

Synthesis Methods for $\text{Ce}(\text{CrO}_4)_2 \cdot x\text{H}_2\text{O}$ and Crystal Structures of K_2CrSO_7 , $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ and $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$

Barbara M. Casari^a, Annika K. Eriksson^b, and Vratislav Langer^b

^a Department of Chemistry, Inorganic Chemistry, Göteborg University, SE-412 96 Göteborg, Sweden

^b Environmental Inorganic Chemistry, Department of Chemical and Biological Engineering, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

Reprint requests to B. M. Casari. Fax: +46(0)317722853. E-mail: casari@chem.gu.se

Z. Naturforsch. **2007**, 62b, 771 – 777; received January 1, 2007

New and quick methods to synthesize $\text{Ce}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Ce}(\text{CrO}_4)_2 \cdot \text{H}_2\text{O}$, giving high yields, are described. The methods are based on exchange reactions by refluxing in water or on solid state reactions. The first crystal structure containing a chromatosulfato ion is presented. K_2CrSO_7 belongs to space group $P2_1/n$ with $a = 7.4024(1)$, $b = 7.3908(1)$, $c = 12.9883(2)$ Å, $\beta = 90.021(1)^\circ$ and $Z = 4$. The CrSO_7^{2-} ion, consisting of one chromate group sharing one oxygen atom with one sulfate group, has a *pseudo syn-C_{2v}* conformation with eclipsed oxygen atoms. K_2CrSO_7 forms a three dimensional network of CrSO_7^{2-} ions held together by the charge balancing potassium ions, with the general structural features common with dichromate-like structures. The redetermination of the structures of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (space group $C2/c$, with hydrogen atoms located) and $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ (space group $P2_1$, with hydrogen atoms located and the absolute structure established) are reported.

Key words: Hydrated Cerium Chromates, Chromatosulfate, Dichromates, Oxidizing Agents, Single Crystal X-Ray Diffraction

Introduction

Chromium(VI) compounds continue to attract interest as they represent the most widely used group of oxidizing agents in organic chemistry, capable of oxidizing almost every organic functional group. Oxidation by cerium(IV) is also a valuable tool [1] in organic chemistry. Various Ce-Cr-O catalysts of different Cr content have been synthesized [2] and used in oxidative dehydrogenation of lower alkanes, a subject of growing interest as a source of inexpensive olefins for industrial applications [3]. Nitrate cerium(IV) chromates(VI) have been used as versatile oxidants or as mild, efficient, and inexpensive catalysts for oxidative deprotection [4]. The combination of Ce(IV) and Cr(VI) in order to synthesize different cerium chromates may produce new powerful oxidation tools with unique properties. Investigations on cerium chromates were started by Lindgren [5] who published $\text{Ce}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$, the only structure determination reported until recently when Kolitsch and Schwendtner [6] reported the structure of $\text{Ce}(\text{CrO}_4)_2 \cdot \text{H}_2\text{O}$. Quick and easy reaction routes for these compounds are presented in this paper.

The chromate, CrO_4^{2-} , and dichromate, $\text{Cr}_2\text{O}_7^{2-}$, ions form the basis for a series of industrially important salts. Solving the crystal structure of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, Byström and Wilhelmi [7] made the first structure determination of a compound with the stoichiometric formula $A_2M_2O_7$, where A is a large cation and M is a small atom with high formal oxidation state. These structures contain M_2O_7 units consisting of two corner sharing MO_4 tetrahedra. Different packing motifs of M_2O_7 units give rise to several polymorphic forms and many new types of $A_2M_2O_7$ structures have been reported since then. Brown and Calvo [8] reported a scheme of the relation between these structure types, and Clark and Morely [9] published a review on inorganic pyrocompounds, $M_a(X_2O_7)_b$. Sodium dichromate has been reported in two triclinic modifications [10]. Three polymorphic forms for potassium dichromate [11] and four modifications for rubidium dichromate [12] have been reported. One crystal structure of ammonium dichromate has been published [7, 13]. Sporadic cases of hydrated dichromates have been structurally characterized until now: the sodium dichromate tetrahydrate [14], three modifications of lithium dichromate dihydrate [15] and the

sodium dichromate dihydrate [16]. Only three structures with pyrosulfate anions were known [17] until recently when Ståhl *et al.* [18] published the structures of $\text{Na}_2\text{S}_2\text{O}_7$, $\text{K}_2\text{S}_2\text{O}_7$ and KNaS_2O_7 .

There is evidence for the existence of a “chromo sulfate” anion [19], but no structures of compounds containing CrSO_7^{2-} ions have been reported until now. Here we present the crystal structure of K_2CrSO_7 and the redetermination of the structures of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ and $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$.

Results and Discussion

Synthesis methods for $\text{Ce}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$ (**1**) and $\text{Ce}(\text{CrO}_4)_2 \cdot \text{H}_2\text{O}$ (**2**)

New and quick methods to synthesize compounds **1** and **2**, giving high yields, are described in the experimental section. One method is based on exchange reactions from commercially available starting materials by refluxing the reactants in water solution. The second method is based on an addition reaction in the solid state. Compound **1** has previously been synthesized by Lindgren [5] from water solution by slow evaporation at r. t. Compound **2** has unexpectedly been synthesized by Kolitsch and Schwendtner [6] by slowly evaporating an aqueous solution, using a Ce(III) species and CrO_3 , where the reaction involved a slow oxidation of Ce(III) by Cr(VI), also encountered in our previous work [20].

The structure of **1** is essentially different from that of **2**. Compound **1** is built up by layers of $[\text{Ce}(\text{CrO}_4)_2 \cdot (\text{H}_2\text{O})_2]_n$ held together by hydrogen bonds, while the structure of **2** forms a three-dimensional network mediated by oxygen bridges. As a consequence of the structural differences their properties differ. The density of **2** (3.75 g cm^{-3}) is higher than that of **1** (3.37 g cm^{-3}) and the solubility of **1** in water is much higher than the solubility of **2**.

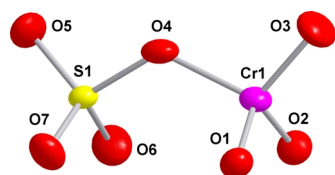


Fig. 1. Coordination geometry for CrSO_7^{2-} in **3**. The displacement ellipsoids are drawn at 50 % probability level.

Structural description of K_2CrSO_7 (**3**)

Compound **3** crystallizes in the space group $P2_1/n$ with $a = 7.4024(1)$, $b = 7.3908(1)$, $c = 12.9883(2) \text{ Å}$, $\beta = 90.021(1)^\circ$ and $Z = 4$. The crystal under investiga-

Table 1. Bond lengths (Å) in **3**.

Cr1–O1	1.595(5)	S1–O4	1.577(6)
Cr1–O2	1.604(6)	S1–O5	1.471(6)
Cr1–O3	1.592(6)	S1–O6	1.495(6)
Cr1–O4	1.807(6)	S1–O7	1.481(6)
K1–O1 ⁱⁱ	2.800(5)	K2–O1 ⁱ	2.755(6)
K1–O1 ⁱⁱⁱ	2.810(5)	K2–O2	2.722(6)
K1–O2	2.870(6)	K2–O4 ^{iv}	3.117(5)
K1–O2 ⁱⁱⁱ	2.966(6)	K2–O5 ^{iv}	2.966(7)
K1–O3 ^{iv}	2.804(6)	K2–O5 ^{vi}	3.111(7)
K1–O5 ^v	2.821(6)	K2–O6 ⁱⁱⁱ	2.843(7)
K1–O6	2.828(7)	K2–O6 ^{vi}	2.921(7)
K1–O7 ⁱ	2.747(6)	K2–O7 ⁱ	2.809(6)

Symmetry transformations for equivalent atoms: ⁱ $x+1, y, z$; ⁱⁱ $x+1/2, -y+1/2, z+1/2$; ⁱⁱⁱ $-x+1, -y+1, -z+1$; ^{iv} $-x+1, -y, -z+1$; ^v $-x+1/2, y+1/2, -z+3/2$; ^{vi} $x+1/2, -y+1/2, z-1/2$.

tion was twinned, mimicking the orthorhombic symmetry due to the closeness of the β angle to 90° , twin law: $[(1\ 0\ 0)\ (0\ \bar{1}\ 0)\ (0\ 0\ \bar{1})]$. The twin volume ratio was refined to 0.505(4)/0.495(4). There are two potassium cations and one chromatosulfato, CrSO_7^{2-} , anion in the asymmetric unit. The CrSO_7^{2-} ion, consisting of one chromate tetrahedron sharing one oxygen atom with one sulfate tetrahedron, has a *pseudo syn-C_{2v}* conformation with eclipsed oxygen atoms (Fig. 1). This conformation is the usual one for both the dichromate and the disulfate compounds. The Cr–O bridging distance is longer [$d = 1.807(6) \text{ Å}$] than the terminal Cr–O distances with an average of $1.597(6) \text{ Å}$. The mean Cr–O distance within the chromium tetrahedra ($1.65(10) \text{ Å}$) is in accordance with distances reported for dichromate compounds [7, 10–16]. Also the S–O bridging distance is longer [$d = 1.577(6) \text{ Å}$] than the terminal distances which average to $1.48(1) \text{ Å}$. The mean S–O distance within the sulfate moiety [$1.50(5) \text{ Å}$] is in accordance with distances within pyrosulfate compounds [17, 18]. The bond-valence sums are 6.08 and 5.84 valence units for Cr1 and S1, respectively (using the parameters from Brown and Altermatt [21]). For a complete list of bond lengths see Table 1. The Cr1–O4–S1 bond angle is $125.8(3)^\circ$. The potassium ions (K1 and K2) are in contact with eight oxygen atoms at distances ranging between 2.722(6) and $3.117(5) \text{ Å}$ (Table 1). The K1 and K2 ions connect to six and five different CrSO_7^{2-} units, respectively. Each terminal oxygen atom within the CrSO_7^{2-} units is linked to two or three potassium ions. The bridging oxygen atom, O4, has one cation contact, which is common in most of the chromate-like structures [9] but not found in the pyrosulfate structures [18].

Compound **3** forms a three dimensional network of CrSO_7^{2-} ions held together by the charge bal-

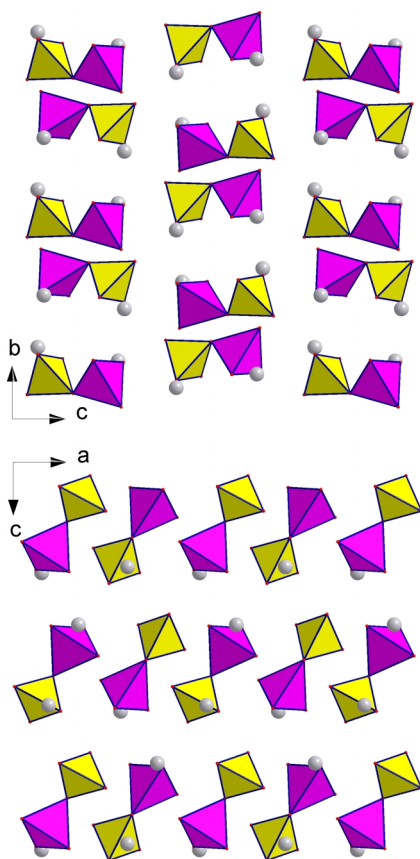


Fig. 2. Packing of the CrSO_7^{2-} units and the potassium ions for **3**, the purple (dark) tetrahedra are chromate units and the yellow tetrahedra (light) are sulfate units.

ancing potassium ions (Fig. 2), with structural features common with $A_2M_2O_7$ compounds. Brown and Calvo [8] proposed a scheme for classifying $A_2M_2O_7$ structure types, where the structures are described in terms of the possible ways of stacking sheets. These sheets are composed of centrosymmetrically related $A_2M_2O_7$ groups forming a basic unit. The structure of **3** can be described in terms of two alternating sheets parallel to the ab plane, with the composition $[\text{K}_2\text{CrSO}_7]_n$ (Fig. 2). In this structure, adjacent sheets are related by two-fold screw axes between them and glide planes perpendicular to them. According to the scheme proposed by Brown and Calvo [8], who predicted this structure type before it had been observed, this structure belongs to type VII. A high temperature phase of $\text{K}_2\text{Cr}_2\text{O}_7$ belonging to this structure type is supposed to exist [11a,f], but its structure has not been solved. However, the structure of $\text{Rb}_2\text{Cr}_2\text{O}_7$ (space group $P2_1/n$) [12b] has the key pack-

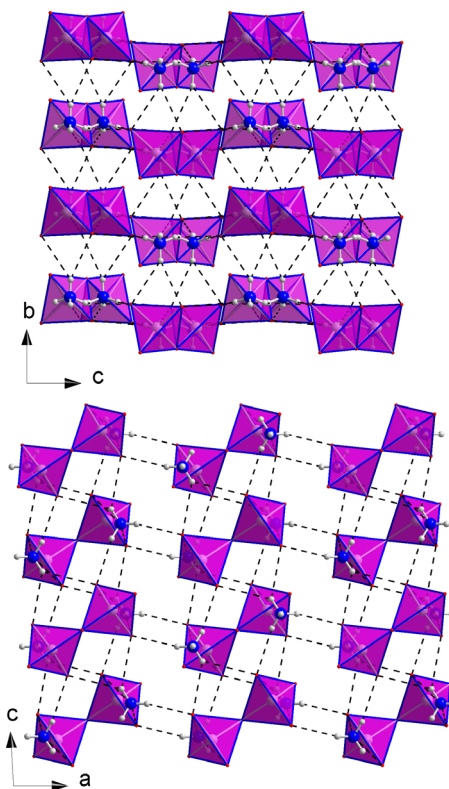


Fig. 3. Packing of the $\text{Cr}_2\text{O}_7^{2-}$ units and the ammonium ions in **4** showing the hydrogen bonding contacts with dashed lines.

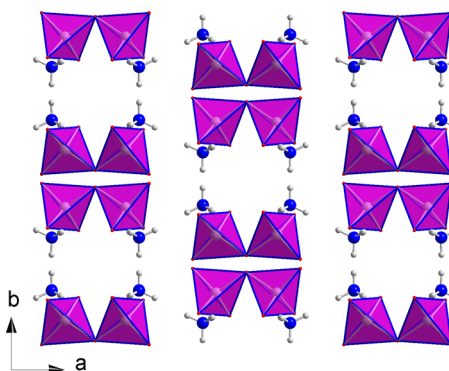


Fig. 4. View of **4** in the c direction showing adjacent sheets with the composition $[(\text{NH}_4)_2\text{Cr}_2\text{O}_7]_n$ related by C -centering.

ing features common with the structure of **3**. The structure of $\text{K}_2\text{S}_2\text{O}_7$ [18] belongs to the structure type X [8] together with the structures of $\text{K}_2\text{Cr}_2\text{O}_7$ [11e], $\text{Rb}_2\text{Cr}_2\text{O}_7$ [12c] and $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (**4**) [7, 13]. Within these structures the sheets are more symmetric, due to the twofold axes through the bridging oxygen atoms,

Table 2. Bond lengths (Å) in **4** and **5**.

4		Cr2–O21	1.631(2)
Cr1–O1	1.7864(9)	Cr2–O22	1.616(2)
Cr1–O2	1.6235(14)	Cr2–O23	1.617(3)
Cr1–O3	1.6292(14)	Cr3–O30	1.800(2)
Cr1–O4	1.6053(14)	Cr3–O31	1.622(2)
5		Cr3–O32	1.627(3)
Cr1–O10	1.794(2)	Cr3–O33	1.622(2)
Cr1–O11	1.620(2)	Cr4–O30	1.800(2)
Cr1–O12	1.626(3)	Cr4–O41	1.619(2)
Cr1–O13	1.618(2)	Cr4–O42	1.628(2)
Cr2–O10	1.817(2)	Cr4–O43	1.628(3)

Table 3. Hydrogen bonds for **4** (Å and deg).

D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠(DHA)
N1–H1...O2	0.83(2)	2.04(2)	2.832(2)	158(3)
N1–H2...O3 ⁱ	0.81(2)	2.08(2)	2.872(2)	167(3)
N1–H3...O3 ⁱⁱ	0.82(2)	2.29(3)	2.939(2)	137(3)
N1–H3...O2 ⁱⁱⁱ	0.82(2)	2.37(3)	2.994(2)	134(3)
N1–H4...O3 ^{iv}	0.81(2)	2.14(2)	2.902(2)	158(3)

Symmetry transformations used for equivalent atoms: ⁱ $-x + 1/2$, $-y + 1/2$, $-z + 1$; ⁱⁱ x , y , $z - 1$; ⁱⁱⁱ $-x + 1$, y , $-z + 1/2$; ^{iv} x , $-y + 1$, $z - 1/2$.

and adjacent sheets are related by a translation operation, see Figs. 3 and 4 for the packing of **4**.

Structural description of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (**4**)

A redetermination of the structure of **4** [7, 13] with the hydrogen atoms located is presented. Compound **4** belongs to the monoclinic space group $C2/c$, with $a = 13.2741(3)$, $b = 7.4831(2)$, $c = 7.7125(1)$ Å, $\beta = 93.305(1)^\circ$ and $Z = 4$. The structure is composed of ammonium cations and discrete chromate dimers, in which the two CrO_4 tetrahedra are related by a twofold axis through the shared oxygen atom, O1. The Cr–O bridging distance is longer ($d = 1.7865(9)$ Å) than the terminal Cr–O bridging distances ($d_{\text{mean}} = 1.62(1)$ Å) and the mean Cr–O distance within the individual tetrahedra is 1.66(8) Å (Table 2). The tetrahedral ammonium ions in **4** are surrounded by eight nearest oxygen atoms belonging to six different dichromate units (distances range: 2.832(2)–3.161(2) Å). The hydrogen atoms in the ammonium ion show mono- (H1, H2 and H4) and bi-furcated (H3) interactions with oxygen atoms in the $\text{Cr}_2\text{O}_7^{2-}$ units, presented in Fig. 3 and Table 3. The structure can be regarded as sheets [8] with the composition $[(\text{NH}_4)_2\text{Cr}_2\text{O}_7]_n$, parallel to the bc plane. The sheets have a twofold axis along b and a glide plane along c , and adjacent sheets are related by a C -centering translation (Fig. 4). This structure is isomorphous with its chemical analogues $\text{K}_2\text{Cr}_2\text{O}_7$ [11e] and $\text{Rb}_2\text{Cr}_2\text{O}_7$ [12c] and $\text{K}_2\text{S}_2\text{O}_7$ [18]. The bridging

oxygen atoms within this structure type do not connect to cations, which is atypical for dichromate compounds.

Structural description of $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ (**5**)

Neither e.s.d.'s nor anisotropic displacement parameters were given by Kharitonov *et al.* [16] in the paper on the $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ structure and the R value was reported to be 0.083, based on film data. Here we present a redetermination of the $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ structure where the hydrogen atoms have been located and the absolute structure has been established. Compound **5** belongs to the non-centrosymmetric space group $P2_1$, with $a = 6.1216(1)$, $b = 10.7868(1)$, $c = 12.7175(1)$ Å, $\beta = 95.080(1)^\circ$ and $Z = 4$. The struc-

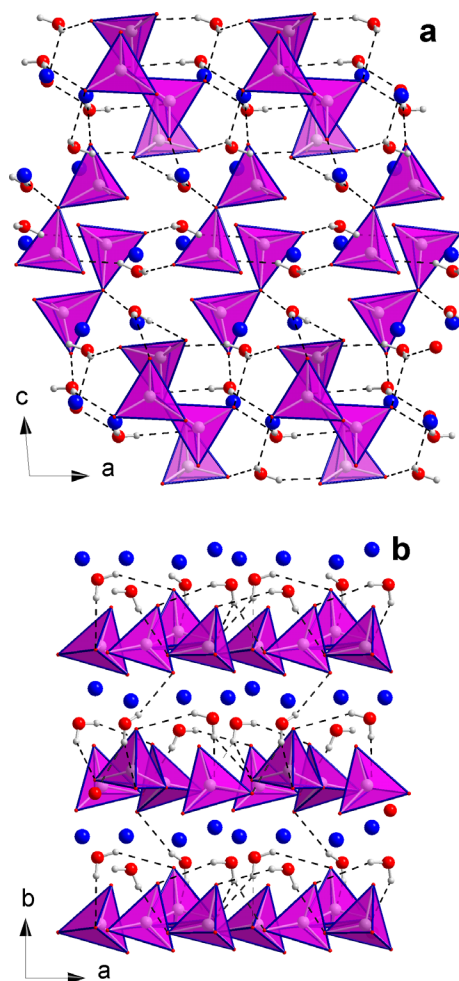


Fig. 5. View of the structure of **5** along the b (top) and c (bottom) axis showing the hydrogen bonding contacts with dashed lines.

Table 4. Hydrogen bonds for **5** (Å and deg).

D—H...A	<i>d</i> (D—H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠(DHA)
O1—H11...O41 ^v	0.81(3)	2.44(4)	3.113(4)	141(5)
O1—H11...O22 ⁱⁱ	0.81(3)	2.46(4)	3.025(4)	128(4)
O1—H12...O43 ⁱⁱ	0.82(3)	2.28(4)	2.989(3)	145(5)
O1—H12...O31	0.82(3)	2.58(5)	3.076(4)	120(4)
O2—H21...O13 ^{iv}	0.80(3)	2.18(3)	2.925(4)	154(5)
O2—H22...O11 ^{vi}	0.83(3)	2.06(3)	2.865(4)	164(5)
O3—H31...O33 ⁱ	0.85(3)	2.20(4)	2.930(4)	144(5)
O3—H32...O32 ⁱⁱ	0.86(3)	2.23(3)	2.991(4)	147(5)
O4—H41...O10 ⁱⁱⁱ	0.79(3)	2.50(4)	3.096(4)	132(5)
O4—H42...O31 ^{iv}	0.82(3)	2.21(3)	3.005(4)	162(5)

Symmetry transformations for equivalent atoms: ⁱ $-x, y-1/2, -z-1$; ⁱⁱ $-x-1, y-1/2, -z-1$; ⁱⁱⁱ $x, y-1, z+1$; ^{iv} $-x, y-1/2, -z$; ^v $-x-2, y-1/2, -z-1$; ^{vi} $-x+1, y-1/2, -z$.

ture is composed of sodium cations, discrete chromate dimers, joined by sharing corners, and water molecules. There are two non-equivalent Cr₂O₇ units, four sodium atoms and four water molecules in the asymmetric unit. The Cr—O bridging distances are longer ($d_{\text{mean}} = 1.80(1)$ Å) than the terminal Cr—O distances ($d_{\text{mean}} = 1.623(5)$ Å). Despite the variation of bond lengths, the mean Cr—O distance within the individual tetrahedra remains constant ($d_{\text{mean}} = 1.668(8)$ Å) (Table 2). Each sodium ion within Na₂Cr₂O₇ · 2H₂O is connected to two water molecules and four oxygen atoms belonging to four different dichromate units (distances range: 2.344(3)–2.512(3) Å). The crystal structure of **5** can be described as intercalating sheets in the *ac* plane of discrete dichromate units, water molecules and sodium ions (Fig. 5a). The water molecules in the *ac* plane interact mainly with the adjacent layer of chromate units (Fig. 5b), and the three dimensional framework is formed by the ionic interactions between the chromate groups and the potassium ions. The hydrogen bonding contacts are listed in Table 4.

Experimental Section

Sample preparations

Ce(CrO₄)₂ · 2H₂O (1), from water solution: Ce(SO₄)₂ · 4H₂O (0.50 g, 1.27 mmol), CrO₃ (0.38 g, 3.8 mmol) and water (5.0 mL) were mixed in a micro round bottom flask connected to a reflux water condenser. The reaction mixture was refluxed for 24 h until orange crystals of **1** were formed. Powder diffraction analysis showed evidence of a pure product.

Ce(CrO₄)₂ · 2H₂O (1), solid state synthesis: Ce(SO₄)₂ · 4H₂O (3.0 g, 7.5 mmol) was dissolved in water (20 mL) and Ce(OH)₄ was precipitated with 15 M ammonia. Ce(OH)₄ and CrO₃ (molar ratio 1 : 2) were milled in dry atmosphere, using a glove bag filled with nitrogen gas. The sample was placed

in a crucible with a lid and heated in a furnace over the weekend at 150 °C. The temperature was then raised to 188 °C for 19 h. The hygroscopic part of the powder was rinsed and the remaining part was dried. Powder diffraction revealed that the dark powder consisted mainly of Ce(CrO₄)₂ · 2H₂O.

Ce(CrO₄)₂ · H₂O (2): Powders of (NH₄)₂[Ce(NO₃)₆] (0.50 g, 0.91 mmol) and CrO₃ (0.28 g, 2.8 mmol) were mixed in water (5.0 mL) and poured into a micro round-bottom flask connected to a reflux water condenser. The reaction mixture was refluxed for 24 h until dark red and bipyramidally formed crystals of **2** were produced. Powder diffraction analysis showed evidence of a pure product.

K₂CrSO₇ (3): Crystals of K₂Cr₂O₇ were formed during an attempt to prepare hydrated cerium chromates. Ce(OH)₄ was precipitated with ammonia as in the solid state synthesis of **1**. Ce(OH)₄ (0.15 g, 0.95 mmol) was added to a saturated solution of K₂CrO₄ (1.5 mL), then concentrated sulphuric acid was added until the cerium hydroxide was completely dissolved. An additional amount (1.5 mL) of saturated solution of K₂CrO₄ was then added. This particular sample was left covered, and after a year light yellow-orange crystals, shaped as parallelepipeds with square faces, started to periodically form and dissolve. Finally, one of these metastable crystals was suitable for single crystal X-ray analysis.

(NH₄)₂Cr₂O₇ (4): Crystals of **4** were produced during investigations on the CeO₂–CrO₃–H₂O system. Ce(OH)₄ was produced using the same recipe as in the solid state synthesis of **1**. (NH₄)₂(CrO₄)₂ (2.0 g, 13.7 mmol) and Ce(OH)₄ (1.0 g, 6.3 mmol) were added to water (20 mL). After stirring, the solid residue was removed by filtration. Evaporation resulted in an orange crystalline material. After recrystallization from water solution, orange plate shaped single crystals were formed.

Na₂Cr₂O₇ · 2H₂O (5): A solution of Ce(CrO₄)₂ · 2H₂O (see synthesis of **1**) (0.15 g, 0.37 mmol), NaCr₂O₇ (0.15 g, 0.57 mmol) and ten drops of hydrochloric acid (15 M) was refluxed in a micro round bottom flask for 10 h. The mixture was left to evaporate until orange plate shaped crystals of Na₂Cr₂O₇ · 2H₂O were formed.

Single crystal X-ray analysis

Data were collected using a Siemens SMART CCD diffractometer equipped with a Siemens LT-2A low temperature device, at 22 °C for **3**, at –90 °C for **4**, and at –100 °C for **5**. Full spheres of the reciprocal space were scanned by 0.3° steps in ω with a crystal-to-detector distance of 3.97 cm and exposure times per frame of 20 s for **3**, 5 s for **4**, and 1 s for **5**. Preliminary orientation matrices were obtained using SMART [22]. The collected frames were integrated with the orientation matrices updated every 100 frames. Final cell parameters were obtained by refinement on the position of 8192 (**3**), 6379 (**4**) and 7764 (**5**) reflections with $I \geq 10\sigma(I)$ after integration of all the data using SAINT [22]. The data

Empirical formula	K_2CrSO_4 (3)	$(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (4)	$\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ (5)	Table 5. Crystal data and structure refinement for 3 , 4 and 5 .
Formula weight	274.26	252.08	298.01	
Temperature [K]	295(2)	183(2)	173(2)	
Wavelength [Å]	0.71073	0.71073	0.71073	
Crystal system	monoclinic	monoclinic	monoclinic	
Space group	$P2_1/n$	$C2/c$	$P2_1$	
Unit cell dimensions [Å, deg]	$a = 7.4024(1)$ $b = 7.3908(1)$ $c = 12.9883(2)$ $\beta = 90.021(1)$	$a = 13.2741(3)$ $b = 7.4831(2)$ $c = 7.7125(1)$ $\beta = 93.31$	$a = 6.1216(1)$ $b = 10.7868(1)$ $c = 12.7175(1)$ $\beta = 95.080(1)$	
Volume [Å ³]	710.585(17)	764.82(3)	836.469(17)	
Z	4	4	4	
Density (calculated) [g cm ⁻³]	2.56	2.19	2.37	
Absorption coefficient [mm ⁻¹]	3.1	2.8	2.7	
$F(000)$ [e]	536	504	584	
Crystal size [mm ³]	$0.40 \times 0.36 \times 0.07$	$0.64 \times 0.22 \times 0.03$	$0.30 \times 0.30 \times 0.10$	
θ range for data collection [deg]	1.57 to 32.97	3.07 to 32.50	1.61 to 32.83	
Index ranges	$-11 \leq h \leq 10$, $-11 \leq k \leq 10$, $-19 \leq l \leq 19$	$-19 \leq h \leq 19$, $-11 \leq k \leq 11$, $-11 \leq l \leq 11$	$-9 \leq h \leq 8$, $-16 \leq k \leq 16$, $-19 \leq l \leq 19$	
Reflections collected	10375	6379	14609	
Independent reflections/ $R(\text{int})$	2549/0.0755	1341/0.0403	5817/0.0446	
Completeness to $\theta = 31.00^\circ$ [%]	99.6	99.8	100.0	
Absorption correction	multi-scan	multi-scan	multi-scan	
Max. and min. transmission	0.814 and 0.374	0.920 and 0.264	0.773 and 0.496	
Data / restraints / parameters	2549/0/101	1341/10/65	5817/9/262	
Goodness-of-fit on F^2	0.999	1.003	1.003	
Final R indices [$I \geq 2\sigma(I)$]	$R1 = 0.0709$, $wR2 = 0.2007$	$R1 = 0.0286$, $wR2 = 0.0732$	$R1 = 0.0371$, $wR2 = 0.0775$	
R indices (all data)	$R1 = 0.0752$, $wR2 = 0.2064$	$R1 = 0.0386$, $wR2 = 0.0786$	$R1 = 0.0550$, $wR2 = 0.0856$	
Largest diff. peak and hole [e Å ⁻³]	1.547/−1.173	0.393/−0.546	0.596/−0.662	
Absolute structure param.	—	—	−0.014(17)	
Extinction coefficient	—	—	0.0231(11)	

were corrected empirically for absorption and other effects using SADABS [23]. The structures were solved by Direct Methods and refined by full-matrix least-squares on all F^2 data using SHELXTL [24]. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms in **4** and **5** were located from difference Fourier maps and refined isotropically with restraints (common O–H distances and a common displacement parameter). The Flack parameter [25] was refined

to −0.014(17) on 2699 Friedel pairs for **5**. Details on data collections and refinements are given in Table 5. Molecular graphics: DIAMOND [26].

Further details of the crystal structures may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number: CSD-417522 for **3**, CSD-417523 for **4** and CSD-417524 for **5**.

- | | |
|---|--|
| <p>[1] G. A. Molander, <i>Chem. Rev.</i> 1992, 92, 29–68.</p> <p>[2] P. Moriceau, B. Grzybowska, Y. Barbaux, G. Wrobel, G. Hecquet, <i>Appl. Catal. A</i> 1998, 168(2), 269–277.</p> <p>[3] F. Cavani, F. Trifirò, <i>Catal. Today</i> 1995, 24, 307–313.</p> <p>[4] M. M. Heravi, H. A. Oskooie, M. Ghassemzadeh, F. F. Zameni, <i>Monath. Chem.</i> 1999, 130, 1253–1256.</p> <p>[5] O. Lindgren, <i>Acta Chem. Scand. A</i> 1977, 31, 167–170.</p> <p>[6] U. Kolitsch, K. Schwendtner, <i>Acta Crystallogr.</i> 2004, C60, i89–i90.</p> <p>[7] A. Byström, K.-A. Wilhelmi, <i>Acta Chem. Scand.</i> 1951, 5, 1003–1010.</p> | <p>[8] I. D. Brown, C. Calvo, <i>J. Solid State Chem.</i> 1970, 1, 173–179.</p> <p>[9] G. M. Clark, R. Morely, <i>Chem. Soc. Rev.</i> 1976, 5, 269–295.</p> <p>[10] a) N. C. Panagiotopoulos, I. D. Brown, <i>Acta Crystallogr.</i> 1972, B28, 1352–1357; b) N. C. Panagiotopoulos, I. D. Brown, <i>Acta Crystallogr.</i> 1973, B29, 890–894.</p> <p>[11] a) U. Klement, G.-M. Schwab, <i>Z. Kristallogr.</i> 1960, 114, 170–199; b) L. A. Zhukova, Z. G. Pinsker, <i>Kristallografiya</i> 1964, 9, 44–49; c) J. K. Brandon, I. D. Brown, <i>Can. J. Chem.</i> 1968, 46, 933–941;</p> |
|---|--|

- d) G. Brunton, *Mat. Res. Bull.* **1973**, 8, 271–274;
e) S. V. Krivovichev, E. V. Kir'yanova, S. K. Filatov, P. C. Burns, *Acta Crystallogr.* **2000**, C56, 629–630;
f) T. J. R. Weakley, E. R. Ylvisaker, R. J. Yager, J. E. Stephens, R. D. Wiegel, M. Mengis, M. R. Bauer, P. Wu, P. Photinos, S. C. Abrahams, *Acta Crystallogr.* **2004**, B60, 705–715.
- [12] a) U. Kolitsch, *Z. Kristallogr.* **2003**, 218, 401–402;
b) P. Löfgren, *Acta Chem. Scand.* **1971**, 25, 44–58;
c) P. Löfgren, K. Waltersson, *Acta Chem. Scand.* **1971**, 25, 35–43; d) N. C. Panagiotopoulos, I. D. Brown, *Can. J. Chem.* **1970**, 48, 537–543.
- [13] G. A. P. Dalgaard, A. C. Hazell, R. G. Hazell, *Acta Chem. Scand. A* **1974**, 28, 541–545.
- [14] H. Ruben, I. Olovsson, A. Zalkin, D. H. Templeton, *Acta Crystallogr.* **1973**, B29, 2963–2964.
- [15] a) I. D. Datt, N. V. Rannev, T. G. Balicheva, R. P. Ozerov, *Kristallografiya* **1970**, 15, 949–952; b) I. D. Datt, R. P. Ozerov, *Kristallografiya* **1974**, 19, 110–117;
c) M. Simonov, Yu. Z. Nozik, N. A. Yamnova, E. L. Belokoneva, N. V. Belov, *Dokl. Akad. Nauk SSSR* **1978**, 240, 85–87; d) L. E. Fykin, Yu. Z. Nozik, *Kristallografiya* **1983**, 28, 1033–1034.
- [16] Yu. A. Kharitonov, E. A. Kuz'min, N. V. Belov, *Kristallografiya* **1970**, 15, 942–948.
- [17] a) H. Lynton, M. R. Truter, *J. Chem. Soc.* **1960**, 5112–5118; b) W. Höenle, *Z. Kristallogr.* **1991**, 196, 279–288; c) M. A. Simonov, S. V. Shkovrov, S. I. Troyanov, *Kristallografiya* **1988**, 33, 502–503.
- [18] K. Ståhl, T. Balic-Zunic, F. da Silva, K. M. Eriksen, R. W. Berg, R. Fehrmann, *J. Solid State Chem.* **2005**, 178, 1697–1704.
- [19] a) D. G. Donald, R. Stewart, *J. Am. Chem. Soc.* **1964**, 86, 3051–3056. b) L. S. A. Dikshitulu, D. Satyanarayana, *J. Inorg. Nucl. Chem.* **1976**, 38, 1843–1845.
- [20] a) B. M. Casari, A. Eriksson, V. Langer, *Z. Anorg. Allg. Chem.* **2006**, 632, 101–106; b) B. M. Casari, E. Wingstrand, V. Langer, *J. Solid State Chem.* **2006**, 179, 296–301.
- [21] I. D. Brown, D. Altermatt, *Acta Crystallogr.* **1985**, B41, 244–347.
- [22] SMART and SAINT. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) **1995**.
- [23] G. M. Sheldrick, SADABS (version 2.03), University of Göttingen, Göttingen (Germany) **2002**.
- [24] G. M. Sheldrick, SHELXTL (version 6.10), Bruker AXS Inc., Madison, Wisconsin (USA) **2003**.
- [25] a) H. D. Flack, G. Bernardinelli, *Acta Crystallogr.* **1999**, A39, 908–915; b) H. D. Flack, G. Bernardinelli, *J. Appl. Crystallogr.* **2000**, 33, 1143–1148.
- [26] K. Brandenburg, DIAMOND (version 2.1c), Crystal and Molecular Structure Visualization, Crystal Impact - K. Brandenburg & H. Putz GbR, Bonn (Germany) **2000**.