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New mixed-valence chromium structure type: $NH_4Cr(CrO_4)_2$

Barbara M. Casari[a,*], Erica Wingstrand[b], Vratislav Langer[c]

[a]Department of Chemistry, Inorganic Chemistry, Göteborg University, SE-421 96 Göteborg, Sweden
[b]Department of Chemistry, Organic Chemistry, Royal Institute of Technology, SE 100 44 Stockholm, Sweden
[c]Department of Chemical and Biological Engineering, Division of Material and Surface Chemistry, Subdivision of Inorganic Environmental Chemistry, Chalmers University of Technology, SE-421 96 Göteborg, Sweden

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Abstract

Synthesis and crystal structure of a new structure type of mixed Cr(III)/Cr(VI) chromates is reported. $NH_4Cr(CrO_4)_2$ was prepared from CrO_3 in the presence of $(NH_4)_2Ce(NO_3)_6$. Since this is the first preparation of mixed valence ternary chromium oxides from aqueous solution, a reaction pathway for this synthesis is suggested. The crystal structure of $NH_4Cr(CrO_4)_2$ has been determined from three-dimensional X-ray data collected at low temperature, 173 K. The structure belongs to the orthorhombic space group *Pnma*, with $a = 14.5206(10)$, $b = 5.4826(4)$, $c = 8.7041(7)$ Å and $Z = 4$. The title compound consists of corner-sharing chromium(III) octahedra and chromium(VI) tetrahedra forming a three-dimensional network with the composition $[Cr(CrO_4)_2]_n^{n-}$, containing channels in which zigzag rows of ammonium ions balance the net charge.

Keywords: $NH_4Cr_3O_8$; Mixed-valence ternary oxide; Mixed-valence chromate; Cr(VI)/Ce(III) redox reaction; X-ray diffraction

1. Introduction

Mixed-valence chromium compounds are of current interest as cathode materials in rechargeable lithium batteries because of the very high-energy density and high capacity of these materials [1–3]. These compounds have also attracted interest as precursors to chemicals for spintronic device applications [4] as magnetoresistive random access memory, spin-based light-emitting diodes and field-effect transistors. Mixed-valence chromium oxides are very attractive also due to the complexity of their structural arrangements with both tetrahedral and octahedral oxygen coordination.

Intermediate binary oxides prepared by thermal decomposition of CrO_3 under different conditions have been subject to numerous studies [5–21] during the past 50 years. The starting material, CrO_3, contains tetrahedrally coordinated Cr(VI), while the final thermal decomposition product is Cr_2O_3 with octahedrally coordinated Cr(III). One of the intermediate decomposition products is CrO_2, a well-known ferromagnetic compound. Further, many oxides with compositions between the trioxide and the monoxide were suggested as a result of these studies; both Cr_2O_5 and Cr_3O_8 have frequently been reported [6,16–18]. Many questions remain concerning the identities of the various stable intermediate oxides, their characterisation and whether non-stoichiometric regions exist. The instability of the intermediate oxidation states toward disproportionation indicate that most of the stable chromium oxides between CrO_3 and CrO_2 are mixed Cr(III)/Cr(VI) compounds [15,17,19]. Crystal structures have so far only been determined for Cr_5O_{12} [9] and Cr_8O_{21} [19], these chromium oxides being better described as $Cr(III)_2(Cr(VI)O_4)_3$ and $Cr(III)_2(Cr(VI)O_4)_2(Cr_4(VI)O_{13})$, respectively.

Mixed III and VI oxidation states for chromium are also found in the structurally related ternary oxides, $MCr(CrO_4)_2$ ($M =$ Li, Na, K, Rb and Cs), all prepared by solid syntheses. The first structural studies in this field were conducted by Wilhelmi [6,7,10–12] who showed that these compounds crystallise in three different structural types, the Li-, K- and Cs-type. Common for these types are Cr(III) octahedra and Cr(VI) octahedra arranged by sharing corners. Here we present a new compound,

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[*] Corresponding author. Fax: +46(0)317722853.
E-mail address: casari@chem.gu.se (B.M. Casari).

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$NH_4Cr(CrO_4)_2$, which does not belong to the earlier described types.

2. Experimental

2.1. Sample preparation

Powder of $(NH_4)_2Ce(NO_3)_6$ (2.19 g, 4.00 mmol) was dissolved, under heating and stirring, in water (2.0 mL); dried CrO_3 (0.80 g, 7.97 mmol) was dissolved in water (2.0 mL). These solutions, mixed in the volumetric ratio of 1:2, were heated in a sealed autoclave in an oven at 53 °C for 48 h. After cooling (30 min), the mixture was filtered. The small amount of solid product obtained, dark brown coloured crystals, was washed carefully with a few drops of cold distilled water.

In spite of many trials we were not able to recrystallise the product to get better crystals. Due to the great difficulties in achieving good single crystals suitable for X-ray analysis directly from the autoclave, many experiments were preformed, varying the amount of starting materials and reaction conditions. The experiments with CrO_3 (0.80–1.59 g) and reaction volumetric ratio of 1:2–1:4 all gave the same product as detected by X-ray diffraction. The best single crystals were obtained with the reaction conditions presented above.

2.2. Single crystal X-ray diffraction

Data were collected using a Siemens SMART CCD diffractometer equipped with a Siemens LT-2A low-temperature device at 173 K. Almost a full sphere of the reciprocal space was scanned by 0.3° steps in ω with a crystal-to-detector distance of 3.97 cm and exposure time per frame 40 s. A preliminary orientation matrix was obtained using SMART [22]. The collected frames were integrated using this orientation matrix, updated every 100 frames. Final cell parameters were obtained by refinement on the position of 1250 reflections with $I > 10\sigma(I)$ after integration of all the data using SAINT [22]. The data were corrected empirically for absorption and other effects using SADABS [23]. The structure was solved by direct methods and refined by full-matrix least squares on all F^2 data using SHELXTL [24]. The non-H atoms were refined anisotropically. The ammonium H atoms were located from difference Fourier maps and refined with restraint to an ideal tetrahedron with a common temperature factor, fixed at 2.5 times the U_{eq} for N(1). Details on data collection and refinement are given in Table 1. Further details of the crystal structure may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-415681. Molecular graphics: DIAMOND [25].

Table 1
Crystal data and structure refinement

Empirical formula	$NH_4Cr(CrO_4)_2$
Formula weight	302.03
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*Pnma*
Unit cell dimensions	$a = 14.5206(10)$ Å
	$b = 5.4826(4)$ Å
	$c = 8.7041(7)$ Å
Volume	692.94(9) Å^3
Z	4
Density (calculated)	2.895 Mg/m^3
Absorption coefficient	4.631 mm^{-1}
$F(000)$	588
Crystal size	$0.03 \times 0.03 \times 0.01$ mm^3
θ range for data collection	2.73–25.05°
Index ranges	$-17 \leqslant h \leqslant 17$, $-6 \leqslant k \leqslant 6$
	$-10 \leqslant l \leqslant 10$
Reflections collected	5533
Independent reflections	684 (R(int) = 0.1443)
Completeness to $\theta = 25.05°$	100.0%
Max. and min. transmission	0.9552 and 0.8736
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	684/10/75
Goodness-of-fit on F^2	0.995
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0594$, w$R_2 = 0.1337$
R indices (all data)	$R_1 = 0.0983$, w$R_2 = 0.1553$
Largest diff. peak and hole	0.875 and -1.105 e Å^3

3. Result and discussion

3.1. Synthesis

The title compound was synthesised from a water solution of $(NH_4)_2Ce(NO_3)_6$ and CrO_3, with the concentrations varied between 0.50–0.66 M for $(NH_4)_2Ce(NO_3)_6$ and 2.66–8.00 M for CrO_3. When the concentration ratio $(NH_4)_2Ce(NO_3)_6$ versus CrO_3 was increased, cerium(IV) dichromate hydrate started to form.

The influence from the presence of Ce(IV) in the reduction of Cr(VI) have to be considered. Cerium(IV) is capable of undergoing rapid changes in oxidation state upon changes in redox potential. Cerium(IV) in acidic aqueous solutions is metastable with respect to the oxidation of water to produce gaseous oxygen, so in an acidic aqueous media cerium(III) will form. Cerium(III) is known to inhibit chromium(VI) oxidation of organic compounds. This effect is attributed to the chromic acid oxidation of the cerium(III) species [26–30] encountered also in the synthesis of $(NH_4)_2[CrCl_5H_2O]$ and $K_2[CrCl_5H_2O]$ from CrO_3 in the presence of Ce(IV) [31]. We believe that during the synthesis of the title compound the reduction of Cr(VI) is promoted by the oxidation of cerium(III). A reasonable mechanism for reaction of the three-equivalent oxidising agent chromium(VI) with the one-equivalent reducing agent cerium(III) is the sequence of three one-equivalent redox equilibria:

$$\mathrm{Cr(VI)} + \mathrm{Ce(III)} \leftrightarrow \mathrm{Cr(V)} + \mathrm{Ce(IV)}, \tag{1}$$

$$\mathrm{Cr(V)} + \mathrm{Ce(III)} \leftrightarrow \mathrm{Cr(IV)} + \mathrm{Ce(IV)}, \tag{2}$$

$$\mathrm{Cr(IV)} + \mathrm{Ce(III)} \leftrightarrow \mathrm{Cr(III)} + \mathrm{Ce(IV)}. \tag{3}$$

These systems are able to produce a variety of transient and intermediate species and several competing redox reactions are reported [26,30,32–34] to occur in these systems of which the following [26,30,33] are the most relevant:

$$\mathrm{Cr(IV)} + \mathrm{Ce(III)} \rightarrow \mathrm{Cr(III)} + \mathrm{Ce(IV)}, \tag{4}$$

$$\mathrm{Cr(IV)} + \mathrm{Ce(IV)} \rightarrow \mathrm{Cr(V)} + \mathrm{Ce(III)}, \tag{5}$$

$$\mathrm{Cr(V)} + \mathrm{Ce(IV)} \rightarrow \mathrm{Cr(VI)} + \mathrm{Ce(III)}. \tag{6}$$

It has been shown [30,33] that small amounts of Ce(III) or Ce(VI) effectively exchanges Cr(IV) species, acting as a catalyst for the disproportionation of chromium(IV). Reaction (4) is much faster than reactions (5) and (6) [30]. At very low cerium(III) concentrations, when almost all available Ce(III) is converted into Ce(IV), the net result of reactions (4)–(6) is reported as follows [30]:

$$3\mathrm{Cr(IV)} - \mathrm{Ce(IV)} \rightarrow 2\mathrm{Cr(III)} + \mathrm{Cr(VI)}. \tag{7}$$

Taking into account the high concentration ratio of Cr(VI) and Ce(IV) versus Cr(V), Cr(IV), Cr(III) and Ce(III) we suggest reactions (1), (2) and (7) as the most dominant, during the formation of $NH_4Cr(CrO_4)_2$. Thus, the synthesis of the title compound may be described by following reactions:

$$2\mathrm{Ce}^{4+} + \mathrm{H_2O} \rightarrow 2\mathrm{Ce}^{3+} + 2\mathrm{H}^+ + \tfrac{1}{2}\mathrm{O_2},$$

$$3\mathrm{CrO_3} + 3\mathrm{Ce}^{3+} + \mathrm{NH_4}^+ + 2\mathrm{H}^+ \rightarrow \mathrm{NH_4Cr(CrO_4)_2} + 3\mathrm{Ce}^{4+} + \mathrm{H_2O}.$$

3.2. Structurally related compounds

The oxygen coordination around chromium in oxides prepared by conventional methods is dependent on the chromium oxidation states [35]: octahedral for Cr(III), tetrahedral or octahedral for Cr(IV) and tetrahedral for Cr(V) and Cr(VI). Three different classes of mixed-valence Cr(III)/Cr(VI) compounds, thus containing both octahedral and tetrahedral oxygen coordination, have been structurally characterised until now: the binary oxides Cr_5O_{12} [9] and Cr_8O_{21} [19], the oxyhydroxides $Na_2Cr_3O_8OH$ and $K_2Cr_3O_8OH$ [15] and the ternary oxides $M\mathrm{Cr(CrO_4)_2}$ (M = Li, Na, K, Rb and Cs) [6,7,10–12,20].

The binary oxides are characterised by pairs of edge-sharing $\mathrm{Cr(III)O_6}$ octahedra linked together by corner-sharing chromate(VI) groups and/or tetrachromate chains. The structure of the two isomorphous oxyhydroxides, $Na_2Cr_3O_8OH$ and $K_2Cr_3O_8OH$ [15], can be visualised as shown in Fig. 1a. It can be described as strings of edge-sharing $\mathrm{Cr(III)O_6}$ linked to $\mathrm{Cr(VI)O_4}$ tetrahedra forming chains with the formula $[Cr_3O_8OH]_n^{2n-}$. Their charge is counterbalanced by the intercalating alkali metal ions. The ternary oxides are divided into three different types. The Li-type, including $\mathrm{LiCr(CrO_4)_2}$ only [10,11], crystallising in the orthorhombic space group *Cmcm*, can be described as strings of edge-sharing octahedra occupied randomly by Li^+ and Cr^{3+}, held together by corner-sharing $\mathrm{Cr(VI)O_4}$ tetrahedra to form a three-dimensional network (Fig. 1b). In the K-type structures ($M\mathrm{Cr(CrO_4)_2}$ with M = Na, K and Rb) [7,10,20], belonging to the monoclinic space group $C2/m$, octahedral $\mathrm{Cr(III)O_6}$ and tetrahedral $\mathrm{Cr(VI)O_4}$ are corner-linked to form layers held together by the alkali metal ions, see Fig. 1c. The Cs-type, with $\mathrm{CsCr(CrO_4)_2}$ [10,12], which crystallises in the orthorhombic space group *Pnma*, forms layers essentially in the same way as the K-type. However, the orientation of half of the tetrahedra differs and every second layer of the Cs-type is rotated by 180° compared with the K-type (Fig. 1d).

3.3. Structural description

Here we present a new structure-type among the mixed-valence ternary chromium oxides, $NH_4Cr(CrO_4)_2$, which is orthorhombic with the space group *Pnma*. The structure of the title compound is build up of chromium-oxygen octahedra $\mathrm{Cr^{III}(1)O_6}$ and tetrahedra, $\mathrm{Cr^{VI}(2)O_4}$ and $\mathrm{Cr^{VI}(3)O_4}$, whose charge is counterbalanced by ammonium ions. There is an expected significant difference between the

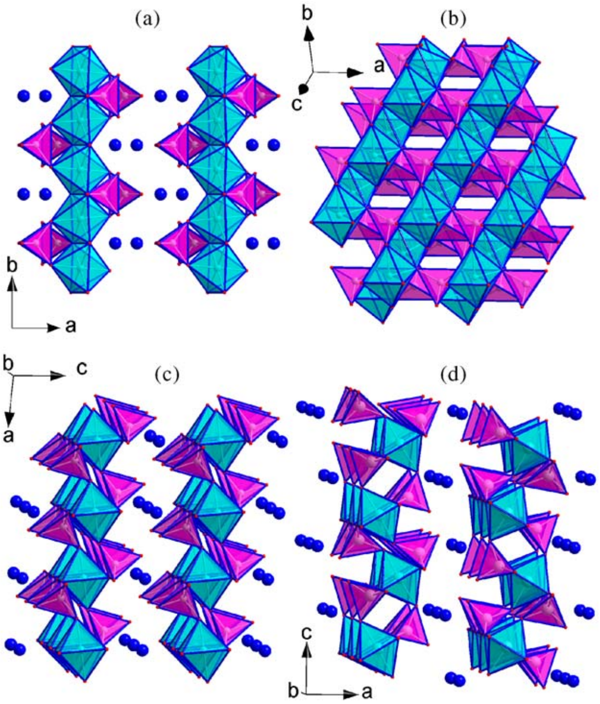

Fig. 1. Packing within: $K_2Cr_3O_8OH$ [15] (a), $\mathrm{LiCr(CrO_4)_2}$ [11] (b), $\mathrm{KCr(CrO_4)_2}$ [20] (c) and $\mathrm{CsCr(CrO_4)_2}$ [12] (d).

Cr–O distances within the Cr(III) octahedron and the two Cr(VI) tetrahedra, as can be seen from Table 2. All the oxygen atoms within the Cr(1)O_6 unit are bridging to a corner-sharing Cr(2)O_4 or Cr(3)O_4 tetrahedra, see Fig. 2. There is one non-bridging oxygen atom within each Cr(2)O_4 and Cr(3)O_4 unit, O(22) and O(33), marked by the shorter Cr–O distances (Table 2). Bond-valence sums for the chromium atoms were calculated [36] using the bond-valence parameters from Brese and O'Keeffe [37]. These sums are 2.91(6) [Cr^{III}(1)], 5.80(14) [Cr^{VI}(2)] and 5.97(14) [Cr^{VI}(3)] valence units (v.u.), all reasonably close to ideal valences. Further, taking into account the bond valence sums on the oxygen atoms a valence of 1.12(26) v.u. may be assigned to the ammonium ion. The ammonium ion is surrounded by ten nearest oxygen atoms belonging to neighbouring $Cr^{III}O_6$ or $Cr^{VI}O_4$ units. The N–O distances ranges between 2.870(16) and 3.181(8) Å, shown in Fig. 3 together with the hydrogen bonds, for details see Table 3.

Table 2
Cr–O bond lengths

Atom labels	Distances (Å)
Cr(1)–O(12)	2.002(9)
Cr(1)–O(13)	2.010(10)
Cr(1)–O(21)^{iii}	1.998(7)
Cr(1)–O(21)^{iv}	1.998(7)
Cr(1)–O(31)^{i}	1.974(7)
Cr(1)–O(31)^{ii}	1.974(7)
Cr(2)–O(12)	1.694(10)
Cr(2)–O(21)	1.662(7)
Cr(2)–O(21)^{v}	1.662(7)
Cr(2)–O(22)	1.614(11)
Cr(3)–O(13)	1.648(10)
Cr(3)–O(31)	1.676(7)
Cr(3)–O(31)^{v}	1.676(7)
Cr(3)–O(33)	1.591(10)

Symmetry transformations: (i) $-x, y+\frac{1}{2}, -z$ (ii) $-x, -y, -z$ (iii) $-x+\frac{1}{2}, y+\frac{1}{2}, z+\frac{1}{2}$ (iv) $-x+\frac{1}{2}, -y, z+\frac{1}{2}$ (v) $x, -y+\frac{1}{2}, z$.

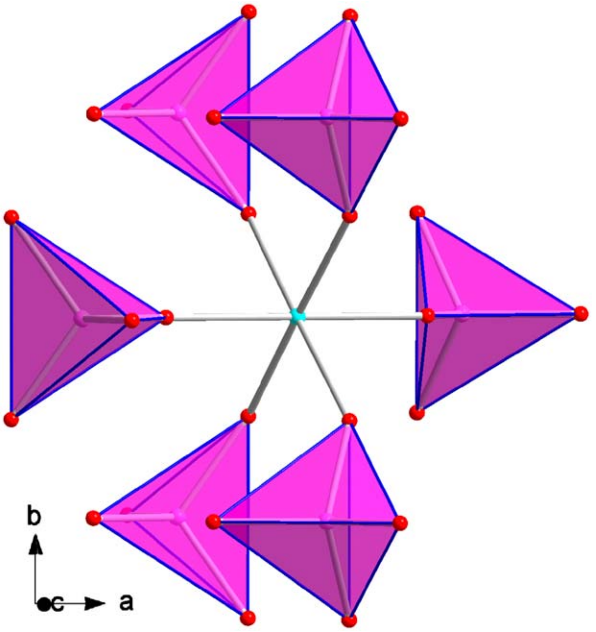

Fig. 2. Eight chromate groups giving an almost regular octahedral coordination around the Cr^{3+} ion, forming one $[Cr(CrO_4)_6]^{9-}$ unit.

The crystal structure of the title compound is build up by corner-sharing chromium octahedra and tetrahedra forming a three-dimensional network with the composition $[Cr(CrO_4)_2]_n^{n-}$, containing channels in the *b* direction. These channels are occupied by ammonium ions, see Figs. 3 and 4b. Despite the crystallographical similarities between $NH_4Cr(CrO_4)_2$ (this paper) and $CsCr(CrO_4)_2$ [12], both belonging to space group *Pnma* with three non-equivalent chromium atoms in special position 4*c*, the structural arrangement is essentially different. Within the structure of $CsCr(CrO_4)_2$ the Cr(III) octahedron and the Cr(VI) tetrahedra are more distorted than in the $NH_4Cr(CrO_4)_2$ structure. The Cr^{III}–O bonding distances and O–Cr^{III}–O angles ranges are 1.976(23)–2.015(21) Å and 87.7–92.1°, 175.5–178.2° within $CsCr(CrO_4)_2$ [12] compared to 1.974(7)–2.010(10) Å and 88.1(4)–91.8(3)°, 178.6(3)–179.5(4)° in the $NH_4Cr(CrO_4)_2$ structure. The Cr^{VI}–O bonding distances and O–Cr^{IV}–O angles ranges are 1.571(20)–1.705(17) Å and 101.6–116.3° within $CsCr(CrO_4)_2$ [12] compared to 1.591(10)–1.694(10) Å and

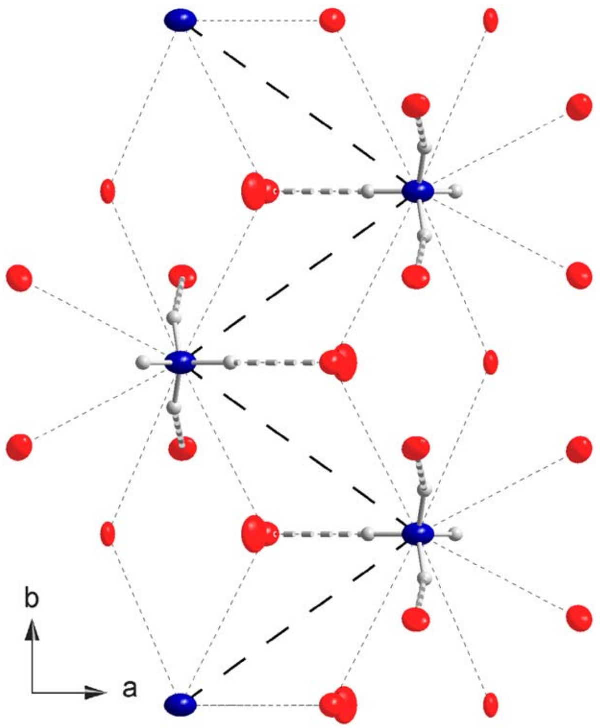

Fig. 3. Zigzag rows of ammonium ions (black dashed lines), surrounded by their ten nearest oxygen atoms (dotted lines), inside the channels of the $[Cr(CrO_4)_2]_n^{n-}$ network. Hydrogen mediated contacts are shown by thicker grey dashed lines. The displacement ellipsoids are drawn at 50% probability level.

Table 3
Hydrogen bonds (Å and °)

D–H···A	d(D–H)	D(H···A)	d(D···A)	<(DHA)
$N(1)–H(11)\cdots O(31)^{i}$	0.87(7)	2.31(6)	3.022(13)	140(3)
$N(1)–H(11)^{ii}\cdots O(31)^{iii}$	0.87(7)	2.31(6)	3.022(13)	140(3)
$N(1)–H(12)\cdots O(33)$	0.87(7)	2.01(7)	2.870(16)	169(13)

Symmetry transformations used to generate equivalent atoms: (i) $-x, -y, -z+1$ (ii) $x, -y+\frac{1}{2}, z$ (iii) $-x, y+\frac{1}{2}, -z+1$.

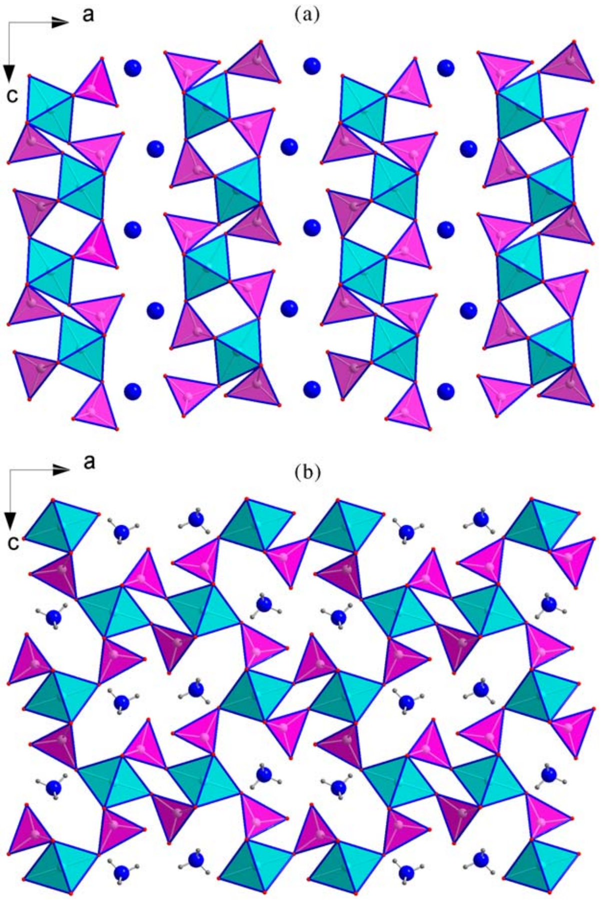

Fig. 4. Packing of the $CsCr(CrO_4)_2$ structure [12], forming layers (a). Packing of the $NH_4Cr(CrO_4)_2$, forming a network with channels enclosing NH_4^+ ions (b).

108.1(5)–111.2(5)° in the structure of $NH_4Cr(CrO_4)_2$. Most apparent are the differences in the mutual orientation between the Cr(III) octahedra and the Cr(VI) tetrahedra perceived by the differences between the Cr^{III}–O–Cr^{VI} angles, shown in Table 4. Further, in the structure of $CsCr(CrO_4)_2$, Cr(III)O_6 and Cr(VI)O_4 units are corner-linked to form layers intercalated by the cesium ions (Fig. 4a), while the structure of $NH_4Cr(CrO_4)_2$ forms channels containing the ammonium ions, shown in Fig. 4b.

4. Conclusions

In summary, for the first time from water solution, we have synthesised a new mixed-valence chromium ternary oxide from CrO_3 at 53 °C and ambient atmospheric pressure. We believe the reduction of the Cr(VI) into Cr(III) is achieved by two one-equivalent reducing steps promoted by Ce(III) followed by a Ce(VI) catalysed disproportionation of a Cr(IV) species. The title compound constitutes a new structure type among the Cr(III)/Cr(VI) ternary oxides, the NH_4-type.

Table 4
Cr^{III}–O–Cr^{VI} bond angles

Atom labels	Angles (deg)
Within $CsCr(CrO_4)_2$ [12]	
Cr(1)–O(3)–Cr(2)	138.9
Cr(1)–O(4)–Cr(3)	126.9
Cr(1)–O(5)–Cr(2)	134.4
Cr(1)–O(6)–Cr(3)	165.6
Within $NH_4Cr(CrO_4)_2$ (this work)	
Cr(1)–O(12)–Cr(2)	134.4(5)
Cr(1)–O(13)–Cr(3)	161.4(7)
Cr(1)–O(21)–Cr(2)	147.6(4)
Cr(1)–O(31)–Cr(3)	144.3(4)

O(3), O(4), O(12) and O(13) are in special position 4*c* while O(5), O(6), O(21) and O(31) are in general position.

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