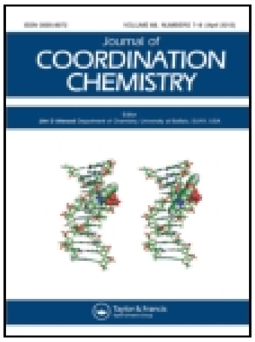

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Crystallographic new light on an old complex: $NaMg[Cr(oxalato)_3]\cdot 9H_2O$ and structure redetermination of the isomorphous aluminum(III) compound

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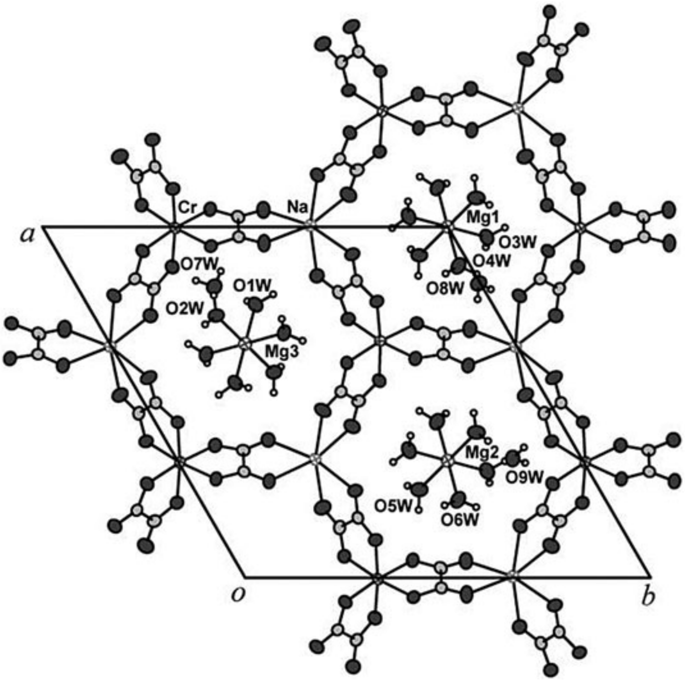

The crystal structure of sodium and magnesium *tris*(oxalato)chromato(III) nona hydrate, $NaMg[Cr(C_2O_4)_3]\cdot 9H_2O$, has been determined by X-ray diffraction methods. It crystallizes in the trigonal $P\bar{3}c1$ space group with (in the hexagonal setting) $a = b = 16.9635(4)$, $c = 12.5247(3)$ Å, and $Z = 6$

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molecules per unit cell. The Cr(III) and sodium ions are in octahedral environments coordinated to three oxalate molecules and arranged in a honeycomb-like layered structure perpendicular to the crystal *c*-axis. There are three different octahedral $[Mg(H_2O)_6]^{2+}$ hydrated ions that fill the honeycomb holes giving rise to electrically neutral $Na[Mg(H_2O)_6][Cr(oxalato)_3]$ crystal slabs. Neighboring slabs are bridged by the remaining three water molecules through H-bonds and therefore the whole crystal can be more properly described as $Na[Mg(H_2O)_6][Cr(oxalato)_3]\cdot 3H_2O$. Also, the structure of isomorphous $NaMg[Al(C_2O_4)_3]\cdot 9H_2O$ compound has been re-examined and compared with the chromium(III) complex. Infrared and Raman spectra of both complexes were also recorded and briefly discussed.

Keywords: *Tris*(oxalato)chromato(III); *Tris*(oxalato)aluminato(III); Na/Mg salts; Crystal structures; Vibrational spectra

1. Introduction

Fascinated in part by their beautiful colors, transition metal complexes attracted the scientist's attention since the late eighteenth century. Their (by then) enigmatic bond structure and physical and chemical properties were initially explained within the framework of the classic coordination theory developed since 1893 by Alfred Werner (1866–1919) [1–3]. With cobalt, chromium complexes were intensively studied because of its ability to bind a great variety of ligands. Among these complexes, the $[Cr^{III}(C_2O_4)_3]^{3-}$ ion has been the subject of continuous studies, in part due to the use of sodium *tris*(oxalato)chromate(III) as an industrial dye [4].

The corresponding potassium salt was also known from the beginnings of the nineteenth century [4] and its chemical structure was definitively established when Alfred Werner succeeded in isolating their optical isomers and proposed a bonding structure for the $[Cr(C_2O_4)_3]^{3-}$ complex that turned out to be essentially correct [5].

The first complete structural determination of $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$ by X-ray diffraction methods was reported by van Niekerk and Schoening [6]. This work revealed the molecular architecture and dimensions of the *tris*(oxalato)chromate(III) anion, showing that the metal is in an octahedral environment coordinated to three $^{-}OOC–COO^{-}$ oxalate anions acting as bidentate ligands through their oxygens in a propeller-like conformation. Confirming Werner's results, the structural study also found that there are two possibilities, namely right- or left-handed ligand conformations.

The *tris*(oxalato)chromate(III) salts of alkaline metals and ammonia have been synthesized and extensively studied both chemically and by X-ray crystallography [7–10]. In general, this is not the case of the corresponding salts of alkaline-earth metals and after about 60 years of structural research, uncertainties still remain about their crystal structure, hydrates, and details on the important role of both coordinated and crystallization water molecules in the solid complexes. This is particularly the case of the double sodium and magnesium salt of *tris*(oxalato)chromate(III).

This compound was first obtained by Frossard [4] while attempting to synthesize the $Mg_3[Cr(C_2O_4)_3]_2$ salt, obtaining instead $NaMg[Cr(C_2O_4)_3]$. From chemical composition analysis, Frossard reports eight water molecules in the solid and therefore the minimal chemical formula $NaMg[Cr(C_2O_4)_3]\cdot 8H_2O$. Furthermore, using photographic X-ray diffraction data, he determined the crystal system as trigonal and from the observed extinction of reflections the space group to be either *P*-31*c* of *P*31*c* (differing only in the presence of an inversion center in the former group) with cell constants (in the hexagonal basis) $a = b = 9.78(4)$ Å, $c = 12.5(2)$ Å, $V = 1033(26)$ Å^3 and $Z = 2$ molecules per unit cell.

Frossard ruled out the non-center $P31c$ space group on the basis of the crystal pyroelectric behavior. Some years later, Mortensen [11] reported that the double salt is in fact a nona rather than an octa hydrate, namely $NaMg[Cr(C_2O_4)_3]\cdot 9H_2O$, and that it crystallizes in either the $P\text{-}3c1$ or $P3c1$ space group with $a = b = 16.90(7)$ Å, $c = 12.52(2)$ Å, $V = 3097(31)$ Å^3 and $Z = 6$. As for Frossard's work, no complete data-set of X-ray diffraction intensities was collected to unravel the detailed molecular structure of the salt.

Finally, Suh *et al.* [12] carried out a structural single crystal X-ray diffraction study (employing MoKα radiation) where they report yet another hydrate, $NaMg[Cr(C_2O_4)_3]\cdot 10H_2O$, the same centro-symmetric $P\text{-}3c1$ space group as above and cell constants $a = b = 16.969(3)$ Å and $c = 12.521(3)$ Å. The authors could not locate the water H-atoms in their electron density maps. In a more recent work by Riesen and Rae [13], where the crystal structure of the isomorphous $NaMg[Al(C_2O_4)_3]\cdot 9H_2O$ compound is reported, the authors confirm the non-center $P3c1$ space group and the nine water molecules, a conclusion that clearly extends to the chromium complex. Probably, because the authors employed in their X-ray experiments MoKα radiation that produces relatively small anomalous dispersion they could not determine the absolute crystal structure. They were also unable to locate experimentally the water hydrogens.

We remove here the remaining structural uncertainties on the $NaMg[Cr(C_2O_4)_3]\cdot 9H_2O$ solid by X-ray crystallography, confirming the non-center $P3c1$ space group, the nine water molecules, the site symmetry C_1 for the $[Cr(C_2O_4)_3]^{3-}$ complex, and uncovering the absolute structure of the salt and its rich H-bonding network as revealed by experimental electron density maps. Also, the structure of the isomorphous $NaMg[Al(C_2O_4)_3]\cdot 9H_2O$ compound has been re-examined and compared with that of the chromium(III) complex.

2. Experimental

2.1. *Materials and methods*

All reagents, of analytical grade, were purchased commercially and used without purification. Elemental analyses (C, H, and N) were performed on a Carlo Erba model EA 1108 elemental analyzer. The infrared spectra in the spectral range 4000 and 400 cm^{-1} were recorded as KBr pellets with a FTIR-Bruker-EQUINOX-55 spectrophotometer. Raman spectra were obtained with a Perkin Elmer FT-Raman RFs 110/s spectrometer, using the 1064 nm line of a solid state Nd:YAG laser for excitation.

2.2. *Synthesis of the complexes*

The investigated chromium complex, $NaMg[Cr(C_2O_4)_3]\cdot 9H_2O$, was obtained by the reaction of an aqueous solution of $Na_3[Cr(C_2O_4)_3]$ (prepared by reaction of CrO_3, $H_2C_2O_4$ and Na_2CO_3) with a great excess of $MgCl_2$, as described in detail by Frossard [4]. After a few days, well-formed rhombohedric violet crystals of the complex begin to deposit. Anal. Calcd for $C_6H_{18}CrMgNaO_{21}$: C, 13.70; H, 3.43. Found: C, 13.66; H, 3.45%.

The corresponding Al(III) complex, $NaMg[Al(C_2O_4)_3]\cdot 9H_2O$, was obtained from the reaction in water of stoichiometric amounts of $Al_2(SO_4)_3$, $Ba(OH)_2$, NaOH, MgO and $H_2C_2O_4\cdot 2H_2O$ [14, 15], according to $Al_2(SO_4)_3\cdot 18H_2O + 3Ba(OH)_2\cdot 8H_2O + 2NaOH + 2MgO + 6H_2C_2O_4\cdot 2H_2O \rightarrow 2NaMg[Al(C_2O_4)_3]\cdot 9H_2O + 3BaSO_4 + 35H_2O$ using the following procedure: in 50 mL of water, heated at 80 °C, 1 mmol of hydrated aluminum sulfate, 2 mmol of sodium hydroxide, 2 mmol of magnesium oxide and 6 mmol of oxalic acid dihydrate were dissolved under stirring. To this solution 3 mmol of hydrated barium hydroxide was slowly added, under continuous stirring, and then cooled to room temperature. After removal of the precipitated $BaSO_4$, the solution was concentrated to 25 mL by heating and then left to evaporate at room temperature. After a few days, well-formed colorless crystals of the complex were obtained. Anal. Calcd for $C_6H_{18}AlMgNaO_{21}$: C, 14.39; H, 3.60. Found: C, 14.30; H, 3.65%.

2.3. *X-ray crystallographic studies*

The measurements were performed on an Oxford Xcalibur, Eos, Gemini CCD diffractometer with graphite-monochromated MoKα (λ = 0.71073 Å) and CuKα (λ = 1.54184 Å) radiation. X-ray diffraction intensities were collected (ω scans with ϑ and κ-offsets), integrated and scaled with CrysAlisPro [16] suite of programs. The unit cell parameters were obtained by least-squares refinement (based on the angular settings for all collected reflections with intensities larger than seven times the standard deviation of measurement errors) using CrysAlisPro. Data were corrected empirically for absorption employing the multi-scan method implemented in CrysAlisPro.

Despite the presence of heavy atoms (Cr), it was more convenient to use CuKα radiation to enhance the atomic anomalous dispersion of the pseudo-centrosymmetric crystal thus improving the reliability of its absolute structure determination. On the other hand, the

Table 1. Crystallographic and structure refinement data for the isomorphous $NaMg[M(C_2O_4)_3]\cdot 9H_2O$ (M = Cr, Al) complexes.

	M = Cr	M = Al
Empirical formula	$C_6H_{18}CrMgNaO_{21}$	$C_6H_{18}AlMgNaO_{21}$
Formula weight	525.50	500.48
Temperature (K)	293(2)	293(2)
Wavelength (Å)	1.54184	1.54184
Crystal system	Trigonal	Trigonal
Space group	*P*3*c*1	*P*3*c*1
Unit cell dimensions		
$a = b$ (Å)	16.9635(4)	16.7567(2)
c (Å)	12.5247(3)	12.6466(2)
Volume (Å^3)	3121.3(1)	3075.26(8)
Z, density (calcd, mg m^{-3})	6, 1.677	6, 1.621
Absorption coefficient (mm^{-1})	5.956	2.323
F(000)	1614	1548
Crystal color	Violet	Colorless
Crystal size (mm^3)	0.237 × 0.164 × 0.033	0.305 × 0.259 × 0.239
θ-range for data collection (°)	5.21–71.99	6.10–72.44
Index range	−12, 20; −20, 20; −10, 15	−20, 20; −18, 20; −15, 14
Reflections collected	7629	12,046
Independent reflections	2703 [R(int) = 0.0266]	3350 [R(int) = 0.0303]
Obs. reflections [$I > 2\sigma(I)$]	2302	2905
Completeness (%)	99.5 (to θ = 71.99°)	99.8 (to θ = 72.44°)
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	2703/28/325	3350/28/325
Goodness-of-fit on F^2	1.074	1.069
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0379$, $wR2 = 0.1054$	$R1 = 0.0480$, $wR2 = 0.1351$
R indices (all data)	$R1 = 0.0456$, $wR2 = 0.1126$	$R1 = 0.0542$, $wR2 = 0.1450$
Absolute structure parameter	0.113(8)	0.17(9)
Largest diff. peak and hole (e Å^{-3})	0.221 and −0.772	0.611 and −0.419

intrinsically higher intensity of CuKα as compared with MoKα radiation from the employed standard X-ray tube sources afforded a clearer experimental determination of H-atom positions.

The structure of the chromium complex was solved in the *P*3*c*1 space group by direct methods with the SHELXS-97 program of the SHELX package [17] and the corresponding molecular models developed by alternated cycles of Fourier methods and full-matrix least-squares refinement with the program SHELXL-97 of the same package. The aluminum compound is isomorphous to the chromium complex. In fact, an initial molecular model assuming the same positions of non-H atoms as in the chromium-containing crystal with the identity of the transition metal changed to aluminum leads to smooth convergence of the structural parameters for this latter compound during the least-squares refinement against the corresponding X-ray data-set.

All water hydrogens in the chromium complex were located among the first 18 more intense peaks of a Fourier difference map phased on the heavier atoms. The hydrogens in the aluminum compound were less defined and all of them appeared at approximate locations among the first 27 peaks of the corresponding map. The hydrogens were refined at their found positions with OW–H and H···H distances restrained to target values of 0.86(1) and 1.36(1) Å and isotropic displacement parameters equal to 1.5 times the one of the corresponding water oxygen. Crystal data, data collection procedure, and refinement results for the isomorphous pair are summarized in table 1.

We further confirm the correctness of space group (*P*3*c*1) and structure determination by an independent procedure, implemented in the recently available SHELXT program (see [18] and references therein). The new development is a radical departure of standard structure determination procedures where normally the space group is determined first and the crystal structure afterward. Now, with the only prior knowledge (besides cell constants) of the Laue group and the atom species present in the solid:

(1) The X-ray diffraction data-set is expanded to the subgroup *P*1 of all space groups where the structure is solved from an initial trial constellation of peaks provided by Patterson superposition methods. This is followed by dual-space recycling to obtain optimal electron density and phases.
(2) The phases are then employed to determine both the correct space group and the translation necessary to refer the electron density to the proper unit cell origin.
(3) The phases are then averaged in every possible space group compatible with the known Laue group and used to calculate improved maps.
(4) The integrated electron density around the peaks of the maps is assigned to atomic species and thus the chemical formula is determined.

Table 2. Candidate space groups with the best figures of merit obtained with SHELXT [18] from the two centrosymmetric and five non-centrosymmetric trigonal space groups with the Laue group *P*-3*m*1 (D_{3d}) of isomorphous $NaMg[M(C_2O_4)_3]\cdot9H_2O$ (M = Cr, Al).

	$NaMg[Cr(C_2O_4)_3]\cdot9H_2O$				$NaMg[Al(C_2O_4)_3]\cdot9H_2O$			
S.G.	*R*1	*R*(weak)	*α*	Formula	*R*1	*R*(weak)	*α*	Formula
P-3*c*1	0.177	0.007	0.058	$C_{10}O_{18}CrNaMg$	0.187	0.002	0.054	$C_{30}O_{54}Al_4Na_3Mg_2$
*P*3*c*1	0.100	0.002	0.024	$C_6O_{21}CrNaMg$	0.117	0.001	0.012	$C_6O_{19}AlNa_3Mg$
*P*321	0.163	0.002	0.055	$C_9O_{19}CrNaMg$	0.170	0.001	0.059	$C_{27}O_{57}Al_4Na_3Mg_2$

Note: The table also includes the corresponding chemical formulas derived from the integrated electron density around the peaks of the maps.

(5) The correct space group and structure solution is selected among the trials on the basis of several figures of merit, including the standard agreement $R1$-factor, R_{weak} (average of calculated E^2_{calcd} for the 10% of unique reflections with the smallest observed normalized structure factors E_{obs}), and the phase error (α), all of which should be the smallest for the right choice.

The results of these procedures applied to X-ray diffraction data of the isomorphous $NaMg[M(C_2O_4)_3]\cdot 9H_2O$ (M = Cr, Al) crystals, assuming the Laue group $P\text{-}3m1$ (D_{3d}) and the presence in the solid of (Cr, Al), Mg, Na, O, and C atomic species is shown in table 2. From this table it can be appreciated that the procedure clearly selects the non-centrosymmetric space group $P3c1$ as having the best indicators. Interestingly, in the case of the chromium complex the program also determines for this group the correct (non-H) chemical formula. For the aluminum-containing complex, however, the program misassigned two oxygens as sodium, a minor problem that probably arises in part because of the closeness in the number of electrons for both elements.

3. Results and discussion

3.1. *Description of crystal structures*

Except otherwise stated, we shall refer in what follows to the better refined structure of the chromium-containing member of the isomorphous $NaMg[M(C_2O_4)_3]\cdot 9H_2O$ (M = Cr, Al)

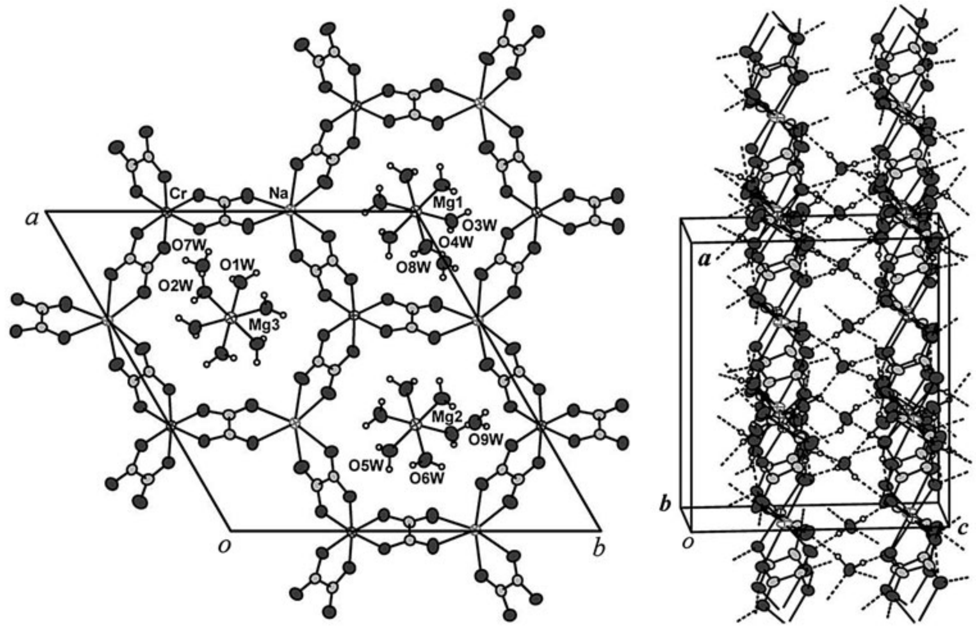

Figure 1. *Left*: view of $Na[Mg(H_2O)_6][Cr(oxalato)_3]\cdot 3H_2O$ down the crystal trigonal axis, showing the displacement ellipsoids at the 50% probability level. Oxygens and carbons are indicated by light and dark gray disks. *Right*: view perpendicular to the trigonal axis. The crystal layered arrangement is seen edge-on and H-bonding structure linking neighboring layers through bridging waters indicated by dashed lines.

Table 3. Bond lengths (Å) and angles (°) around the metals in $NaMg[Cr(C_2O_4)_3]\cdot 9H_2O$.

Cr–O(11)	1.975(4)	O(21)–Cr–O(31)	93.8(2)
Cr–O(12)	1.985(4)	O(12)–Cr–O(31)	92.8(2)
Cr–O(21)	1.978(4)		
Cr–O(22)	1.971(4)	O(14)#2–Na–O(33)	99.6(2)
Cr–O(31)	1.982(4)	O(14)#2–Na–O(34)	164.8(2)
Cr–O(32)	1.973(4)	O(33)–Na–O(34)	70.2(1)
		O(14)#2–Na–O(23)#3	99.9(2)
Na–O(33)	2.371(5)	O(33)–Na–O(23)#3	96.7(2)
Na–O(34)	2.392(5)	O(34)–Na–O(23)#3	92.5(2)
Na–O(14)#2	2.362(6)	O(14)#2–Na–O(24)#3	90.3(2)
Na–O(23)#3	2.390(6)	O(33)–Na–O(24)#3	165.5(2)
Na–O(24)#3	2.398(5)	O(34)–Na–O(24)#3	102.0(2)
Na–O(13)#2	2.396(6)	O(23)#3–Na–O(24)#3	70.9(1)
		O(14)#2–Na–O(13)#2	70.7(2)
Mg(1)–O(3W)	2.072(4)	O(33)–Na–O(13)#2	95.3(2)
Mg(1)–O(4W)	2.061(4)	O(34)–Na–O(13)#2	98.5(2)
		O(23)#3–Na–O(13)#2	165.9(1)
Mg(2)–O(5W)	2.086(5)	O(24)#3–Na–O(13)#2	98.1(2)
Mg(2)–O(6W)	2.049(4)		
		O(4W)–Mg(1)–O(3W)	89.5(2)
Mg(3)–O(1W)	2.069(4)	O(4W)–Mg(1)–O(4W)#5	91.0(2)
Mg(3)–O(2W)	2.065(4)	O(4W)–Mg(1)–O(3W)#5	89.7(2)
		O(4W)–Mg(1)–O(3W)#4	179.2(3)
O(22)–Cr–O(32)	93.2(2)	O(3W)–Mg(1)–O(3W)#4	89.8(2)
O(22)–Cr–O(11)	94.1(2)		
O(32)–Cr–O(11)	93.5(2)	O(6W)–Mg(2)–O(5W)	89.4(2)
O(22)–Cr–O(21)	81.9(1)	O(6W)–Mg(2)–O(6W)#7	91.0(2)
O(32)–Cr–O(21)	91.5(2)	O(6W)#6–Mg(2)–O(5W)	90.1(2)
O(11)–Cr–O(21)	173.8(1)	O(6W)–Mg(2)–O(5W)#6	178.9(3)
O(22)–Cr–O(12)	91.6(1)	O(5W)–Mg(2)–O(5W)#6	89.6(2)
O(32)–Cr–O(12)	173.6(1)		
O(11)–Cr–O(12)	81.9(2)	O(2W)–Mg(3)–O(2W)#3	90.4(2)
O(21)–Cr–O(12)	93.4(2)	O(2W)#1–Mg(3)–O(1W)	179.7(2)
O(22)–Cr–O(31)	174.1(2)	O(2W)–Mg(3)–O(1W)	89.8(2)
O(32)–Cr–O(31)	82.8(1)	O(2W)–Mg(3)–O(1W)#2	179.6(2)
O(11)–Cr–O(31)	90.5(1)	O(1W)–Mg(3)–O(1W)#2	90.4(2)

Symmetry transformations used to generate equivalent atoms: (#1) $-y+2, x-y, z$; (#2) $-x+y+1, -x+1, z$; (#3) $-x+y+2, -x+2, z$; (#4) $-y+1, x-y, z$; (#5) $-y+1, x-y-1, z$; (#6) $-x+y+2, -x+1, z$.

pair. Figure 1 shows ORTEP [19] drawings of the complex and corresponding bond distances and angles around the metals are presented in tables 3 (Cr) and 4 (Al). The chromium and sodium ions are at crystal general positions, in octahedral environments coordinated to three oxalate molecules acting as bidentate ligands through oxygens of their opposite carboxylic groups in a propeller-like conformation. Cr–O bond lengths are 1.970 (4) to 1.986(4) Å [corresponding Al–O distances are in the 1.893(3)–1.909(3) Å interval] and Na–O contact distances are 2.364(6)–2.396(5) Å [for the aluminum compound, Na–O distances are 2.375(4)–2.421(4) Å]. Because the crystal 3-fold axes, these metal ions are in a honeycomb-like layered arrangement conformed by alternated chromium and sodium ions linked through sharing oxalate ligands (see figure 1).

There are three different Mg(II) ions positioned at the three special lattice sites of C_3 symmetry in $P3c1$ space group (Wyckoft a, b and c sites) and they are at the honeycomb plane. These alkaline-earth metal ions are in an octahedral environment coordinated to water through their oxygen lone pairs. Mg–OW distances are 2.048(4) to 2.089(4) Å [in the aluminum compound, Mg–OW contacts are 2.040(4)–2.084(3) Å]. The three $Mg(H_2O)_6$

Table 4. Bond lengths (Å) and angles (°) around the metals in NaMg[Al(C_2O_4)$_3$]·9H_2O.

Al–O(11)	1.893(4)	O(21)–Al–O(31)	91.9(2)
Al–O(12)	1.895(3)	O(12)–Al–O(31)	91.0(2)
Al–O(21)	1.899(3)		
Al–O(22)	1.893(3)	O(14)#3–Na–O(33)	99.1(2)
Al–O(31)	1.909(3)	O(14)#3–Na–O(34)	164.2(1)
Al–O(32)	1.902(4)	O(33)–Na–O(34)	70.72(8)
		O(14)#3–Na–O(23)#4	98.9(2)
Na–O(33)	2.380(4)	O(33)–Na–O(23)#4	96.3(2)
Na–O(34)	2.401(4)	O(34)–Na–O(23)#4	94.3(2)
Na–O(14)#3	2.375(4)	O(14)#3Na–O(24)#4	91.7(1)
Na–O(23)#4	2.387(5)	O(33)–Na–O(24)#4	164.8(2)
Na–O(24)#4	2.421(4)	O(34)–Na–O(24)#4	100.9(2)
Na–O(13)#3	2.418(5)	O(23)#4–Na–O(24)#4	71.20(9)
		O(14)#3–Na–O(13)#3	70.7(1)
Mg(1)–O(3W)	2.057(3)	O(33)–Na–O(13)#3	96.1(1)
Mg(1)–O(4W)	2.083(3)	O(34)–Na–O(13)#3	97.8(2)
		O(23)#4–Na–O(13)#3	164.9(1)
Mg(2)–O(5W)	2.040(4)	O(24)#4–Na–O(13)#3	97.6(2)
Mg(2)–O(6W)	2.105(3)		
		O(4W)–Mg(1)–O(3W)	89.8(1)
Mg(3)–O(1W)	2.080(3)	O(4W)–Mg(1)–O(4W)#6	89.8(2)
Mg(3)–O(2W)	2.060(3)	O(4W)–Mg(1)–O(3W)#6	179.1(2)
		O(3W)#5–Mg(1)–O(3W)	91.0(2)
O(22)–Al–O(32)	91.0(2)	O(3W)#6–Mg(1)–O(4W)#5	89.1(2)
O(22)–Al–O(11)	91.3(2)		
O(32)–Al–O(11)	91.2(2)	O(5W)#1–Mg(2)–O(5W)	91.6(2)
O(22)–Al–O(21)	84.1(1)	O(5W)#3–Mg(2)–O(6W)#1	178.1(2)
O(32)–Al–O(21)	93.1(2)	O(5W)–Mg(2)–O(6W)#1	89.4(1)
O(11)–Al–O(21)	173.7(1)	O(5W)–Mg(2)–O(6W)	89.9(1)
O(22)–Al–O(12)	93.9(1)	O(6W)#1–Mg(2)–O(6W)	89.1(2)
O(32)–Al–O(12)	173.4(1)		
O(11)–Al–O(12)	84.3(2)	O(2W)–Mg(3)–O(2W)#2	90.3(2)
O(21)–Al–O(12)	91.8(2)	O(2W)#4–Mg(3)–O(1W)#2	179.8(2)
O(22)–Al–O(31)	173.8(2)	O(2W)–Mg(3)–O(1W)#2	89.9(2)
O(32)–Al–O(31)	84.45(9)	O(2W)#2–Mg(3)–O(1W)#2	89.7(1)
O(11)–Al–O(31)	93.0(1)	O(1W)#2–Mg(3)–O(1W)	90.1(2)

Symmetry transformations used to generate equivalent atoms: (#1) $-y + 2, x - y, z$; (#2) $-x + y + 1, -x + 1, z$; (#3) $-x + y + 2, -x + 2, z$; (#4) $-y + 1, x - y, z$; (#5) $-y + 1, x - y - 1, z$; (#6) $-x + y + 2, -x + 1, z$.

hydrated ions fill the honeycomb holes hence giving an electrically neutral layered structure of about 2.4 Å in thickness (measured between surface non-H atoms) or about 5.5 Å considering van der Waals layer contours. These layers can be conveniently described as Na[Mg(H_2O)$_6$][Cr(oxalate)$_3$] and the whole crystal as Na[Mg(H_2O)$_6$][Cr(oxalate)$_3$]·3H_2O. Neighboring layers are $c/2 = 6.26$ Å apart and weakly bonded to each other mainly through H-bonding bridges involving the remaining three water molecules (see below). This explains the easy-cleavage plane parallel to (0 0 1) observed in NaMg[Cr(C_2O_4)$_3$]·9H_2O single crystals (see figure 1).

The nine water molecules per chemical formula can be nicely split into two sets. One of them contains six coordinated-to-magnesium water molecules (O1W–O6W in figure 1) which in turn can be arranged into three subsets with two molecules each: (O1W, O2W), (O3W, O4W), and (O5W, O6W) respectively coordinated to the three independent Mg(II) ions at the three C_3 lattice sites giving rise to the above mentioned Mg(H_2O)$_6$ hydrated ions. The other set contains the remaining three molecules which act as crystallization waters (O7W to O9W), sandwiched between neighboring Na[Mg(H_2O)$_6$][Cr(oxalate)$_3$]

Table 5. Hydrogen bonds in $NaMg[Cr(C_2O_4)_3]\cdot 9H_2O$.

D–H	d(D–H)	d(H···A)	<(D–H···A)	d(D···A)	A	Symm. operat.
O1W–H1A	0.860	1.936	153.53	2.733	O7W	
O1W–H1B	0.859	1.988	173.17	2.843	O23	$[-y+1, x-y, z]$
O2W–H2A	0.856	2.093	162.34	2.921	O32	
O2W–H2B	0.856	1.883	177.04	2.738	O7W	$[-y+1, -x+1, z-1/2]$
O3W–H3A	0.855	1.930	156.63	2.736	O8W	
O3W–H3B	0.858	2.005	172.92	2.858	O12	$[x, y+1, z]$
O4W–H4A	0.858	2.022	160.58	2.845	O24	$[x, y+1, z]$
O4W–H4B	0.858	1.891	169.86	2.740	O8W	$[x, x-y+1, z-1/2]$
O5W–H5A	0.855	1.948	153.73	2.742	O9W	$[x, x-y+1, z+1/2]$
O5W–H5B	0.859	2.122	174.09	2.978	O31	$[x-1, y, z]$
O6W–H6A	0.856	2.013	156.77	2.820	O13	$[-x+y+1, -x+2, z]$
O6W–H6B	0.853	1.894	176.21	2.746	O9W	$[-y+1, x-y+1, z]$
O7W–H7A	0.858	2.064	143.17	2.798	O21	
O7W–H7B	0.857	1.912	161.44	2.738	O34	$[x, x-y, z+1/2]$
O8W–H8A	0.855	1.901	177.97	2.756	O22	$[-y+1, -x+2, z+1/2]$
O8W–H8B	0.855	1.894	168.13	2.736	O14	$[-y+1, x-y, z]$
O9W–H9A	0.857	1.890	168.95	2.736	O33	$[-y+1, -x+2, z - 1/2]$
O9W–H9B	0.858	1.941	165.64	2.780	O11	$[-x+y+1, -x+2, z]$

crystal slabs bridging through relatively strong H-bonds. In fact, all three water molecules act as H-donors in O(ox)···H–OW–H···O(ox) bridges with oxalate oxygens [OW···O(ox) distances in the 2.736–2.798 Å range] and also as H-acceptors in OW–H···OW···H–OW bridges with coordinated-to-magnesium water molecules [OW···OW lengths from 2.736 to 2.744 Å]. The H-bonding structure is detailed in table 5.

3.2. *Vibrational spectra*

As the vibrational spectra of these two complexes have so far not been investigated, we have recorded their infrared and Raman spectra in order to extend our knowledge of their general physicochemical properties. This information seems particularly interesting in the case of the $NaMg[Al(C_2O_4)_3]\cdot 9H_2O$ complex, as this compound has often been used as a host material for different spectroscopic studies [11, 14, 15, 20–22].

The spectra of both complexes are rather similar in general structure, band patterns and intensity distribution, although those of the Al(III) complex appear better defined, probably as a consequence of the colorless crystals.

The obtained spectra have been analyzed on the basis of the classic papers of Fujita *et al.* on $K_2[M^{II}(C_2O_4)_2]\cdot nH_2O$ and $K_3[M^{III}(C_2O_4)_3]\cdot 3H_2O$ [23, 24] (cf also [25]) and also using information derived from our numerous previous studies on metallic oxalato complexes [15].

As the $[M(C_2O_4)_3]^{3-}$ skeleton of these complexes posses approximately D_3-symmetry, its 51 internal vibrational modes are distributed as follows:

$$\Gamma_{\text{vib}} = 8A_1 + 9A_2 + 17E$$

where the A_1 species are Raman active, the A_2 species infrared active and the E species are active in both the Raman and the infrared [26]. Therefore, in the experimental spectra one should see vibrations which present similar energies in both spectra and others which can be found in only one of the spectra.

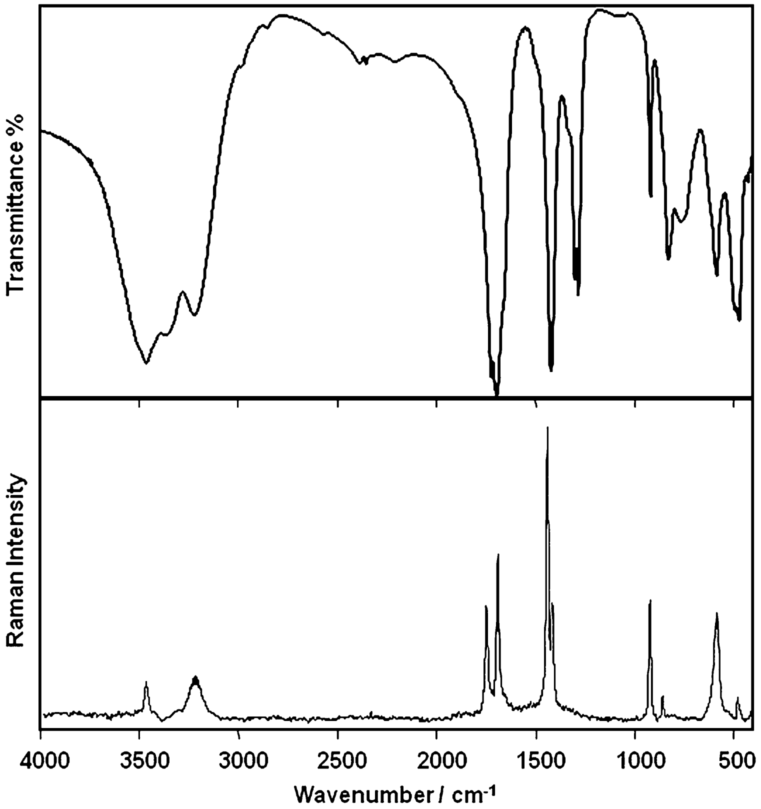

Figure 2. FTIR (above) and FT-Raman spectra (below) of $Na[Mg(H_2O)_6]$ $[Al(oxalato)_3]\cdot 3H_2O$ in the spectral range between 4000 and 400 cm^{-1}.

The FTIR and FT-Raman spectra of the $NaMg[Al(C_2O_4)_3]\cdot 9H_2O$ complex are shown in figure 2 and the assignments proposed for this and the isomorphous Cr(III) complex are presented in table 6 and briefly discussed as follows:

- The characteristic O–H stretching vibrations of the water molecules are seen as a strong band multiplet in the IR spectra and, as usual, only in the form of some weak signals in the respective Raman spectra. The band broadening and the appearance of different well-defined peaks are surely related to the presence of the different kinds of water molecules in the structures, as discussed above. The measured wavenumbers for these vibrations clearly satisfy known correlations between OH-stretching frequencies and hydrogen bond distances (cf for example [27]) and from the spectroscopic point of view these hydrogen bridges classify as mean strength bridges [28]. The deformational mode of the H_2O molecules are surely overlapped by the strong IR bands located above 1600 cm^{-1}, whereas bands related to $\rho(H_2O)$ modes could also not be identified.
- The antisymmetric C=O stretches generate three spectral bands, one in the form of a well-defined doublet in the Raman spectra and other two in the IR spectra. One of these bands shows an additional weak splitting in the case of the Cr(III) complex (the 1681/1666 cm^{-1} pair).

Table 6. Assignment of the vibrational spectra of the two investigated isomorphous complexes (band positions in cm^{-1}).

$NaMg[Cr(C_2O_4)_3]\cdot 9H_2O$		$NaMg[Al(C_2O_4)_3]\cdot 9H_2O$		
Infrared	Raman	Infrared	Raman	Assignment
3502 sh		3510 sh		
3451 vs	3480 m	3462 vs	3470 m	ν(OH) water
3350 sh		3356 m		
3222 m		3217 m	3211 m	
	1745 s,1677 m		1746 s, 1692 vs	ν_{as}(C=O)
1707 s		1720 vs		ν_{as}(C=O)
1681/1666 vs		1692 vs		ν_{as}(C=O)
1403 vs	1470 vs	1416 vs	1441 vs, 1417 s	ν_s(CO) + ν(CC)
1268 s		1299/1281 s		ν_s(CO) + δ(OC=O)
907 m	923 m	916 s	924 s	ν_s(CO) + δ(OC=O)
820 m, 770 sh	851 m/816 w	827/763 s	859 w	δ(O–C=O)
629 w,546 m	564 s	581 s	587 s	ν(MO) + ν(CC)
476 w	480 w	477 sh/469 s	480 w	δ_{ring} + δ(O–C=O)
415 m	414 w	424 w	422 sh, 390 w	ν(MO) + δ(O–C=O)

Note: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

- As shown by theoretical studies [23, 24], and as a consequence of the low symmetry of the chelate ring and the fact that the force constants for the ν(C–O), ν(C–C) and ν(M–O) vibrations are of similar magnitude, bands related to the symmetric C–O stretches are strongly coupled with some other vibrations.
- Although partially coupled with other motions, bands assigned to the ν(MO) stretches lie somewhat higher in the case of the Al(III) complex, in agreement with shorter Al–O than Cr–O bonds (cf again tables 3 and 4). This relative reinforcement of the Al–O bonds has an additional spectral impact on the oxalate vibrations. As can be seen from table 6, ν(C=O) vibrations are always at higher energies in the case of the Al(III) complex. Essentially one may expect that a reinforcement of the M–O bond causes a slight decrease in the strength of the C–O bonds and a concomitant reinforcement of the uncoordinated C=O bonds [15, 23]. The decrease in energy of the C–O bonds is not clearly visible in the present case, surely due to the strong coupled nature of this vibration.
- Interestingly, one of the characteristic ν(Cr–O) bands, found at 415 cm^{-1} in the IR spectrum, was found at this same energy in the case of $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$ [24].

4. Conclusion

The determination of the crystal structure of $NaMg[Cr(C_2O_4)_3]\cdot 9H_2O$ by X-ray diffraction methods allowed the definitive knowledge of the structural characteristics and peculiarities of this Cr(III) complex, which may be better described as $Na[Mg(H_2O)_6][Cr(oxalato)_3]\cdot 3H_2O$. The chromium and sodium ions are at crystal general positions, in octahedral environments coordinated to three oxalate anions acting as bidentate ligands through oxygens of their opposite carboxylic groups in a propeller-like conformation. The structure of the isomorphous $NaMg[Al(C_2O_4)_3]\cdot 9H_2O$ compound has also been re-examined and compared with that of the Cr(III) complex. Infrared and Raman spectra of both complexes were recorded and briefly discussed on the basis of the structural results.

Supplementary material

CCDC Nos. 1057600 and 1057601 contain the supplementary crystallographic data for the Cr(III) and Al(III) complex, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Disclosure statement

No potential conflict of interest was reported by the authors.

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