

Preparations and Characterizations of μ_3 -Oxo-hexakis(μ_2 -carboxylatopyridine-*O,O*)-triaquatrichromium(III) Perchlorates

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Abstract

The preparations of 2- and 4-carboxylatopyridine (HPyCO₂) complexes of the type [Cr₃O(HPyCO₂)₆(H₂O)₃](ClO₄)₇·XNaClO₄·YHPyCO₂·ZH₂O are reported. A single-crystal X-ray structural characterization of the 2-HPyCO₂ species (*X* = 1, *Y* = 0, *Z* = 6) is described. [Cr₃O(C₆H₅NO₂)₆(H₂O)₃](ClO₄)₇·NaClO₄·6H₂O, *M* = 1885.35, *P*6₃/*m*, *a* = 13.978(1), *c* = 24.506(3) Å, *V* = 4146.3(11) Å³, *Z* = 2, *D* = 1.510 g/cm³, λ (Mo Kα) = 0.71073 Å, *F*(000) = 1902, *T* = 298 K, final *R* = 0.034 for 1024 reflections with *I* > 2σ(*I*). The complex lies on a $\bar{6}$ symmetry operator. The three O_h chromium atoms share a common vertex O(3) at 1.918(2) Å; two picolinic acid zwitterions bridge each pair of Cr(III) ions through the carboxylate oxygen atoms, Cr–O_{br} = 1.961(7) Å; and terminal water molecules round out the O_h geometry, Cr–O_t = 2.058(10) Å. Vis–UV–IR absorption spectra for the 2-, 3-, and 4-HPyCO₂ complexes are reported. These data are discussed in terms of the corresponding properties of ‘basic chromic acetate’ and related species.

Introduction

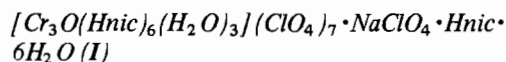
As a matter of historical interest, oxo-centered, trinuclear complex ions of the type Cr_{*n*}Fe_{3–*n*}-(RCO₂)₆(L)₃]^{*n+*} (*n* = 3) were first reported in 1908 and (*n* = 0, 1, 2) in 1909 by Weinland *et al.* [1, 2]. Subsequently, a variety of their physical properties were studied, beginning with their magnetic properties [3]; vibrational [4], luminescence [5], Vis–UV [3i, 4d, 5, 6a] and CD [7] spectral studies followed, as did heat capacity measurements [3f, 8]. However, it was not until 1965 that two independent X-ray crystal structures [9] were finally reported. Additional crystal structures have since been published [3h, 4d, 6b, 10]. Since the publication of reviews by Catterick and Thornton [11] and by

Müller *et al.* [12], a resurgence of interest in the chemistry of oxo-centered trinuclear metal complexes has occurred, especially for chromium(III) and iron(III). Pragmatic interest in these complexes continues for purposes of modeling the ferritin core [6h, 10a, 13], testing Cr-glucose tolerance factor activity [10d] and catalyzing epoxidation reactions [14]. Basic research interests continue, too. First, mixed oxidation state complexes [3e,i, 8b, 10e,h] afford possibilities for investigating cooperative redox and magnetic phenomena. Second, Mössbauer studies [3d, e; 10h] can add further characterization of the iron containing species. and third, a modern theory [15] now addresses such complexes.

Following reports on the preparations and X-ray crystal structures of the iron(III)–amino acid and the chromium(III)–nicotinic acid species [10a–d] and noting the similarities between the chemistries of chromium(III) and iron(III) so elegantly exploited by Raymond [16], we set out to complete the preparations and characterizations of the series of carboxylatopyridine analogs and to extend these syntheses to amino acids. Herein, we report the preparations of the perchlorate salts of the 2- and 4-carboxylatopyridine complexes, the X-ray crystal structure of the former (picolinic acid) species, and the V–UV and infrared spectral properties of the entire series.

Experimental

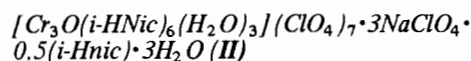
Materials



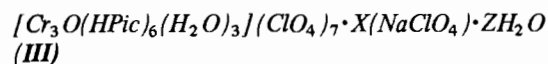
The synthesis and recrystallization of I was carried out essentially by the method of Gonzalez-Vergara *et al.* [10d] except that amounts of reactants were scaled up five times. (CAUTION: Metal perchlorates with oxidizable organic substituents are potentially explosive [17]. Sintered disc filters should be avoided in filtration procedures [17d]). *Anal.* Calc. for I: Cr, 7.74; C, 25.04; H, 2.65; N, 4.86. Formula mass, 2014.65. Found: Cr, 7.40; C, 24.11; H, 2.17; N, 4.45%; [HNic]/[Cr], 2.26 ± 0.05.

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II was prepared exactly as **I** except that the complex was washed directly with anhydrous ether rather than with ethyl alcohol due to the high solubility of **II** in the latter. *Anal. Calc.* for **II**: Cr, 6.83; C, 20.50; H, 2.05; N, 3.99; formula mass, 2284.41. Found: Cr, 6.61; C, 20.93; H, 1.98; N, 3.93; [i-Hnic]; [Cr], 2.18 ± 0.05 .



The trinuclear picolinic acid–chromium(III) complex was prepared and recrystallized by the same procedure as for **I** and treated as **II** above. *Anal. Calc.* for **III** ($X = 6$, $Z = 3$): Cr, 6.37; C, 17.65; H = 1.73; N, 3.34; formula mass, 2499.73. Found: Cr, 6.23; C, 17.73; H, 1.75; N, 3.41; [Hpic]: [Cr], 2.12 ± 0.05 .

X-ray Structural Determination

A suitable single crystal of **III** ($X = 1$, $Z = 6$, formula mass = 1885.35) was formed by slow evaporation of an aqueous solution of **III**. The unwashed crystal was found to have crystallized in a hexagonal lattice having a symmetry consistent with space groups $P6_3/m$ or $P6_3$. The unit cell dimensions, $a = 13.978(1)$, $c = 24.506(3)$ Å, $V = 4146.3(11)$ Å³, $Z = 2$, were determined by twenty-five reflections ($\theta = 12.8$ to 21.5°) whose setting angles were measured on an Enraf Nonius CAD-4F diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The calculated density is 1.510 Å g/cm³. Systematic extinctions ($00l$, $l = 2n + 1$) were observed and show consistency with the possible space groups. Intensity data were collected ($3^\circ < 2\theta < 50^\circ$, h : 0–16, k : 0–16, l : 0–29) using the ω – 2θ scan technique with a variable scan rate of 0.38 to $3.35^\circ \text{ min}^{-1}$. Selected reflections (1, $\bar{4}$, $\bar{3}$, and 3, 1, 9) were monitored every two hours of exposure time and revealed only random deviations in intensity (<1.0%). Lorentz and polarization corrections were applied, but due to the low absorption coefficient (0.7399 mm^{-1}), absorption was ignored. Averaging of equivalent reflections ($R_{\text{int}} = 0.034$) and rejection of systematic extinctions produced 1770 unique reflections, 1024 having $I > 2\sigma(I)$. The zero moment test of Howells *et al.* [18] was applied to the unique data and supplied inconclusive evidence for the presence of an inversion center. The centric structure reported by Gonzalez-Vergara *et al.* [10d] was used to initiate the refinement of the present structure. After several series of full-matrix refinements on F values, the highest peaks on a difference Fourier map indicated that six positions attributable to disordered water molecules were missing from our model. Inclusion of six oxy-

gen atoms at 50% population decreased the residual from 0.125 to 0.083. The populations were refined individually for several cycles of least-square refinement, then fixed (populations O(11): 0.58(3), O(12): 0.55(3), O(13): 0.76(4), O(14): 0.60(2), O(15): 0.58(4), O(16): 0.54(4). Hydrogen atom positions were calculated for the pyridine ring and included in structure factor calculations but were not refined. The least-squares refinement was terminated when the R factors stabilized and the maximum ratio of parameter shift to parameter error, $(\Delta_i/\sigma(i))$, was less than 0.02. The final reliability indices were $R = \Sigma F/\Sigma |F_o| = 0.077$ and $R_\omega = [\Sigma \omega^{1/2}(\Delta F)^2/\Sigma \omega^{1/2}(F_o)^2] = 0.073$, where $\Delta F = |F_o| - |F_c|$ and $\omega = \sigma^{-2}(F_o)$. The ‘goodness-of-fit’ value (Σ_2) was 1.979, and the largest ratio of shift to error was 0.014. The quantity minimized in the refinement was $\omega|F_o| - |F_c|$. Residual electron density revealed by a difference Fourier map was less than $0.8(1) \text{ e}\text{\AA}^{-3}$ which is attributed to random fluctuation. Computer programs used in the structural analysis were supplied by Enraf-Nonius [19]. Atomic scattering factors and anomalous dispersion correction factors for all atoms were taken from the International Tables of X-ray Crystallography [20].

Comparison of the structure at various stages of refinement in each of the two potential space groups confirmed the selection of the centric space group $P6_3/m$. The atomic positional and equivalent isotropic thermal parameters are given in Table I. In Table II are presented the interatomic distances and angles.

Analyses

Microanalyses for C, H and N were performed by Guelph Analytical Laboratories. Chromium was determined spectrophotometrically as CrO_4^{2-} after the method of Haupt [21] following oxidation of duplicate aliquots of complex ion solutions in alkaline H_2O_2 . The three carboxylatopyridines were determined spectrophotometrically in 0.1 M HClO_4 solution after first decomposing the complexes with base. Concentrations were obtained from a standard curve of absorbance versus [carboxylatopyridine], where the absorbances were measured at 264, 270, and 261 nm, respectively, for the 2-, 3-, and 4-carboxylatopyridines. Beer’s law was obeyed in all cases.

Spectral measurements

Visible and UV spectra were measured on a Cary 14 recording spectrophotometer using water or perchloric acid solutions of the complexes. Infrared spectra of samples in KBr discs were recorded on a Perkin-Elmer Model 521 recording spectrophotometer.

TABLE I. Positional Parameters ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\times 10^3$) for the $[\text{Cr}_3\text{O}(\text{O}(\text{C}_2\text{H}_3\text{O}_2)_6(\text{H}_2\text{O})_3)](\text{ClO}_4)_7 \cdot \text{NaClO}_4 \cdot 6\text{H}_2\text{O}$ Complex

Atom	x	y	z	U_{eq}^a
Cr	5151(2)	2177(2)	2500	30(1)
C(11)	10065(3)	2140(3)	915(2)	73(2)
C(12)	6667	3333	482(3)	53(2)
Na	10000	0	0	26(3)
O(1)	4698(6)	2834(6)	1918(3)	35(3)
O(2)	5972(6)	4660(6)	1926(4)	37(3)
O(3)	6667	3333	2500	20(4)
O(4)	3527(9)	930(10)	2500	50(5)
O(5)	10654(9)	1653(9)	1061(7)	150(6)
O(6)	10801(9)	3266(9)	786(6)	118(6)
O(7)	9469(11)	1567(11)	447(5)	128(7)
O(8)	9269(9)	2038(10)	1278(5)	126(6)
O(9)	5639(9)	3010(11)	361(7)	161(8)
O(10)	6667	3333	1035(9)	167(7)
O(11)	0	0	1933(20)	139(15)
O(12)	3320(28)	-1021(23)	2500	123(16)
O(13)	1841(29)	1872(44)	2500	457(26)
O(14)	2414(17)	4719(24)	1663(12)	212(16)
O(15)	3290(38)	4261(32)	2500	314(23)
O(16)	3333	6667	3579(37)	247(35)
N	3747(8)	3092(8)	1027(5)	45(4)
C(1)	5135(9)	3801(9)	1739(5)	32(4)
C(2)	4586(9)	3988(9)	1260(5)	33(4)
C(3)	3195(11)	3193(12)	608(6)	60(6)
C(4)	3500(11)	4175(11)	391(6)	64(6)
C(5)	4339(12)	5083(11)	613(7)	71(6)
C(6)	4913(12)	4998(12)	1036(6)	61(6)

$$^a U_{\text{eq}} = (U_{11} + U_{22} + U_{33} + U_{12} \cos \gamma + U_{13} \cos \beta + U_{23} \cos \alpha) / 3.$$

Results and Discussion

X-ray Structure

In Fig. 1 is presented a stereo drawing of the heptacation of **III** with the asymmetric unit labeled. A central feature of the structure is oxygen atom O(3) which is trigonally coordinated to three chromium(III) ions. Within experimental error the atoms of the Cr_3O unit lie in the same plane. Each of the chromium atoms lies on an equivalent position having two-fold site symmetry. The chromium atoms are six coordinate, having slightly distorted octahedral geometry with three different sets of oxygen donor atoms. For example, the labeled Cr atom in Fig. 1 has an equatorial plane of the octahedron formed by four bridging carboxyl oxygen atoms (O(1), O(2'), O(1'), O(2'')) from four symmetry related picolinic acid ligands at an average Cr–O bond length of 1.961(11) Å. The apical atoms are (i) the

TABLE II. Selected Bond Distances and Bond Angles Determined for the μ_3 -Oxo-hexakis(μ_2 -picolinic acid-*O,O*)triaqua-trichromium(III) Perchlorate^a

Distances (Å)			
Cr–O(1)	1.965(7)	O(1)–C(1)	1.252(11)
Cr–O(2)	1.958(7)	O(2)–C(1)	1.271(11)
Cr–O(3)	1.918(2)	N–C(2)	1.342(12)
Cr–O(4)	2.058(10)	N–C(3)	1.333(14)
Cl(1)–O(5)	1.352(10)	C(1)–C(2)	1.495(14)
Cl(1)–O(6)	1.421(9)	C(2)–C(6)	1.365(15)
Cl(1)–O(7)	1.408(11)	C(3)–C(4)	1.329(16)
Cl(1)–O(8)	1.375(9)	C(4)–C(5)	1.341(16)
Cl(2)–O(9)	1.307(10)	C(5)–C(6)	1.351(15)
Cl(2)–O(10)	1.354(20)		
Angles (°)			
O(1)–Cr–O(1')	93.1(4)	O(7)–Cl(1)–O(8)	104.4(7)
O(1)–Cr–O(2)	86.6(3)	O(9)–Cl(2)–O(9')	115.0(5)
O(1)–Cr–O(2')	170.1(3)	O(9)–Cl(2)–O(10)	103.1(7)
O(1)–Cr–O(3)	94.8(2)	C(2)–N–C(3)	120.7(10)
O(1)–Cr–O(4)	85.4(3)	O(1)–C(1)–O(2)	128.0(10)
O(2)–Cr–O(2')	92.0(4)	O(1)–C(1)–C(2)	116.6(11)
O(2)–Cr–O(3)	95.0(2)	O(2)–C(1)–C(2)	115.3(10)
O(2)–Cr–O(4)	84.8(3)	N–C(2)–C(1)	117.2(10)
O(3)–Cr–O(4)	179.7(6)	N–C(2)–C(6)	118.6(10)
Cr–O(3)–Cr'	120.0(6)	C(1)–C(2)–C(6)	124.2(11)
O(5)–Cl(1)–O(6)	109.3(7)	N–C(3)–C(4)	121.1(12)
O(5)–Cl(1)–O(7)	105.4(8)	C(3)–C(4)–C(5)	119.4(12)
O(5)–Cl(1)–O(8)	116.3(9)	C(4)–C(5)–C(6)	120.5(12)
O(6)–Cl(1)–O(7)	110.1(8)	C(2)–O(6)–C(5)	119.6(12)
O(6)–Cl(1)–O(8)	111.0(7)	Cr–O(1)–C(1)	131.4(7)
		Cr–O(2)–C(1)	131.4(7)

^aO(1') and O(2') are generated by the $x, y, \frac{1}{2} - z$ symmetry operation and Cr' and O(9') by the $1 - x, x - y, z$ operation.

three-fold bridging oxygen atom O(3) which has the shortest average Cr–O distance of 1.918(2) Å; and (ii) the terminal oxygen atom O(4) (coordinated water) at an average Cr–O distance of 2.058(10) Å. Interestingly, the chromium atom is displaced 0.17 Å from the equatorial plane toward O(3) as are the metal atoms in $[\text{Cr}_2\text{FeO}(\text{CH}_3\text{CO}_2)_2(\text{H}_2\text{O})_3]\text{NO}_3 \cdot \text{CH}_3\text{CO}_2\text{H}$ [10b]. The displacement of the chromium(III) ions toward O(3) necessarily requires the O(3)–Cr–O(i) ($i = 1, 2$) angles to be greater than 90° and the O(4)–Cr–O(i) angles to be less than 90° in accord with values given in Table II.

In Table III are compared the related bond distances for species of the type $[\text{Cr}_n\text{Fe}_{3-n}\text{O}(\text{R}(\text{CO}_2)_6(\text{L})_3)]^{m+}$, $n = 0 - 3$. The sums of ionic radii for O^{2-} (CN = 3) and either $\text{O}_h \text{Cr}^{3+}$ or Fe^{3+} (high spin) average 1.98 and 2.00 Å, respectively. For the most part, the metal–bridging oxygen distances $\text{M}-\text{O}_{\text{br}}$ in column 3 of Table III are in accord with summations of these ionic radii. However, the M_3-O distances in column 2 are substantially shorter, lying outside any experimental error whereas the

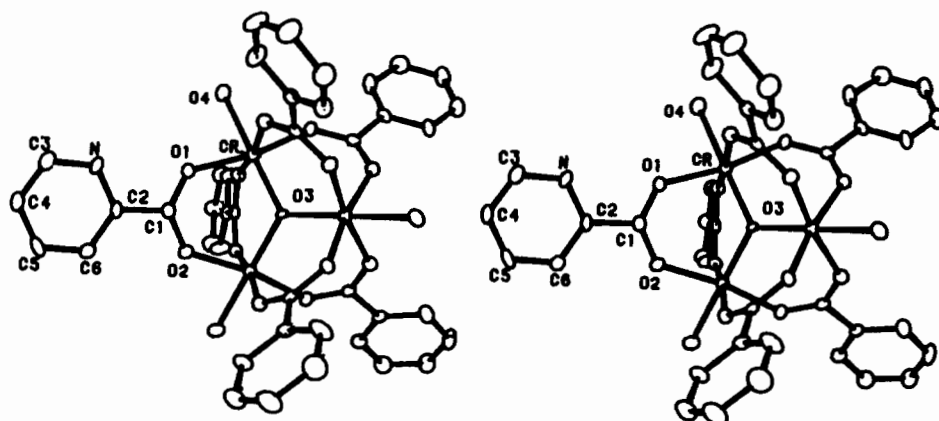


Fig. 1. Stereodrawing of the μ_3 -Oxo-hexakis(μ_2 -2-carboxylatopyridine-*O,O*)-triaquatrichromium(III) ion.

TABLE III. Metal-Ligand Structural Comparisons of $[\text{Cr}_n\text{Fe}_{3-n}\text{O}(\text{RCO}_2)_6(\text{L})_3]^{m+}$ Ions ($n = 0-3$)

Complex ion ^a	Average r_o (Å)			Reference
	M_3-O	$\text{M}-\text{O}_{\text{br}}^{\text{b}}$	$\text{M}-\text{L}_t^{\text{c}}$	
1 $[\text{Cr}_3\text{O}(\text{Hpic})_6(\text{H}_2\text{O})_3]^{7+}$	1.918(2)	1.961(7)	2.058(10)	^d
2 $[\text{Cr}_3\text{O}(\text{Hnic})_6(\text{H}_2\text{O})_3]^{7+}$	1.906(6)	1.98(2)	2.05(2)	10d
3 $[\text{Cr}_3\text{O}(\text{OAc})_6(\text{H}_2\text{O})_3]^+$	1.89(2)	1.98(2)	2.05(1)	9d
4 $[\text{Cr}_2\text{FeO}(\text{OAc})_6(\text{H}_2\text{O})_3]^+$	1.894(8) ^e	1.987(8) ^e	2.091(10) ^e	10b
	1.89 ^f	1.98 ^f	2.09 ^f	10g
5 $[\text{CrFe}_2\text{O}(\text{HGly})_6(\text{H}_2\text{O})_3]^{7+}$	1.900(2)	2.03(2)	2.043(9)	10f
(see ⁵)	1.915(6)	2.01(1)	2.066(13)	10f
6 $[\text{Fe}_3\text{O}(\text{HGly})_6(\text{H}_2\text{O})_3]^{7+}$	1.90(2)	2.02(2)	2.09(2)	10c
7 $[\text{Cr}_3\text{O}(\text{F}_2-\text{OAc})_6(\text{B})_3]^0$	1.938(1)	2.034(7)	2.158(7) ^h	10e
	1.926(1)	2.028(4)	2.155(5) ⁱ	10e

^aAnions are ClO_4^- (1, 2, 5, 6), Cl^- (3), NO_3^- (4a) and FeCl_4^- (4b); Hpic and Hnic = 2- and 3-carboxylatopyridines, OAc = acetate and HGly = glycine. ^bMetal-bridging carboxylate oxygen. ^cMetal-terminal atom (O of H_2O or N of pyridine base). ^dThis work. ^eAverage bond distances and errors calculated from Table III of ref. 10b; Cr and Fe positions are statistical, therefore, indistinguishable. ^fNo errors reported. ^gCr and Fe positions are ordered, therefore, distinguishable; Cr distances given first, then Fe distances. ^hB = pyridine. ⁱB = 4-cyanopyridine.

$\text{M}-\text{O}_t$ bond lengths (column 4) are corresponding longer than the predicted values. The shorter M_3-O bond lengths may be rationalized on the basis of significant $d\pi-p\pi$ interactions between the respective 3d orbitals of the metal ions and the $2p_z$ orbital of O(3). Additionally, the magnetic exchange parameters are indicative of metal ion coupling via the central oxide ion.

These arguments are further strengthened by the observation that a one electron reduction of the $\text{Cr}_3^{\text{III}}\text{O}$ core (entry 7 in Table III) leads to slightly elongated (by 0.03–0.04 Å) Cr–O(3) bond distances. However, all the Cr–O(3) distances are equivalent. Thus, at least one electron is delocalized over the $\text{Cr}_2^{\text{III}}\text{Cr}^{\text{II}}\text{O}$ core.

Conversely, the enhancement of M_3-O bonding interactions of the $d\pi-p\pi$ type necessarily places extra electron density in the 3d orbital of the metal which in turn should repel ligands *trans* to the central

oxide ion, *i.e.* the terminal oxygen atoms (or N for entries 7a,b in Table III). Thus, the slightly longer $\text{M}-\text{O}_t$ (or N_t) bonds (column 4) are also accommodated by invoking the $d\pi-p\pi$ interactions. Finally, it is noteworthy that the skeletal replacement of Cr(III) by Fe(III) (*cf.* entries 1–3 with entries 4–6) has very little, if any, effect on the essential features of the $[\text{M}_3\text{O}(\text{RCO}_2)_6(\text{L})_3]^{m+}$ complex ion skeleton. The Cr–Cr minimum separation in the core is 3.28 Å; it has already been noted [12] that the metal ions are too far separated to allow for significant direct metal ion interactions.

Moving now to the peripheral atoms in the structure, one finds that the picolinic acid molecule is zwitter ionic and bridges the chromium centers through the carboxylate oxygen atoms. Both COO_{br} bond lengths in the bridging carboxylate are identical (1.26(1) Å) within experimental error. These values are in accord with those found in the struc-

TABLE IV. Vis-UV Absorption Spectra for μ_3 -Oxo-hexakis(μ_2 -carboxylatopyridine-*O,O*)triaquatrichromium(III) Complexes in Aqueous Solution^a

λ_{\max} (nm) (ϵ ($M^{-1} \text{ cm}^{-1}$)))					Assignment ^b
2-HpyCO ₂	3-HpyCO ₂	4-HpyCO ₂	OAc ^{-b}	Hgly ^c	
1 721(7)	721(9)	724(8)	712 ^d	720 ^d	⁴ B ₁ → ² E(² T _{1g})
2 701(13)	701(13)	701(13)	702	710	
				695	
3 685(18)	685(20)	685(19)	—	685	⁴ B ₁ → ¹ A ₂ (cluster states)
4 670(39)	670(43)	670(49)	671	666	
				645	
5 583(107)	583(121)	590(126)	585	585	⁴ B ₁ → ⁴ B ₂ , ⁴ E(⁴ T _{2g})
6 440(146)	440(153)	440(157)	442	434	
					⁴ B ₁ → ⁴ A ₂ (⁴ T _{1g})
7 360(179)	360(138)	360(199)	358		
8 348(251)	348(174)	350(285)	339		⁴ B ₁ → [⁴ B ₁ , (² A ₁) ₂]; [⁴ B ₁ , (² B ₁) ₂]; [⁴ B ₁ , ² A ₁ , ² B ₁]
9 349(321)	339(214)	340(420)	332		
10 270(70,100)	264(37,800) ^e	272(19,800) ^e	—		
11 220(36,700)	228(74,900) ^e	218(95,200) ^e	—		

^a2-, 3-, 4-HpyCO₂ are 2-, 3-, and 4-carboxylatopyridines, OAc⁻ = acetate; Hgly = glycine. ^bRef. 5. ^cRef. 4d. ^dDiffuse reflectance spectrum. ^eSee text.

tures included in Table III. Surprisingly, the C—O_{br} bond distances are equivalent to the sum of the C-atom and O-atom double bond covalent radii, 1.27 Å whereas one might have expected them to be an average of C—O and C=O bond distances, 1.38 Å. Entirely similar, short carbon—oxygen distances were observed by Ardon *et al.* [22] in two crystal structures involving glycine bridged, binuclear complexes of chromium(II). The pyridine ring is free of distortion, having a maximum deviation from the mean plane of 0.023 Å, an average bond distance of 1.344 Å, and an average bond angle of 120.0°. The C(1)—C(2) distance (1.495(14) Å) is that of an ideal C—C single bond (1.50 Å). The C—N and C—C bond distances in the ring are all within the range 1.329–1.365 Å. Such values are entirely in accord with the corresponding values reported for 7a in Table III. Further, they fall below the average of a C—N (1.49 Å) and a C=N (1.29 Å) covalent bond length. The asymmetric unit contains one perchlorate counterion at a general position within the cell and a second at a special position with 3-fold rotational symmetry. The two perchlorate anions are angularly distorted with angles ranging from 104.4 to 116.3° and 103.1 to 115.0° for each perchlorate ion, respectively. The bond distances found in each show some variance; however, all values are in agreement with perchlorate Cl—O distances compiled in BIDICS [23].

Vis-UV Absorption Spectra

In Table IV are given the Vis-UV absorption bands for the three complexes investigated. Additionally, the reported spectra of the corresponding acetate [5] and glycine [4d] species are included for purposes of comparison. The bulk of the band

assignments given in Table IV were taken from the detailed single crystal, polarized spectral study reported for the acetate species. The basic features of the aqueous solution spectra of these oxo-centered species are these: (i) Four low-energy bands (entries 1–4) in the range of 670–725 nm ($\epsilon = 8–49 M^{-1} \text{ cm}^{-1}$) interpreted as spin forbidden transitions. (ii) Two typical chromium(III) d–d absorption bands (entries 5 and 6) at 583–590 nm (ϵ values = 107–126 $M^{-1} \text{ cm}^{-1}$) and 440 nm ($\epsilon = 146–157 M^{-1} \text{ cm}^{-1}$). (iii) Three high energy bands (entries 7–9) in the near UV at 339–360 nm ($\epsilon = 138–420 M^{-1} \text{ cm}^{-1}$) interpreted to involve double excitations. (iv) Two intense UV bands (entries 10 and 11) characteristic of the pyridine carboxylic acids. Except for the last two bands, the pyridine carboxylic acid species exhibit remarkably similar spectral characteristics to those of the basic chromic acetate [5] and the recently reported [4d] glycine analog. Only the 2-carboxylatopyridine species is free of adduct carboxylatopyridine; thus, the two UV bands for the 3- and 4-carboxylatopyridine species represent some average of adduct and coordinated acid.

IR Spectra

In Table V the IR spectra of the 2-, 3-, and 4-carboxylatopyridine complexes are compared to the isostructural 'basic chromic acetate' [4b] and glycine [4d] analogs. The assignments are based on the more recent work of Johnson *et al.* [4b]. The absorption bands for $\nu_{\text{as}}(\text{CO}_2)$ appear at substantially higher wavenumbers, 1644–1678 cm^{-1} , than that for the acetate species (*cf.* 1610 cm^{-1}). Taylor [24] observed similar anomalies for the IR spectra of 2-, 3- and

TABLE V. Selected Infrared Spectral Bands of the μ_3 -Oxo-hexakis(μ_2 -carboxylatopyridine-*O,O*)triquatrichromium(III) Complexes^a

IR assignment	2-HpyCO ₂	3-HpyCO ₂	4-HpyCO ₂	OAc ^{-b}	HGly ^c
B ₁ ν_{as} CO ₂	1678	1649	1644	1610	1650
A ₁ ν_s CO ₂	1440	1431	1420	1454	1410
δ OCO	683	678	682		
ν_{as} M ₃ O	675	670	675	660	630
π CO ₂	622	620	622	621	610
E _u ν_d MO	416	412	416	411	450
A _{1g} ν_2 MO	360	(359)	355	360	
δ_s M ₃ O	288	283	273	283	

^aAll spectra recorded for KBr discs; units, cm⁻¹. ^bRef. 4b. ^cRef. 4d.

4-carboxylatopyridines in KBr pellets and concluded that hydration of the pellets causes a shift from the zwitterion to the unionized form of these acids. The tendency toward hydration was attributed to the positive charge on the nitrogen center. The same vibrational band for the glycine complex (at 1650 cm⁻¹) [4d] serves to strengthen the argument. By contrast, all the ν_s (CO₂) bands are below that of the acetate complex, including the glycine complex. Although the differences become greater as the carboxylate substituent is moved away from the nitrogen center (from the 2 to the 3 to the 4 position), note that glycine yields the greatest difference. It is tempting to ascribe the greater (by 10–15 cm⁻¹) wavenumber ν_{as} (M₃O) bands in the carboxylatopyridine species to a greater $d\pi-p\pi$ M^{III}-O interaction; however, the structural results in Table III mitigate against this. The remaining skeletal vibrations are strikingly parallel to those of the 'basic chromic acetate'.

Supplementary Material

Listings of the structure factor amplitudes for the μ_3 -oxo-hexakis(μ_2 -carboxylatopyridine-*O,O*)triquatrichromium(III) perchlorate·sodium perchlorate·hexahydrate have been deposited with the British Library Document Supply Centre as a Supplementary Publication (10 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, U.K.

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Note Added in Proof

Several oxo-centered Cr(III) and Fe(III) trinuclear complexes of the biologically active ligand, trimethylamine-carboxylatoborane, have been prepared and characterized (Vis, IR, Magnetic Susceptibility) by V. M. Norwood and K. W. Morse, *Inorg. Chem.*, **25**, 3690 (1986).