The Crystal Structures of Potassium Tris(oxalato)-chromate(III) and -aluminate(III) Trihydrate: a Reinvestigation

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Abstract

The crystal structures of the isomorphous complexes K₃ [M(oxalate)₃],3H₂O, M = Cr^{III} and Al^{III}, have been determined from three-dimensional diffractometer intensity data by conventional Patterson and difference Fourier techniques. The crystals are monoclinic; M = Cr, $a \ 7.714(1)$, $b \ 19.687(4)$, $c \ 10.361(2)$ Å, $\beta \ 108.06(3)^{\circ}$; M = Al, $a \ 7.712(1)$, $b \ 19.518(3)$, $c \ 10.286(2)$ Å, $\beta \ 108.21(3)^{\circ}$; space group $P2_1/c$ with Z = 4. Block-diagonal least-squares refinement of all non-hydrogen atoms converged at $R \ 0.040$, $R_w \ 0.051$ (M = Cr); $R \ 0.048$, $R_w \ 0.056$ (M = Al). The structures are comprised of discrete M(ox)₃³⁻ anions, K⁺ cations and water molecules. One potassium ion and one water molecule appear to be cooperatively disordered over two possible pair sites (α , β) with occupancy ratios $\alpha/\beta c$. 3 : 1. The geometries within the M(ox)₃³⁻ anions are as expected with $\langle \text{Cr-O} \rangle 1.969(13)$, $\langle \text{Al-O} \rangle 1.896(15)$ Å. The oxalate ligands are non-planar with $\langle \text{C-O}(\text{inner}) \rangle 1.224(6)$, 1.279(12); $\langle \text{C-O}(\text{outer}) \rangle 1.223(5)$, 1.223(10) and $\langle \text{C-C} \rangle 1.538(16)$, 1.534(21) Å for the two structures.

Introduction

The e.p.r. spectra of the tris(oxalato) transition metal complex ions, $[Cr(ox)_3]^{3-1}$ and $[Fe(ox)_3]^{3-}$, doped in a K₃ $[Al(ox)_3], 3H_2O$ host lattice, have revealed the presence of four magnetically distinguishable sites for substitution.^{1,2} The four sites are grouped into two energetically distinct, non-symmetry related pairs, α and β , the sites within each pair being related by a glide plane or screw axis symmetry element. The ratio of the α/β sites for the substitution of chromium was estimated from the relative intensities of the e.p.r. signals to be $2 \cdot 2(5)$.¹ This result is in conflict with the known crystal structure of K_3 [Cr(ox)₃],3H₂O³ with which the host material is reportedly isomorphous.^{4,5} The space group was determined as $P2_1/c$ with four molecules in the unit cell. Since, in general, e.p.r. spectroscopy cannot distinguish entities related by an inversion centre, only one pair of substitution sites should be magnetically distinguishable, not two pairs as observed.^{1,2} However, a close examination of the crystal structure analysis of K_3 [Cr(ox)₃],3H₂O as reported by van Niekerk and Schoening³ revealed some unsatisfactory features. Although it was acknowledged that the correct space group was $P2_1/c$, the structure was determined in the highersymmetry space group C2/c with the coordinates determined from two-dimensional

¹ Doetschman, D. C., J. Chem. Phys., 1974, 60, 2647.

² Doetschman, D. C., and McCool, B. J., Chem. Phys., 1975, 8, 1.

³ Niekerk, J. N., van, and Schoening, F. R. L., Acta Crystallogr., 1952, 5, 196.

⁴ Herpin, P., Bull. Soc. Fr. Mineral. Crystallogr., 1958, 81, 245.

⁵ Gillard, R. D., Laurie, S. H., and Mitchell, P. R., J. Chem. Soc., 1969, 19, 3006.

electron density projections. Furthermore, there was considerable doubt concerning the presence of the third water molecule in that the electron-density maximum of the supposed oxygen atom was considerably less than other oxygen atoms in the structure.

This uncertainty regarding the degree of hydration in these complexes has been compounded by the results of a low-temperature proton magnetic resonance study of ${}^{K}_{3}[Al(ox)_{3}], 3H_{2}O'.^{6}$ The study indicated the presence of at least two molecules of water per complex anion with the authors tentatively assigning a shoulder in the spectrum to the third water molecule *which is probably unstable*'.⁶

In order to resolve some of these problems and to provide a definitive structural basis for further e.p.r. and photochemical studies of the $M(ox)_3^{3-}$ systems, we have reinvestigated the crystal structure of K_3 [Cr(ox)₃],3H₂O and report here the results together with the structural analysis of the isomorphous aluminium complex K_3 [Al(ox)₃],3H₂O.

Experimental

Crystals of K_3 [Cr(ox)₃],3H₂O and K_3 [Al(ox)₃],3H₂O suitable for X-ray study were readily found from the material synthesized for the e.p.r. experiments.¹ In view of the doubt surrounding the degree of hydration of these complexes, the bulk crystalline samples were chemically analysed (M = Cr; Found: C, 14.7; H, 1.1; Cr, 10.7; K, 24.0. Calc. for C₆CrK₃O₁₂,3H₂O: C, 14.8; H, 1.2; Cr, 10.7; K, 24.1%. M = Al; Found: C, 15.7; H, 1.3; Al, 5.6; K, 25.4. Calc. for C₆AlK₃O₁₂,3H₂O: C, 15.6; H, 1.3; Al, 5.8; K, 25.4%).

The crystals were mounted on quartz fibres and coated with epoxy cement to prevent loss of water of hydration. Weissenberg and precession photography confirmed the space group of each compound to be $P2_1/c$ which is uniquely defined by the systematic absences k = 2n+1 for (0k0) data and l = 2n+1 for (hol) data. Long exposure X-ray photographs gave no evidence for crystal disorder or small deviations from $P2_1/c$. The previously observed strong relationship to a centred cell of higher symmetry, C2/c,³ was also noted. Reflection intensity data were measured on a Picker FACS-I diffractometer; the $\theta/2\theta$ moving crystal/counter technique was used. The method of data collection and reduction to observed structure factors has been presented in detail elsewhere;⁷ relevant experimental data are summarized below with data for the chromium complex preceding that of the aluminium complex where the values differ.

Crystal data.—C₆H₆CrK₃O₁₅, C₆H₆AlK₃O₁₅; *M*, 487·4, 462·4; monoclinic, a 7·714(1), 7·712(1); b 19·687(4), 19·518(3); c 10·361(2), 10·286(2) Å; β 108·06(3), 108·21(3)°, *V* 1495·8, 1470·7 Å³; ρ_{obs} 2·15, 2·10 g cm⁻³, ρ_{calc} 2·16, 2·09 g cm⁻³; *Z* 4; space group *P*₂₁/c (C_{2h}⁵, No. 14); crystal dimensions [perpendicular distance (cm) betweem faces (*hkl*) and (*hkl*)] (031), 0·0099, 0·0106; (031), 0·0138, 0·0162; (301), 0·0426, 0·0264; μ (Mo K α) 16·7, 10·3 cm⁻¹.

Data collection.—Mo K α radiation; $\lambda 0.71069$ Å; take-off angle 3.0° ; graphite crystal monochromator $2\theta_{\rm m} = 12.13^{\circ}$; data collected at 2θ speed of 2° min⁻¹ over 2θ range from 3° to 60° , 55° ; individual 2θ scan width $(1.90+0.692 \tan \theta)^{\circ}$; total background count time 20 s; standard reflection intensities remeasured every 40 reflections with no significant variation; number of data collected 4990, 3475; number of unique data with $I \ge 3\sigma(I)$, 2751, 1674; $\rho 0.002$ (the constant ρ is used in the calculation of $\sigma(F_{\rm o})$, see^{7,8}); $R_{\rm s}^{9} 0.026$, 0.036.

Solution and Refinement of the Structure

The structure of the chromium complex was solved initially and then the atomic parameters were used as a basis for the refinement of the aluminium complex. The Patterson function was readily solved for the position of the chromium atom which closely approximated the pseudo-special position $(\frac{1}{4}, y, \frac{1}{4})$. A succession of difference Fouriers located the three oxalate ligands, the three potassium ions, and two of the supposed three water molecules. Block-diagonal least-squares of this model

- ⁶ Rangarajan, T., and Ramakrishna, J., J, Chem. Phys., 1968, 49, 5336.
- ⁷ Martin, R. L., and Taylor, D., Inorg. Chem., 1976, 15, 2970.
- ⁸ Corfield, P. W. R., Doedens, R. J., and Ibers, J. A., Inorg. Chem., 1967, 6, 197.
- ⁹ Taylor, D., Aust. J. Chem., 1976, 29, 723.

gave $R \ 0.142$ and $R_w \ 0.152.$ ⁺ The potassium ion, K(3), appeared to be in some doubt, as the temperature factor was twice that of K(1) or K(2) and the difference Fourier showed a substantial negative residual density. K(3) was removed from the scattering model and another difference Fourier carefully examined. In the region of the removed K(3), there were four major peaks A, B, C, and D with peak height ratios A : C \approx D : B, A : D \approx C : B \approx 3 : 1 and with the shortest interpeak distances of A-B 1 · 5, A-C 2 · 8, B-C 1 · 4, B-D 2 · 7, and C-D 1 · 6 Å (A is the position of the removed K(3)). A difference Fourier calculated after the reflection data had been corrected for absorption, and further cycles of refinement with anisotropic thermal parameters and individual reflection weights equal to $[\sigma(F_0)]^{-2}$ had reduced the residuals to $R \ 0.062$, $R_w \ 0.073$, showed essentially identical features. At this stage the scattering model was deficient from the expected formulation by one potassium and one water molecule.

	K ₃ [Cr(ox) ₃],3H ₂ O				K ₃ [Al(ox) ₃],3H ₂ O				
Atom	. x	У	Z	Atom	x	У	Z		
Cr	0.23745(6)	0.13137(2)	0.24992(5)	Al	0.23688(22)	0.13035(7)	0.25038(17)		
K(1)	0.53639(10)	0.07655(4)	-0.16422(8)	K(1)	0.53537(17)	0.07746(7)	-0.16512(13)		
K(2)	-0.02122(10)	0.07263(4)	0.66431(8)	K(2)	-0.02205(17)	0.07428(7)	0.66510(13)		
K(3) ^A	0.74031(15)	0.08740(6)	0.24100(11)	K(3) ^A	0.74091(26)	0.08898(9)	0.24272(20)		
K(3*) ^B	0.6206(6)	0.2629(2)	0.1034(5)	K(3*) ^B	0.6183(12)	0.2612(4)	0.1003(10)		
O(1)	0.1726(3)	0.0619(1)	0.3655(2)	O(1)	0.1706(4)	0.0631(2)	0.3617(3)		
O(2)	0.4685(3)	0.1316(1)	0.3974(2)	O(2)	0.4621(5)	0.1299(2)	0.3899(3)		
O(3)	0.2702(4)	0.0224(1)	0.5779(2)	O(3)	0.2632(5)	0.0224(2)	0.5752(3)		
O(4)	0.6030(3)	0.0851(1)	0.5999(2)	O(4)	0.6008(5)	0.0851(2)	0.5967(4)		
O(5)	0.3378(3)	0.0705(1)	0.1378(2)	O(5)	0.3370(5)	0.0724(2)	0.1421(3)		
O(6)	0.0096(3)	0.1157(1)	0.1032(2)	O(6)	0.0158(4)	0.1149(2)	0.1103(3)		
O(7)	0.2625(3)	0.0302(1)	-0.0739(2)	O(7)	0.2647(5)	0.0313(2)	-0.0707(4)		
O(8)	-0.0964(3)	0.0644(1)	-0.0978(2)	O(8)	-0.0969(5)	0.0665(2)	-0.0954(3)		
O(9)	0.1202(3)	0.2006(1)	0.3304(2)	O(9)	0.1205(5)	0.1970(2)	0.3282(4)		
O(10)	0.3083(3)	0.2122(1)	0.1652(2)	O(10)	0.3114(5)	0.2083(2)	0.1704(4)		
O(11)	0.0565(5)	0.3105(1)	0.3191(3)	O(11)	0.0584(9)	0.3084(2)	0.3209(5)		
O(12)	0.3006(4)	0.3251(1)	0.1729(3)	O(12)	0.3003(7)	0.3224(2)	0.1727(5)		
C(1)	0.2909(4)	0.0552(1)	0.4833(3)	C(1)	0.2880(8)	0.0550(2)	0.4817(5)		
C(2)	0.4721(4)	0.0931(2)	0.4992(3)	C(2)	0.4688(7)	0.0929(2)	0.4952(5)		
C(3)	0.2246(4)	0.0583(1)	0.0198(3)	C(3)	0.2262(7)	0.0594(2)	0.0236(5)		
C(4)	0.0270(4)	0.0810(1)	0.0031(3)	C(4)	0.0276(7)	0.0815(2)	0.0062(5)		
C(5)	0.1325(5)	0.2610(2)	0.2903(3)	C(5)	0.1337(9)	0.2575(3)	0.2901(6)		
C(6)	0.2567(4)	0.2688(2)	0 2026(3)	C(6)	0.2598(8)	0.2659(3)	0 · 2046(6)		
O _w (1)	-0.1190(5)	0.1660(2)	0.4692(4)	O _w (1)	-0.1206(9)	0.1713(4)	0.4711(6)		
O _w (2)	0.7048(5)	0.2865(2)	0.3369(4)	0 _w (2)	0.7073(9)	0.2852(3)	0.3312(7)		
O _w (3) ^A	0.5821(7)	0.1836(2)	0.0509(5)	$O_w(3)^A$	0.5785(10)	0.1848(4)	0.0456(7)		
O _w (3*) ^B	0.664(2)	0.129(1)	0.129(2)	O _w (3*) ^B	0.667(3)	0.128(1)	0.132(4)		

 Table 1. Final atomic fractional coordinates

^A Occupancy factors for K(3) and $O_w(3)$ were 0.75 (Cr), 0.76 (Al).

 B Occupancy factors for K(3*) and $O_{w}(3*)$ were 0.25 (Cr), 0.24 (Al).

With the knowledge that $K \cdots O$ contact distances are generally greater than $c. 2 \cdot 6 \text{ Å}$,¹⁰ the residual peaks were interpreted in a strictly pairwise disorder of a potassium ion and water molecule, A = K(3), $D = K(3^*)$, $C = O_w(3)$ and $B = O_w(3^*)$ with occupation of the K(3) and $O_w(3)$ sites being mutually exclusive of occupation of the K(3^{*}) and $O_w(3^*)$ sites. The occupancy factors were refined from initial values of 0.75 and 0.25 (based on the observed peak heights) so that their sum remained equal to unity. Refinement of this model converged at $R \cdot 0.040$, $R_w \cdot 0.051$ with all parameter shift/e.s.d. being less than 0.05. The difference Fourier exhibited residual density in the range -0.52 to 0.92 e/Å³; the largest positive peak was in the vicinity of K(3) with other positive peaks close ($c. 1 \cdot 0 \text{ Å}$) to water oxygen atoms $O_w(1)$ and $O_w(2)$, indicative of possible hydrogen atoms. However, hydrogen atoms were not included in the model. Examination of the weighting scheme showed that $w\Delta^2$ was not dependent on either $|F_o|$ or $\sin(\theta/\lambda)$. The cooperative disorder of one potassium ion and one water molecule in the aluminium complex was confirmed by locating the aforementioned peaks A-D in a difference Fourier. Refinement converged at residuals $R \cdot 0.048$, $R_w \cdot 0.056$ with final difference Fourier peaks in the range -0.50 to 0.76 e/Å³.

† Unit reflection weights $R = \sum \Delta / \sum |F_o|$, $R' = (\sum w \Delta^2 / \sum w |F_o|^2)^{1/2}$ where $\Delta = ||F_o| - |F_c||$.

¹⁰ Brown, I. D., Brown, M. C., and Hawthorne, F. C., 'Bond Index to the Determinations of Inorganic Crystal Structures, 1976' p. 70 (McMaster University: Canada 1977).

Environ- ment	Atoms	Distan M = Cr	M = Al	Atoms	Distar M = Cr	nce (Å) M = Al
Metal	M-O(1) M-O(2) M-O(5) ⟨M-O⟩	$ \begin{array}{r} 1 \cdot 981(2) \\ 1 \cdot 955(2) \\ 1 \cdot 985(2) \\ 1 \cdot 969(13) \end{array} $	1 · 913(4) 1 · 876(3) 1 · 911(4) 1 · 896(15)	M-O(6) M-O(9) M-O(10)	1 · 959(2) 1 · 959(3) 1 · 975(2)	1 · 881(3) 1 · 894(5) 1 · 903(4)
Ligand 1	C(1)–O(1) C(2)–O(2) C(1)–O(3)	1 · 284(4) 1 · 292(4) 1 · 224(4)	1 · 292(6) 1 · 289(6) 1 · 217(7)	C(2)-O(4) C(1)-C(2)	$1 \cdot 217(3)$ $1 \cdot 548(5)$	1 · 219(5) 1 · 546(8)
Ligand 2	C(3)–O(5) C(4)–O(6) C(3)–O(7)	$1 \cdot 285(3)$ $1 \cdot 283(4)$ $1 \cdot 230(4)$	1 · 276(5) 1 · 281(6) 1 · 230(7)	C(4)–O(8) C(3)–C(4)	1 · 221(3) 1 · 546(4)	1 · 214(5) 1 · 546(8)
Ligand 3	C(5)–O(9) C(6)–O(10) C(5)–O(11)	$1 \cdot 274(4)$ $1 \cdot 283(4)$ $1 \cdot 221(5)$	$1 \cdot 259(7)$ $1 \cdot 277(7)$ $1 \cdot 241(9)$	C(6)-O(12) C(5)-C(6)	1 · 227(4) 1 · 519(6)	1 · 219(7) 1 · 510(10)
All ligands	$\langle C-O(inner) \rangle$ $\langle C-O(outer) \rangle$ $\langle C-C \rangle$	$1 \cdot 284(6)$ $1 \cdot 223(5)$ $1 \cdot 538(16)$	$1 \cdot 279(12)$ $1 \cdot 223(10)$ $1 \cdot 534(21)$			

Table 2. Principal bond distances in the $[M(ox)_3]^{3-}$ ions

Table 3. Interbond angles in the $[M(ox)_3]^{3-}$ ions

Environ-	Atoms	Angles (degrees)		Atoms	Angles (degrees)	
ment		M = Cr	M = Al		M = Cr	M = Al
Metal	O(1)-M-O(2)	82.5(1)	84.0(3)	O(1)-M-O(9)	89.2(1)	88.2(2)
	O(5)-M-O(6)	82.5(1)	83.9(2)	O(2)-M-O(5)	91.8(1)	89 · 8(2)
	O(9)-M-O(10)	81 · 8(1)	83.1(2)	O(2)-M-O(9)	95 · 5(1)	97.3(2)
	O(1)-M-O(10)	169.0(1)	168.8(2)	O(2)-M-O(10)	92.0(1)	90.1(2)
	O(2)-M-O(6)	171.0(1)	$170 \cdot 5(2)$	O(5)-M-O(10)	9 0 · 8(1)	89.4(2)
	O(5)-M-O(9)	169.7(1)	169.7(2)	O(6)-M-O(9)	91 · 1(1)	89.9(2)
	O(1)-M-O(5) O(1)-M-O(6)	98·9(1) 91·5(1)	$100 \cdot 1(2)$ 90 \cdot 1(2)	O(6)-M-O(10)	95.0(1)	96.9(2)
Ligand 1	C(1)-O(1)-M C(2)-O(2)-M O(1)-C(1)-C(2) O(1)-C(1)-O(3)	$ \begin{array}{c} 114 \cdot 0(2) \\ 114 \cdot 8(2) \\ 113 \cdot 8(2) \\ 125 \cdot 8(3) \end{array} $	$ \begin{array}{c} 114 \cdot 7(3) \\ 115 \cdot 5(3) \\ 111 \cdot 7(5) \\ 125 \cdot 6(5) \end{array} $	O(3)-C(1)-C(2) O(2)-C(2)-C(1) O(2)-C(2)-O(4) O(4)-C(2)-C(1)	$120 \cdot 4(3) \\114 \cdot 0(2) \\125 \cdot 3(3) \\120 \cdot 7(3)$	$122 \cdot 7(4) \\113 \cdot 2(4) \\126 \cdot 4(5) \\120 \cdot 3(5)$
Ligand 2	C(3)-O(5)-M C(4)-O(6)-M O(5)-C(3)-C(4) O(5)-C(3)-O(7)	$113 \cdot 3(2) 114 \cdot 6(2) 114 \cdot 1(3) 125 \cdot 3(3)$	$ \begin{array}{r} 113 \cdot 7(3) \\ 116 \cdot 0(3) \\ 113 \cdot 5(5) \\ 125 \cdot 9(5) \end{array} $	O(7)-C(3)-C(4) O(6)-C(4)-C(3) O(6)-C(4)-O(8) O(8)-C(4)-C(3)	120.6(2) 114.2(2) 125.8(3) 119.9(3)	$120 \cdot 5(4) \\ 111 \cdot 8(4) \\ 126 \cdot 8(5) \\ 121 \cdot 4(5)$
Ligand 3	C(5)-O(9)-M C(6)-O(10)-M O(9)-C(5)-C(6) O(9)-C(5)-O(11)	$ \begin{array}{r} 114 \cdot 8(3) \\ 114 \cdot 3(2) \\ 114 \cdot 5(3) \\ 125 \cdot 2(4) \end{array} $	$114 \cdot 7(4) 115 \cdot 0(4) 114 \cdot 4(6) 125 \cdot 5(7)$	O(11)-C(5)-C(6) O(10)-C(6)-C(5) O(10)-C(6)-O(12) O(12)-C(6)-C(5)	$120 \cdot 3(3) \\113 \cdot 9(3) \\125 \cdot 0(4) \\121 \cdot 1(3)$	$120 \cdot 0(6) \\ 112 \cdot 2(5) \\ 126 \cdot 5(7) \\ 121 \cdot 3(6)$
Aver- ages	<c-o-m> <o-c-o> <o(inner)-c-c> <o(outer)-c-c></o(outer)-c-c></o(inner)-c-c></o-c-o></c-o-m>	$114 \cdot 3(6) 125 \cdot 4(3) 114 \cdot 1(3) 120 \cdot 5(4)$	114 · 9(8) 126 · 1(5) 112 · 8(11) 121 · 0(10)			

Atoms	Distances (Å)		Atoms	Distances (Å)		
	M = Cr	M = Al		M = Cr	M = Al	
K(1)-O(4) ⁱ	2.654(3)	2.656(4)	K(1)-O(12) ¹¹¹	2.828(3)	2.828(4)	
K(1)-O(8) ¹¹	2.710(2)	2.707(4)	$K(1)-O_w(2)^{iii}$	2.991(4)	2.995(7)	
K(1)-O(7)	2.720(3)	2.717(5)	$K(1) - O_W(3)$	3.008(5)	2.958(8)	
$K(2)-O_{w}(1)$	2.662(4)	2.683(6)	K(2)–O(4) ^v	2.776(3)	2.778(4)	
K(3)O(8) ^{iv}	2.706(3)	2.704(4)	K(2)–O(3)	2.843(3)	2.826(5)	
K(2)-O(11)	2.762(3)	2.752(5)	$K(2)-O(1)^{vi}$	2.873(2)	2.895(4)	
$K(3) - O_w(3)$	2.733(5)	2.755(7)	K(3)-O(7) ^{viii}	2.886(3)	2.932(4)	
$K(3) - O_W(1)^{ii}$	2.752(5)	2.769(6)	K(3)–O(6) ⁱⁱ	2.916(3)	2.900(5)	
K(3)-O(3) ^{vii}	2.881(3)	2.876(4)	K(3)–O(5)	2.973(2)	2 977(4)	
$K(3^*) - O_w(2)$	2.349(7)	$2 \cdot 306(12)$	K(3*)-O(2) ⁱⁱⁱ	2.949(5)	3.005(9)	
$K(3^*) - O_w(3^*)$	2.654(13)	2.635(22)	K(3*)-O(4) ⁱⁱⁱ	2.995(5)	3.003(9)	
K(3*)-O(10)	2.858(6)	2.873(11)				
$O_{w}(1)-K(2)$	$2 \cdot 662(4)$	2.683(6)	$O_{w}(1) - O(9)$	2.753(5)	2.752(9)	
$O_{W}(1)-K(3)^{v}$	2.752(4)	2.769(6)	$O_{W}(1) - O_{W}(2)^{v}$	2.863(6)	2.754(9)	
$O_w(2) - K(3^*)$	2.349(7)	2.306(12)	$O_{w}(2) - O_{w}(1)^{ii}$	2.863(6)	2.754(9)	
$O_w(2) - O_w(3)^{ix}$	2.731(8)	2.750(12)	$O_{w}(2)-K(1)$	2.991(4)	2.995(7)	
$O_{W}(2)-O(11)^{ii}$	2.816(6)	2.780(10)				
$O_w(3) - O_w(2)^{iii}$	2.731(8)	2.750(12)	O _w (3)–O(10)	2.780(7)	2.784(10)	
O _w (3)-K(3)	2.733(5)	2.755(7)	$O_{w}(3)-K(1)$	3.008(5)	2.958(8)	
$O_w(3^*) - K(3^*)$	2.654(13)	2.635(22)	$O_{w}(3^{*}) - O(5)$	2.793(15)	2.795(29)	
$O_{w}(3^{*}) - O(6)^{11}$	2.777(16)	2.782(31)				

Table 4. The environments of the potassium ions and water molecules

Contact distances less than c. 3 Å. Transformations of the coordinates (x, y, z) are denoted by superscripts: i (x, y, z-1); ii (1+x, y, z); iii $(x, \frac{1}{2}-y, z-\frac{1}{2})$; iv (x, y, 1+z); v (x-1, y, z); vi $(\bar{x}, \bar{y}, 1-z)$; vii $(1-x, \bar{y}, 1-z)$; viii $(1-x, \bar{y}, \bar{z})$; ix $(x, \frac{1}{2}-y, \frac{1}{2}+z)$; x $(\bar{x}, \bar{y}, \bar{z})$

Table 5. Weighted least-squares planes

Planes are defined as LX+MY+NZ = d where (X, Y, Z) are orthogonal (Å) coordinates derived from the fractional cell coordinates (x, y, z) by $X = xa+cz\cos\beta$, Y = yb and $Z = zc\sin\beta$. The inplane atoms are printed in *italics* and are weighted according to $w = 3/[\sigma^2(X) + \sigma^2(Y) + \sigma^2(Z)]$. Data are presented as pairs of values with the value for the chromium complex preceding that of the aluminium complex

Plane		Parameters	Atom	Deviation (Å)	Atom	Deviation (Å)
1		0.4867, 0.4708	O(1)	0.067(2), 0.065(3)	O(3)	-0.076(2), -0.065(4)
	N N d	-0.3775, -0.3725 -2.3101, -2.2937	C(1) C(2) O(2)	0.001(3), -0.006(5) -0.070(2), -0.065(4)	M	-0.156(1), -0.171(2)
2	L M	0.3108, 0.3033 0.8664, 0.8737	O(5) C(3)	-0.077(2), -0.065(3) 0.015(3), 0.012(5)	O(7) O(8)	0.080(2), 0.064(4) - $0.081(2), -0.065(4)$
	N d	-0.3908, -0.3803 1.4221, 1.4204	C(4) O(6)	$\begin{array}{ccc} 0.010(3), & 0.005(5) \\ 0.074(2), & 0.059(3) \end{array}$	Μ	0.176(1), 0.182(1)
3	L M	-0.5836, -0.5720 -0.0698, -0.0745	0(9) C(5)	-0.079(3), -0.059(4) 0.027(4), 0.029(6)	O(11) O(12)	0.126(4), 0.098(6) -0.102(3), -0.079(5)
	N d	-0.8090, -0.8169 -2.7515, -2.7745	$\begin{array}{c} C(6) \\ O(10) \end{array}$	$\begin{array}{c} -0.008(3), -0.015(6) \\ 0.065(2), 0.052(4) \end{array}$	M	-0.021(1), 0.002(2)

Atomic scattering factors were taken from ref.¹¹ and were corrected for anomalous dispersion $(\Delta f', \Delta f'')$.¹² All calculations were performed on the Univac-1108 computer of the Australian National University using the ANUCRYS (1975) suite of crystallographic programs. The final atomic parameters are given in Table 1. The anisotropic thermal parameters and the final observed and calculated structure factor amplitudes are available.[†]-

Results and Discussion

The principal bond lengths and interbond angles in the $M(ox)_3^{3-}$ anions are presented in Tables 2 and 3 while the environments of the K⁺ ions and H₂O molecules are characterized by their nearest neighbour contacts (Table 4). The results of weighted least-squares planes through the oxalate ligands are given in Table 5. The $Cr(ox)_3^{3-}$ anion and the crystal packing of K₃ [Cr(ox)₃],3H₂O are illustrated as stereoviews in Figs 1 and 2 respectively. All discussion of the crystal structures will be given in terms of the chromium complex and the aluminium complex will be mentioned only where there is a significant difference.

The X-ray structural analysis confirms the composition of the complex as the trihydrate, K_3 [Cr(ox)₃], $3H_2O$. The crystal structure is composed of discrete Cr(ox)₃³⁻ anions, K⁺ cations and water molecules. These species appear to interact through electrostatic attractions and hydrogen bonding, although definitive proof of the latter is lacking since the hydrogen atoms of the water molecules were not located. In the following discussion an $O \cdots O$ separation less than $3 \cdot 0$ Å, which is twice the van der Waals radius of oxygen,¹³ will be taken as prima facie evidence of hydrogen bonding.‡ The structural analysis demonstrates that one of each of the three unique K^+ ions and H_2O molecules are cooperatively disordered over two pair sites (α, β) with an occupancy ratio of α : β sites of c. 3:1. The disorder can be readily rationalized from consideration of the disordered water molecule sites, $O_w(3)$ which is the α site and $O_w(3^*)$ which is the β site. A water molecule in the α site has potential for hydrogen bonding to another water molecule $O_w(2)^{iii}$ (2.731(8) Å) and an inner oxalate oxygen atom O(10) (2.780(7) Å) whereas, in the β site, hydrogen bonding may occur to two inner oxalate oxygen atoms, $O(6)^{ii}$ (2.78(2) Å) and O(5) (2.79(2) Å). Whilst it may appear that occupation of the two sites by individual ordered H_2O molecules is possible, the separation of the $O_w(3)$ and $O_w(3^*)$ sites, 1.37 Å, precludes such an eventuality. That is, the $O_w(3)$ and $O_w(3^*)$ sites are mutually exclusive. Furthermore, as the third K⁺ ion is also situated in this restricted region of the crystal structure, occupation by a water molecule of a β site necessarily requires the K⁺ ion to occupy a site, K(3^{*}), in order to avoid the uncomfortably close $O_w(3^*)$ -K(3) contact of 1.40 Å! Therefore the K^+ ion and the H_2O molecule are cooperatively disordered. As regards the relative occupancy of the α and β sites, it should be noted that whereas in the α sites K(3) and $O_w(3)$ have 'normal' contact distances, in the β sites K(3^{*}) has one short contact

[†] Copies are available on application to the Editor-in-Chief, Editorial and Publications Service, CSIRO, 314 Albert Street, East Melbourne, Vic. 3002.

 \ddagger For a cautionary note on the use of this criterion when hydrogen atoms have not been located see ref.¹⁴

¹¹ Cromer, D. T., and Mann, J. B., Acta Crystallogr., Sect. A, 1968, 24, 321.

¹² Cromer, D. T., and Liberman, D., J. Chem. Phys., 1970, 53, 1891.

¹³ Bondi, A., J. Chem. Phys., 1964, 68, 441.

¹⁴ Olovsson, I., and Jönsson, P.-G., in 'The Hydrogen Bond II' (Eds P. Schuster, G. Zundel and C. Sandorfy) p. 401 (North-Holland: Amsterdam 1976).

 $K(3^*)\cdots O_w(2)$, 2.35 Å, which is unusual but not uniquely so.^{10,15} The implication that this $K\cdots O$ contact is sterically unfavourable may result in the observed lower relative occupancy of the β sites. The causal effects of the disorder may be further revealed from a neutron diffraction study of the isomorphous iron(III) complex, K_3 [Fe(ox)₃],3H₂O.¹⁶



Fig. 1. A stereoview of the $Cr(ox)_3^{3-}$ anion down the approximate trigonal axis. The ellipsoids are drawn at the 50% probability level.



Fig. 2. A stereoview of the unit cell of K_3 [Cr(ox)₃],3H₂O. The origin is located on the left-hand front corner of the unit cell outline: the vertical and horizontal axes are *b* and *c* respectively with the view approximately along the *a* axis. The apparently isolated oxalate groups are from neighbouring Cr(ox)₃³⁻ anions which project into the unit cell illustrated. The disordered atoms have partly dotted outlines. OW, oxygen of H₂O.

The disorder phenomenon, particularly of the charged K^+ ion, will create two different crystal field environments for the $Cr(ox)_3^{3-}$ anion. This is corroborated by the e.p.r. spectra of $Cr(ox)_3^{3-}$ and $Fe(ox)_3^{3-}$ doped into a K_3 [Al(ox)₃],3H₂O host



¹⁶ Howard, C. J., Power, L. F., and Thompson, N., unpublished data.

lattice.^{1,2} The spectra clearly show that the anions are in two energetically distinct sites which are *not* related by the crystallographic symmetry. For the chromium derivative the relative intensities of the signals for the α : β sites was estimated at $2 \cdot 2(5)$.¹

The crystallographic environment of the remaining K⁺ ions and H₂O molecules is normal (Table 4). For K(1) and K(2) there are six contacts less than 3 Å to oxygen atoms of both water molecules and oxalate anions. The water molecules have four contact distances less than 3 Å, involving other oxygen atoms, presumably through hydrogen bonding, and K⁺ ions, presumably through electrostatic interaction. There is one further feature of the crystal packing that does not appear to have been reported previously. There are a number of short O(outer oxalate)…C(oxalate) contacts (e.g. $C(3) \dots O(8)^x$, $2 \cdot 822(4)$, $C(4) \dots O(11)^{111} 2 \cdot 919(5)$ Å), involving only carbon atoms of oxalate ions 1 and 2, which are considerably shorter than the estimated van der Waals $C \dots O$ distance of $3 \cdot 20$ Å.¹³ These could arise from electrostatic attractions of the type $C(\delta +) \dots O(\delta -)$.

The chromium atoms of the $Cr(0x)_3^{3-}$ anions are located near $(\frac{1}{4}, 0.131, \frac{1}{4})$ and symmetry-related sites, with a virtual C_2 axis of the anion coincident with the crystallographic *b* axis (Fig. 2). These features give rise to the space group approximation of C2/c which is of higher symmetry than the actual space group $P2_1/c$.

The metal atom in the $M(ox)_3^{3-}$ anion is octahedrally coordinated by three bidentate oxalate groups (Fig. 1). Perturbations from an exact MO₆ octahedron can be described in terms of the twist angle, 47.9° (Cr), 47.4° (Al), and the compression ratio, s/h, 1.260 (Cr), 1.211 (Al), which in the undistorted octahedral geometry have values of 60° and 1.225 respectively.¹⁷ The average M–O bond lengths, 1.969 (Cr), 1.896 Å (Al), are in good agreement with appropriate values of 1.951 Å in Cr(acac)₃,¹⁸ 1.965 Å in $Cr(glycine)_3^{19}$ and 1.889 Å in $[Ag(PPh_3)_2]_3Al(O_2C_2S_2)_3^{20}$ In the complex ion, Cr(catecholate)₃³⁻, the Cr-O distance appears to be marginally longer at 1.986 Å.²¹ The oxalate ligands are non-planar with a maximum atom deviation of 0.13 Å from the plane (Table 5). Only in the case of ligand 3 is the metal atom in the approximate ligand plane. Oxalate ligand 3 is also unusual in that the C-C bond length in both structure determinations is significantly shorter at $\langle 1.515 \text{ Å} \rangle$ than for the other oxalate ligands, $\langle 1.546 \text{ Å} \rangle$. The C–O bond lengths exhibit their expected asymmetry with the inner C-O bonds, where the oxygen is coordinated to the metal atom, being c. 0.06 Å longer than the outer C–O bonds ($\langle 1.282 \text{ Å} \rangle$ compared to <1 · 223 Å>).

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¹⁷ Stiefel, E. I., and Brown, G. F., Inorg. Chem., 1972, 11, 434.

¹⁸ Morosin, B., Acta Crystallogr., 1965, 19, 131.

¹⁹ Bryan, R. F., Green, P. T., Stokely, P. F., and Wilson, E. W., Inorg. Chem., 1971, 10, 1468.

²⁰ Hollander, F. J., and Coucouvanis, D., Inorg. Chem., 1974, 13, 2381.