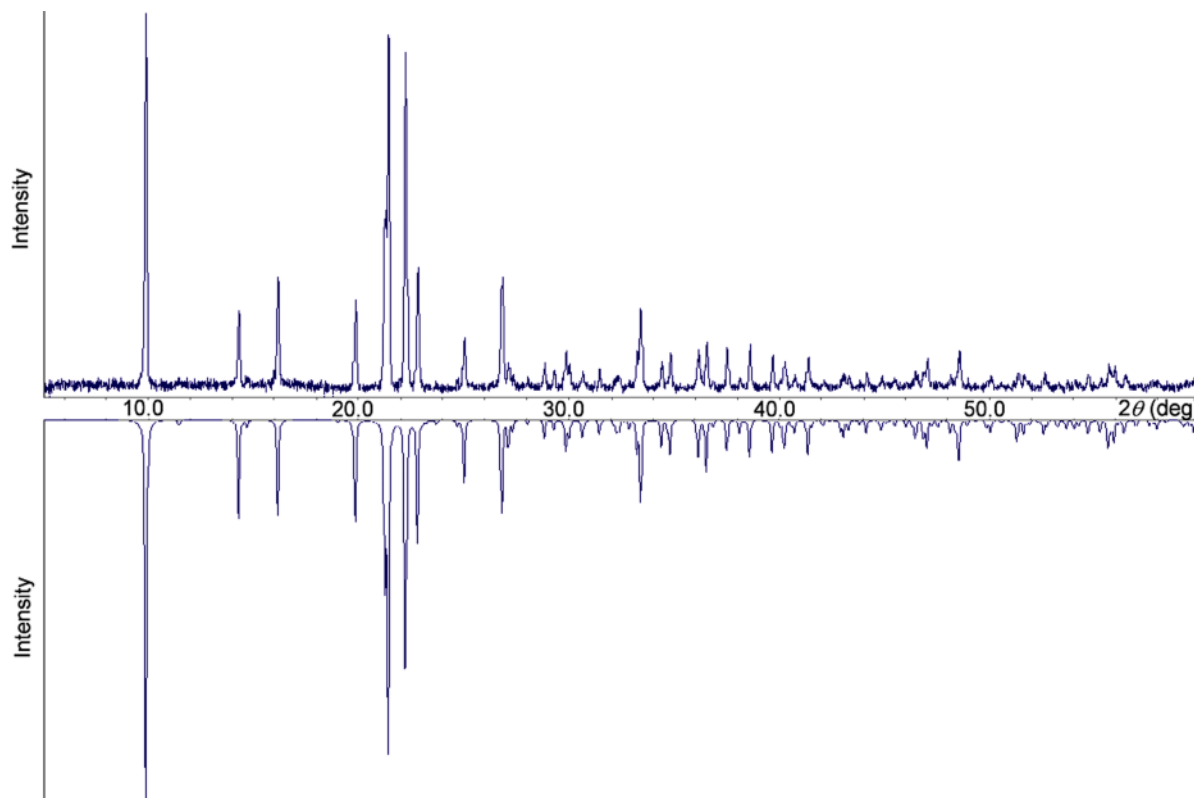
Fig. 6 (color online). Experimental (upper half) and calculated (upside-down in the lower half) powder diffraction pattern of the title compound. The calculated pattern was generated by WinXpow [32].

sults and Discussion). We therefore refrained from further analytical investigations.

Crystal data, measurement parameters, bond lengths and atomic parameters are given in Tables 1 to 5. Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de. http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-426368.

That the crystal structure obtained at 170 K is the same as the one at room temperature can be seen from Fig. 6

where the experimental powder diffraction pattern of **2** at room temperature is compared to the theoretical one calculated from the 170 K single-crystal structure but with lattice parameters as determined from the experimental pattern by means of WinXpow [32]: $a = 15.461(2)$, $b = 10.966(2)$, $c = 8.362(1)$ Å, $\beta = 92.71(1)°$.

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