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Potassium Tris(oxalato)ruthenate(III)

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Abstract

The structure of the title compound has been found by single-crystal X-ray analysis to be a 4.5 hydrate, isomorphous with the rhodium and iridium analogs (triclinic space group $P\bar{1}$, a = 6.813(5), b = 10.519(1), c = 12.470(2) Å, α = 76.28(1)°, β = 84.26(1)°, γ = 85.60(1)°, Z = 2). The structure was refined to a conventional R value of 0.025 by using 2271 significant reflections. The structure contains the expected tris-bidentate oxalatoruthenate(III) anion with an average Ru–O bond length of 2.028(7) Å. Two methods of preparing this salt free of chloride ions are described. The powder diffraction pattern is tabulated with the three most intense lines of 6.05-(100), 13.62(46), and 3.033(38) Å. The reduction potential was measured by cyclic voltammetry to be −0.456 V, which differs from that previously reported.

Introduction

Charonnat [1] reported a synthesis of potassium tris(oxalato)ruthenate(III) in 1931. The product of the reaction between solutions of $K_2[RuCl_5H_2O)$ and potassium oxalate in sealed tubes at 100 °C was correctly identified as $K_3[Ru(C_2O_4)_3]\cdot 4.5H_2O$. In addition, Charonnat isolated from the reaction mixture a product of composition $K_3[Ru(C_2O_4)_3]\cdot 4.5KCl\cdot 4H_2O$.

Because it is difficult to prepare the chloride-free salt by Charonnet's method, alternative syntheses have been developed. One is to reflux a mixture of ammonium pentabromohydroxyruthenate(IV), oxalic acid dihydrate and formaldehyde for 45 min, followed by the addition of K_2CO_3 to the reaction mixture [2]. Another method, reported briefly, is to dissolve ruthenium(III) hydroxide in boiling aqueous oxalic acid [3]. The absence of a reliable and detailed preparative method has led some workers to use freshly prepared but crude products in subsequent syntheses [4–6].

There have been some studies of the chemical and physical properties of the complex. The infrared absorption spectrum of the solid was reported for the region 200–1800 cm^{-1} [7, 8]. The electronic absorption spectrum of $[Ru(C_2O_4)_3]^{3-}$ generated in solution was described as comprising four peaks on the edge of a charge-transfer band [3]. The magnetic moment of 2.03 BM indicates a low-spin d^5 electron configuration [2, 3]. A polarographic study found a reversible one-electron reduction with $E_{1/2}$ of −0.56 V versus NHE [9].

No structural study of the complex appears to have been reported. In the present work two detailed preparative methods are given which enabled single crystals to be obtained. In the first method hydrated ruthenium trichloride was used directly and the chloride was eliminated by reprecipitation of the product. In the second method the chloride was eliminated by preliminary isolation of ruthenium hydroxide with thorough washing. The crystals obtained by the two methods were found to be identical. The structure has been determined by X-ray diffraction and the X-ray powder diffraction pattern was recorded. The infrared and electronic spectra and the polarography have been reexamined using this material.

Experimental

Syntheses

Potassium tris(oxalato)ruthenate(III)

In Method A a solution of hydrated ruthenium trichloride (5.0 g) and potassium oxalate (11.8 g) in water (100 ml) was refluxed with rapid stirring for 7 h. During this time the solution changed color from black to olive-green. A black solid was obtained by the addition of the hot solution to ethanol (250 ml). The mixture was filtered warm. If the mixture were cooled overnight in a refrigerator, as described previously [5], the product was contaminated with KCl. The crude product (6.3 g) was dissolved in water (10 ml) and the solution poured into ethanol (100 ml). The precipitated product was collected by filtration and the filtrate tested with $AgNO_3$ for the

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presence of chloride ions. Usually there was no trace of chloride after three reprecipitations.Recrystallization of the residue from water, by the slow evaporation of the solvent over silica gel in a desiccator, gave olive-green needles and plates.

In Method B ruthenium trichloride was first converted to $Ru(OH)_3(aq)$ to eliminate Cl^- [3]. A solution of potassium hydroxide (3.2 g) in water (2 ml) was added dropwise with stirring to a solution of $RuCl_3 \cdot xH_2O$ (5.0 g) dissolved in water (40 ml). The resulting mixture was stirred for 15 min, then the $Ru(OH)_3 \cdot xH_2O$ precipitate was filtered from the supernatant KCl solution and washed with water (4 X 250 ml). Each washing involved stirring a suspension of $Ru(OH)_3 \cdot xH_2O$ in water for 15 min. This was followed by the separation of the solid by filtration on a Buchner funnel and rinsing the residue with water. This procedure required 6 h and rendered the intermediate free from Cl^-.

The ruthenium(III) hydroxide was added to a boiling solution of oxalic acid (8.2 g) in water (40 ml) and the mixture was refluxed for 20 min, by which time the precipitate had dissolved. Potassium carbonate (4.4 g) was added in small quantities to the solution. The solution was refluxed for another 20 min, then cooled (40 °C) and poured into ethanol (250 ml). The resulting precipitate (6.3 g) was collected by filtration and recrystallized from water to give olive-green needles and plates.

Both procedures were tested quantitatively for the removal of all chloride. The chloride content of the starting material was determined to be 43.8%. All of this chloride was found in the filtrates of the two procedures.

Spectroscopy

Some electronic absorption spectra were obtained using a Cary 17D spectrophotometer interfaced with a Commodore 4016 computer and a Hewlett-Packard 7470A plotter. Other spectra were recorded using a Beckman Instruments Acta V spectrophotometer interfaced with a Hewlett-Packard 9835A computer and 7225A plotter. Infrared spectra (potassium bromide discs: 0.4 mg compound, 200.0 mg KBr) were recorded on a Perkin-Elmer 457 Grating Infrared Spectrophotometer.

Electrochemistry

Water used in electrochemical measurements was doubly distilled from potassium permanganate. Sodium perchlorate and KCl were twice recrystallized from distilled water and vacuum-dried over silica gel. Phosphate buffer solutions were prepared by established procedures [10]. Solutions were deoxygenated by bubbling with dry argon, which was purified by passage through a column of BASF R3-11 catalyst. All measurements were made at room temperature (20.0 ± 0.5 °C).

Electrochemical half-wave potentials were obtained by cyclic voltammetry with a precision triangle wave generator [11] and a CMOS FET input operational amplifier based on a potentiostat with positive feedback *iR* compensation. Oxidative measurements were made in a medium of 0.1 M potassium nitrate/water using a Teflon shrouded platinum disk working electrode [12], a platinum wire auxiliary electrode and a silver/silver chloride (saturated KCl) reference electrode in a three-compartment cell with medium porosity frit separators. Reductive measurements were made in a medium of 0.1 M KCl/H_2O using a Princeton Applied Research Model 303 SMDE operated from the voltammetry apparatus with a hanging drop electrode (HMDE).

Crystallography

Powder diffraction

X-ray powder diffractograms were recorded on a Philips PW 1370 powder diffractometer fitted with a PW 1373 goniometer, with Cu Kα radiation, a 1° slit divergence, 0.2 mm receiving slit, and 1° scatter slit. Peak positions were recorded at a scan speed of 1°/min and chart speed such that 2.0 cm represented 1°.

The d spacings were calculated via the Bragg equation $d = \lambda/2 \sin \theta$, where 2θ is the measured angle of X-ray reflections from the crystals and λ, the appropriate wavelength of radiation. For reflections at low angle (small θ), λ will be the weighted mean of $\lambda(K\alpha_1)$ and $\lambda(K\alpha_2)$. For a high reflection angle where the α_1 and α_2 doublet is resolved, the appropriate wavelength must be used. Thus, d was calculated with either of the following: (i) $\lambda K\alpha$ = 1.5418 Å; or (ii) $\lambda K\alpha_1$ = 1.5405 Å and $\lambda K\alpha_2$ = 1.5443 Å.

Single crystal data

Precession photography was employed in order to check crystal quality and to determine the space group. All of the data were collected on a computer-controlled Enraf-Nonius CAD4 automatic diffractometer equipped with a graphite monochromator. Lattice parameters at 21 °C were determined by a least-square fit to the setting parameters at 25 independent reflections in the range $19° < 2\theta < 30°$. Three standard reflections, monitored after every 4000 s of data collection, showed that no decomposition occurred during data collection. The intensities were corrected for Lorentz, polarization and adsorption effects [13].

Structure solution and refinement

The structure was solved by heavy atom methods; the position of the ruthenium atom was determined by Harker analysis of a Patterson map. All other atoms, including hydrogen atoms, were located in subsequent difference Fourier maps. One water oxygen [O(27)] lies only 1.2 Å from its symmetry related ($-x$, $1-y$, $1-z$) image and, therefore, cannot be present at 100% occupancy. A group occupancy factor for the oxygen and hydrogen atoms of this water refined to 47(1)%.

A blocked-matrix least-squares refinement of an overall scale factor, a weighting scheme, and positional and thermal parameters (anisotropic for non-hydrogen, isotropic for hydrogen atoms) converged (all shifts less than 0.5σ) with $R = 0.025$. At this stage the largest peaks in a final difference map were less than 0.6 e Å^{-3} in height.

All the calculations were performed using the SHELX [14] system of programs, while the scattering factors (neutral Ru for Ru^{III}) and anomalous dispersion terms were taken from International Tables [15]. The data collection and refinement parameter are listed in Table 1, while the final least-squares positional parameters are collected in Table 2. See also 'Supplementary Material'.

Results

Description of the Structure

A stereo view of the unit cell of $K_3[Ru(C_2O_4)_3]\cdot 4.5H_2O$ is shown in Fig. 1. The structure consists of the $[Ru(C_2O_4)_3]^{3-}$ anions, potassium cations, and water molecules with bonds connecting the potassium atoms to the oxalate oxygen atoms and to the water oxygen atoms. Tables 3 and 4 give the intramolecular bond lengths and bond angles. There are also a number of hydrogen bonds between the water molecules and the oxalate oxygen atoms, and between water molecules (Table 5). The water molecules occupy a channel running down the centre of the unit cell in the direction of *a*. The compound is isostructural with that of $K_3[Rh(C_2O_4)_3]\cdot 4.5H_2O$ [16].

TABLE 1. Summary of the data collection and processing parameters

Space group	triclinic, $P\bar{1}$
Cell constants	$a = 6.813(5)$ Å
	$b = 10.519(1)$ Å
	$c = 12.470(2)$ Å
	$\alpha = 76.28(1)^\circ$
	$\beta = 84.26(1)^\circ$
	$\gamma = 85.60(1)^\circ$
	$U = 862.5$ Å, $Z = 2$
Molecular formula	$C_6H_9K_3RuO_{16.5}$
Formula mass	563.5
Density	2.170 M gm^{-3}
Absorption coefficient	16.62 cm^{-1}
Crystal dimensions	0.17 × 0.17 × 0.12 mm
Radiation	Mo Kα, $\lambda = 0.71069$ Å
$F(000)$	550 electrons
Temperature	292 K
Data collection range	$2^\circ < 2\theta < 50^\circ$
Scan width	$(1.00 + 0.35 \tan\theta)^\circ$
Horizontal scan aperture	$(2.40 + 00.50 \tan\theta)$ mm
Scan type	$\omega{-}4\theta/3$
Total data collected	3301
Data with $I > 2.5\sigma(I)$	2271
Total variables	282
$R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma(\lvert F_o\rvert)$	0.025
$R_w = \Sigma(\lvert F_o\rvert F_c\rvert)w^{1/2}/\Sigma(\lvert F_o\rvert w^{1/2})$	0.029
Weighting scheme	$w = 1.62/(\sigma^2 F_o + 0.0030 F_o^2)$

All of the potassium cations are coordinated to seven oxygen atoms: K(3) and K(4) are each bound to three water molecules, three free oxalato oxygens and one coordinated oxalate oxygen. K(2) is bound to three free oxalato oxygens and four coordinated oxygens, three of which are bonded to the same anion, which results in a short ruthenium–potassium contact of 3.99(1) Å. This penetration of potassium into the coordination sphere has been observed in the structures of a number of other tris(oxalato) metal complexes [16].

The X-ray crystal structure confirms that the complex anion is formulated correctly as $[Ru(C_2O_4)_3]^{3-}$, with all of the oxalato groups acting as

TABLE 2. Final positional parameters (×10^4) for $K_3[Ru(C_2O_4)_3]\cdot 4.5H_2O$

	x	y	z
Ru(1)	1650(1)	1876(1)	2007(1)
K(2)	7490(1)	2450(1)	491(1)
K(3)	4461(1)	−1302(1)	4021(1)
K(4)	2990(1)	3241(1)	8255(1)
O(5)	240(3)	3668(2)	1755(2)
O(6)	4039(3)	2989(2)	1547(2)
C(7)	1390(5)	4624(3)	1458(2)
C(8)	3612(5)	4234(3)	1384(2)
O(9)	4827(4)	5059(3)	1166(2)
O(10)	824(4)	5772(2)	1255(2)
O(11)	−931(3)	1016(2)	2535(1)
O(12)	1585(3)	1886(2)	3637(2)
C(13)	−1562(4)	1057(3)	3542(2)
C(14)	−57(4)	1540(3)	4197(2)
O(15)	−3156(3)	729(2)	3988(2)
O(16)	−482(3)	1559(2)	5168(2)
O(17)	1597(3)	1739(2)	410(2)
O(18)	3058(3)	83(2)	2115(2)
C(19)	2200(4)	594(3)	242(2)
C(20)	3059(4)	−368(3)	1249(3)
O(21)	2158(4)	276(2)	−622(2)
O(22)	3682(4)	−1452(2)	1165(2)
O^w(23)	8393(4)	8147(3)	3004(3)
O^w(24)	3242(6)	6575(4)	3282(3)
O^w(25)	3957(7)	3508(4)	4398(3)
O^w(26)	7575(11)	4553(8)	3490(7)
O^w(27)	817(23)	4775(29)	4891(15)

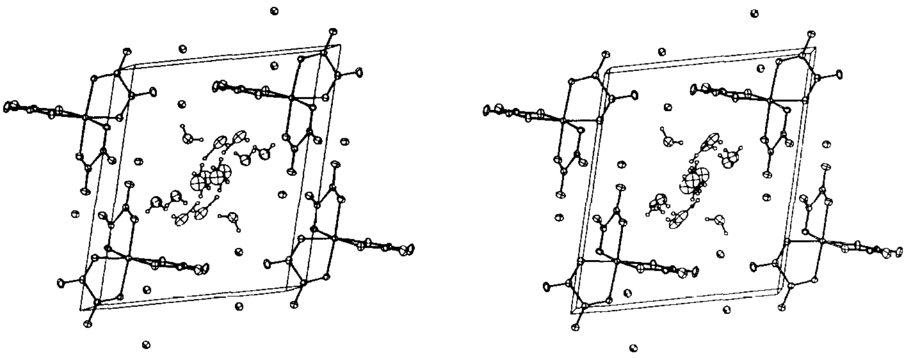

Fig. 1. A stereo view of the unit cell of $K_3[Ru(C_2O_4)_3]\cdot 4.5H_2O$.

TABLE 3. Bond lengths (Å) for $K_3[Ru(C_2O_4)_3]\cdot 4.5H_2O$

O(5)–Ru(1)	2.019(2)
O(6)–Ru(1)	2.033(2)
O(11)–Ru(1)	2.019(2)
O(12)–Ru(1)	2.030(2)
O(17)–Ru(1)	2.034(2)
O(18)–Ru(1)	2.031(2)
O(5)–K(2)	3.092(2)
O(6)–K(2)	2.667(2)
O(11)–K(2)	2.899(2)
O(17)–K(2)	2.838(2)
O(10)–K(2)	2.731(2)
O(21)–K(2)	2.825(2)
O(22)–K(2)	2.736(2)
O(15)–K(3)	2.771(3)
O(18)–K(3)	2.700(2)
O(23)–K(3)	2.924(3)
O(24)–K(3)	2.816(5)
O(15)–K(3)	2.740(2)
O(16)–K(3)	2.806(2)
O(25)–K(3)	2.880(2)
O(17)–K(4)	2.885(2)
O(9)–K(4)	2.677(2)
O(10)–K(4)	2.788(2)
O(22)–K(4)	2.869(2)
O(23)–K(4)	2.660(2)
O(24)–K(4)	3.036(2)
O(26)–K(4)	2.812(2)
C(7)–O(5)	1.284(4)
C(8)–O(6)	1.292(4)
C(8)–C(7)	1.537(4)
O(10)–C(7)	1.213(4)
O(9)–C(8)	1.210(4)
C(13)–O(11)	1.295(3)
C(14)–O(12)	1.288(3)
C(14)–C(13)	1.556(5)
O(15)–C(13)	1.206(4)
O(16)–C(14)	1.222(4)
C(19)–O(17)	1.300(4)
C(20)–O(18)	1.282(4)
C(20)–C(19)	1.546(4)
O(21)–C(19)	1.207(4)
O(22)–C(20)	1.209(4)

TABLE 4. Valence angles (°) for $K_3[Ru(C_2O_4)_3]\cdot 4.5H_2O$

O(6)–Ru(1)–O(5)	81.1(1)
O(11)–Ru(1)–O(5)	90.8(1)
O(11)–Ru(1)–O(6)	171.2(1)
O(12)–Ru(1)–O(5)	88.2(1)
O(12)–Ru(1)–O(6)	94.6(1)
O(12)–Ru(1)–O(11)	81.4(1)
O(17)–Ru(1)–O(5)	94.1(1)
O(17)–Ru(1)–O(6)	89.5(1)
O(17)–Ru(1)–O(11)	94.8(1)
O(17)–Ru(1)–O(12)	175.6(1)
O(18)–Ru(1)–O(5)	174.9(1)
O(18)–Ru(1)–O(6)	98.5(1)
O(18)–Ru(1)–O(11)	89.8(1)
O(18)–Ru(1)–O(12)	96.9(1)
O(18)–Ru(1)–O(17)	80.8(1)
C(7)–O(5)–Ru(1)	114.4(2)
C(8)–O(6)–Ru(1)	113.9(2)
C(8)–C(7)–O(5)	115.5(2)
O(10)–C(7)–O(5)	124.3(3)
O(10)–C(7)–C(8)	120.2(3)
C(7)–C(8)–O(6)	114.8(3)
O(9)–C(8)–O(6)	124.3(3)
O(9)–C(8)–C(7)	120.9(3)
C(13)–O(11)–Ru(1)	113.8(2)
C(14)–O(12)–Ru(1)	113.9(2)
C(14)–C(13)–O(11)	114.9(2)
O(15)–C(13)–O(11)	125.2(3)
O(15)–C(13)–C(14)	119.9(3)
C(13)–C(14)–O(12)	114.8(2)
O(16)–C(14)–O(12)	125.4(3)
O(16)–C(14)–C(13)	119.8(3)
C(19)–O(17)–Ru(1)	113.9(2)
C(20)–O(18)–Ru(1)	114.6(2)
C(20)–C(19)–O(17)	114.8(3)
O(21)–C(19)–O(17)	124.6(3)
O(21)–C(19)–C(20)	120.6(3)
C(19)–C(20)–O(18)	115.0(2)
O(22)–C(20)–O(18)	125.3(3)
O(22)–C(20)–C(19)	119.6(3)

TABLE 5. Close intermolecular contacts (Å)

A–H...B	A...B	H...B
O(23)–H(23A)...O(16)^{i}	2.893	2.19
O(23)–H(23B)...O(11)^{ii}	2.997	2.41
O(23)–H(23B)...O(21)^{iii}	3.081	2.38
O(24)–H(24A)...O(27)	2.891	2.22
O(24)–H(24B)...O(22)^{iv}	2.950	2.34
O(25)–H(25B)...O(26)	2.799	1.68
O(25)–H(25B)...O(12)	2.814	2.13
O(26)–H(26A)...O(27)^{v}	3.005	1.90
O(27)–H(27A)...O(26)^{i}	2.648	1.87

$^{i}1 - x, 1 - y, 1 - z$; $^{ii}1 + x, 1 + y, z$; $^{iii}1 - x, 1 - y, -z$; $^{iv}x, 1 + y, z$; $^{v}1 + x, y, z$.

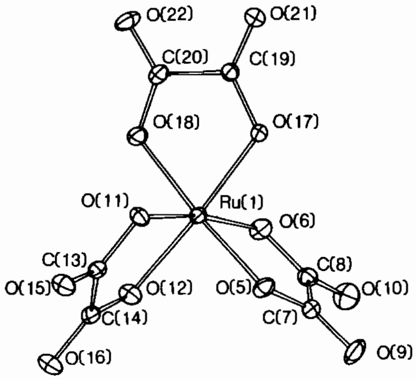

Fig. 2. An ORTEP plot of the $[Ru(C_2O_4)_3]^{3-}$ anion with the atom numbering scheme.

bidentate chelating ligands. An ORTEP [17] plot of the complex cation, giving the atomic numbering scheme, is shown in Fig. 2. The geometry around ruthenium can be described as distorted octahedral, with the distortion arising because of the small bite angle (average 81.4(3)°) of the oxalato ligand. The ruthenium–oxygen bond lengths do not show any significant variation and average to 2.028(7) Å. This is very similar to the rhodium–oxygen distance (2.016 Å) observed in the isostructural complex [16]. The least-squares planes through each of the oxalato ligands (Table SII) reveal no deviations greater than 0.025 Å from planarity (see 'Supplementary Material'). However, for two of the oxalato groups (atoms 11–16 and 17–22), the ruthenium atom is found to deviate from these planes by 0.17 and 0.10 Å, respectively. Presumably, these distortions are a consequence of the interactions of these ligands with potassium cations and water molecules.

Infrared and Electronic Spectra

The infrared spectrum of the complex (KBr disc) is in good agreement with that reported previoulsy [7, 8]. The electronic spectrum is characterised by a strong absorption band at 285 nm, with an apparent molar absorptivity of 6.0 × 10^3 M^{-1} cm^{-1}, and a shoulder at 353 nm with ϵ of 2.0 × 10^3 M^{-1} cm^{-1}. In the visible region the spectrum displays a shoulder at about 588 nm with ϵ of 4 M^{-1} cm^{-1}. These features are qualitatively similar to those reported earlier [3]. In the earlier work the charge transfer background was subtracted before calculated extinction coefficients were reported. Consequently, the previously reported spectrum does not describe the experimentally observed features.

TABLE 6. X-ray powder pattern data for $K_3[Ru(C_2O_4)_3]\cdot 4.5H_2O$

Diffraction angles 2θ (°)	Interplanar distances d (Å)	Relative intensity I/I_0^{a}
6.55	13.62	46
7.80	11.36	28
9.15	9.70	34
11.80	7.54	30
13.60	6.56	25
14.75	6.06	100
15.25	5.87	26
16.40	5.46	25
17.25	5.20	31
21.67	4.17	32
25.20	3.62	30
25.85	3.54	34
26.45	3.46	24
27.40	3.35	22
30.55	3.03	38
31.75	2.93	27
34.25	2.72	22
41.30	2.33	20
44.45	2.20	22
46.95	2.11	19

^{a}The peak corresponding to a d-spectrum of 6.06 Å was assigned an intensity of 100%.

Powder Diffraction Pattern

The powder diffraction patterns of samples prepared by the two different synthetic methods are identical. The interplanar spacings d and the relative intensities are summarized in Table 6. No reference values have been reported in the ASTM File Index [18]. The three most intense reflections for the complex are 6.05(100), 13.62(46) and 3.033(38) Å.

Cyclic Voltammetry

In the cyclic voltammogram of 3 × 10^{-4} M $K_3[Ru(C_2O_4)_3]\cdot 4.5H_2O$ at a scan rate of 200 and 500 mV/s and iR compensation of 0.2, the electrochemical half wave $E_{1/2}$ of the Ru^{III}/Ru^{II} couple was determined to be −0.653 V versus Ag/AgCl (20.0 ± 0.1 °C) or −0.456 V relative to the hydrogen electrode. The peak to peak potential separations

ΔE_p were observed to be 61 mV, which indicates a reversible one-electron redox reaction.

These results differ markedly from those previously reported [9]. In the previous study, however, the tris-oxalato complex was not isolated, but generated by the reaction of RuO_4 with oxalic acid. A mixture of products was obtained.

The reduction reaction was not reversible on a gold electrode. It was only quasi-reversible on carbon, with a broad wave at about 0.1 V more positive than is observed on a mercury electrode.

Oxidative measurements for a Ru^{IV}/Ru^{III} couple were attempted under identical conditions as above, except in a medium of 0.1 M KNO_3/H_2O with a platinum electrode. This experiment showed no oxidation response before the onset of water oxidation, at 1.00 V versus the Ag/AgCl/sat. KCl reference electrode.

Discussion

Potassium tris(oxalato)ruthenate crystallizes in a triclinic habit with 4.5 waters of hydration, isomorphous with its rhodium analog. It is not monoclinic, as described by Herpin [19] and Gouteron [8]. The iridium analog is also an isomorphous 4.5 hydrate [20] presenting nearly identical low-frequency infrared absorption spectra [21]. In contrast, optically active potassium tris(oxalato)-rhodate and -iridate crystallize as dihydrates [20]. Although single crystal structures were described, the reported metal–oxygen distances of 1.96 Å for both rhodium and iridium are somewhat shorter than expected, compared with the rhodium–oxygen distance of 2.02 Å observed more recently for the racemic 4.5 hydrate [16].

In contrast with these heavier spin-paired transition metal complexes, the lighter potassium tris-(oxalato)metal(III) salts of aluminium [22], vanadium [23], chromium [22], manganese [24] and iron [19] are isomorphous monoclinic trihydrates. Potassium tris(oxalato)cobaltate(III) is apparently anomalous, not isomorphous with either the trihydrate or 4.5 hydrate series [23]; Herpin describes it as a 3.5 hydrate [20], but Jaeger originally formulated it as a triclinic trihydrate [25].

Other tris(oxalato)metal(III) salts for which crystal structures have been reported include $Na_3[M(ox)_3]\cdot 5H_2O$ for M = Al and Cr [26], $(NH_4)_3[Cr(ox)_3]\cdot 2H_2O$ [27], $K[Ni(phen)_3][Co(ox)_3]\cdot 2H_2O$ [28], $K_2[Ge(ox)_3]\cdot 2H_2O$ [29] and $M_3[Sb(ox)_3]\cdot 4H_2O$, where $M = (NH_4)^+$ and K^+ [30].

Precise metal–oxygen distances have been determined only for Al (1.96 Å), Cr (1.971 Å), Ru (2.028 Å) (this work), Rh(2.016 Å) and Ge (1.882 Å). The structure of $[Mn(ox)_3]^{3-}$ is Jahn–Teller distorted, as expected, and hence not strictly isomorphous with the other trihydrate structures. Two Co–O distances of 1.90(3) and 1.95(3) Å are perhaps longer than might be expected for low-spin Co(III). The reported Fe–O distance of 2.04 Å is also not very precisely determined; furthermore, the dihedral angle β of 105.6° of the monoclinic crystal differs significantly from the values of 108° found for the four other isomorphous compounds of Al, V, Cr and Mn.

Tris(oxalato)ruthenate(III) ion has not been resolved into optical isomers. Attempts using strychnine, quinine, $[Ni(phen)_3]^{2+}$, and the method of 'active racemates' have all failed [2]. In contrast, tris(ethylenediamine)ruthenium(III) is quite optically inert [31]. Oliff and Odell [32] report that there is no exchange with labelled free oxalate ligand within twenty minutes, before decomposition of the complex ion had become serious. It may be that failure to resolve the complex has been the consequence of some photodecomposition processes.

Supplementary Material

Tables SI and SII listing thermal parameters and the least-squares planes for the oxalato ligands and tables of observed and calculated structure factors are available form the authors on request.

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