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LETTER

Crystal structure of a μ_3-oxo-hexakis-(μ_2-carboxylatopyridine-*O*,*O*)-triaquatrichromium(III) perchlorate, $\{[Cr_3O(i\text{-}C_6H_5O_2N)_6(H_2O)_3](ClO_4)_7 \cdot 3NaClO_4 \cdot 3H_2O\}$

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Initial studies of oxygen trinuclear metal complex ions of the formula $[M_3O(RCO_2)_6(L)_3]^{n+}$ have been presented elsewhere [1, 2]. Our research has dealt with a study of oxo-centered trinuclear chromium(III) complexes with nicotinic acid and its structural isomers, picolinic acid and isonicotinic acid. The latter was used in the preparation of the perchlorate salt of 4-carboxylatopyridine, the title compound. Since chromium(III) has been classified as an essential element of the glucose tolerance factor (GTF) which is a dietary agent needed to sustain normal glucose levels in the human body, it is apparent that trinuclear chromium(III) complexes would be of interest [3]. Applied and basic research investigations dealing with synthesis and structural characterization of oxo-centered trinuclear chromium(III) complexes are needed in order to test chromium-GTF activity. For this reason, the crystal and molecular structure of the title trinuclear isonicotinic acid–Cr(III) complex was determined.

Experimental

Clear green irregular shaped crystals of $\{[Cr_3O(i\text{-}C_6H_5O_2N)_6(H_2O)_3](ClO_4)_7 \cdot 3NaClO_4 \cdot 3H_2O\}$ (**I**) which crystallizes in the hexagonal space group *P*6$_3$/*m* (No. 176, C^2_{6h}) were synthesized by Bradshaw [1]. The experimental density was determined pycnometrically by flotation in a mixture of bromoform and 1-hexene, 1.66(5) Mg m^{-3} (calc. 1.665 Mg m^{-3}). UV–Vis and IR spectral data of **I** have been published elsewhere [2]. The uniaxial classification for the system was confirmed by a conoscopic examination, which was performed by crystal rotation between two crossed polarizers on a Zeiss Photomicroscope II. A Debye-Scherrer cylindrical camera (114.6 mm, 298 K) using V-filtered Cr K$\bar{\alpha}$ radiation ($\lambda = 2.29100$ Å), was employed to obtain refined powder lattice constants [3], $a = 13.838(3)$ and $c = 25.038(8)$ Å (see Table 1).

An optically pure single crystal of the trinuclear chromium(III) complex of 4-carboxylatopyridine-(isonicotinato) was mounted on an Enraf-Nonius CAD4-F autodiffractometer (Mo K$\bar{\alpha}$, 0.71073 Å; $T = 292$ K), which is equipped with a dense graphite monochromator (take-off angle of 5.8°). A SEARCH routine [4] was used to obtain the θ values for 25 well-centered reflections. These reflections were used in the program INDEX [4] in order to acquire a working orientation matrix. Final lattice dimensions were obtained at high θ angles (>20°, see Table 1). Measured intensities were collected over the range of $3.0 < 2\theta < 50.0°$ utilizing the ω–2θ scan method at a variable scan speed of 0.38–3.35° min^{-1} in ω. The ω scan range was $1.25° + 0.35 \tan\theta$. Reflections having less than 75 counts above background during the prescan (3.35° min^{-1}) were considered unobserved. No significant variations were observed in the intensities of the two monitored check reflections (every 2 h of exposure time: $\bar{1}\,0\,\bar{5}$, $2\,6\,5$, dev. <1.0%). Thus, the reliability of the electronic hardware and crystal stability were verified. Of the 2842 collected reflections (h: 0→14, k: 0→14, l: 0→29),

TABLE 1. Experimental and statistical summaries

	Powder	Single crystal
Formula	$C_{36}H_{42}O_{59}N_6Cl_{10}Na_3Cr_3$	
Space group	*P*6$_3$/*m* (No. 176, C^2_{6h})	
Radiation	Cr K$\bar{\alpha}$	Mo K$\bar{\alpha}$
λ_{mean} (Å)	2.29100	0.71073
a (Å)	13.838(3)	13.840(4)
c (Å)	25.038(8)	25.037(7)
V (Å^3)	4152.2	4153.2
D_m (Mg m^{-3})	1.66(5)	1.66(5)
D_x (Mg m^{-3})	1.665	1.668
M_r		2082.2
Z		2
$F(000)$ (e$^-$)		2094
Crystal size (mm)		0.28×0.35×0.12
μ (Mo K$\bar{\alpha}$)(mm^{-1})		0.823
$\Delta\theta$ (°)		1.5–25.0
$\Delta\omega$ (°) (ω–2θ scan)		$1.25 + 0.35 \tan\theta$
R_{int}		0.068
R		0.079
R_w		0.079
Unique reflections		1517
No. variables		204
Shift/error		0.050

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2503 were independent. After averaging the data ($R_{\mathrm{int}} = 0.068$), 1517 fitted $F_i > 6.0\sigma(F_i)$. The standard deviations of the averaged data were determined as $\sigma(F_i) = \Sigma[1.02(F_i)]/N$, where N is the number of redundant measurements and $\sigma(F_i)$ is the standard deviation for each individual measurement. Lorentz and polarization effects were corrected, but since the absorption coefficient was extremely small (0.823 mm^{-1}), an absorption correction was ignored. Careful examination of the resultant data revealed the reflection condition $00l$ where $l = 2n$. Therefore, the possible space groups were $P6_3$, $P6_3/m$ and $P6_322$. However, the $6/mmm$ Laue group was quickly eliminated due to $hk0 \neq kh0$. Further examination using an N(Z) analysis (cumulative probability distribution test) provided evidence of a centrosymmetric symmetry [5], concluding $P6_3/m$ as the assigned space group. Crystal data experimental conditions and statistical data are presented in Table 1.

The structure was solved by direct methods using Siemens SHELXTL-PC-1989 [6] and electron density calculations. The skeletal surroundings of Cr_3O(i-nicotinic acid)$_6(H_2O)_3{}^{7+}$ were initially found, and successive Fourier mapping located the remaining non-hydrogen atoms, which were refined anisotropically by the full-matrix least-squares method. The quantity minimized in the refinement was $\Sigma w \Delta F^2$ where $\Delta F = \| F_o | - | F_c \|$. The idealized hydrogen atoms were constrained (0.96 Å) to ride on their connected carbon and nitrogen atoms with isotropic temperature factors fixed arbitrarily at $U_{\mathrm{iso}} = 0.08$ Å^2. There was no indication in the final difference Fourier map as to the location which would have yielded the orientation of the hydrogen atoms associated with the water molecules. Therefore, these hydrogen atoms are missing from our model. There were 204 parameters refined ($R = 0.079$; $R_w = 0.079$), which constituted a data to parameter ratio of 7.7:1. Residual electron density of 0.86 e$^-$ Å^{-3} was found in the vicinity of the chromium atom; elsewhere the Δ-Fourier map was virtually featureless displaying a random fluctuating background in the range of −0.28 to 0.32 e$^-$ Å^{-3}. Atomic scattering factors and anomalous-dispersion correction terms were taken from the usual source [7].

TABLE 2. Fractional atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) with e.s.d.s in parentheses

Atom	x	y	z	U_{eq}
Cr	2210(2)	7079(2)	2500	32(1)
O(1)	3333	6667	2500	34(4)
O(2)	1007(9)	7529(9)	2500	54(5)
O(3)	1316(5)	6045(6)	1936(3)	42(3)
O(4)	2915(6)	8203(6)	1942(3)	44(3)
C(1)	4075(7)	9431(8)	1268(4)	40(4)
C(2)	3145(8)	9376(10)	1027(4)	57(5)
C(3)	3314(9)	10043(10)	585(4)	70(6)
N	4362(8)	10755(9)	435(4)	68(5)
C(4)	5261(9)	10817(10)	663(4)	73(6)
C(5)	5147(8)	10119(9)	1084(4)	58(5)
C(6)	3893(9)	8712(8)	1756(4)	39(4)
Cl(1)	6667	3333	5425(2)	50(2)
O(11)	7233(9)	2783(9)	5226(4)	90(5)
O(12)	6667	3333	5984(6)	79(5)
Na(1)	0000	0000	5000	88(9)
Na(2)	0000	0000	6975(13)	296(16)
Cl(2)	2245(4)	2098(4)	4186(2)	93(2)
O(21)	1477(10)	992(5)	4312(7)	196(7)
O(22)	3326(6)	2269(12)	4258(6)	175(7)
O(23)	2089(13)	2312(14)	3655(2)	219(8)
O(24)	2079(13)	2831(10)	4522(4)	188(8)
Cl(3)	6667	3333	3422(6)	223(6)
O(31)[a]	5661(27)	2465(42)	3226(7)	332(10)
O(32)[b]	6667	3333	3982(7)	264(4)
O(33)[c]	7267(32)	2812(33)	3606(7)	269(9)
O(34)[d]	6667	3333	2861(7)	283(17)
O(1W)	3956(38)	4951(41)	7500	161(9)
O(2W)	4075(35)	3007(39)	2500	168(9)
H(1)[e]	4476	11261	147	80
H(2)[e]	2406	8887	1160	80
H(3)[e]	2693	9989	389	80
H(4)[e]	5993	11343	534	80
H(5)[e]	5780	10116	1240	80

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor. [a]O(31) refined to 0.46(1) occupancy. [b]O(32) refined to 0.42(1) occupancy. [c]O(33) refined to 0.45(1) occupancy. [d]O(34) refined to 0.46(1) occupancy. [e]Hydrogen atoms not refined.

Results and discussion

The composition of the bulk sample used for elemental analyses differs in minor respects from that of the single crystal used in X-ray structure determination. However, the differences reside in the type and amounts of adducts trapped in the channels formed by packing of the complex ions in the crystalline lattice. The best fit to the elemental analyses for C, H, N (done commercially, Guelph Analytical Laboratories), Cr and isonicotinic acid is $[Cr_3O(i\text{-}C_6H_5O_2N)_6(H_2O)_3](ClO_4)_7 \cdot 4NaClO_4 \cdot 0.5(i\text{-}C_6H_5O_2N) \cdot 4H_2O$, $M_r = 2284.4$. The average percentage compositions and the attendant average deviations for duplicate analyses are: Found: C, 20.93±0.02; H, 1.98±0.08; N, 3.93±0.03; Cr, 6.61±0.06. Calc.: C, 20.50; H, 2.05; N, 3.99; Cr, 6.83%. $[C_6H_5O_2N]/[Cr]$: found 2.18±0.05; calc. 2.17. By contrast, the single crystal analysis indicates the absence of the $0.5(i\text{-}C_6H_5O_2N)$ and three rather than four molecules each of sodium perchlorate and water. The high degree of adduct trapping in the bulk material versus that in the single crystal specimen is not unexpected due to the slower rate of crystal growth for the latter.

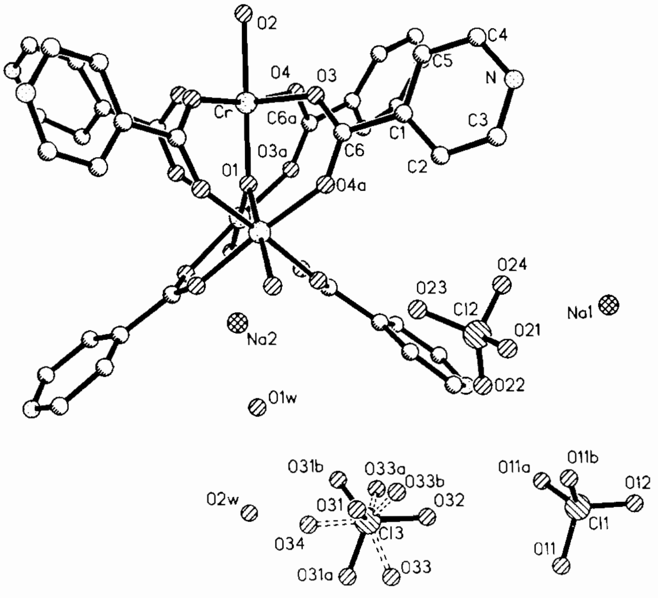

Fig. 1. Computer generated drawing of the title compound showing the atom-labeling scheme with H atoms omitted for clarity.

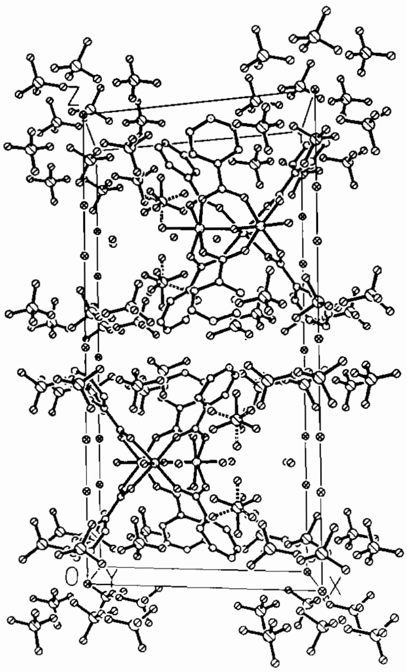

Fig. 2. A detailed packing plot of **I** showing the contents of the unit cell with only H atoms omitted.

TABLE 3. Relevant bond lengths (Å) and angles (°) with e.s.d.s in parentheses

Cr–O(1)	1.903(3)	Cl(1)–O(11)	1.428(14)
Cr–O(2)	2.046(15)	Cl(1)–O(12)	1.399(16)
Cr–O(3)	1.948(7)	Cl(2)–O(21)	1.394(8)
Cr–O(4)	1.950(7)	Cl(2)–O(22)	1.404(11)
O(3)–C(6a)	1.259(16)	Cl(2)–O(23)	1.402(10)
O(4)–C(6b)	1.260(13)	Cl(2)–O(24)	1.422(17)
C(1)–C(6)	1.515(15)	Cl(3)–O(31)	1.396(32)
C(1)–C(2)	1.388(16)	Cl(3)–O(32)	1.402(23)
C(2)–C(3)	1.383(17)	Cl(3)–O(33)	1.421(52)
C(3)–N	1.336(13)	Cl(3)–O(34)	1.406(23)
N–C(4)	1.331(18)	C–H(2–5)	0.960
C(4)–C(5)	1.383(18)	N–H(1)	0.960
C(5)–C(1)	1.380(12)		
O(1)–Cr–O(2)	179.7(3)	C(2)–C(1)–C(5)	122.5(10)
O(1)–Cr–O(3)	95.4(3)	C(1)–C(2)–C(3)	118.0(9)
O(1)–Cr–O(4)	94.6(3)	C(2)–C(3)–N	118.4(12)
O(2)–Cr–O(3)	84.8(4)	C(3)–N–C(4)	124.1(11)
O(2)–Cr–O(4)	85.2(4)	N–C(4)–C(5)	120.3(9)
O(3)–Cr–O(4)	87.0(3)	C(4)–C(5)–C(1)	116.4(11)
O(3)–Cr–O(3a)	92.9(4)	O(1)–C(6)–C(4)	116.4(11)
O(4)–Cr–O(4a)	91.5(4)	C(1)–C(6)–O(3a)	117.0(9)
Cr–O(1)–Cr	120.0(1)	O(4)–C(6)–O(3a)	126.5(10)
Cr–O(3)–C(6a)	131.5(8)	O–Cl(1)–O (av.)	109.5(10)
Cr–O(4)–C(6)	132.8(9)	O–Cl(2)–O (av.)	109.5(8)
C(6)–C(1)–C(2)	118.0(8)	O–Cl(3)–O (av.)	109.5(6)
C(6)–C(1)–C(5)	119.5(10)	O–Cl(3′)[a]–O (av.)	109.5(12)

[a] Cl(3′) is the inversion disordered form of the Cl(3) perchlorate.

The fractional atomic coordinates and equivalent isotropic displacement coefficients (U_{eq}) with e.s.d.s. are listed in Table 2. Figure 1 presents the atom-labelling scheme and Fig. 2 is a packing diagram of the contents of the unit cell with an extended artistical effect which yields a more meaningful arrangement; SHELXTL-PC (TELP and PACK) [6]. Selective bond length and angles are given in Table 3. All bond lengths and angles are internally consistent and agree quite well with corresponding values found in similar trinuclear chromium(III) complexes [2, 8].

The three chromium(III) ions are bonded trigonally to the central oxygen atom, O(1), which is evidenced by the Cr–O(1)–Cr bond angles of 120.0(1)°. The Cr_3O unit is planar and the mean Cr–O bond distance is in accord with other experimental values found in the Cambridge Structure Database [9] and BIDICS [10]. Further, when considering the summation of the involved radii of Cr(III) and oxygen ions found in the work of Shannon [11], i.e. 1.965 Å, the mean experimental value of 1.962 Å is in excellent agreement. Each Cr atom is octahedrally coordinated to oxygen atoms, O(1) through O(4). The bond angles are slightly distorted ranging from 84.8 to 95.4°, see Table 3. The displacement of the Cr atoms toward the central oxygen atom, O(1), requires the inner angle to be greater than 90°. The interatomic bond distances and angles of the pyridine ring system are within expected values (mean C–C of 1.384 Å, mean N–C of 1.334 Å, and mean angles of 120.0°). The perchlorate anions are angularly distorted, however, the mean O–Cl–O angle in each anion is 109.5°. All Cl–O bond values (range, 1.394 to 1.428 Å) are in accord with published perchlorate bond lengths [9] (mean Cl–O, 1.407 Å). The $Cl(3)O_4^-$ group is disordered by an inversion, see Figs. 1 and 2.

Other oxo-centered, trinuclear complexes which have been prepared are in the process of being structurally investigated by X-ray diffractometry.

Supplementary material

Additional material comprising all bond distances and angles, thermal parameters, and structure factor amplitudes are available from author D.F.M. on request.

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