

# [Cr<sub>3</sub>O(CH<sub>3</sub>COO)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]NO<sub>3</sub>·HNO<sub>3</sub>·H<sub>2</sub>O, TRIAQUA-HEXAKIS(μ-ACETATO)-μ<sub>3</sub>-OXO-TRICHRONIUM(III) NITRATE NITRIC ACID SOLVATE MONOHYDRATE

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**Abstract:** Reaction in methanol solution of the trinuclear ‘basic’ chromium(III) acetate with Pr(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and further extraction by chloroform-acetone mixture led to the formation of novel unusual [Cr<sub>3</sub>O(CH<sub>3</sub>COO)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]NO<sub>3</sub>·HNO<sub>3</sub>·H<sub>2</sub>O (**1**) cluster with one “free” molecule of nitric acid. Complex **1** crystallizes in the monoclinic space group *P*2<sub>1</sub>/*c* with, at room temperature, *a* = 13.624(2), *b* = 15.032(2), *c* = 15.180(2) Å, β = 112.98(3)°, *Z* = 4, and *V* = 2862.09 Å<sup>3</sup>. The obtained crystalline compound has been synthesized and characterized by IR and UV/Vis methods.

**Keywords:** Chromium carboxylate, Polynuclear complex, UV-Vis

## 1. Introduction

Oxo-centered triangular complexes of the general type [M<sub>3</sub>O(OOCR)<sub>6</sub>L<sub>3</sub>]<sup>n+</sup> are particularly valuable as frameworks for a systematic study of metal-metal interactions in clusters. They have been characterized for a wide variety of first-row and heavier transition metals, with mixed-metal combinations and with mixed-valence combinations [1]. ‘Basic’ chromium carboxylates is a general name for a family of chromium(III) complexes in which only RCOO<sup>-</sup> and oxo/hydroxo/aquo ligands are present. For many years, the only representative of this group was the classical oxo-centered trinuclear complex [Cr<sub>3</sub>O(CH<sub>3</sub>COO)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]<sup>+</sup>, whose structure was reported almost four decades ago by Figgis and Robertson [2].

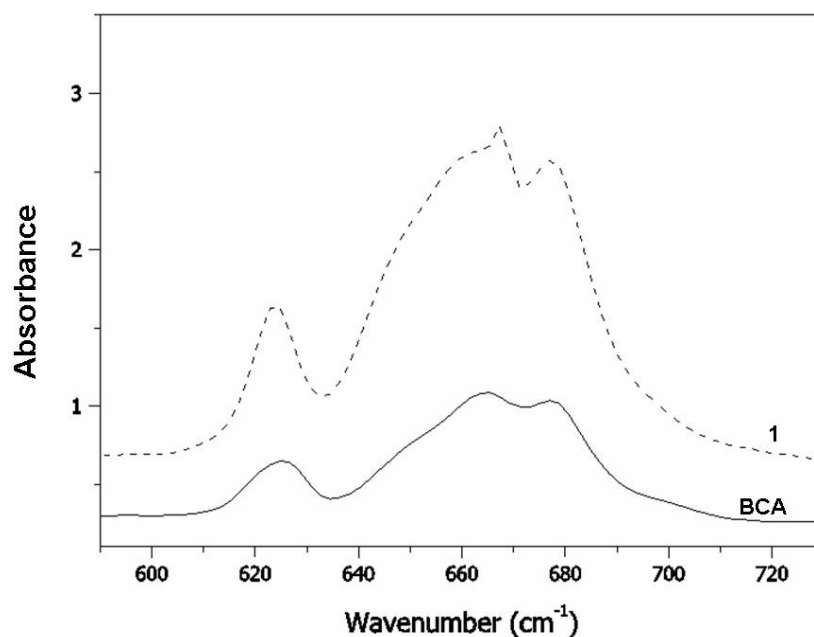
Chromium(III) carboxylates have been used extensively for various applications as polymerization and oxidation catalysts [3], suitable building block of zeotype polyoxometalate-macrocations for shape-selective adsorption of water [4], materials in processing of fir bark extract for air fresheners [5], possible DNA-cleaving agents and nutritional supplements [6] and for many other uses [7-10]. Ever since the discovery of chromium as an essential human nutrient, Cr(III) acetates containing [Cr<sub>3</sub>O(CH<sub>3</sub>COO)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]<sup>+</sup> cation have been administered to animals in biological intake experiments [11], to produce DNA strand breaks in peripheral lymphocytes [12] and in phosphate ester cleavage reactions [13].

Here, we report the crystal structural determination of a new cationic trinuclear Cr(III) complex, which represents a new type of ‘basic’ chromium carboxylate.

## 2. Results and discussion

It needs to be mentioned that this synthetic route for the title compound can be realized only in the presence of Pr(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O. Using other lanthanide nitrates (Ln = La, Eu) clusters with other structures have been obtained. The reasons for this behavior and the nature of these different products are being investigated.

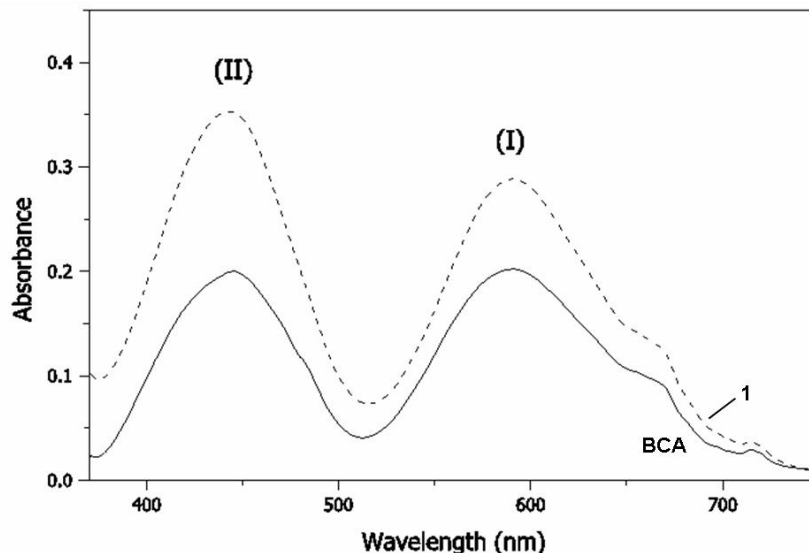
On the basis of the results of elemental analysis, in the first step of our research it has been assumed that the obtained product is a new ‘Cr(III,III,IV)-acetate’ cluster. But the absence of splitted components A<sub>1</sub> and B<sub>2</sub> of E' [1] in the region 700-500 cm<sup>-1</sup> of IR spectrum (Fig.1) and typical profile of the electronic absorption spectra (Fig.2) for such trichromium(III) complexes [1] confirm that a member of the investigated class of substances of symmetrical complexes with “Cr<sup>III</sup><sub>3</sub>O”-core has been obtained. Other IR bands are definitely assigned to vibrations of CH<sub>3</sub>COO<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and H<sub>2</sub>O groups, but do not represent essential interest for the discussion in the present communication.



**Figure 1.** The  $\nu_{as}(\text{Cr}_3\text{O})$  band of complexes  $[\text{Cr}_3\text{O}(\text{Ac})_6(\text{H}_2\text{O})_3]\text{NO}_3 \cdot \text{HNO}_3 \cdot \text{H}_2\text{O}$  (1) and  $[\text{Cr}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3] \cdot \text{CH}_3\text{COO}$  (BCA)

The electronic spectrum of **1** in acetone solution shows the familiar two peaks in the visible (Fig.2, bands I and II), corresponding to the  ${}^4A_{2g} \rightarrow {}^4T_{2g}$  and  ${}^4A_{2g} \rightarrow {}^4T_{1g}$  transitions of Cr(III) in octahedral symmetry.

No spectral features relative to other oxidation states of chromium are present in the UV-Vis-NIR absorption spectra.



**Figure 2.** Electronic spectra of  $[\text{Cr}_3\text{O}(\text{Ac})_6(\text{H}_2\text{O})_3]\text{NO}_3 \cdot \text{HNO}_3 \cdot \text{H}_2\text{O}$  (1) and  $[\text{Cr}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3] \cdot \text{CH}_3\text{COO}$  (BCA), in acetone solution.

X-ray study of **1** showed that the structure consists of three chromium atoms connected together by an oxygen atom. In addition two acetate groups connect the three chromium atoms to each other. So every chromium atom adopts a tetrahedral conformation with four atoms of four different acetate groups as base and the common oxygen and a water molecule in apex positions (Fig.3). Bond distances and angles do not deviate significantly from the normal range. The atomic coordinates of the heavy atoms are in Table 2 and their anisotropic thermal parameters are in Table 4. Table 3 reports the coordinates of H atoms with isotropic thermal parameters. The geometrical parameters are in Table 5. A projection of the complex with the labeling scheme is in Fig. 3.

**Table 2. Atomic fractional coordinates ( $\times 10^4$ ) and  $U_{eq}$  ( $\times 10^4 \text{ \AA}^2$ )**

	x/a		y/b		z/c		U <sub>eq</sub>	
CR1	8440	(1)	914	(1)	7170	(1)	314	(2)
CR2	6347	(1)	1475	(1)	7614	(1)	306	(2)
CR3	8661	(1)	2401	(1)	8825	(1)	305	(2)
O1W	9099	(3)	202	(2)	6412	(2)	511	(13)
O2W	4776	(2)	1360	(2)	7367	(3)	483	(12)
O3W	9515	(3)	3299	(2)	9866	(2)	484	(13)
O1	7817	(2)	1597	(1)	7869	(2)	299	(8)
C1A	5610	(5)	1155	(5)	4624	(3)	708	(23)
C2A	6305	(3)	1220	(3)	5670	(2)	394	(14)
O3A	7269	(2)	1096	(2)	5916	(2)	488	(11)
O4A	5847	(2)	1392	(2)	6221	(2)	508	(10)
C1B	6208	(4)	4334	(3)	7510	(4)	529	(20)
C2B	6679	(3)	3427	(2)	7792	(3)	363	(14)
O3B	6084	(2)	2770	(2)	7477	(2)	471	(11)
O4B	7641	(2)	3388	(2)	8336	(2)	475	(11)
C1C	6802	(5)	-1346	(3)	7642	(5)	572	(22)
C2C	7017	(3)	-386	(2)	7558	(2)	371	(13)
O3C	7778	(2)	-202	(2)	7340	(2)	486	(12)
O4C	6414	(2)	167	(2)	7709	(2)	524	(12)
C1D	10205	(4)	3229	(4)	6982	(4)	558	(19)
C2D	9568	(3)	2634	(2)	7342	(3)	362	(13)
O3D	9407	(2)	2896	(2)	8065	(2)	456	(11)
O4D	9224	(2)	1919	(2)	6910	(2)	429	(10)
C1E	11108	(5)	419	(5)	9825	(5)	643	(21)
C2E	10149	(3)	895	(3)	9133	(3)	379	(13)
O3E	9725	(2)	591	(2)	8310	(2)	460	(11)
O4E	9841	(2)	1561	(2)	9445	(2)	473	(10)
C1F	7110	(5)	1508	(4)	10634	(4)	531	(19)
C2F	7256	(3)	1695	(2)	9725	(2)	364	(15)
O3F	8112	(2)	2040	(2)	9790	(2)	478	(11)
O4F	6516	(2)	1491	(2)	8958	(2)	536	(11)
N1G	2252	(3)	1273	(3)	5554	(3)	693	(19)
O1G	3120	(4)	1094	(4)	5549	(4)	1362	(27)
O2G	1455	(3)	1141	(4)	4918	(4)	1483	(29)
O3G	2220	(5)	1516	(5)	6284	(4)	1682	(36)
N1H	3592	(6)	1562	(5)	9199	(5)	1263	(38)
O1H	3885	(7)	1524	(10)	10241	(6)	3135	(91)
O2H	4182	(6)	1507	(7)	8841	(5)	2292	(56)
O3H	2419	(8)	1762	(9)	8569	(8)	2838	(76)
O4W	11146	(5)	-5	(4)	6885	(7)	1076	(35)

**Table 3 . Atomic fractional coordinates ( $\times 10^4$ ) and Uiso ( $\times 10^4 \text{ \AA}^2$ ).**

	x/a		y/b		z/c		Uiso	
H1A	568	(6)	63	(5)	425	(6)	1341	(289)
H2A	491	(7)	113	(5)	444	(5)	1209	(262)
H3A	568	(5)	170	(4)	437	(4)	899	(209)
H1B	560	(6)	437	(4)	735	(5)	1018	(229)
H2B	654	(6)	466	(5)	802	(6)	1345	(288)
H3B	635	(5)	455	(5)	711	(5)	1051	(245)
H1C	615	(5)	-147	(3)	762	(3)	663	(143)
H2C	729	(4)	-163	(3)	801	(3)	586	(149)
H3C	676	(6)	-160	(5)	712	(5)	1257	(274)
H1D	999	(7)	350	(6)	646	(6)	1415	(300)
H2D	1058	(6)	345	(5)	739	(5)	1118	(276)
H3D	1047	(6)	295	(6)	656	(6)	1247	(271)
H1E	1158	(5)	58	(5)	984	(5)	888	(269)
H2E	1119	(6)	43	(5)	1050	(6)	1289	(264)
H3E	1105	(5)	-14	(5)	969	(4)	1085	(241)
H1F	761	(6)	120	(4)	1104	(5)	960	(210)
H2F	709	(5)	202	(5)	1095	(5)	951	(217)
H3F	663	(6)	135	(5)	1051	(5)	1007	(286)
H1W1	886	(4)	-10	(3)	605	(4)	558	(164)
H2W1	982	(5)	9	(4)	663	(4)	778	(172)
H1W2	439	(5)	121	(5)	693	(5)	1021	(249)
H2W2	455	(4)	145	(3)	780	(4)	693	(162)
H1W3	934	(4)	341	(4)	1030	(4)	715	(178)
H2W3	1011	(5)	333	(4)	994	(4)	690	(180)
H1W4	1111	(8)	-37	(7)	636	(7)	1638	(360)
H2W4	1133	(4)	-21	(4)	704	(4)	164	(130)
H1NH	4491	(5)	802	(4)	9221	(4)	1386	(133)

**Table 4. Anisotropic thermal parameters ( $\times 10^4 \text{ \AA}^2$ ).**

	$U_{11}$		$U_{22}$		$U_{33}$		$U_{23}$		$U_{13}$		$U_{12}$	
CR1	294	(3)	314	(3)	353	(3)	-33	(2)	149	(2)	-21	(2)
CR2	251	(3)	337	(3)	326	(3)	-34	(2)	108	(2)	-25	(2)
CR3	271	(3)	315	(3)	316	(3)	-36	(2)	100	(2)	-35	(2)
O1W	448	(17)	553	(19)	583	(18)	-225	(16)	256	(15)	-37	(15)
O2W	298	(14)	658	(20)	479	(17)	-80	(15)	137	(14)	-56	(13)
O3W	395	(16)	562	(19)	488	(17)	-168	(13)	163	(14)	-120	(14)
O1	271	(11)	292	(12)	327	(11)	-37	(9)	110	(9)	-36	(9)
C1A	562	(31)	1127	(52)	337	(22)	-23	(27)	70	(21)	23	(32)
C2A	398	(20)	415	(21)	334	(18)	-17	(15)	104	(16)	-37	(16)
O3A	384	(15)	720	(19)	345	(13)	-85	(12)	126	(11)	-11	(13)
O4A	313	(13)	850	(22)	322	(13)	-96	(13)	79	(11)	1	(13)
C1B	479	(26)	402	(25)	721	(33)	63	(23)	252	(26)	107	(20)
C2B	398	(19)	342	(19)	415	(19)	1	(15)	229	(17)	21	(15)
O3B	306	(13)	368	(15)	687	(17)	-29	(13)	136	(12)	14	(11)
O4B	382	(14)	316	(14)	613	(16)	-84	(12)	69	(13)	19	(11)
C1C	499	(28)	351	(24)	860	(37)	47	(25)	259	(27)	-40	(21)
C2C	353	(18)	331	(19)	393	(18)	24	(15)	107	(15)	-16	(15)
O3C	547	(16)	312	(14)	740	(18)	-71	(12)	405	(15)	-43	(12)
O4C	425	(15)	352	(14)	874	(21)	-15	(14)	338	(15)	-55	(12)
C1D	578	(28)	627	(31)	514	(27)	-32	(24)	263	(25)	-240	(24)

C2D	277	(16)	384	(20)	389	(18)	69	(16)	92	(15)	-18	(14)
O3D	503	(16)	468	(16)	446	(14)	-78	(12)	237	(12)	-183	(12)
O4D	443	(14)	411	(16)	490	(14)	-28	(12)	243	(12)	-87	(12)
C1E	394	(26)	654	(37)	720	(36)	157	(28)	42	(24)	75	(25)
C2E	273	(16)	415	(21)	426	(20)	60	(16)	109	(15)	-1	(15)
O3E	399	(14)	502	(16)	449	(14)	-6	(12)	134	(12)	136	(12)
O4E	391	(14)	492	(16)	410	(14)	-28	(12)	21	(12)	64	(12)
C1F	485	(28)	726	(37)	444	(25)	25	(23)	248	(23)	-72	(26)
C2F	403	(20)	365	(19)	362	(18)	-9	(14)	189	(16)	24	(15)
O3F	453	(15)	650	(18)	369	(13)	-123	(12)	201	(12)	-198	(14)
O4F	354	(14)	912	(23)	359	(14)	-35	(14)	158	(12)	-137	(14)
N1G	422	(22)	895	(32)	639	(25)	-205	(22)	74	(20)	13	(21)
O1G	589	(27)	2204	(65)	1182	(38)	-188	(39)	225	(25)	200	(33)
O2G	523	(24)	1932	(54)	1467	(43)	-1080	(41)	-184	(26)	313	(29)
O3G	1198	(46)	2471	(82)	1271	(46)	-947	(49)	367	(37)	-59	(46)
N1H	1254	(55)	1720	(66)	1077	(46)	-325	(43)	738	(45)	-512	(47)
O1H	1759	(82)	6318	(239)	1226	(59)	-561	(89)	471	(55)	-1211	(108)
O2H	1294	(52)	4826	(154)	1151	(44)	-642	(63)	905	(42)	-176	(67)
O3H	1668	(85)	3735	(148)	2688	(111)	1487	(103)	391	(76)	-254	(90)
O4W	673	(32)	644	(35)	1995	(69)	-137	(36)	611	(37)	142	(24)

**Table 5. Bond distances (Å) and angles (°).**

CR1 - O1W	2.021	(4)	C1B - C2B	1.496	(6)
CR1 - O1	1.898	(3)	C2B - O3B	1.249	(4)
CR1 - O3A	1.968	(2)	C2B - O4B	1.248	(4)
CR1 - O3C	1.969	(3)	C1C - C2C	1.487	(6)
CR1 - O4D	1.977	(3)	C2C - O3C	1.237	(5)
CR1 - O3E	1.982	(2)	C2C - O4C	1.252	(5)
CR2 - O2W	2.030	(3)	C1D - C2D	1.490	(8)
CR2 - O1	1.894	(2)	C2D - O3D	1.262	(5)
CR2 - O4A	1.956	(3)	C2D - O4D	1.251	(4)
CR2 - O3B	1.975	(3)	C1E - C2E	1.500	(7)
CR2 - O4C	1.970	(3)	C2E - O3E	1.242	(4)
CR2 - O4F	1.960	(3)	C2E - O4E	1.247	(5)
CR3 - O3W	2.058	(3)	C1F - C2F	1.496	(8)
CR3 - O1	1.894	(2)	C2F - O3F	1.244	(5)
CR3 - O4B	1.968	(3)	C2F - O4F	1.245	(4)
CR3 - O3D	1.958	(3)	N1G - O1G	1.216	(7)
CR3 - O4E	1.971	(3)	N1G - O2G	1.155	(6)
CR3 - O3F	1.963	(3)	N1G - O3G	1.183	(9)
C1A - C2A	1.502	(5)	N1H - O1H	1.474	(11)
C2A - O3A	1.231	(5)	N1H - O2H	1.135	(13)
C2A - O4A	1.250	(5)	N1H - O3H	1.538	(12)

O4D - CR1 - O3E	90.0	(1)	O3W - CR3 - O3D	86.3	(1)
O3C - CR1 - O3E	88.3	(1)	O3W - CR3 - O4B	84.3	(1)
O3C - CR1 - O4D	171.2	(1)	O3W - CR3 - O1	177.4	(1)
O3A - CR1 - O3E	169.9	(1)	CR2 - O1 - CR3	119.7	(1)
O3A - CR1 - O4D	89.8	(1)	CR1 - O1 - CR3	120.2	(1)
O3A - CR1 - O3C	90.3	(1)	CR1 - O1 - CR2	120.1	(1)
O1 - CR1 - O3E	94.6	(1)	C1A - C2A - O4A	116.6	(3)
O1 - CR1 - O4D	95.3	(1)	C1A - C2A - O3A	117.9	(3)
O1 - CR1 - O3C	93.5	(1)	O3A - C2A - O4A	125.5	(3)

O1 - CR1 - O3A	95.4	(1)	CR1 - O3A - C2A	132.9	(2)
O1W - CR1 - O3E	86.0	(1)	CR2 - O4A - C2A	133.0	(2)
O1W - CR1 - O4D	84.0	(1)	C1B - C2B - O4B	117.0	(3)
O1W - CR1 - O3C	87.2	(1)	C1B - C2B - O3B	118.0	(3)
O1W - CR1 - O3A	84.0	(1)	O3B - C2B - O4B	125.0	(3)
O1W - CR1 - O1	179.1	(1)	CR2 - O3B - C2B	132.4	(2)
O4C - CR2 - O4F	87.3	(1)	CR3 - O4B - C2B	133.6	(2)
O3B - CR2 - O4F	92.3	(1)	C1C - C2C - O4C	117.7	(4)
O3B - CR2 - O4C	172.8	(1)	C1C - C2C - O3C	117.0	(3)
O4A - CR2 - O4F	167.1	(1)	O3C - C2C - O4C	125.3	(3)
O4A - CR2 - O4C	90.1	(1)	CR1 - O3C - C2C	134.4	(2)
O4A - CR2 - O3B	88.7	(1)	CR2 - O4C - C2C	131.7	(2)
O1 - CR2 - O4F	95.8	(1)	C1D - C2D - O4D	118.4	(3)
O1 - CR2 - O4C	93.8	(1)	C1D - C2D - O3D	117.1	(3)
O1 - CR2 - O3B	93.4	(1)	O3D - C2D - O4D	124.5	(3)
O1 - CR2 - O4A	96.9	(1)	CR3 - O3D - C2D	134.4	(2)
O2W - CR2 - O4F	83.2	(1)	CR1 - O4D - C2D	132.3	(2)
O2W - CR2 - O4C	86.8	(1)	C1E - C2E - O4E	116.5	(3)
O2W - CR2 - O3B	86.0	(1)	C1E - C2E - O3E	117.7	(4)
O2W - CR2 - O4A	84.1	(1)	O3E - C2E - O4E	125.8	(3)
O2W - CR2 - O1	178.8	(1)	CR1 - O3E - C2E	133.9	(2)
O4E - CR3 - O3F	86.8	(1)	CR3 - O4E - C2E	131.7	(2)
O3D - CR3 - O3F	168.9	(1)	C1F - C2F - O4F	117.8	(4)
O3D - CR3 - O4E	90.6	(1)	C1F - C2F - O3F	117.6	(3)
O4B - CR3 - O3F	94.1	(1)	O3F - C2F - O4F	124.7	(3)
O4B - CR3 - O4E	170.7	(1)	CR3 - O3F - C2F	132.4	(2)
O4B - CR3 - O3D	86.8	(1)	CR2 - O4F - C2F	134.3	(2)
O1 - CR3 - O3F	95.8	(1)	O2G - N1G - O3G	117.9	(6)
O1 - CR3 - O4E	95.4	(1)	O1G - N1G - O3G	117.8	(5)
O1 - CR3 - O3D	95.2	(1)	O1G - N1G - O2G	123.8	(5)
O1 - CR3 - O4B	93.7	(1)	O2H - N1H - O3H	118.3	(7)
O3W - CR3 - O3F	82.8	(1)	O1H - N1H - O3H	117.1	(7)
O3W - CR3 - O4E	86.7	(1)	O1H - N1H - O2H	124.4	(7)

**Table 6. Possible H bonds and contacts <2.5 (D= donor, A = acceptor)**

D-H (Å)	D...A (Å)	H...A (Å)	D-H...A (°)	
O1W-H2W1	0.91(7)	O1W...O4W 2.612(8)	H2W1...O4W 1.71(7)	O1W-H2W1...O4W 171(5)
O2W-H1W2	0.70(6)	O2W...O1G 2.828(5)	H1W2...O1G 2.14(6)	O2W-H1W2...O1G 167(7)
O2W-H2W2	0.83(7)	O2W...O2H 2.670(9)	H2W2...O2H 1.85(7)	O2W-H2W2...O2H 171(5)
O1W-H1W1	0.69(5)	O1W...O2Gi 2.745(7)	H1W1...O2Gi 2.07(5)	O1W-H1W1...O2Gi 164(6)
O3W-H2W3	0.76(7)	O3W...O2Gii 2.746(6)	H2W3...O2Gii 2.02(7)	O3W-H2W3...O2Gii 158(11)

Equivalent positions: i = -x+1,-y,-z+1; ii = x+1,-y+1/2,z+1/2

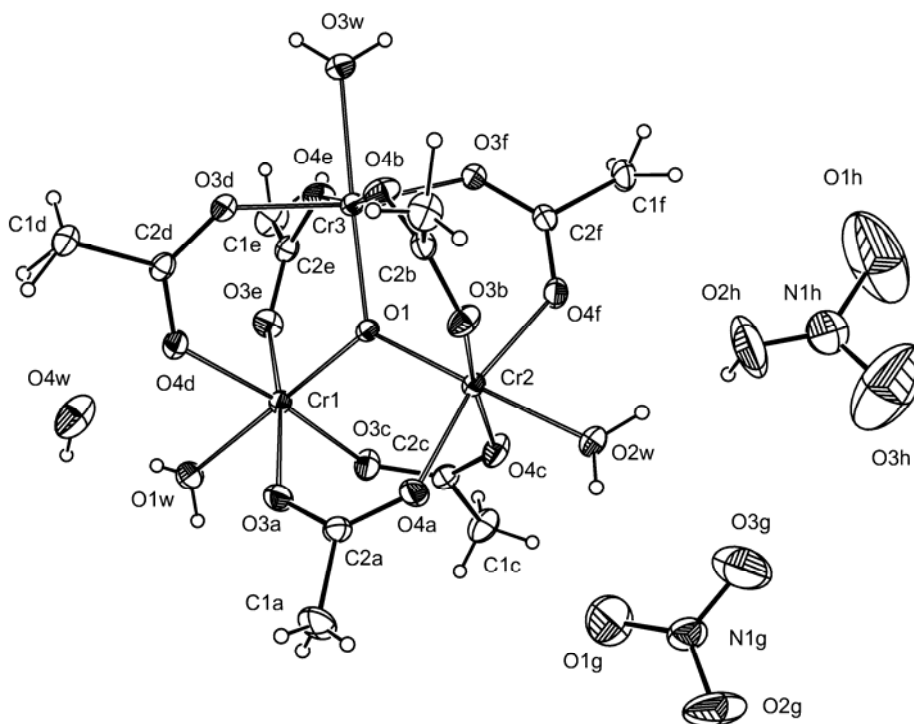


Figure 3. Projection of the complex with arbitrary numbering. The ellipsoids are at 20% probability level.

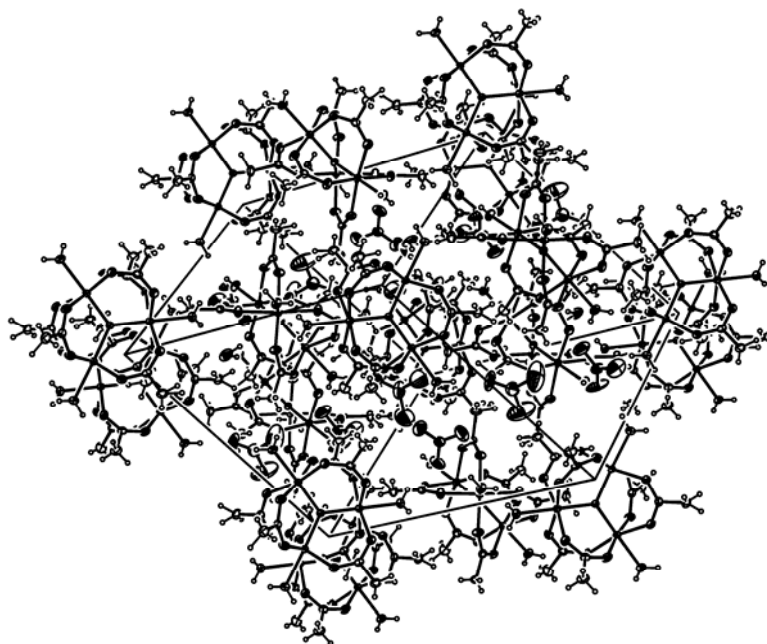


Fig. 4. Packing of the complex 1.

The single acetate groups are planar and the dihedral angles formed by the couples which connect Cr1 with Cr2, Cr1 with Cr3 and Cr2 with Cr3 are 88.1(3), 93.5(2) and 103.8(2)°, respectively.

In the solid state the molecules are connected by intermolecular and intramolecular H-bonds (Fig.4).

### 3. Conclusion

In summary, new basic chromium acetate has been isolated and characterised by spectroscopic techniques. This novel compound contains the well-known  $[\text{Cr}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]^+$  triangular cation, but is characterised by the unusual presence of a "free"  $\text{HNO}_3$  molecule. This could give rise to differences in the interaction of this compound with biological molecules, with respect to other basic chromium carboxylates.

*Supporting information available:* IR data, listing crystallographic parameters in CIF format, atomic coordinates, bond distances and angles, thermal parameters and hydrogen atom positions for the title complex. This material is available free of charge from the authors.

#### 4. Experimental

*General:* All chemicals and solvents were used as received. All preparations and manipulations were performed under aerobic conditions.  $[\text{Cr}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\cdot\text{CH}_3\text{COO}$  was prepared as previously described [14].

The *UV-Visible absorption spectra* were measured with a conventional double beam UVIKON 941 plus spectrophotometer using a resolution of 1 nm. The solvent (acetone) was used as a reference.

The *diffuse reflectance spectra* in the medium infrared region ( $4000\text{--}400\text{ cm}^{-1}$ ) were measured using a Nicolet Magna 740 FTIR spectrometer. The powders of the samples under investigation were dispersed in KBr in a 1:100 mass ratio and the spectra were measured using KBr as a reference. All the spectroscopic measurements were performed at room temperature.

*Synthesis* of  $[\text{Cr}_3\text{O}(\text{Ac})_6(\text{H}_2\text{O})_3]\text{NO}_3\cdot\text{HNO}_3\cdot\text{H}_2\text{O}$  (**1**). Solutions of  $[\text{Cr}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\cdot\text{CH}_3\text{COO}$  ('basic' chromium acetate, 0.8176 g, 1.279 mmol) and  $\text{Pr}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$  (1.6001 g, 3.836 mmol) in methanol (ca. 10 mL) were added with continuous stirring (30–45 min.) to 40 mL of acetonitrile – toluene (1 : 3). After 4–5 days the obtained dark green viscous mass was dissolved in part in a chloroform-acetone mixture (2:1, ca. 25 mL) and filtered off. During the first 3 days the transparent solution of dark green color was separated constantly until the first crystals have appeared. A microcrystalline product was obtained, which was recrystallized from a mixture of acetone and toluene (4:1, ca. 15 mL). After 1 week the resultant dark green crystals were collected by filtration, washed with toluene, and dried in vacuum. Yield: ~30% (270 mg) Calc. for  $\text{C}_{12}\text{H}_{27}\text{N}_2\text{Cr}_3\text{O}_{23}$ : C, 19.93; H, 3.76; N, 3.87%. Found: C, 19.99; H, 3.42; N, 3.78%.

*Crystallographic data:* The structure was solved by direct methods with SIR97 [15]. The refinement was carried out with SHELX97 [16]. After some full-matrix anisotropic cycles all H atoms were found in a  $\Delta F$  map and all refined isotropically. The ORTEP drawings were performed with ORTEP-3 program [17]. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. CCDC reference number 612714. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk]. The crystal data and pertinent details of the experimental conditions are summarized in Table 1.

**Table 1. Experimental and crystallographic information for 1.**

Formula	$(\text{CH}_3\text{COO})_6\cdot\text{O}\cdot\text{NO}_3\cdot\text{HNO}_3\cdot(\text{H}_2\text{O})_3\cdot\text{Cr}_3\cdot(\text{H}_2\text{O})$
Formula weight	723.36
Crystal: color	dark green
shape	prismatic
dimensions (mm)	0.19x0.23x0.34
Crystal system	Monoclinic
Space Group	P21/c
Cell Constants: a (Å)	13.624(2)
b (Å)	15.032(2)
c (Å)	15.180(2)
$\beta$ (°)	112.98(3)
Cell volume (Å <sup>3</sup> )	2862.09
Formula units	4
Temperature	room
Diffractometer	Bruker AXS
Radiation, wavelength (Å)	MoK $\alpha$ , 0.71069
Reflections measured	27926
Unique reflections, $R_{\text{int}}$	6461, 0.055
Reflections. observed [ $I > 2\sigma(I)$ ]	4547
$2\theta$ max (°)	56.7
Indices range: h, k, l	-18/17, -19/19, -19/19
No. of refined parameters	465
R	0.048
$R_w$	0.14
Weights	$w=1/[(\sigma^2 F_o+0.099P^2+0.22P)]$
GOF	0.84
$\Delta\rho_{\text{min/max}}(e/\text{Å}^3)$	-0.57/0.50

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(<http://www.edu.md/?lng=ro&MenuItem=5&SubMenu0=2>). V. Mereacre thanks also the AvH foundation. The authors gratefully thank Erica Viviani (Univ. Verona) for expert technical assistance.

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