

*Sodium 2-hydroxy-3-butenylglucosinolate O-pentaacetates* (II, R = A = CH<sub>3</sub>CO·O; B = H) and (II, R = B = CH<sub>3</sub>CO·O; A = H). Non-purified thiohydroxamic acid, containing about 1.3 g, was stirred overnight in pyridine (40 ml) with SO<sub>3</sub>:pyridine complex (3.0 g). The mixture was neutralized with 10 % NaHCO<sub>3</sub> (50 ml) and extracted with ether. The aqueous phase was concentrated to dryness at <40°. The sirupy residue was combined with additional material, obtained by resulphonation of the material obtained from the ether extracts, and passed, in aqueous solution, through acid alumina (200 g) (Woelm). The column was rinsed with water (350 ml) and the glucosinolate acetates were eluted with 1 % NaOH. The whole procedure was repeated, yielding, after evaporation to dryness, a lightly yellow syrup (812 mg) which was taken up in ethanol. Addition of ether and prolonged cooling resulted in the separation of a crystalline glucosinolate pentaacetate fraction (340 mg) which was recrystallized twice from 2-propanol before analysis (m.p. 162–170° (rapid heating)), [α]<sub>D</sub><sup>22</sup> – 12.5° (c 2.0, H<sub>2</sub>O). (Found: C 40.23; H 4.68; N 2.16; S 10.10. Calc. for C<sub>21</sub>H<sub>28</sub>NO<sub>15</sub>S<sub>2</sub>Na: C 40.57; H 4.54; N 2.25; S 10.32). On paper chromatography in butanol : ethanol : water (4 : 1 : 4), and spraying with ammoniacal AgNO<sub>3</sub>, only one spot was observed.

*Deacetylation and enzymic hydrolysis.* The above pentaacetate mixture (56 mg) was dissolved in MeOH (3 ml), saturated at 0° with ammonia. Paper chromatography served to establish when ammonolysis of the ester groupings had gone to completion. The residue from the reaction mixture was dissolved in a citrate buffer (pH 6.4), a few drops of a cell-free myrosinase solution and a trace of ascorbic acid were added, and the mixture set aside at room temperature for 3 h. The solution was extracted twice with CHCl<sub>3</sub>. Evaporation, after drying, gave a residue (4.5 mg) from which traces of elementary S were removed by extraction with CS<sub>2</sub>. The crystalline residue (3.8 mg) gave one spot on TLC-chromatography, indistinguishable from that of (+)- or (-)-5-vinyl-2-oxazolidinethione, (III<sub>R</sub>) and (III<sub>S</sub>), and possessed the rotation value [α]<sub>D</sub><sup>20</sup> – 5° (c 0.3, CHCl<sub>3</sub>). The mass spectrum was identical with that of the authentic compounds (III<sub>R</sub>) and (III<sub>S</sub>).

Microanalyses were performed by Mr. G. Cornali and his staff.

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## On the Crystal Structures of Rb<sub>2</sub>Cr<sub>3</sub>O<sub>10</sub> and Rb<sub>2</sub>Cr<sub>4</sub>O<sub>13</sub>

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The crystal structures of rubidium trichromate(VI), Rb<sub>2</sub>Cr<sub>3</sub>O<sub>10</sub>, and rubidium tetrachromate(VI), Rb<sub>2</sub>Cr<sub>4</sub>O<sub>13</sub>, have been investigated. Three-dimensional intensity data were collected with a Siemens automatic diffractometer with Nb-filtered MoK $\alpha$  radiation. The structures were determined from three-dimensional Patterson syntheses, and the atomic positions were refined by use of full-matrix least-squares program. The results are summarized in Tables 1 and 2. For the sake of brevity isotropic temperature factors are given although anisotropic factors were finally used as indicated by the figures.

The trichromate ion consists of three CrO<sub>4</sub> tetrahedra sharing corners (Fig. 1). The Cr–O (terminal) distances range from

Table 1. The crystal structure of  $\text{Rb}_2\text{Cr}_3\text{O}_{10}$ . Unit cell dimensions:  $a=19.04$ ,  $b=11.52$ ,  $c=9.36$  Å and  $Z=8$ . Space group:  $Pbca$  (No. 61) all atoms in  $8(c)$ .

	$x$	$y$	$z$	$B$ (Å <sup>2</sup> )
Rb(1)	0.4161 (1)	0.5481 (2)	0.6521 (2)	2.15
Rb(2)	0.3178 (1)	0.2243 (2)	0.7806 (2)	2.45
Cr(1)	-0.0263 (1)	0.1934 (3)	0.0088 (3)	1.74
Cr(2)	0.1118 (1)	0.1281 (3)	0.2069 (3)	1.70
Cr(3)	0.2329 (1)	0.0042 (3)	0.0108 (3)	1.72
O(1)	-0.0734 (7)	0.1122 (12)	0.1096 (15)	3.06
O(2)	-0.0566 (8)	0.3227 (14)	0.0073 (18)	3.83
O(3)	-0.0241 (9)	0.1444 (16)	-0.1453 (17)	4.40
O(4)	0.0624 (6)	0.1964 (12)	0.0822 (14)	2.48
O(5)	0.1635 (8)	0.2248 (11)	0.2704 (16)	3.44
O(6)	0.0637 (7)	0.0751 (11)	0.3322 (14)	3.15
O(7)	0.1616 (6)	0.0158 (11)	0.1363 (14)	2.56
O(8)	0.2077 (7)	0.0294 (13)	0.8518 (14)	2.83
O(9)	0.2938 (7)	0.0931 (12)	0.0550 (13)	2.52
O(10)	0.2593 (7)	-0.1275 (12)	0.0253 (14)	3.36

Table 2. The crystal structure of  $\text{Rb}_2\text{Cr}_4\text{O}_{13}$ . Unit cell dimensions:  $a=17.67$ ,  $b=7.69$ ,  $c=9.49$  Å,  $\beta=92.0^\circ$  and  $Z=4$ . Space group:  $P2_1/c$  (No. 14) all atoms in  $4(e)$ .

	$x$	$y$	$z$	$B$ (Å <sup>2</sup> )
Rb(1)	0.0698 (1)	0.8353 (2)	0.3219 (1)	2.37
Rb(2)	0.4244 (1)	0.3595 (2)	0.1838 (1)	2.33
Cr(1)	0.0878 (1)	0.3162 (2)	0.4404 (2)	1.81
Cr(2)	0.2485 (1)	0.1386 (2)	0.3191 (2)	1.73
Cr(3)	0.2459 (1)	-0.1894 (3)	0.0921 (2)	2.10
Cr(4)	0.4175 (1)	-0.1856 (3)	0.0392 (2)	1.99
O(1)	0.0164 (5)	0.1862 (12)	0.4244 (9)	2.63
O(2)	0.0893 (6)	0.4047 (14)	0.5940 (11)	3.33
O(3)	0.0808 (6)	0.4600 (14)	0.3197 (10)	3.31
O(4)	0.1727 (5)	0.1818 (12)	0.4180 (9)	2.38
O(5)	0.3260 (5)	0.1479 (13)	0.4109 (10)	3.07
O(6)	0.2551 (5)	0.2702 (13)	0.1940 (10)	2.98
O(7)	0.2373 (5)	-0.0748 (11)	0.2513 (9)	2.44
O(8)	0.1784 (6)	-0.3215 (14)	0.0794 (11)	3.74
O(9)	0.2407 (6)	-0.0582 (15)	-0.0349 (11)	3.79
O(10)	0.3304 (5)	-0.2990 (11)	0.0879 (8)	2.13
O(11)	0.4230 (7)	-0.0091 (17)	0.1265 (13)	4.79
O(12)	0.4130 (7)	-0.1487 (15)	-0.1255 (12)	4.23
O(13)	0.4887 (5)	-0.3101 (12)	0.0780 (9)	2.41

1.55 to 1.61 Å and the Cr—O (bridging) distances from 1.70 to 1.82 Å. Rubidium trichromate is isostructural with the ammonium trichromate  $(\text{NH}_4)_2\text{Cr}_3\text{O}_{10}$  structure, determined by Seiter<sup>1</sup> in 1957.

The tetrachromate ion consists of four  $\text{CrO}_4$ -tetrahedra sharing corners (Fig. 2). The Cr—O (terminal) distances range from 1.56 to 1.62 Å and the Cr—O (bridging) distances from 1.70 to 1.86 Å.

A full description of the structure analyses and a further discussion of the results will be published in the near future.<sup>2</sup>

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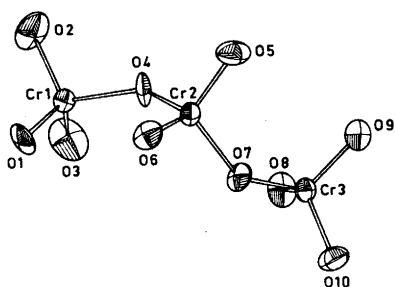


Fig. 1. The trichromate ion.

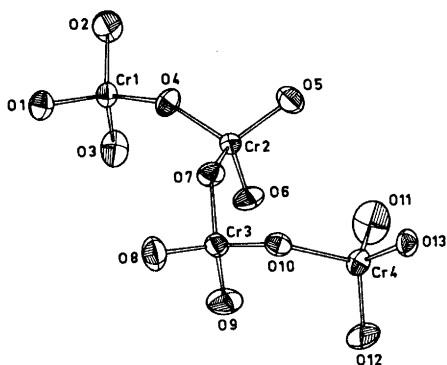


Fig. 2. The tetrachromate ion.

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## Comments on the Use of InSb as Standard for $^{121}\text{Sb}$ Mössbauer Spectroscopy

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The Mössbauer chemical shift ( $\delta$ ) is a function of the total  $s$  electron density at the relevant nucleus. The observed variations in  $\delta$  values for different chemical environments result from changes in the population of the valence orbitals. The orbitals of  $p$  and  $d$  character affect  $\delta$  by virtue of their shielding properties. The  $\delta$  value for a given compound is only meaningful when referred to a standard. The choice of such a standard is not arbitrary — it must fulfil certain requirements. The most important of these are good reproducibility and maximum accuracy in the determination of its  $\delta$  value. The latter condition precludes compounds which possess unresolved quadrupole and/or magnetic interactions or a large line-width.

For  $^{121}\text{Sb}$  Mössbauer spectroscopy InSb, which satisfies the above requirements, is widely accepted as a standard. The environments of both kinds of atoms in InSb are of  $T_d$  symmetry as a consequence of its ZnS zinc blende type crystal structure. Hence, there is no quadrupole interaction in this compound. An additional feature favouring the selection of InSb as a standard is its highly covalent nature. This is a direct result of the close proximity of In to Sb in the Periodic System and the average electron to atom ratio of four. These features have led a number of investigators to postulate  $5s^15p^3$  as the outer electronic configuration for Sb in InSb. It does not necessarily follow, however, that four tetrahedral covalent bonds between the In and Sb atoms imply an  $sp^3$  hybridization or 25%  $s$  character per bond as has been inferred by, *e.g.*, Refs. 1, 2. In fact, the differences in  $s$  and  $p$  orbital electronegativities in the actual molecule cause an electron flow towards or away from the ligands; *cf.*, *e.g.*, Refs. 3–5. Theoretical calculations<sup>6</sup> and electron spin resonance data<sup>7</sup> appear to be compatible with the assumption of zero charge on the atoms in InSb.