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The Crystal Structure of Rubidium Tetrachromate, $Rb_2Cr_4O_{13}$

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The crystal structure has been determined and refined to a final R value of 0·038 from 2089 independent reflexions registered with a diffractometer (Mo $K\alpha$ radiation). The space group is $P2_1/c$ (No. 14) with cell constants $a=17·624$ (2), $b=7·688$ (2), $c=9·492$ (2) Å, $\beta=91·95°$ (1), $V=1285$ Å^3, and $Z=4$. The structure contains $Cr_4O_{13}^{2-}$ ions composed of four CrO_4 tetrahedra joined by shared corners. The Cr–O (bridge) distances are in the range 1·691–1·846 Å, mean value 1·77 Å. They are significantly longer than the Cr–O (non-bridging) distances, ranging from 1·576–1·621, mean value 1·61 Å. The Cr–O–Cr angles exhibit great variation: 147·2, 139·3, and 120·5°. The two crystallographically independent rubidium ions are each irregularly coordinated to eleven oxygen atoms with Rb–O distances in the range 2·88–3·47 Å. The Cr–O distances and the conformation of the $Cr_4O_{13}^{2-}$ ions are compared with those observed in other related chromium compounds.

Introduction

Chromium oxides and chromates have long been studied at this Institute. A review of the early work in this field has been given by Wilhelmi (1966*a*). Subsequent studies within this program by the present author have been concerned with the crystal structures of various polychromates. The conditions of formation of the alkali polychromates have been thoroughly analysed by Schreinemakers & Filippo (1906). The methods described by these authors were adapted to the preparation of rubidium polychromates. The results of crystal-structure studies on two modifications of $Rb_2Cr_2O_7$ ($C2/c$ and $P2_1/n$ respectively) have been described in previous articles (Löfgren & Waltersson, 1971; Löfgren, 1971*a*). A preliminary note on the crystal structures of $Rb_2Cr_3O_{10}$ and $Rb_2Cr_4O_{13}$ has also been published (Löfgren, 1971*b*).

Experimental

Rubidium tetrachromate was prepared by adding 55 g chromium trioxide to a hot solution containing 2·7 g rubidium dichromate in 45 ml water. Dark red prismatic crystals were obtained by fractional crystallization at room temperature. The main part of the mother liquor was removed from the crystals by treatment on an unglazed clay plate. Washing with water or diluted CrO_3 solutions is excluded because of the limited area of stability for $Rb_2Cr_4O_{13}$ in the three-component system.

The amount of chromium in the samples was determined by titration with thiosulphate. The percentage by weight of chromium found in different fractions was in the range 36·4 ± 0·2 (calculated value 35·4). The density of the compound was determined from the loss of weight in diethyl phthalate, with a technique developed by Hörlin, Kihlborg & Niklewski. The observed density 3·01 ± 0·01 g cm^{-3} is in good agreement with the calculated value 3·033 g cm^{-3} for four formula units per cell. The deviations of the observed values for the chromium content and the density from the calculated values obviously arise from the difficulties in totally removing the mother liquor from the crystals.

The powder photographs were taken in a Guinier–Hägg focusing camera with Cu $K\alpha_1$ radiation, $\lambda=1·54050$ Å, and potassium chloride, $a(20°C)=6·2919$ Å as an internal standard. The refinement of the cell parameters (*cf.* Table 1) was performed by the method of least squares. The powder pattern is listed in Table 2.

Table 1. *Crystal data for* $Rb_2Cr_4O_{13}$

Space group: $P2_1/c$ (No. 14)
a = 17·624 (2), b = 7·688 (2), c = 9·492 (2) Å, β = 91·95° (1),
V = 1285·4 Å^3 and Z = 4.

Table 2. *Powder pattern of* $Rb_2Cr_4O_{13}$

Cu $K\alpha_1$ radiation, λ = 1·54050 Å

h	k	l	d_{obs}	10^5 $\sin^2\theta_{obs}$	10^5 $\sin^2\theta_{calc}$	I_{obs}
0	1	1	5·982	1658	1663	*vvw*
1	1	$\bar{1}$	5·699	1827	1830	*vvw*
1	1	1	5·619	1879	1878	*vvw*
2	1	$\bar{1}$	4·996	2377	2379	*vw*
2	1	1	4·896	2475	2476	*vw*
2	0	$\bar{2}$	4·241	3299	3305	*m*
3	1	$\bar{1}$			3312	
2	0	2	4·117	3501	3499	*m*
0	1	2	4·036	3643	3641	*w*
1	1	$\bar{2}$	3·962	3780	3783	*vvw*
1	1	2	3·910	3881	3880	*vvw*
0	2	0	3,846	4010	4015	*m*
2	1	2	3·632	4497	4502	*s*
0	2	1	3·562	4676	4674	*vw*
4	1	1	3·506	4827	4820	*vw*
1	2	$\bar{1}$			4841	
2	2	$\bar{1}$	3·318	5389	5391	*s*
4	0	$\bar{2}$	3·282	5509	5503	*m*
3	1	2			5507	
4	0	2	3·172	5895	5890	*vw*
4	1	$\bar{2}$	3·020	6504	6507	*m*
6	0	0	2·935	6889	6884	*m*
4	2	1	2·751	7840	7831	*w*
3	2	$\bar{2}$	2·682	8249	8228	*vvw*
6	1	1	2·612	8699	8693	*vvw*
6	0	2	2·458	9816	9812	*vvw*
6	1	$\bar{2}$	2·4052	10256	10234	*vvw*
0	0	4	2·3688	10573	10547	*vvw*
2	2	$\bar{3}$			10568	
0	1	4	2·2656	11559	11551	*w*
4	3	1	2·1481	12857	12850	*vvw*
0	3	3	1·9908	14970	14967	*w*
2	2	4	1·9552	15519	15521	*vvw*
2	3	3	1·9333	15874	15877	*vvw*
8	1	2	1·9104	16256	16267	*vvw*
6	2	$\bar{3}$	1·9023	16395	16397	*vvw*
0	4	1	1·8834	16725	16720	*w*
8	2	$\bar{1}$			16720	
6	3	1			16723	
10	1	$\bar{2}$	1·6323	22267	22280	*vw*
6	3	3			22287	
12	0	0	1·4676	27545	27538	*vw*
11	2	1	1·4533	28089	28080	*vvw*
4	3	$\bar{5}$			28089	
6	2	5			28106	

The crystal used for the X-ray diffraction work had the dimensions 0·11 × 0·12 × 0·11 mm. The X-ray intensity data were collected on a Siemens automatic 4-circle diffractometer (Nb-filtered Mo $K\alpha$ radiation, λ = 0·71069 Å) with the b axis parallel to the φ (goniometer-head) axis, by a scintillation counter with a pulse-height analyser. The instrument was operated in the θ–2θ mode with the five-values method (scan range $-\Delta\theta = 0{\cdot}40 + 0{\cdot}25 \tan\theta$; $+\Delta\theta = 0{\cdot}40 + 0{\cdot}40 \tan\theta$). Altogether, 4378 lattice points within $\theta \leq 30°$ were measured and two standard reflexions were checked after every 23rd measurement.

Corrections for Lp and absorption effects (μ = 114·0 cm^{-1}) were applied to the data with the program *DATA PH* (Coppens, Leiserowitz & Rabinovich, local version by I. Carlbom).

The Gaussian integration method was used with 10 × 12 × 10 grid points. The transmission factors varied between 0·29 and 0·38. The scattering factors for Rb^+, Cr^{3+}, and O^- were taken from McMaster, Kerr del Grande, Mallett & Hubbell (1969) and $\Delta f'$ and $\Delta f''$ values for anomalous dispersion from *International Tables for X-ray Crystallography* (1962). The calculations were performed on the IBM 360/75 and IBM 1800 computers. The programs used are briefly described elsewhere (*cf.* Löfgren, 1973).

Determination of the structure

The Weissenberg photographs indicated monoclinic symmetry with the following reflexions systematically missing:

$$h0l \text{ for } l = 2n+1$$
$$0k0 \text{ for } k = 2n+1$$

The only space group with these extinctions is $P2_1/c$ (No. 14). The appearance of the Patterson function excluded for the metal atoms all point positions except the general position 4(e): $\pm(x,y,z;\bar{x},\tfrac{1}{2}+y,\tfrac{1}{2}-z)$ From the Harker section at $v=\tfrac{1}{2}$, it was possible to derive approximate x and z parameters for the metal atoms. These were refined by the method of least squares *versus* 71 observed $h0l$ reflexions. After three cycles of refinement the conventional R index defined by $R=\sum||F_o|-|F_c||/\sum|F_o|$ was 0·19. From several trials, tentative y parameters for the metal atoms were derived from the three-dimensional Patterson function. Only one model gave a satisfactory explanation of all main peaks. The metal positions were tested and refined, and the oxygen atoms were also located by successive electron density calculations which finally included 1964 independent reflexions.

The positions of all atoms, their individual isotropic temperature factors and the scale factor were refined with the full-matrix least squares program *LINUS* (Busing, Martin & Levy, local version by I. Carlbom). After four cycles the R index dropped to 0·071. When corrections for secondary extinction and anisotropic temperature factors for the metal atoms were introduced the R value was 0·054. Introduction of anisotropic temperature factors for all atoms reduced the R index to 0·038. The weighted R_w value, defined by the expression $R_w=(\sum w\Delta^2)^{1/2}/(\sum w|F_o|^2)^{1/2}$, was then 0·048. Only the 2089 independent reflexions with $\sigma(|F_o|)/|F_o| \leq$ 0·125 were included in the refinement. The structure factors were weighted according to the formula

$$w=(\sigma|F_o|^2+a+b|F_o|^2+c|F_o|^4)^{-1}$$

with a = 2·5, $b = 10^{-4}$ and $c = 5 \times 10^{-8}$. The final atomic parameters with their standard deviations are listed in

Table 3, and observed and calculated structure factors in Table 4.

Description and discussion of the structure

The structure of $Rb_2Cr_4O_{13}$ consists of Rb^+ and $Cr_4O_{13}^{2-}$ ions (Fig. 1). The latter are composed of four CrO_4 tetrahedra joined by shared corners (Fig. 2).

The thermal parameters are given in Table 3 and the numerical values of the root mean square displacements in Table 5. Fig. 2 is a pictorial representation of the thermal vibrations of the atoms within the tetrachromate ion. On the whole the thermal vibrations of the non-bridging oxygens are larger than those of the bridge oxygens O(4), O(7) and O(10). The average r.m.s. radial thermal displacement values are 0·303 Å

Table 3. *Final coordinates and anisotropic thermal parameters β_{ij} with standard deviations resulting from the least-squares refinement*

The β_{ij} values given are defined by the temperature factor $\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\right]$. β_{ij} values for Rb and Cr are × 10^5 and for O, × 10^4.

	x	y	z
Rb(1)	0·06994 (5)	0·83521 (10)	0·32196 (8)
Rb(2)	0·42448 (5)	0·35928 (10)	0·18377 (9)
Cr(1)	0·08775 (7)	0·31625 (16)	0·44064 (14)
Cr(2)	0·24852 (7)	0·13870 (17)	0·31910 (13)
Cr(3)	0·24584 (7)	−0·18927 (18)	0·09221 (14)
Cr(4)	0·41749 (7)	−0·18520 (17)	0·03944 (14)
O(1)	0·0166 (3)	0·1868 (8)	0·4246 (6)
O(2)	0·0896 (4)	0·4035 (10)	0·5932 (7)
O(3)	0·0805 (4)	0·4609 (9)	0·3204 (8)
O(4)	0·1730 (3)	0·1821 (8)	0·4173 (6)
O(5)	0·3260 (4)	0·1472 (9)	0·4109 (7)
O(6)	0·2548 (4)	0·2703 (9)	0·1940 (6)
O(7)	0·2371 (3)	−0·0752 (8)	0·2520 (6)
O(8)	0·1787 (4)	−0·3211 (10)	0·0790 (7)
O(9)	0·2404 (4)	−0·0583 (10)	−0·0345 (7)
O(10)	0·3308 (3)	−0·2986 (7)	0·0881 (6)
O(11)	0·4228 (5)	−0·0101 (10)	0·1270 (10)
O(12)	0·4132 (4)	−0·1494 (12)	−0·1251 (8)
O(13)	0·4888 (3)	−0·3095 (8)	0·0779 (6)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rb(1)	229 (3)	984 (14)	646 (9)	−52 (5)	32 (4)	39 (9)
Rb(2)	233 (3)	828 (13)	693 (9)	−29 (4)	17 (4)	− 27 (9)
Cr(1)	148 (4)	698 (19)	638 (14)	20 (7)	35 (6)	−127 (14)
Cr(2)	145 (4)	905 (21)	452 (13)	9 (7)	18 (5)	− 49 (14)
Cr(3)	165 (4)	1099 (23)	572 (14)	43 (8)	2 (6)	−194 (15)
Cr(4)	180 (4)	700 (19)	700 (15)	−11 (8)	60 (6)	85 (14)
O(1)	20 (2)	110 (11)	86 (8)	− 5 (4)	5 (3)	0 (7)
O(2)	24 (2)	213 (16)	104 (9)	14 (5)	2 (4)	− 79 (10)
O(3)	22 (2)	113 (12)	150 (11)	4 (4)	3 (4)	49 (9)
O(4)	19 (2)	94 (10)	74 (7)	8 (4)	13 (3)	6 (7)
O(5)	21 (2)	191 (15)	78 (7)	6 (5)	− 6 (3)	− 15 (9)
O(6)	29 (2)	163 (13)	65 (7)	− 7 (5)	5 (3)	26 (8)
O(7)	24 (2)	116 (11)	59 (7)	3 (4)	5 (3)	− 25 (7)
O(8)	20 (2)	197 (15)	119 (9)	− 7 (5)	1 (4)	− 57 (10)
O(9)	38 (3)	204 (16)	71 (8)	41 (6)	2 (4)	26 (9)
O(10)	19 (2)	87 (9)	63 (7)	2 (3)	1 (3)	5 (6)
O(11)	45 (4)	112 (13)	217 (15)	−14 (5)	28 (6)	− 71 (11)
O(12)	37 (3)	296 (21)	88 (9)	− 8 (7)	5 (4)	84 (11)
O(13)	12 (2)	139 (11)	83 (7)	4 (4)	1 (3)	14 (8)

Table 4. *Observed and calculated structure factors for* $Rb_2Cr_4O_{13}$

for the bridging oxygen atoms and 0·375 Å for the non-bridging oxygens. The Cr–O distances cited as 'thermally corrected' in Table 6 have been calculated, assuming the riding-motion model, with the program *ORFFE* (Busing, Martin & Levy, local version by Kihlborg & Klug). As can be seen there is no apparent influence on the equilibrium bridge distances, the corrections not exceeding the e.s.d.'s. This is also observed in $^1_\infty(CrO_3)$* (Stephens & Cruickshank, 1970*a*). On the other hand the thermal motions of the non-bridging oxygens require a slight correction of the corresponding Cr–O distances.

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* Terminology according to Machatschki (1946).

Table 5. *R.m.s. components* (R_i) *of thermal displacement along the ellipsoid axes and r.m.s. radial thermal displacements* (R) (*in* Å)

	R_1	R_2	R_3	R
Rb(1)	0·163	0·175	0·194	0·308
Rb(2)	0·156	0·177	0·191	0·304
Cr(1)	0·134	0·155	0·177	0·271
Cr(2)	0·140	0·154	0·166	0·266
Cr(3)	0·146	0·157	0·195	0·290
Cr(4)	0·140	0·163	0·189	0·284
O(1)	0·168	0·187	0·201	0·322
O(2)	0·150	0·198	0·296	0·386
O(3)	0·160	0·187	0·276	0·370
O(4)	0·142	0·166	0·208	0·302
O(5)	0·168	0·196	0·245	0·355
O(6)	0·156	0·212	0·233	0·352
O(7)	0·141	0·196	0·202	0·315
O(8)	0·171	0·194	0·279	0·380
O(9)	0·160	0·196	0·299	0·391
O(10)	0·158	0·172	0·174	0·291
O(11)	0·155	0·244	0·344	0·449
O(12)	0·155	0·242	0·323	0·432
O(13)	0·136	0·186	0·213	0·314

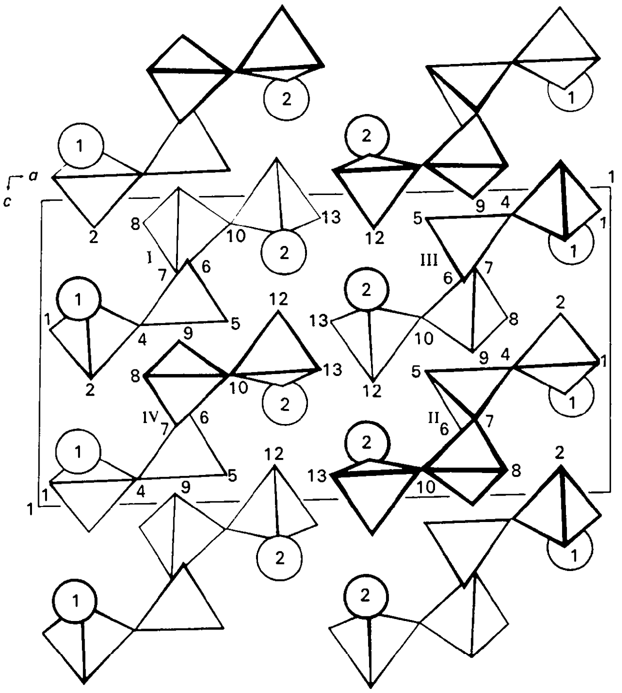

Fig. 1. Projection of the structure of $Rb_2Cr_4O_{13}$ along [010]. Rubidium atoms are shown as circles and the different tetrachromate ions are distinguished by Roman numerals.

Table 6. *Distances* (Å) *and angles* (°) *within the tetrachromate ion with estimated standard deviations*

The O–O distances are given without correction for thermal effects.

Distances

	Uncorrected	Corrected		Uncorrected	Corrected
Cr(1)–Cr(2)	3·383 (2)		Cr(2)–O(7)	1·772 (6)	1·779
Cr(2)–Cr(3)	3·315 (2)		Cr(3)–O(7)	1·764 (6)	1·768
Cr(3)–Cr(4)	3·083 (2)		Cr(3)–O(8)	1·560 (7)	1·576
Cr(1)–O(1)	1·605 (6)	1·613	Cr(3)–O(9)	1·569 (7)	1·591
Cr(1)–O(2)	1·596 (7)	1·618	Cr(3)–O(10)	1·718 (6)	1·718
Cr(1)–O(3)	1·596 (7)	1·614	Cr(4)–O(10)	1·832 (6)	1·832
Cr(1)–O(4)	1·842 (6)	1·846	Cr(4)–O(11)	1·583 (8)	1·621
Cr(2)–O(4)	1·684 (6)	1·691	Cr(4)–O(12)	1·585 (7)	1·618
Cr(2)–O(5)	1·595 (6)	1·612	Cr(4)–O(13)	1·610 (6)	1·617
Cr(2)–O(6)	1·567 (7)	1·582			

O(1)–O(2)	2·618 (9)	O(4)–O(7)	2·788 (8)	O(8)—O(10)	2·684 (8)
O(1)–O(3)	2·601 (9)	O(5)–O(6)	2·555 (9)	O(9)—O(10)	2·679 (9)
O(1)–O(4)	2·761 (8)	O(5)–O(7)	2·737 (9)	O(10)–O(11)	2·764 (10)
O(2)–O(3)	2·627 (10)	O(6)–O(7)	2·733 (9)	O(10)–O(12)	2·778 (9)
O(2)–O(4)	2·831 (9)	O(7)–O(8)	2·686 (9)	O(10)–O(13)	2·791 (8)
O(3)–O(4)	2·828 (9)	O(7)–O(9)	2·726 (9)	O(11)–O(12)	2·621 (12)
O(4)–O(5)	2·712 (8)	O(7)–O(10)	2·876 (8)	O(11)–O(13)	2·627 (10)
O(4)–O(6)	2·691 (8)	O(8)–O(9)	2·551 (10)	O(12)–O(13)	2·613 (10)

Angles

Cr(1) -O(4)—Cr(2)	147·2 (4)	O(4)–Cr(2)–O(5)	111·5 (3)	O(8)—Cr(3)–O(9)	109·2 (4)
Cr(2) -O(7)—Cr(3)	139·3 (4)	O(4)–Cr(2)–O(6)	111·7 (3)	O(8)—Cr(3)–O(10)	109·8 (3)
Cr(3) -O(10)–Cr(4)	120·5 (3)	O(4)–Cr(2)–O(7)	107·5 (3)	O(9)—Cr(3)–O(10)	109·1 (3)
O(1)—Cr(1) -O(2)	109·8 (3)	O(5)–Cr(2)–O(6)	107·8 (4)	O(10)–Cr(4)–O(11)	107·9 (4)
O(1)—Cr(1) -O(3)	108·7 (3)	O(5)–Cr(2)–O(7)	108·6 (3)	O(10)–Cr(4)–O(12)	108·6 (3)
O(1)—Cr(1) -O(4)	106·2 (3)	O(6)–Cr(2)–O(7)	109·7 (3)	O(10)–Cr(4)–O(13)	108·1 (3)
O(2)—Cr(1) -O(3)	110·8 (4)	O(7)–Cr(3)–O(8)	107·7 (3)	O(11)–Cr(4)–O(12)	111·7 (5)
O(2)—Cr(1) -O(4)	110·7 (3)	O(7)–Cr(3)–O(9)	109·6 (3)	O(11)–Cr(4)–O(13)	110·7 (4)
O(3)--Cr(1) -O(4)	110·5 (3)	O(7)–Cr(3)–O(10)	111·4 (3)	O(12)–Cr(4)–O(13)	109·7 (4)

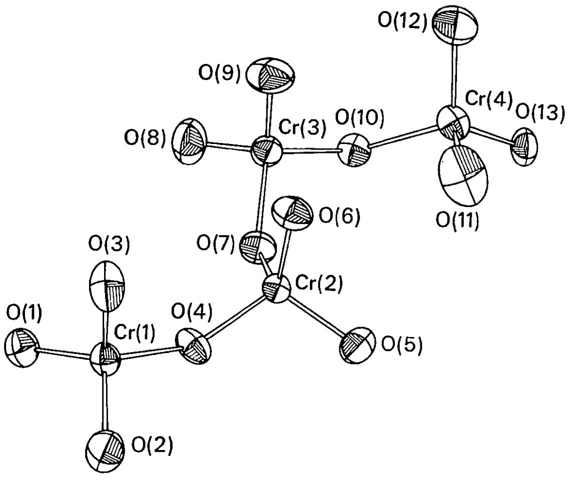

Fig. 2. Configuration of the tetrachromate ion.

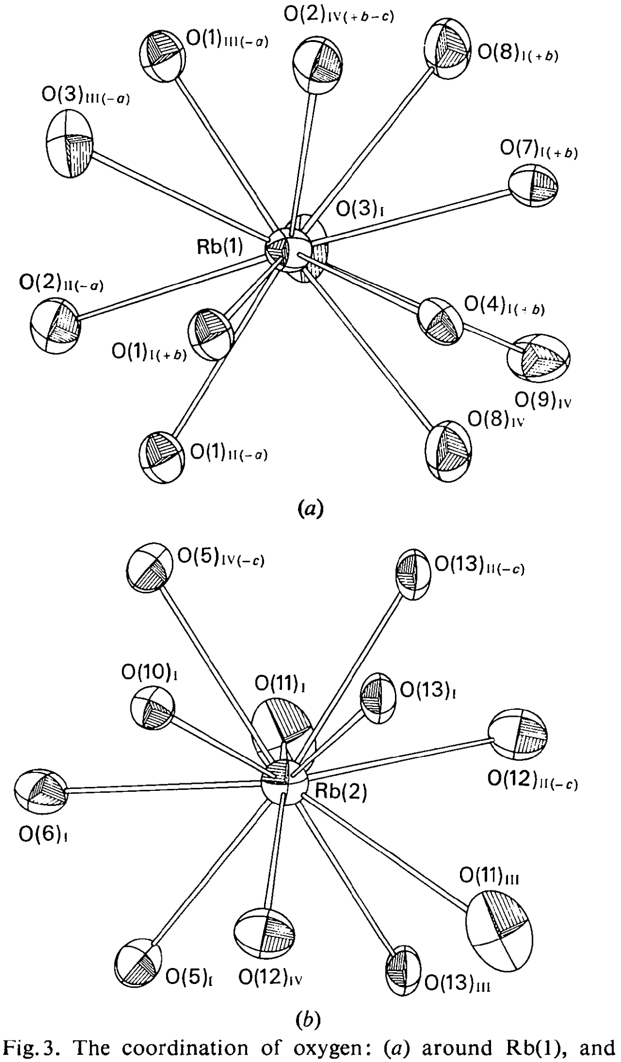

Fig. 3. The coordination of oxygen: (*a*) around Rb(1), and (*b*) around Rb(2).

The considerable distortion of the CrO_4 tetrahedra of the anion is obvious from the range of O–O distances. The range is smallest, 0·18 Å, around Cr(4) and largest, 0·33 Å, around Cr(3). It is of interest to compare these data with those reported for CrO_4 tetrahedra in $(NH_4)_2CrO_4$ (Stephens & Cruickshank, 1970*b*). $Rb_2Cr_2O_7$ ($P2_1/n$), $Rb_2Cr_3O_{10}$, and CrO_3, where the spread of the O–O distances is 0·04, 0·19, 0·20–0·24, and 0·31 Å respectively. These values indicate that the deformation of the tetrahedra increases with the numver of polyhedra forming the chain.

The Cr–O distances also reflect the distortion of the tetrahedra. There is a significant and expected difference between the bridging and non-bridging Cr–O distances with averages of 1·77 and 1·61 Å respectively and considerable spread around these averages (Table 6).

The terminal tetrahedra containing Cr(1) and Cr(4) exhibit Cr–O (non-bridging) distances between 1·613 and 1·621 Å (mean value 1·62 Å). These are in fair agreement with corresponding distances in $Rb_2Cr_3O_{10}$ (mean value 1·60 Å) and in the various modifications of $Rb_2Cr_2O_7$ of symmetries $P\bar{1}$ (Panagiotopoulos & Brown, 1970) $C2/c$, and $P2_1/n$ (mean value 1·62 Å, the latter two based on estimated thermal corrections). These Cr–O distances show an expected shortening compared with those in $(NH_4)_2CrO_4$ (mean value 1·66 Å) and in Ag_2CrO_4 (Hackert & Jacobson, 1971) with a mean value of 1·67 Å (estimated thermal correction applied on the published data). The Cr–O (non-bridging) values of the inner Cr(2) and Cr(3) tetrahedra are even shorter (1·575–1·612 Å, mean value 1·59 Å). This shortening is also reasonable as the chromium atoms are involved in two long bonds to bridge oxygens. The two corresponding distances in CrO_3 are 1·594 and 1·603 Å, mean value 1·60 Å.

It is observed that in $Rb_2Cr_4O_{13}$ the bridge distances vary in a characteristic way along the tetrachromate ion. The longest distances, 1·846 and 1·832 Å, occur at the terminal tetrahedra which possess three contacts between chromium and non-bridging oxygens. Next to these long distances are the two shortest Cr–O bridges, 1·691 and 1·718 Å.

The main feature of the distortion of the terminal tetrahedra is primarily due to an elongation of the Cr–O (bridging) distances. A different situation is found in $K_2S^{VI}_5O_{16}$ (de Vries & Mijlhoff, 1969) where the sulphur atoms of the terminal tetrahedra lie nearly in the plane of the three O (non-bridging) atoms such that the O(br)–S–O(non-br) angles are about 100°. The corresponding angles in the tetrachromate ion are 106·2–110·7° close to the value 109·5° of a regular tetrahedron. The Cr–O–Cr angles are remarkably variable: 147·2, 139·3 and 120·5°, average 135·7°. In the dichromates the majority of the bridge angles are in the range 123–124°; in $Rb_2Cr_3O_{10}$ they are 140 and 136°, and in CrO_3, 143°. It is interesting to note that on the whole the bridging angles seem to increase with the number of tetrahedra sharing corners. However, in

$Rb_2Cr_2O_7$ ($P\bar{1}$) there is a large difference between the bridge angles 123 and 138° of the two crystallographically independent ions. Thus the angles at the bridging oxygen atoms seem also influenced by the packing of the oxygen and rubidium atoms.

The rubidium–oxygen coordination is complex with no directional bond character [Fig. 3(*a*), (*b*)]. The Rb(1) and Rb(2) atoms are each surrounded by eleven oxygen atoms (Table 7). The Rb(1)–O distances range from 2·883 Å to 3·474 Å and the eleven oxygen atoms belong to six different tetrachromate ions. The Rb(2) distances to oxygen atoms from five tetrachromate ions range from 2·887 to 3·348 Å. The Rb–O coordination in $Rb_2Cr_4O_{13}$ can be compared with the ten- and eleven-coordination in $Rb_2Cr_3O_{10}$ and an eight- or ninefold coordination in the rubidium dichromates. The relatively high coordination number of the rubidium ions in rubidium tetrachromate seems to be correlated with the oxygen-rubidium ratio.

The results of the investigation of the structure of $Rb_2Cr_4O_{13}$ can be summarized as follows. Fig. 4 compares schematically the conformation of the tetrachromate ion with those of the dichromate ions, the trichromate ion, and ${}^{1}_{\infty}(CrO_3)$. The alkali dichromates contain ions of the shape shown in Fig. 4(*a*). Strontium dichromate (Wilhelmi, 1966*b*) contains both this type of dichromate ion, and also ions of the shape illustrated in Fig. 4(*b*). The latter evidently resembles the arrangement of the Cr(1) and Cr(2) tetrahedra in $Cr_3O_{10}^{2-}$ [Fig. 4(*c*)]. In the tetrachromate ion [Fig. 4(*d*)] the chromate tetrahedra containing Cr(1), Cr(2), and Cr(3) all have this type of orientation and are arranged in nearly the same way as the tetrahedra of CrO_3 [Fig. 4(*e*)]. The main difference is in the orientation of the terminal Cr(4)-tetrahedron. The mean value of the Cr–O (non-bridging) distances within the inner tetrahedra, Cr(2) and Cr(3), is 1·59 Å and within the error limit the same as the corresponding value in CrO_3 (1·60 Å); nor is there a significant difference among the Cr–O (bridge) distances in the inner tetrahedra (mean value 1·74 Å) and the value observed in CrO_3 [1·748 (5) Å].

The structural relationships between the chromates, dichromates, polychromates and ${}^{1}_{\infty}(CrO_3)$ are further discussed in a forthcoming publication.

The author is indebted to Dr K.-A. Wilhelmi for his continuous interest in this research and for many

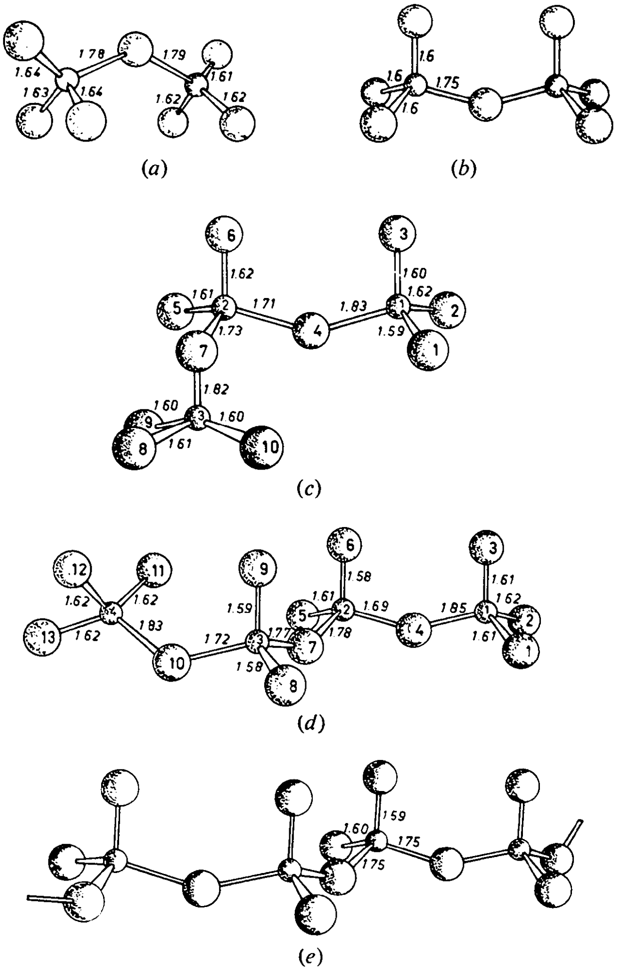

Fig. 4. Shapes and dimensions (Å) of polychromate chains in (*a*) $Rb_2Cr_2O_7$ ($P\bar{1}$), (*b*) $SrCr_2O_7$ [also ions as in (*a*)], (*c*) $Rb_2Cr_3O_{10}$, (*d*) $Rb_2Cr_4O_{13}$, (*e*) ${}^{1}_{\infty}(CrO_3)$.

Table 7. Rb–O *distances* (Å) *less than* 4·0 Å *with estimated standard deviations*

The numbering of the atoms is that of Fig. 1. The vairous tetrachromate ions involved are distinguished by Roman numerals. The notation $-a$, $+b$, and $-c$ indicates an atom translated $-a$, $+b$, and $-c$ respectively.

Rb(1)–O(3)$_{\mathrm{I}}$	2·883 (7)	Rb(2)–O(12)$_{\mathrm{V}}$	2·887 (8)
Rb(1)–O(1)$_{\mathrm{II}(-a)}$	2·896 (6)	Rb(2)–O(11)$_{\mathrm{I}}$	2·891 (8)
Rb(1)–O(1)$_{\mathrm{III}(-a)}$	2·977 (6)	Rb(2)–O(13)$_{\mathrm{I}}$	2·976 (6)
Rb(1)–O(2)$_{\mathrm{IV}(+b-c)}$	2·987 (7)	Rb(2)–O(13)$_{\mathrm{III}}$	2·984 (6)
Rb(1)–O(1)$_{\mathrm{I}(+b)}$	3·034 (6)	Rb(2)–O(13)$_{\mathrm{II}(-c)}$	2·985 (6)
Rb(1)–O(8)$_{\mathrm{V}}$	3·053 (7)	Rb(2)–O(5)$_{\mathrm{IV}(-c)}$	3·069 (6)
Rb(1)–O(3)$_{\mathrm{III}(-a)}$	3·089 (7)	Rb(2)–O(6)$_{\mathrm{I}}$	3·072 (7)
Rb(1)–O(7)$_{\mathrm{I}(+b)}$	3·119 (6)	Rb(2)–O(10)$_{\mathrm{I}}$	3·220 (6)
Rb(1)–O(8)$_{\mathrm{I}(+b)}$	3·277 (7)	Rb(2)–O(5)$_{\mathrm{I}}$	3·252 (7)
Rb(1)–O(4)$_{\mathrm{I}(+b)}$	3·334 (6)	Rb(2)–O(11)$_{\mathrm{III}}$	3·340 (9)
Rb(1)–O(2)$_{\mathrm{II}(-a)}$	3·474 (7)	Rb(2)–O(12)$_{\mathrm{II}(-c)}$	3·348 (8)
Rb(1)–O(9)$_{\mathrm{V}}$	3·891 (7)		

stimulating discussions. I wish to express my sincere gratitude to Professor Arne Magnéli for his kind interest and constructive comments on the manuscript. I am also grateful to Dr Don Koenig for revising the English text. This investigation has been supported by the Swedish Natural Science Research Council.

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Structure Cristalline et Moléculaire de la Phyllochrysine

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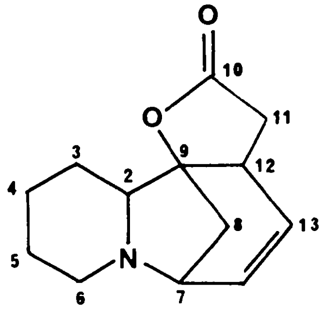
The structure of an alkaloid, phyllochrysine, has been determined by direct methods, using a new approach to the symbolic addition procedure: the phase function. The space group is $P2_12_12_1$ with $a = 8{\cdot}52$, $b = 10{\cdot}60$, $c = 12{\cdot}12$ Å. The final R value is 0·097. The molecular configuration shows that the free electron pair of the nitrogen atom is not directed towards the double bonds, as it was suggested by ultraviolet spectra.

Introduction

Au cours de ces dernières années, l'étude chimique des constituants de différentes espèces végétales de la famille des Euphorbiacées (*Securinega suffraticosa*, *Securinega virosa*, *Phyllantus discoïdes*) a permis de trouver un nouveau type d'alcaloïdes dont le chef de file est la sécurinine.

En 1962, la formule plane de la sécurinine et celle de son antipode optique la virosécurinine avaient été proposées (Saito, Kodera, Sugimoto, Horii & Tamura, 1962; Nakano, Yang & Terao, 1962). L'examen de la formule (I) montre la présence de deux éléments d'asymétrie; l'un est formé par le pont méthylénique 789; l'autre élément d'asymétrie est constitué par le carbone C(2). L'atome d'azote joue également un rôle dans la distribution spatiale des atomes de la molécule par suite d'une conformation préférentielle qui peut être adoptée par son doublet libre.



(I)

Parello, Melera & Goutarel (1963) montraient, à l'aide de la résonance magnétique nucléaire et de certaines dégradations chimiques, qu'un nouvel alcaloïde dénommé phyllochrysine devait être considéré comme un diastéréoisomère de la sécurinine. Les deux isomères diffèrent par la configuration de l'atome de carbone C(2), l'atome d'hydrogène étant en position *cis* ou *trans* par rapport au pont méthylénique.

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