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## The Crystal Structure of $(\text{CrO}_3)_\infty$

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The crystal structure of  $\text{CrO}_3$  has been refined with new three-dimensional X-ray data from a linear diffractometer to an  $R$  index of 0.0234. The structure consists of infinite chains of corner-sharing  $\text{CrO}_4$  tetrahedra running parallel to the  $c$  axis. The bridging Cr–O bond length is 1.748 Å and the terminal Cr–O length is 1.599 Å. The angle at the bridging oxygen atom is  $143^\circ$ . Comparison with other accurately determined structures shows that the angles subtended at tetrahedral chromium(VI) atoms are considerably more regular than those at the sulphur or selenium atoms in analogous compounds.

### Introduction

The crystal structure of chromium trioxide was first determined by Byström & Wilhelmi (1950) who collected two-dimensional photographic data. Vaughan (1955) and Hanic & Štempelová (1960) undertook further refinement of the structure using the original (1950) data. The basic structure was confirmed as being made up of linear chains of corner-sharing  $\text{CrO}_4$  tetrahedra. Unfortunately the limited data did not yield accurate molecular dimensions. A complete redetermination with three-dimensional X-ray diffraction data was therefore undertaken as part of a general study of the structures of tetrahedral oxyanions.

### Experimental

Crystals of  $\text{CrO}_3$  were grown near the surface of a saturated solution of  $\text{Na}_2\text{Cr}_2\text{O}_7$  in concentrated  $\text{H}_2\text{SO}_4$ . The growth was at room temperature over a period of two days during which water vapour was absorbed from the air. These crystals were dark red and grew in the form of long, nearly cylindrical, needles. A small single crystal, 2 mm in length and 0.2 mm in diameter, was selected and sealed inside a 0.3 mm Lindemann-glass capillary. The previously reported crystal data

(Byström & Wilhelmi, 1950), as listed in Table 1, were used throughout this work.

Table 1. *Crystal data*

Chromium trioxide, $\text{CrO}_3$ , F.W. = 100.01
Orthorhombic: $a = 4.789$ (5), $b = 8.557$ (5), $c = 5.743$ (4) Å
$U = 235.4$ (5) Å <sup>3</sup> , $D_x = 2.82$ g.cm <sup>-3</sup> ,
$F(000) = 192$
Absorption coefficient: $47.4$ cm <sup>-1</sup> ( $\lambda = 0.7107$ Å)
Absent spectra: $hkl$ when $h+k$ is odd
$h0l$ when $l$ is odd
Space group: $C2cm$

The intensity data were measured on a Hilger–Watts linear diffractometer, using Mo  $K\alpha$  radiation and balanced Zr/Sr filters with the crystal mounted to rotate around the needle  $c$  axis. All reflexions within a hemisphere in reciprocal space out to a maximum  $\sin \theta/\lambda$  value of 0.92 were recorded. The intensities of symmetry-equivalent reflexions were averaged.

In addition, precession photographs of the ( $hhl$ ) and ( $h, 3h, l$ ) planes were taken with Mo  $K\alpha$  radiation and the intensities of these reflexions measured with the aid of a Joyce–Loebl ‘flying spot’ microdensitometer. A total of 334 independent reflexions were measured, 13 of which did not give a significant number of counts on the diffractometer and were not visible on the photographs. These reflexions were assigned appropriate ‘threshold’ intensities.

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Lorentz and polarization corrections were applied in the usual manner. As  $\mu R$  for this crystal was 0.47, absorption corrections were not considered necessary.

**Refinement**

All least-squares (l.s.) refinement was undertaken with the full-matrix program written by J.S. Stephens for the ATLAS computer. The scattering factors for  $Cr^{3+}$  and  $O^-$  were derived by 4-point interpolation from the values given in *International Tables for X-ray Crystallography* (1962). The parameters of Vaughan (1955) were taken as the starting point for the refinement. The first stages of refinement used isotropic vibration parameters and 11 separate scale factors. The weighting scheme of Cruickshank (1961a) was used, with the parameters selected to yield an approximately constant  $\langle w\Delta^2 \rangle$  over the range of  $|F_o|$ . It became apparent that several of the stronger reflexions were quite seriously

affected by secondary extinction. Extinction coefficients† (Zachariassen, 1963) were refined in the l.s. program in the manner advocated by Larson (1967). In this method, the value of  $F_c^*$  including the extinction correction is given by

$$F_c^* = F_c \cdot (1 + g \cdot \beta(2\theta) \cdot |F_c|^2)^{-1/2}, \quad (1)$$

with

$$\beta(2\theta) = L \cdot A \cdot (dA^*/d\mu) \cdot (1 + \cos^4 2\theta)/(1 + \cos^2 2\theta), \quad (2)$$

where  $L$  is the Lorentz factor. The term  $A \cdot (dA^*/d\mu)$  is very nearly constant over the range of  $\theta$  for the data

† In this case, two extinction coefficients are required as the intensity data were collected by two separate techniques. The difficulty is caused by the two different Lorentz factors. A similar situation will arise for sets of *relative* intensity data collected about two (or more) different axes unless the absorption is negligible or the crystal is spherical in shape.

Table 2. Final parameters from the least-squares refinement

E.s.d.'s are shown in parentheses.

	$x/a$	$y/b$	$z/c$	$U_{11} (\text{Å}^2)$	$U_{22} (\text{Å}^2)$	$U_{33} (\text{Å}^2)$	$U_{12} (\text{Å}^2)$	$U_{13} (\text{Å}^2)$	$U_{23} (\text{Å}^2)$
Cr	0.0	0.40324 (5)	0.25						
O(1)	0.1159 (8)	0.5	0.0						
O(2)	0.1245 (14)	0.2323 (5)	0.25						
O(3)	0.3284 (9)	0.3922 (5)	0.25						
Cr	0.0325 (3)	0.0265 (3)	0.0130 (5)	0.0000 (4)	0.0	0.0	0.0	0.0	0.0
O(1)	0.0442 (13)	0.0493 (17)	0.0164 (9)	0.0	0.0	0.0	0.0	0.0	0.0075 (9)
O(2)	0.0541 (24)	0.0295 (15)	0.0456 (18)	0.0093 (17)	0.0	0.0	0.0	0.0	0.0
O(3)	0.0373 (16)	0.0548 (25)	0.0430 (22)	0.0055 (14)	0.0	0.0	0.0	0.0	0.0

Table 3. Observed and calculated structure factors

The third and fourth columns are  $10|F_o|$  and  $10|F_c^*|$  respectively. The 13 unobserved reflexions are preceded by asterisks.

H	K	L = 0	10 F <sub>o</sub>	10 F <sub>c</sub> *	H	K	L = 8	10 F <sub>o</sub>	10 F <sub>c</sub> *
1	3	402 414	3 3	103 99	5	7	83 81	0 10	45 39
1	5	151 149	3 5	273 279	6	2	118 114	1 1	215 209
0	2	300 289	1 1	7 82 85	6	4	65 65	1 3	255 254
0	4	265 260	1 1	9 136 135	3	9	153 134	1 5	469 49
0	6	377 369	1 1	1 27 46	3	9	272 273	1 5	179 182
0	8	149 146	2 2	2 384 398	4	2	167 162	4	2 86 84
0	10	194 192	2 2	4 276 280	4	4	145 144	4	4 81 84
1	1	473 466	2 2	6 157 157	4	6	101 105	4	4 6 73 73
1	3	249 247	2 2	8 205 203	4	8	28 29	4	8 20 20
1	5	371 361	2 10	4 41	5	1	163 165	5	1 102 103
1	7	92 92	3 3	1 262 256	5	3	21 15	5	3 22 11
1	9	151 150	3 3	3 430 448	5	5	100 101	5	5 73 71
1	11	191 191	3 3	5 27 25	5	7	45 44	6	6 88 89
2	0	547 560	3 7	200 202	6	0	144 145	6	2 0 168 166
2	2	206 203	3 9	121 122	6	2	54 53	2	4 104 103
2	4	294 298	4 2	253 250	6	4	84 84	2	6 99 99
2	6	78 78	4 4	154 152	6	6		2	8 28 22
2	8	146 146	4 6	70 70	7	0	369 370	3	1 107 107
3	1	377 378	5 1	79 81	2	2	132 132	3	3 55 52
3	3	211 210	5 3	166 163	2	4	207 208	0	6 149 148
3	5	354 359	5 5	127 118	2	6	189 188	0	6 92 90
3	7	158 158	5 7	86 87	2	8	116 116	3	9 50 47
3	9	119 121	6 2	132 130	2	10	113 114	4	0 82 85
4	0	189 180	6 6	74 74	2	10	117 117	4	2 22 23
4	2	77 75	6 2	132 130	3	1	247 244	1	3 185 183
4	4	245 240	6 4	74 74	3	3	129 126	1	5 35 36
4	6	165 164	6 4	74 74	3	5	250 252	1	7 121 121
4	8	27 14	1 1	332 318	3	7	99 99	1	9 69 69
4	10	113 113	1 3	106 100	3	9	89 91	2	2 172 171
5	1	377 378	1 5	231 234	3	11	144 144	3	5 74 70
5	3	211 210	1 7	117 116	4	2	132 132	3	1 107 107
5	5	354 359	0 2	486 523	4	4	49 50	0	2 202 220
5	7	158 158	0 4	458 448	4	6	49 50	0	6 149 148
5	9	119 121	0 6	229 228	4	8	92 96	0	6 92 90
6	0	189 180	0 8	229 228	4	10	116 116	0	8 116 116
6	2	77 75	0 10	117 117	4	12	113 114	0	10 23 19
6	4	245 240	0 12	209 207	4	14	113 114	1	1 134 134
6	6	165 164	0 14	48 44	4	16	67 66	1	3 185 183
6	8	27 14	0 16	247 244	4	18	49 53	1	5 35 36
6	10	113 113	0 18	106 100	4	20		1	7 121 121
7	0	377 378	0 20	231 234	4	22	99 99	1	9 69 69
7	2	211 210	0 22	486 523	4	24	89 91	2	2 172 171
7	4	354 359	0 24	458 448	4	26	144 144	3	5 74 70
7	6	158 158	0 26	229 228	4	28	132 132	3	1 107 107
7	8	119 121	0 28	209 207	4	30	49 50	0	2 202 220
8	0	189 180	0 30	48 44	4	32	49 50	0	6 149 148
8	2	77 75	0 32	247 244	4	34	92 96	0	6 92 90
8	4	245 240	0 34	106 100	4	36	116 116	0	8 116 116
8	6	165 164	0 36	231 234	4	38	113 114	1	1 134 134
8	8	27 14	0 38	486 523	4	40	67 66	1	3 185 183
8	10	113 113	0 40	458 448	4	42	49 50	1	5 35 36
9	0	377 378	0 42	229 228	4	44	99 99	1	7 121 121
9	2	211 210	0 44	209 207	4	46	89 91	2	2 172 171
9	4	354 359	0 46	48 44	4	48	144 144	3	5 74 70
9	6	158 158	0 48	247 244	4	50	132 132	3	1 107 107
9	8	119 121	0 50	106 100	4	52	49 50	0	2 202 220
9	10	189 180	0 52	231 234	4	54	49 50	0	6 149 148
9	12	77 75	0 54	458 448	4	56	92 96	0	6 92 90
9	14	245 240	0 56	229 228	4	58	116 116	0	8 116 116
9	16	165 164	0 58	209 207	4	60	113 114	1	1 134 134
9	18	27 14	0 60	48 44	4	62	67 66	1	3 185 183
9	20	113 113	0 62	247 244	4	64	49 50	1	5 35 36
9	22	113 113	0 64	106 100	4	66	99 99	1	7 121 121
9	24	377 378	0 66	231 234	4	68	89 91	2	2 172 171
9	26	211 210	0 68	209 207	4	70	144 144	3	5 74 70
9	28	354 359	0 70	48 44	4	72	132 132	3	1 107 107
9	30	158 158	0 72	247 244	4	74	49 50	0	2 202 220
9	32	119 121	0 74	106 100	4	76	49 50	0	6 149 148
9	34	189 180	0 76	231 234	4	78	92 96	0	6 92 90
9	36	77 75	0 78	458 448	4	80	116 116	0	8 116 116
9	38	245 240	0 80	229 228	4	82	113 114	1	1 134 134
9	40	165 164	0 82	209 207	4	84	67 66	1	3 185 183
9	42	27 14	0 84	48 44	4	86	49 50	1	5 35 36
9	44	113 113	0 86	247 244	4	88	99 99	1	7 121 121
9	46	113 113	0 88	106 100	4	90	89 91	2	2 172 171
9	48	377 378	0 90	231 234	4	92	144 144	3	5 74 70
9	50	211 210	0 92	209 207	4	94	132 132	3	1 107 107
9	52	354 359	0 94	48 44	4	96	49 50	0	2 202 220
9	54	158 158	0 96	247 244	4	98	49 50	0	6 149 148
9	56	119 121	0 98	106 100	4	100	92 96	0	6 92 90
9	58	189 180	0 100	231 234	4	102	116 116	0	8 116 116
9	60	77 75	0 102	458 448	4	104	113 114	1	1 134 134
9	62	245 240	0 104	229 228	4	106	67 66	1	3 185 183
9	64	165 164	0 106	209 207	4	108	49 50	1	5 35 36
9	66	27 14	0 108	48 44	4	110	99 99	1	7 121 121
9	68	113 113	0 110	247 244	4	112	89 91	2	2 172 171
9	70	113 113	0 112	106 100	4	114	144 144	3	5 74 70
9	72	377 378	0 114	231 234	4	116	132 132	3	1 107 107
9	74	211 210	0 116	209 207	4	118	49 50	0	2 202 220
9	76	354 359	0 118	48 44	4	120	49 50	0	6 149 148
9	78	158 158	0 120	247 244	4	122	92 96	0	6 92 90
9	80	119 121	0 122	106 100	4	124	116 116	0	8 116 116
9	82	189 180	0 124	231 234	4	126	113 114	1	1 134 134
9	84	77 75	0 126	458 448	4	128	67 66	1	3 185 183
9	86	245 240	0 128	229 228	4	130	49 50	1	5 35 36
9	88	165 164	0 130	209 207	4	132	99 99	1	7 121 121
9	90	27 14	0 132	48 44	4	134	89 91	2	2 172 171
9	92	113 113	0 134	247 244	4	136	144 144	3	5 74 70
9	94	113 113	0 136	106 100	4	138	132 132	3	1 107 107
9	96	377 378	0 138	231 234	4	140	49 50	0	2 202 220
9	98	211 210	0 140	209 207	4	142	49 50	0	6 149 148
9	100	354 359	0 142	48 44	4	144	92 96	0	6 92 90
9	102	158 158	0 144	247 244	4	146	116 116	0	8 116 116
9	104	119 121	0 146	106 100	4	148	113 114	1	1 134 134
9	106	189 180	0 148	231 234	4	150	67 66	1	3 185 183
9	108	77 75	0 150	458 448	4	152	49 50	1	5 35 36
9	110	245 240	0 152	229 228	4	154	99 99	1	7 121 121
9	112	165 164	0 154	209 207	4	156</			

because of the small value of  $\mu R$ , and was set equal to unity.

The refinement was continued with anisotropic vibration parameters for all atoms. The final values of the conventional  $R$  index ( $R_1 = \Sigma|\Delta|/\Sigma|F_o|$ ), and the l.s. residual ( $R_2 = [\Sigma w\Delta^2/\Sigma w|F_o|^2]^{1/2}$ ) were 0.0234 and 0.0286 respectively. Weights for the last cycle were calculated as  $w = 1/(0.187 - 0.0333|F_o| + 0.00167|F_o|^2)$ . In this cycle the largest parameter shift was less than 1% of its estimated standard deviation (e.s.d.) and the average shift/error was 0.004. All 13 'unobserved' reflexions had  $|F_c| < |F_{\text{threshold}}|$  and were therefore given zero weight in the refinement.

The final values of the positional and vibrational parameters are listed in Table 2, together with their e.s.d.'s derived from the inverse l.s. matrix. Table 3 shows the agreement between the observed structure factors and those calculated with the parameters of Table 2.

### Discussion

The structure consists of infinite chains of corner-sharing  $\text{CrO}_4$  tetrahedra running in the  $c$  direction, as shown in Figs. 1 and 2. The tetrahedra lie on mirror planes, and adjacent tetrahedra in each chain are related by twofold axes which pass through the bridging oxygen atoms O(1). Adjacent chains are not joined by chemical bonds and are held together only by van der Waals forces. The preferential growth of  $\text{CrO}_3$  in the  $c$  direction to produce cylindrical crystals is thus readily understood.

Each oxygen atom is surrounded by 12 other oxygen atoms, including those within the same tetrahedron. The distances between oxygen atoms from different tetrahedra lie in the range 2.995 to 3.660 Å. The O...O distances within the tetrahedron fall between 2.564 and 2.871 Å. These distances, uncorrected for thermal motion, are shown in Table 4 and Fig. 2.

An analysis of the vibration parameters of the atoms shows that the chain is not rigid, as O(1) has an appreciable  $U_{11}$  value. Motion of O(1) parallel to  $a$  cannot arise from a torsional oscillation of the chain as a whole, as can be seen from Fig. 2. The motion of O(1) is due primarily to a flexing of the Cr-O-Cr bond angle of  $143^\circ$ . This type of motion does not cause an apparent change in the *equilibrium* Cr-O(1) bond length, and no thermal correction to this distance is necessary. The terminal oxygen atoms, O(2) and O(3), have a motion which is consistent with libration about a point close to the chromium atom, and a libration correction (Cruickshank, 1961*b*) is in order here. This reasoning forms the basis for the 'corrected' bond lengths quoted in Table 5.

From Table 5 it can be seen that the bridging Cr-O(1) bond distance of 1.748 Å is 0.15 Å greater than the mean terminal distance of 1.599 Å. This difference may be due to a difference of  $\pi$ -bond order (Cruickshank, 1961*c*). The angle at the bridging oxygen atom is  $143^\circ$ . All O-Cr-O angles are within  $0.9^\circ$  of the ideal

tetrahedral value of  $109.5^\circ$  despite the difference between the terminal and bridging Cr-O bond lengths. A similar situation is found in  $\text{K}_2\text{Cr}_2\text{O}_7$  (Brandon &

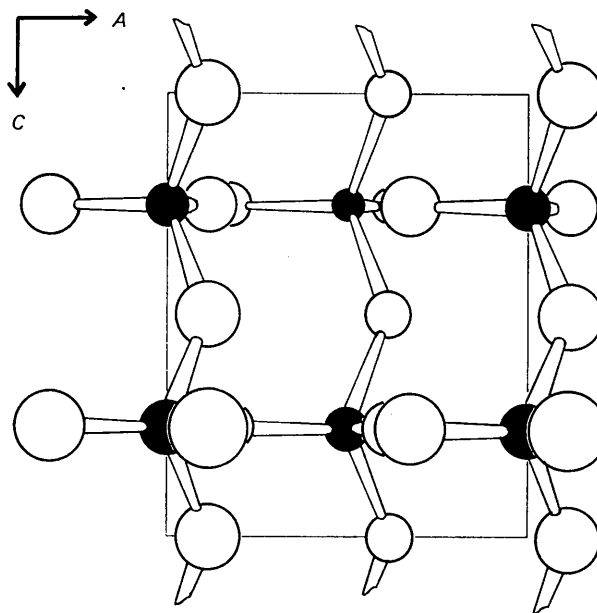


Fig. 1. Projection of the structure down the  $b$  axis showing the parallel non-bonded chains of linked tetrahedra.

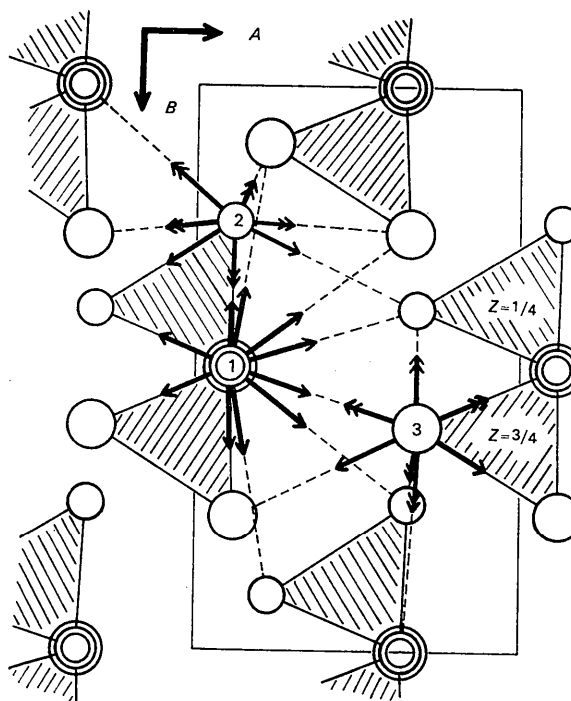


Fig. 2. Projection of the structure down the  $c$  axis (chain direction). Each oxygen atom has 12 near-neighbour contacts with other oxygen atoms. These contacts are shown with solid arrows. Double arrowheads indicate two symmetry-equivalent contacts superimposed in this projection. Concentric circles similarly denote superimposed atoms.

Brown, 1968) where the difference between terminal and bridging bond lengths is 0.16 Å and the O–Cr–O angles have only a 1.3° deviation from their mean of 109.5°. This close constancy of the angles subtended at the central chromium atom is in direct contrast to the analogous sulphates, S<sub>3</sub>O<sub>9</sub> (McDonald & Cruickshank, 1967) and K<sub>2</sub>S<sub>2</sub>O<sub>7</sub> (Lynton & Truter, 1960), where the O···O distances are approximately constant and it is the O–S–O angles which show a wide spread of values. This difference in behaviour cannot be ascribed solely to O···O overcrowding in the sulphates and to the absence of this overcrowding in the chromates, as this sulphate-like behaviour is also found in Se<sub>4</sub>O<sub>12</sub> (Mijlhoff, 1965) where the bond distances are very similar to those in CrO<sub>3</sub>. Summaries of the molecular geometries of these compounds are given in Table 6.

It would seem that the strength of the tetrahedral bonding decreases more rapidly for chromates than for sulphates or selenates when the angles at the central atom are distorted from the ideal tetrahedral value. A simple explanation of this can be seen from a valence-

bond picture of the  $\sigma$ -bonding. In this representation the primary hybridization of sulphur (and selenium) would be  $sp^3$ , but that of chromium would be  $d^3s$ . A tetrahedrally directed  $d^3s$  orbital is 'narrower' than an  $sp^3$  orbital, and a distortion of the bonding angle from the ideal value of 109.5° will result in a greater reduction in the overlap between a  $d^3s$  hybrid and the ligand's  $\sigma$ -orbitals than would occur in the case of  $sp^3$  hybridization. On this basis one would also expect selenates to show angular distortions to a greater extent than chromates. An insufficient number of condensed selenate structures have been reported in the literature to provide complete confirmation, but the results for Se<sub>4</sub>O<sub>12</sub> (see Table 6) show encouraging agreement.

As a final note, it is of interest to compare the average vibrationally-corrected Cr–O bond lengths for isolated CrO<sub>4</sub><sup>2-</sup> groups, singly-linked dichromate ions (Cr<sub>2</sub>O<sub>7</sub>)<sup>2-</sup>, and the doubly-linked CrO<sub>3</sub> chains. For (NH<sub>4</sub>)<sub>2</sub>CrO<sub>4</sub> (Stephens & Cruickshank, 1970) the mean Cr–O bond length is 1.658 Å. In K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (Brandon & Brown, 1968) the mean distance is 1.668 Å and in CrO<sub>3</sub> it is 1.688 Å. The regular increase in the average bond

Table 4. Oxygen···oxygen contact distances

The distances above the broken lines are between oxygen atoms in the same tetrahedron. None of these distances have been corrected for thermal motion.

Distance (Å)		Distance (Å)		Distance (Å)	
O(1)···O(1')	(2) 2.871	O(2)···O(1)	(2) 2.704	O(3)···O(2)	2.564
O(1)···O(2)	(2) 2.704	O(2)···O(3)	2.564	O(3)···O(1)	(2) 2.728
O(1)···O(3)	(2) 2.728	-----		-----	
O(1)···O(3')	(2) 3.160	O(2)···O(3')	2.955	O(3)···O(2')	2.995
O(1)···O(2)	(2) 3.456	O(2)···O(3'')	(2) 3.072	O(3)···O(2'')	(2) 3.072
O(1)···O(3'')	(2) 3.660	O(2)···O(1')	(2) 3.456	O(3)···O(1')	(2) 3.160
		O(2)···O(2')	(4) 3.751	O(3)···O(3')	(2) 3.413
				O(3)···O(1'')	(2) 3.660

Table 5. Distances and angles within the chromate tetrahedron

	Uncorrected distance	Corrected distance	Angle
Cr–O(1)	(2) 1.748 (2) Å	1.748 Å	O(1)–Cr–O(1')
Cr–O(2)	1.579 (5)	1.603	O(1)–Cr–O(2)
Cr–O(3)	1.576 (5)	1.594	O(1)–Cr–O(3)
			O(2)–Cr–O(3)
O(1)···O(1')	2.871	2.871	
O(1)···O(2)	(2) 2.704	2.723	Cr–O(1)–Cr
O(1)···O(3)	(2) 2.728	2.743	
O(2)···O(3)	2.564	2.598	

Table 6. Summaries of the geometries of X<sub>2</sub>O<sub>7</sub> and XO<sub>3</sub> compounds

The values following ± are root-mean-square deviations from the mean.

Average values	K <sub>2</sub> S <sub>2</sub> O <sub>7</sub>	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	S <sub>3</sub> O <sub>9</sub>	(CrO <sub>3</sub> ) <sub>∞</sub>	Se <sub>4</sub> O <sub>12</sub>
Bridge X–O (Å)	1.645	1.786	1.619	1.748	1.77
Terminal X–O (Å)	1.437	1.629	1.395	1.599	1.55
Difference (Å)	0.21	0.16	0.22	0.15	0.22
∠ X–O–X (°)	124.2	125.8	121.5	143.0	123.2
Average X–O (Å)	1.489	1.668	1.507	1.688	1.66
Average O···O (Å)	2.43 ± 0.03	2.70 ± 0.06	2.44 ± 0.04	2.71 ± 0.12	2.69 ± 0.08
∠ O–X–O (°)	109.5 ± 5.0	109.5 ± 1.3	108.9 ± 9.0	109.5 ± 0.8	108.9 ± 5.0

length as the condensation of the chromates increases is undoubtedly significant, and may be compared with similar increases noted for sulphates (Cruickshank & Robinson, 1966).

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## The Crystal Structure of (+)<sub>D</sub>-(N,N,N',N'-Tetrakis-(2'-aminoethyl)-1,2-diaminoethane)cobalt(III) Hexacyanocobaltate(III) Dihydrate

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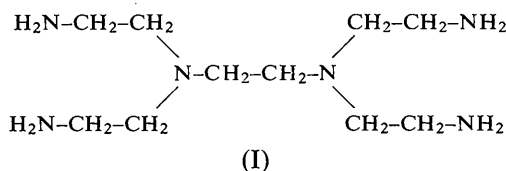
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(+)<sub>D</sub>-(N,N,N',N'-Tetrakis(2'-aminoethyl)-1,2-diaminoethane)cobalt(III) hexacyanocobaltate(III) dihydrate, (+)<sub>D</sub>-[Co(penten)] [Co(CN)<sub>6</sub>].2H<sub>2</sub>O, forms orthorhombic crystals with  $a=15.471$ ,  $b=16.036$ ,  $c=9.253$  Å and four formula units in the unit cell, in space group  $P2_12_12_1$ . The structure has been refined by least-squares methods with anisotropic temperature factors. The structure consists of complex cations, [Co(penten)]<sup>3+</sup>, complex anions, [Co(CN)<sub>6</sub>]<sup>3-</sup> and water molecules. The central cobalt atom of the cation is bonded octahedrally to the six nitrogen atoms of a penten molecule. Three out of the five chelate rings form a girdle about the cobalt atom. Approximately at right angles to the girdle and to one another are two other five-membered chelate rings. All the five-membered chelate rings are not planar. Their conformations are not the same, two of them being enantiomeric with the other three. The absolute configuration of the complex ion, (+)<sub>D</sub>-[Co(penten)]<sup>3+</sup> can be designated as skew chelate pairs, AAA. When applied to this case, the method of ring pairing, together with the octant rule, correctly predicted the sign of the circular dichroism band.

### Introduction

N,N,N',N'-Tetrakis(2'-aminoethyl)-1,2-diaminoethane (I), penten, can function as a sexidentate, giving complexes structurally related to those derived from ethylenediaminetetra-acetic acid (EDTA) (Wiekliem & Hoard, 1959).



Recently the cobalt(III) complex, [Co(penten)]Br<sub>3</sub>, was resolved and the optical properties were examined by Yoshikawa, Fujii & Yamasaki (1967). They confirmed the previous results (Schwarzenbach & Moser, 1953; Emmenegger & Schwarzenbach, 1966). However, the absolute configuration proposed by Yoshikawa, Fujii & Yamasaki (1967) and by Gollogly & Hawkins (1966) is enantiomeric with that proposed by Emmenegger & Schwarzenbach (1966) and by Mason & Norman (1965). Therefore it was highly desired to establish the absolute configuration of the complex ion, [Co(penten)]<sup>3+</sup>. In this paper, the result of the crystal structure analysis of [Co(penten)] [Co(CN)<sub>6</sub>].2H<sub>2</sub>O and the relationship between the absolute configuration of opti-