orthoferrites, -gallates, and -chromites (Quezel-Ambrunaz & Mareschal, 1963).

The materials used in this study were Tb_4O_7, Pr_4O_7, and the sesquioxides of Lu, Tm, Er, Ho, Dy, Gd, Eu, Sm, and Nd and were of at least 99·9% purity. The Rh_2O_3 was supplied by Engelhard. Spectrographic analysis indicated *ca.* 100 p.p.m. each of Fe, Ni, Cr, Si, Al, and Ru and *ca.* 500 p.p.m. Ir, Re, and Pd. The oxides, thoroughly mixed in stoichiometric quantities, were heated in sealed Pt tubes under a pressure of 3 kbar at 1350° for 24 hr. X-ray patterns were obtained at 25° on a Hägg–Guinier camera using monochromatized Cu $K\alpha$ radiation; d values were calculated using (Cu $K\alpha_1$) = 1·54051 Å with a KCl internal standard (a = 6·2931 Å). Cell dimensions were obtained by least-squares refinement of these data using the space group *Pbnm* as determined for $GdFeO_3$ (Geller, 1956) and $YFeO_3$ (Coppens & Eibschütz, 1965). Table 1 lists the cell dimensions and Table 2 lists the crystallographic data for the 11 rare earth orthorhodites.

In Fig. 1 the cell dimensions are plotted *vs.* the effective ionic radii of the trivalent rare earth ions (Shannon & Prewitt, 1969). Cell dimensions of $LaRhO_3$ were taken from Wold, Post & Banks (1957). Effective ionic radii are plotted because it is felt that the variation with radius is more apt to be regular than with atomic number. The plot clearly shows a regular increase in b up to Gd followed by a decrease for Eu, Sm, Nd, Pr, and La. This anomalous behavior has been correlated by Marezio *et al.* (1968) to a regular increase in the average M–O distance of the eight first-nearest neighbors and a decrease in the average M–O distance of the four second-nearest neighbors as M increases from Lu to La. This behavior is also reflected in the plot of r_M^3 *vs.* unit-cell volume for these compounds (Prewitt & Shannon, 1969). Whereas most r^3 *vs.* V plots are linear, r_M^3 *vs.* V plots for the $MM'O_3$ perovskites where M′ = Al, Cr, Ga, Fe, Rh, Sc and In have a pronounced curvature. Plots of $r_m^3{}'$ *vs.* V are linear as expected because the coordination of the M′ cations does not change (Shannon, 1967).

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The refinement of the crystal structure of $Na_2Co_5Mo_4Cl_4O_{16}$.

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The diffraction data of the compound $Na_2Co_5Mo_4Cl_4O_{16}$ have been refined by least-squares methods, using the block-diagonal approximation, to R = 9·6%. The site occupancy factors for the non-oxygen atoms have been investigated and shown to be unity. Although the coordinates of the heavy atoms have changed but little the refined oxygen coordinates have yielded significantly different cation–oxygen distances.

The diffraction data of the compound $Na_2Co_5Mo_4Cl_4O_{16}$, the structural details of which were published in an unrefined form (Smith, 1965) have now been subjected to a full three-dimensional least-squares analysis. For the sake of completeness the crystal data are restated.

Crystal data:

Monoclinic, space group $C2/m$
a = 10·706 ± 0·003 Å
b = 8·852 ± 0·002
c = 10·663 ± 0·003
β = 109° 45′ ± 6′
V = 951 Å³
Z = 2

Atoms are in positions:

4 Na in 4(i)
8 Co(1) in 8(j)
2 Co(2) in 2(c)
4 Mo(1) in 4(i)
4 Mo(2) in 4(i)
8 Cl in 8(j)
8 O(1) in 8(j)
8 O(2) in 8(j)
4 O(3) in 4(i)
4 O(4) in 4(i)
4 O(5) in 4(i)
4 O(6) in 4(i)

Refinement

Starting from the previous atomic parameters an isotropic refinement using the block-diagonal approximation was carried out on 2132 reflexions. Included in this data list were 288 unobserved structure amplitudes which were allocated an F value equivalent to $\frac{1}{2}F_{\text{min}}$. Convergence was reached at $R=11{\cdot}4\%$. The weighting scheme used was $\sqrt{w}=1$ if $|F_o|\le a$ or $a/|F_o|$ if $|F_o|<a$. The form factors used were those due to Hanson, Herman, Lea & Skillman (1964) with corrections for the real part of the dispersion for the Co and Mo atoms. Fractional occupancies of the heavy atom sites were investigated by analogy with sodium cobalt molybdate (Ibers & Smith, 1964) since both compounds were extraced from the same melt. After two further refinement cycles there were no significant changes in the value of R or the temperature factors of these atoms, nor was there a significant difference from unity for the occupancy factors n (Table 1).

Anisotropic temperature factors were then introduced for all the non-oxygen atoms. Only a small improvement in R to 11·0% was obtained with all shifts becoming very small and random. The agreement analysis showed that the inclusion of the weighted unobserved reflexions into the data was the cause and following their exclusion further cycles of refinement were calculated until convergence was obtained at $R=9{\cdot}6\%$.

A single overall scale factor was employed throughout, with interlayer scaling made at intervals. The parameter in the weighting scheme was adjusted to maintain the quantities $\sum w\Delta^2$ constant over the ranges of F_{obs}. The value in the final cycles was $a=60{\cdot}0$. The final atomic parameters are given in Table 1 and the temperature factors in Table 2 which includes the values of B for the non-oxygen atoms obtained in the last isotropic cycle.

Discussion

The atomic positions of the atoms have changed only slightly from the previous published list. In particular the heavier atoms have hardly moved but there have been sufficient shifts in the oxygen parameters to cause significant changes in cation–oxygen distances. Table 3 lists selected interatomic distances. The Mo–O bond distances in the MoO_4 tetrahedra have decreased as a result of refinement. Each tetrahedra now possesses one long bond of 1·81 Å Mo(1)–O(3) and Mo(2)–O(4) and three other shorter bonds. In the tetrahedron about Mo(1) these three bonds are almost equal and the tetrahedron is nearly regular with angles subtended by Mo(1) lying in the range 107·7–111·0°. The Mo(2) tetrahedron is slightly less regular probably as a result of O(5) which has two contacts with the sodium atom. The tetrahedral angles in this case have a slightly greater spread 107·5–111·9°. The standard deviation of all these angles is 0·4°. O(5) and O(6), which are both bonded to the sodium atom, have relatively high temperature factors compared with the other oxygen atoms. Additionally the sodium atom has by far the highest temperature factor since it is free to vibrate, especially in the y direction, in its loose environment, which is in any case unusual. It possesses three close neighbour oxygen atoms, two O(5) atoms and one O(6) atom, and the angles it subtends with them are very unequal, *e.g.* O(5)–Na–O(6) = 110·8°, O(5)–Na–O(5) = 89·8° and O(6)–Na–O(5) = 159·4°. There are also two pairs of chlorine atoms at distances of 2·97 and 3·10 Å both of which are greater than the distance 2·81 Å in sodium chloride. The environment of the sodium atom cannot be described in terms of a single coordination polyhedron; on the one hand there is the planar trigonal arrangement of oxygen atoms and on the other there is a distorted pyramid formed by the chlorine atoms and the O(6) atom with the sodium atom displaced from the base. The chlorine–chlorine distances in this pyramid are 3·48

Table 1. *The final atomic coordinates (fractional) and their standard deviations*
n = occupancy factor

	x	y	z	n
Mo(1)	0·0396 (1)	0·0000	0·1913 (1)	1·015 (7)
Mo(2)	0·4466 (1)	0·0000	0·1532 (1)	1·019 (7)
Co(1)	0·2644 (1)	0·1790 (1)	0·8654 (1)	0·980 (7)
Co(2)	0·0000	0·0000	0·5000	1·004 (16)
Na	0·3260 (10)	0·0000	0·4918 (10)	1·023 (42)
Cl	0·1650 (3)	0·1964 (3)	0·6242 (2)	0·977 (13)
O(1)	0·3523 (7)	0·1629 (8)	0·0845 (7)	
O(2)	0·1025 (8)	0·1621 (9)	0·1399 (7)	
O(3)	0·1404 (10)	0·0000	0·8715 (10)	
O(4)	0·3936 (10)	0·0000	0·8717 (10)	
O(5)	0·4767 (12)	0·0000	0·3218 (12)	
O(6)	0·0955 (12)	0·0000	0·3675 (12)	

Table 2. *Final temperature factor parameters and standard deviations*
Anisotropic temperature factor $=\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{23}kl+\beta_{13}hl)\right]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B
Mo(1)	0·0009 (1)	0·0016 (1)	0·0010 (1)	—	0·0006 (1)	—	0·426
Mo(2)	0·0008 (1)	0·0014 (1)	0·0016 (1)	—	0·0008 (1)	—	0·478
Co(1)	0·0012 (1)	0·0017 (1)	0·0017 (1)	−0·0002 (2)	0·0012 (1)	0·0001 (2)	0·589
Co(2)	0·0020 (2)	0·0039 (3)	0·0019 (2)	—	0·0016 (3)	—	0·864
Na	0·0048 (8)	0·0115 (13)	0·0051 (8)	—	−0·0012 (13)	—	2·278
Cl	0·0035 (2)	0·0042 (3)	0·0021 (1)	−0·0003 (3)	0·0012 (3)	−0·0020 (3)	1·087
O(1)							0·934
O(2)							1·085
O(3)							0·871
O(4)							0·872
O(5)							1·241
O(6)							1·212

and 3·81 Å, the latter distance being greater than the 3·63 Å distance in the octahedra about Co(2). The angle Cl–Co(2)–Cl is 87·6 and has not changed significantly from the previously published result. Also the refinement has not significantly altered the octahedron about Co(1).

Table 3. *Selected interatomic distances with standard deviations*

Mo(1)–O(2)	1·75 Å	(0·008)
–O(3)	1·81	(0·012)
–O(6)	1·77	(0·012)
Mo(2)–O(1)	1·77	(0·007)
–O(4)	1·82	(0·012)
–O(5)	1·72	(0·012)
Co(1) –O(1)	2·06, 2·21	(0·007)
–O(2)	2·02	(0·008)
–O(3)	2·08	(0·008)
–O(4)	2·09	(0·008)
–Cl	2·43	(0·003)
Co(2) –O(6)	2·01	(0·012)
Cl	2·51	(0·003)
Na —O(5)	2·36, 2·80	(0·016)
–O(6)	2·37	(0·016)
–Cl	2·97, 3·10	(0·005)
Cl——Cl	3·48, 3·63, 3·81	(0·004)

All the nearest O–O distances are now confined to a narrower range of values 2·71–3·02 Å with the bulk of these lying between 2·83 and 2·98 Å. The average standard deviation of these distances is 0·01 Å.

The calculations were performed on an ICL-1907 computer using programs written by F. R. Ahmed for the IBM 360 and modified by Dr J. D. Lee (Loughborough Univ.) and by one of us (BGAM).

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On the structure of β-thianthrene dioxide.

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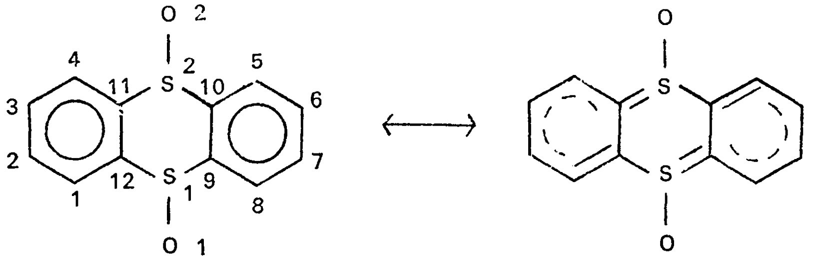
The published X-ray diffraction data for β-thianthrene dioxide have been re-examined. Bond lengths and angles were obtained which are in agreement with the expected symmetry of the central, heterocyclic ring.

In connection with some recent work on the crystal structure of a sulfone (Ammon, Watts, Stewart & Mock, 1968), we have made an extensive literature search for information on carbon–sulfur bond lengths in sulfides, sulfoxides, and sulfones. The four *Csp*^{2}–S distances reported (Hosoya, 1966) for β-thianthrene dioxide (I) showed a symmetrical pattern of short and long bonds and, in conjunction with bond distances in the two benzene nuclei, suggested that structure (II) might make a significant contribution to the resonance hybrid. This represented an intriguing possibility, and we have further studied the data published for β-thianthrene dioxide to check the C–S bond length asymmetry.

Our work started with a recalculation of bond lengths, angles, and their estimated standard deviations using the cell constants and carbon, oxygen, and sulfur coordinates reported by Hosoya (1966). The lengths and angles obtained from this calculation differed markedly from many of those in the original work (Tables 1 and 2).* Several characteristics of the new values relative to the old data were: (*a*) the C–S bond length differences were considerably smaller; (*b*) bond length e.s.d.'s were smaller; (*c*) differences



(I) (II)

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[*] Jackobs & Sundaralingam (1969) have reported a partial list of bond length and angle data which was derived from a similar recalculation.