

**The Crystal Structure of Calcium Potassium  
(+)<sub>589</sub>-Tris(dithiooxalato)cobaltate(III) Tetrahydrate:  
an Application of Anomalous Dispersion Patterson Methods**

BY K. R. BUTLER AND M. R. SNOW

*Department of Physical and Inorganic Chemistry, The University of Adelaide, Adelaide, S.A. 5001, Australia*

(Received 9 September 1974; accepted 13 September 1974)

The crystal structure of  $\text{CaK}(+)\text{[Co(S}_2\text{C}_2\text{O}_2)_3\text{]} \cdot 4\text{H}_2\text{O}$  has been determined by anomalous dispersion Patterson techniques from 2086 counter reflexions. The crystals are orthorhombic, space group  $P2_12_12_1$ , with  $a = 12.381$  (5),  $b = 12.791$  (5) and  $c = 11.801$  (5) Å. The measured density is  $2.01$  (2)  $\text{g cm}^{-3}$  which agrees with the calculated density of 2.03 for  $Z = 4$ . The absorption-corrected data gave an  $R$  of 0.062 on full-matrix least-squares refinement. Bonding to cobalt in the 6-coordinate tris(bidentate chelate) complex is through the sulphur atoms; the average  $\text{Co}^{\text{III}}\text{-S}$  distance is  $2.244$  (5) Å and the average chelate bite angle is  $89.7$  (2)°. The absolute configuration of the complex is  $A$  in accord with spectroscopic prediction. The potassium ion achieves effective 7- and the calcium ion 9-coordination through contacts with sulphur and oxygen.

### Introduction

A knowledge of the structure and absolute configuration of metal complexes is useful in the interpretation of their circular dichroism (Mason, 1963; Piper & Karipides, 1962, 1964; Butler & Snow, 1971*a, b*). It is of interest to obtain structural data for widely different geometries to test competing theories of the origin of their spectra. The structure of  $(+)\text{[Co(thioox)}_3\text{]}^{3-}$  (thioox is 1,2-dithiooxalate) was undertaken to check the spectroscopic prediction of absolute configuration (Hidaka & Douglas, 1964), to confirm that bonding to cobalt was *via* the sulphur atoms, and, since no thioox complexes have been structurally determined, to examine the geometric result of replacing six coordinating oxygens in the oxalato analogue of known structure (Butler & Snow, 1971*c*) by sulphur. A preliminary report of the structure with a discussion of the relationship of structure parameters to circular dichroism for a series of complexes has been published (Butler & Snow, 1972).

### Experimental

The complex ion was prepared and resolved by established methods (Dwyer & Sargeson, 1959) except that the  $\text{Ca}^{2+}$  ion, rather than  $\text{Ba}^{2+}$  was chosen as the co-crystallizing cation with  $\text{K}^+$  in order to reduce the scattering power of the crystals ( $[\text{M}]_{589} = +6680^\circ$ , literature  $+5000^\circ$  for  $\text{KBa}$  salt). Recrystallization of  $\text{KCa}(+)\text{[Co(thioox)}_3\text{]} \cdot 4\text{H}_2\text{O}$  from aqueous solution gave burgundy-coloured rectangular prisms elongated along [001] and bearing (111) and  $(\bar{1}\bar{1}\bar{1})$  bevels at one end; the faces parallel to [001] were  $\{110\}$ .

Preliminary photographic investigation of several crystals revealed that twinning parallel to [001] was a serious problem. Two crystals free from twinning were eventually found, coated with a thin film of Canada

balsam to reduce possible dehydration and mounted about [001] and [100] for data collection. The cell constants were determined on a Buerger-Supper equi-inclination diffractometer, with a pinhole detector aperture from the  $2\theta$  values of the  $K\alpha_1$  components of several axial, high-order zero-layer reflexions. The crystal data are collected in Table 1.

Table 1. *Crystal data*

$\text{C}_6\text{H}_8\text{CaCoKO}_{10}\text{S}_6$	F.W. 570.6
Orthorhombic	Space group $P2_12_12_1$
$a = 12.381$ (5) Å	$F(000) = 1144$
$b = 12.791$ (5)	$D_m = 2.01$ $\text{g cm}^{-3}$
$c = 11.801$ (5)	$D_c = 2.03$
$Z = 4$	$\mu(\text{Cu } K\alpha) = 175$ $\text{cm}^{-1}$

$$[\lambda(\text{Cu } K\alpha_1) = 1.54051 \text{ \AA}]$$

Data were collected by the  $\omega$ -scan and variable scan-speed technique (Freeman, Guss, Nockolds, Page & Webster, 1970; Guss, Nockolds & Wood, 1970), and the control parameters for the scan-range and scan-speed calculations as defined in the references were:  $\Delta\lambda = 0.007$ ,  $X = 0.6^\circ$ ,  $\varphi_m = 1.15^\circ$ ,  $P = 0.001$ ,  $\delta\mu = 0.05$ ,  $\varphi_{\text{max}} = 0.333^\circ \text{ s}^{-1}$ ,  $\varphi_{\text{min}} = 0.05^\circ \text{ s}^{-1}$ , and  $R_e = 4\%$ .

With the crystal mounted along [001], reflexions for layers  $0 \leq l \leq 9$  of both  $hkl$  and  $\bar{h}k\bar{l}$  forms were collected in the range  $10^\circ < \psi < 140^\circ$ . The layers  $0kl$  to  $8kl$  were measured only for the  $hkl$  octant with the [100] mounted crystal. For each reflexion with integrated peak count  $P$  and background counts  $B_1$  and  $B_2$ , the intensity  $I(hkl)$  was given by  $I(hkl) = P - (B_1 + B_2)$  and its standard deviation by  $\sigma[I(hkl)] = (P + B_1 + B_2)^{1/2}$ . Lorentz-polarization and analytical absorption corrections (De Meulenaer & Tompa, 1965; Alcock, 1970) were applied to give a set of corrected structure amplitudes  $|F_o(hkl)|$  and standard deviations  $\sigma|F_o(hkl)|$ . The [001] crystal measured  $0.135 \times 0.137 \times 0.283$  mm,

and had transmission factors in the range 0.125 to 0.210. The [100] crystal measured  $0.129 \times 0.129 \times 0.182$  mm and had transmission factors in the range 0.10 to 0.25. The two sets of data were scaled together (Rae, 1965). 2374 reflexions were obtained including 1226 non-equivalent Friedel pairs. Of these 188 had  $I(hkl) < 3\sigma[I(hkl)]$  and were not included in the refinement.

### Solution and refinement of the structure

A Patterson synthesis employing a data set with averaged  $I(hkl)$  and  $I(\bar{h}\bar{k}\bar{l})$  reflexions could not be solved in view of the very large number of similarly sized peaks on the Harker sections. These sections and the whole Patterson have regularly spaced peaks  $\sim 2.3$  Å apart at the points of a face-centred grid parallel to the unit-cell faces. These suggested an orientation of the  $\text{CoS}_6$  group, but the cobalt atom could not be placed so that other atoms appeared in subsequent Fourier maps. The principal atoms have very similar atomic numbers (Co, 27; Ca, 20; K, 19; S, 16) and the initial choice of substituting Ba (atomic number 56) for Ca rendered the heavy-atom method inapplicable. The alternative methods of solution were direct methods or Patterson syntheses employing Friedel pairs. Since the appropriate data were available and the latter methods yield the absolute configuration directly these methods were chosen. The anomalous dispersion terms  $\Delta f''$  for Cu  $K\alpha$  radiation are Co, 3.95; Ca, 1.34; K, 1.11; and S, 0.58 (Cromer, 1965).

Two anomalous Patterson syntheses were computed: (a) based on  $|\Delta F|^2 = |F_o(\bar{h}\bar{k}\bar{l}) - F_o(hkl)|^2$  for all data showing any difference of the Friedel pairs, 851 terms, and (b) based on  $\Delta I = [I(\bar{h}\bar{k}\bar{l}) - I(hkl)]$  where  $|\Delta I| > 2\sigma|I(hkl)|$ , 417 terms; an analogous significance test should have been applied in case (a). Reflexions with one index zero, and therefore having equivalent Friedel pairs in point group 222, were excluded from the data sets. Synthesis (a) is the anomalous squared synthesis (Ramachandran & Ramachandra Ayyar, 1963) and (b) is a modification of the anomalous difference Patterson (Okaya & Pepinsky, 1961). In principle, synthesis (a) should show only the Harker peaks for the anomalous scatterers whereas (b) also gives peaks due to interaction of the anomalous scatterers with the normal scatterers. Interactions involving normal scatterers only should be absent from both maps.

Although the disposition of peaks was similar in the two maps there were some differences in relative peak heights. Interpretation of the dominant peaks on the Harker sections gave a starting position for Co at  $(\pm 0.078, 0, \pm 0.213)$ , but the usual heavy-atom Fourier procedures would not readily yield further atomic positions. The maps showed the expected mirror in the  $xz$  plane. A  $\beta$ -anomalous synthesis (Ramachandran & Ramachandra Ayyar, 1963) was computed with coefficients  $(\Delta I/F''_{Co}(hkl))\exp i\alpha''_{Co}$ , where  $F''_{Co} = |F''_{Co}| \exp i\alpha''_{Co}$  is the contribution from the imaginary component of the scattering by the cobalt atom

located at  $(0.078, 0, 0.213)$ . This map yielded six sulphur sites which taken with the cobalt site in a structure-factor calculation gave  $R_1 = 0.512$  ( $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ). The  $\beta$ -anomalous synthesis has proved very powerful in situations where false symmetry is generated by the single heavy atom (here and previously; Snow, 1972). The calcium and potassium sites were determined by comparison of the original Patterson and the anomalous squared syntheses since the cobalt and sulphur Harker peaks could now be assigned. Two possible starting positions for these atoms were found and inclusion of one of them as calcium in the above model gave  $R_1 = 0.478$ ; the alternative structure with the mirror image set of sulphur atoms gave  $R_1 = 0.503$ . Positional refinement of this eight-atom model lowered  $R_1$  to 0.305 for the 1548 averaged data. A subsequent difference map located all the remaining atoms. Refinement of this 25-atom model by least-squares calculations minimizing  $\sum w||F_o| - |F_c||^2$ , where the weights  $w$  are equal to  $1/\sigma^2|F_o|$ , and employing isotropic temperature factors, gave  $R_1 = 0.109$  and  $R_2 = 0.100$  ( $R_2$  is  $[w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$ ). The allocation of the  $\text{Ca}^{2+}$  and  $\text{K}^+$  ions to their sites was confirmed by evaluating the close-contact distances with other atoms. The contact distances with  $\text{Ca}^{2+}$ , are 0.3 to 0.4 Å shorter than those with  $\text{K}^+$  (*International Tables for X-ray Crystallography*, 1968) for the same element and coordination number. The opposite absolute configuration gave  $R_1 = 0.148$ , confirming that the correct absolute configuration can be derived from Patterson functions based on Friedel-pair intensity differences. The least-squares calculations employed scattering factors for  $\text{Co}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ , S, O and C (Cromer & Waber, 1965) with allowance for the  $\Delta f'$  and  $\Delta f''$  terms for the first four atoms (Cromer, 1965).

Refinement was continued with anisotropic temperature factors. Computer storage limitations necessitated blocking the parameters; the positional parameters (76) and the temperature parameters (151) were refined alternately with the scale factors included in all cycles. At convergence (parameter shifts less than  $0.1\sigma$ )  $R_1$  was 0.062 ( $R_2 = 0.060$ ), but the anisotropic temperature factors of C(5) and C(6) were non-positive-definite. The distribution of  $w(|F_o| - |F_c|)^2$  averaged in ranges of  $|F_o|$  versus  $|F_c|$  was constant at  $1.6 \pm 0.4$ , but showed a systematic increase to 9.0 and 16.0  $e^2$  for the two highest  $|F_o|$  ranges. There was no evidence of a secondary extinction effect. The standard deviations were derived from counting statistics and did not incorporate an empirical  $(\rho[I(hkl)])^2$  term to allow for errors from other sources (Corfield, Doedens & Ibers, 1967). The problem with the carbon atoms noted above may be due to this omission. Derivation of the estimated standard deviations of the parameters is formally invalid for weighting schemes with this property; the effect is most noticeable for the standard deviations of the thermal parameters (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961).

The large and highly anisotropic temperature factor

for  $\text{K}^+$  could not be better represented as a pair of atoms with multipliers of 0.5. Refinement of the disordered model gave no better agreement on Hamilton's (1965) criterion. A final difference map did show the largest disturbance at this site equivalent to 20% of a carbon atom in previous difference syntheses. The hydrogen atoms of the water molecules were not found; their absence from the model and the unsatisfactory representation of the  $\text{K}^+$  disorder by an anisotropic temperature factor can also be expected to contribute to the trend of  $w(|F_o| - |F_c|)^2$  at high  $|F_o|$ . The observed and calculated structure factors ( $e \times 10$ ) have been deposited.\*

The positional and thermal parameters are given in Table 2 with their estimated standard deviations. Programs used for solution, refinement and geometry calculations were local modifications of the following: Busing & Levy's *ORFLS* and *ORFFE*, Zalkin's *FORDAP*, Johnson's *ORTEP* and Blount's *PLANE* and *BLANDA*.

### Results and discussion

The  $(+)_S89-[\text{Co}(\text{thioox})_3]^{3-}$  anion has the *A* configuration, *IUPAC Information Bulletin*, 1968 predicted from solution circular dichroism correlations (McCaffery, Mason & Ballard, 1965; Hidaka & Douglas, 1964). Both  $A(-)-[\text{Co}(\text{oxalate})_3]^{3-}$  and the thiooxalate complex have a dominant positive circular dichroism in the region of the  $^1A_{1g} \rightarrow ^1T_{1g}$  transition.

\* This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30677 (11 pp). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Fig. 1 shows the (+)  $[\text{Co}(\text{thioox})_3]$  anion and its immediate cation neighbours in projection down *b*. Tables 3, 4 and 5 contain the important molecular and crystal geometry. In space group  $P2_12_12_1$  the complex possesses no crystallographic symmetry and shows small deviations from an idealized 32 geometry. The approximate threefold axis is nearly parallel to *b* and one of the approximate twofold axes is nearly parallel to *a*. The grid pattern of peaks in the Patterson syn-

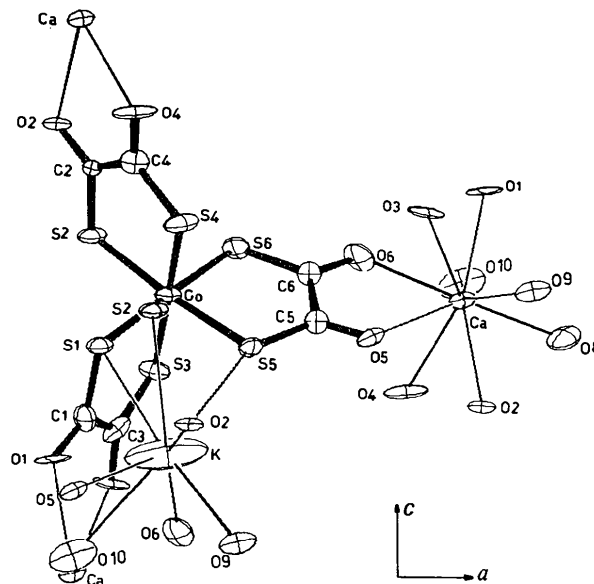


Fig. 1.  $\text{KCa}(+)-A-[\text{Co}(1,2\text{-dithiooxalate})] \cdot 4\text{H}_2\text{O}$ . Projection down the *b* axis showing the anion environment. Atoms are represented as 50% probability ellipsoids [C(5) and C(6) have been represented as spheres corresponding to their isotropic *B* factors].

Table 2. Positional ( $\times 10^4$ ) and thermal ( $\times 10^5$ ) parameters for  $\text{KCa}(+)_S89-[\text{Co}(\text{thioox})_3] \cdot 4\text{H}_2\text{O}$

	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Ca	780 (2)	4397 (2)	-2121 (2)	413 (21)	302 (17)	214 (22)	25 (18)	54 (21)	-7 (19)
K	778 (6)	-2806 (3)	-733 (4)	4089 (118)	507 (34)	704 (46)	274 (58)	538 (74)	80 (33)
Co	774 (2)	-138 (2)	2130 (2)	413 (17)	337 (15)	165 (17)	21 (13)	1 (17)	34 (14)
S(1)	-371 (3)	-1191 (3)	1187 (3)	419 (29)	393 (24)	204 (30)	-36 (21)	15 (25)	58 (24)
S(2)	-529 (3)	587 (3)	3171 (3)	528 (32)	451 (25)	166 (30)	191 (24)	29 (25)	73 (23)
S(3)	558 (3)	1085 (3)	767 (3)	587 (36)	359 (26)	234 (30)	-84 (24)	-82 (28)	75 (22)
S(4)	976 (3)	-1384 (3)	3434 (3)	722 (38)	406 (28)	258 (32)	221 (25)	125 (30)	101 (24)
S(5)	2178 (3)	-869 (3)	1204 (3)	360 (27)	396 (26)	270 (32)	-16 (21)	53 (26)	-141 (24)
S(6)	1910 (3)	961 (3)	2997 (3)	450 (30)	463 (26)	334 (36)	62 (22)	-21 (28)	-195 (27)
O(1)	-1142 (8)	-996 (8)	-860 (7)	796 (100)	578 (79)	55 (78)	-113 (72)	101 (72)	-128 (67)
O(2)	-1154 (8)	100 (8)	5197 (7)	505 (85)	611 (84)	103 (81)	3 (68)	-12 (68)	-38 (67)
O(3)	-146 (8)	815 (7)	-1279 (8)	794 (95)	518 (78)	90 (76)	77 (67)	-123 (73)	93 (68)
O(4)	160 (9)	-1526 (7)	5454 (8)	1187 (120)	350 (68)	144 (80)	31 (75)	118 (80)	79 (67)
O(5)	4217 (7)	-498 (7)	1423 (7)	452 (76)	453 (67)	252 (75)	24 (65)	148 (72)	-18 (61)
O(6)	4004 (8)	1063 (7)	2872 (8)	562 (86)	449 (69)	514 (93)	-34 (63)	-156 (83)	-243 (75)
C(1)	-603 (11)	-620 (11)	-111 (12)	302 (117)	456 (109)	468 (133)	-131 (98)	-51 (109)	4 (104)
C(2)	-553 (10)	-124 (10)	4411 (11)	214 (113)	497 (105)	172 (113)	21 (89)	-15 (92)	19 (92)
C(3)	-70 (11)	452 (11)	-303 (12)	431 (121)	451 (110)	448 (145)	-4 (92)	236 (110)	29 (105)
C(4)	169 (11)	-1051 (10)	4550 (12)	493 (124)	207 (88)	425 (138)	28 (88)	-3 (107)	-54 (99)
C(5)	3288 (10)	-294 (9)	1683 (10)	453 (107)	325 (94)	119 (110)	120 (78)	267 (97)	211 (88)
C(6)	3154 (11)	658 (10)	2556 (10)	504 (114)	264 (83)	105 (115)	-8 (86)	-135 (96)	187 (89)
O(7)	2845 (8)	2792 (7)	721 (8)	691 (96)	470 (77)	374 (93)	-22 (72)	-1 (84)	-41 (70)
O(8)	2553 (8)	3771 (8)	-1470 (8)	701 (95)	693 (89)	416 (98)	175 (73)	148 (78)	291 (81)
O(9)	2995 (8)	4051 (7)	2690 (8)	793 (92)	443 (70)	320 (88)	17 (70)	131 (79)	-24 (70)
O(10)	773 (10)	2505 (7)	-2429 (8)	1336 (125)	271 (64)	695 (110)	-9 (83)	289 (107)	51 (71)

thesis is immediately understandable in terms of the similarity of the Co, Ca and K coordinates and the orientation of the complex ion in the cell.

The calcium ion is 9-coordinated; the arrangement best approximates the favoured tricapped trigonal-prismatic geometry (Helmholz, 1939; Muetterties & Wright, 1967). O(5), O(9) and O(10) are the atoms capping the rectangular faces of the trigonal prism

Table 3. Bond distances (Å) and angles (°)

Ligand 1		Ligand 2		Ligand 3	
Co—S(1)	2.250 (4)	S(1)—Co—S(3)	89.30 (14)	Co—S(5)	2.256 (4)
S(1)—C(1)	1.721 (14)	Co—S(1)—C(1)	106.9 (5)	S(5)—C(5)	1.658 (14)
C(1)—O(1)	1.207 (14)	S(1)—C(1)—O(1)	125.1 (11)	C(5)—O(5)	1.220 (13)
C(1)—C(3)	1.539 (18)	S(1)—C(1)—C(3)	115.9 (10)	C(5)—C(6)	1.603 (16)
C(3)—O(3)	1.246 (15)	O(1)—C(1)—C(3)	119.0 (13)	C(6)—O(6)	1.231 (14)
S(3)—C(3)	1.689 (15)	Co—S(3)—C(3)	104.8 (5)	S(6)—C(6)	1.672 (14)
Co—S(3)	2.259 (4)	S(3)—C(3)—O(3)	123.2 (12)	Co—S(6)	2.237 (4)
		S(3)—C(3)—C(1)	121.0 (10)		
		O(3)—C(3)—C(1)	115.8 (13)		
Ligand 2		Ligand 3			
Co—S(4)	2.230 (4)	S(5)—Co—S(6)	89.84 (15)		
S(4)—C(4)	1.707 (13)	Co—S(5)—C(5)	106.8 (5)		
C(4)—O(4)	1.228 (15)	S(5)—C(5)—O(5)	127.0 (11)		
C(4)—C(2)	1.493 (17)	S(5)—C(5)—C(6)	118.1 (9)		
C(2)—O(2)	1.224 (14)	O(5)—C(5)—C(6)	114.9 (12)		
S(2)—C(2)	1.724 (13)	Co—S(6)—C(6)	106.9 (5)		
Co—S(2)	2.230 (4)	S(6)—C(6)—O(6)	126.5 (11)		
		S(6)—C(6)—C(5)	118.1 (9)		
		O(6)—C(6)—C(5)	115.3 (12)		
Ligand 3					
Co—S(5)	2.256 (4)				
S(5)—C(5)	1.658 (14)				
C(5)—O(5)	1.220 (13)				
C(5)—C(6)	1.603 (16)				
C(6)—O(6)	1.231 (14)				
S(6)—C(6)	1.672 (14)				
Co—S(6)	2.237 (4)				

Table 4. Metal ion and water contacts (Å)

Ca <sup>+</sup> —O(8)	2.460 (10)	K <sup>+</sup> —S(1)	3.380 (6)
O(10)	2.447 (9)	S(5)	3.790 (7)
O(2) <sup>ii</sup>	2.485 (9)	O(1)	3.322 (12)
O(4) <sup>ii</sup>	2.573 (10)	O(6) <sup>vi</sup>	2.784 (10)
O(1) <sup>iii</sup>	2.476 (9)	O(9) <sup>vi</sup>	2.882 (11)
O(3) <sup>iii</sup>	2.733 (10)	S(2) <sup>vii</sup>	3.668 (6)
O(9) <sup>iv</sup>	2.508 (10)	O(2) <sup>vii</sup>	2.791 (11)
O(5) <sup>v</sup>	2.531 (9)	O(10) <sup>viii</sup>	2.924 (13)
O(6) <sup>v</sup>	2.442 (10)	O(5) <sup>ix</sup>	3.017 (11)
Possible hydrogen bonds			
O(7)···O(3) <sup>x</sup>	3.130 (13)	O(9)···O(2)	2.916 (13)
O(4) <sup>vi</sup>	2.971 (14)	O(3)	2.845 (13)
O(8)	2.896 (13)	O(8)	3.034 (13)
O(9)	2.833 (13)	S(1)	3.522 (10)
S(3)	3.576 (11)		
S(4) <sup>vi</sup>	3.558 (11)	O(10)···O(1) <sup>iii</sup>	2.821 (13)
		O(3)	2.795 (13)
O(8)···O(2)	2.854 (13)	O(4) <sup>ii</sup>	2.882 (14)
O(10)	2.959 (15)	O(5) <sup>vi</sup>	2.903 (12)
S(2)	3.216 (10)	O(6) <sup>v</sup>	2.902 (14)
S(4)	3.557 (10)		

i  $x, y, z$ ; ii  $-x, \frac{1}{2} + y, \frac{1}{2} - z$ ; iii  $-x, \frac{1}{2} + y, -\frac{1}{2} - z$ ; iv  $\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z$ ; v  $-\frac{1}{2} + x, \frac{1}{2} - y, -z$ ; vi  $\frac{1}{2} - x, -y, -\frac{1}{2} + z$ ; vii  $-x, -\frac{1}{2} + y, \frac{1}{2} - z$ ; viii  $-x, -\frac{1}{2} + y, -\frac{1}{2} - z$ ; ix  $-\frac{1}{2} + x, -\frac{1}{2} - y, -z$ ; x  $\frac{1}{2} + x, \frac{1}{2} - y, -z$ ; xi  $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$ ; xii  $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$ .

Table 5. Ligand planes and atomic deviations (Å)

Plane equations. Each plane is represented by  $lx' + my' + nz' + p = 0$  with respect to orthogonal axes in Å.

	Ligand 1	Ligand 2	Ligand 3
$l$	0.843	-0.717	-0.062
$m$	-0.440	-0.592	0.654
$n$	-0.310	-0.368	-0.754
$p$	0.229	1.331	1.984
	Ligand 1	Ligand 2	Ligand 3
Co*	0.334	Co* -0.177	Co* -0.085
S(1)	0.077	S(2) -0.021	S(5) 0.020
S(3)	-0.079	S(4) 0.020	S(6) -0.024
O(1)	-0.087	O(2) 0.024	O(5) -0.020
O(3)	0.086	O(4) -0.024	O(6) 0.014
C(1)	-0.010	C(2) 0.000	C(5) -0.010
C(3)	0.013	C(4) 0.001	C(6) 0.021
Ca <sup>iii</sup>	0.808	Ca <sup>ii</sup> -0.612	Ca <sup>v</sup> 0.161

Angles between planes: 1 and 2, 103.31; 1 and 3, 96.08; 2 and 3, 93.76°. For the corresponding planes which include cobalt these angles are 101.1, 94.3 and 91.7°.

\* The cobalt atom was not included in the derivation of the plane equations.

(Fig. 1). The range of calcium to oxygen distances (2.44–2.73 Å) has a mean value of 2.52 Å (Table 4). The mean for those to water oxygen, 2.47 (2) Å, does not differ significantly from that involving oxalate oxygen, 2.54 (4) Å. The thiooxalate is behaving as a bidentate ligand to three calcium ions and it is most likely that this is the cause of the cobalt position deviating significantly from the planes of the ligands (Table 5). Thus the coordinated calcium is on the same side of the ligand plane as the cobalt where the deviations from the plane of the latter are greatest (planes 1 and 2, Table 5) and on the other side where the Ca—O distances are least [plane 3; O(6), Table 4].

The potassium ion has an environment of oxygen and sulphur atoms forming a cylinder of density approximately parallel to  $a$ . The absence of atoms at the ends of the cylinder suggests an explanation for the large apparent thermal anisotropy in this direction. The r.m.s. components of thermal displacement along the  $a$ ,  $b$  and  $c$  directions are 0.564 (8), 0.205 (7) and 0.223 (7) Å. The values for the thermal ellipsoid are 0.197 (7), 0.213 (8) and 0.570 (8) Å, which may be compared with those for cobalt: 0.106 (6), 0.167 (4) and 0.181 (4) Å, and those for calcium: 0.119 (7), 0.157 (5) and 0.183 (5) Å. The mean value of the potassium to oxygen contacts is 2.88 (3) Å excluding O(1) whose length is 0.44 Å greater than this value (Table 4). The K—S(5) contact is similarly 0.4 Å longer than K—S(1), which indicates that the effective coordination number of the potassium is only seven.

No structures containing coordinated thiooxalate ligands have hitherto been reported.\* The mean Co<sup>iii</sup>—S length found here [2.244 (5) Å] is as short as

\* Note added in proof:—The structures of tris(thiooxalate) complexes of iron and aluminium have been reported (Hollander & Coucouvanis, 1974).

previously reported values in cobalt(III) complexes with six ligating sulphur atoms: cobalt(III) tris-(*N,N*-diethylthiocarbamate), 2.258 (3) Å (Merlino, 1968), and tetrakis(ethylthioxanthato)- $\mu$ -bis(ethylthio)dibalt(III), 2.274 Å (xanthate S), 2.247 (2) Å (bridged thiol S) (Lewis, Lippard & Zubietta, 1972). The unsatisfactory thermal refinement of atoms C(5) and C(6) results in S–C and C–C lengths for ligand 3 (Table 3) which deviate significantly from the mean obtained from ligands 1 and 2 only; the C=O lengths seem less affected. The mean lengths for ligands 1 and 2 are S–C 1.710 (8), C–C 1.516 (23), and C=O 1.226 (8) Å. The mean sulphur–carbon length lies mid-way between the sum of the Pauling (1960) covalent radii for C–S (1.812 Å) and for C=S (1.607 Å). The C–C and C–O (non-ligating) lengths are not significantly different from those found [1.495 (10), 1.233 (1) Å] in the best determined metal(oxalate)<sub>3</sub> structure,  $\text{K}_3[\text{Rh}(\text{oxalate})_3] \cdot 4.5\text{H}_2\text{O}$  (Dalzell & Eriks, 1971). The thiooxalate ligands are approximately planar; the dihedral angles about the C–C bonds are 7.8 (1.5)° (ligand 1), 1.5 (1.5)° (ligand 2) and 4.1 (1.2)° (ligand 3). The sense of the twist in the ligand is to make the C–C bond more parallel to the approximate threefold axis of the complex.

The effect of replacing oxygen by sulphur in  $[\text{Co}(\text{thioox})_3]^{3-}$  is to open up the intra-ligand S–Co–S angle to an average value of 89.7 (2)° from 84.3 (1.5)° found in  $[\text{Co}(\text{oxalate})_3]^{3-}$  (Butler & Snow, 1971c). That this angle is very close to 90° is not a sufficient condition for regular octahedral coordination is seen by viewing the angles between the ligand planes (Table 5). They are all greater than 90° and vary over a 10° range. The angles between the intraligand S–Co–S planes are more uniform: 93.79 (15), 91.89 (16) and 93.41 (17)° for the same sequence given in Table 5. The  $\text{CoS}_6$  core atoms more closely approach 32 symmetry than the complex itself. This observation was also made in respect of the  $\text{CoN}_6$  core of the (+)<sub>589</sub>-tris-(biguanide)cobalt(III) ion (Snow, 1974). These angles imply that the  $[\text{Co}(\text{thioox})_3]^{3-}$  complex has a small distortion towards a trigonal prism arrangement for which the corresponding angle is 120°.

The angles of spectroscopic interest  $\theta$  [between the threefold axis and the Co–S bond, 53.79 (0.15)°] and  $\omega$  [the S–Co–S angle projected on to the plane perpendicular to the threefold axis, 57.0 (2)°] have been previously compared with those for oxygen donor complexes (Butler & Snow, 1972). The  $\theta$  angle for  $[\text{Co}(\text{oxalate})_3]^{3-}$  [56.4 (1.5)°] lies on the opposite side of the regular octahedral value (54.75°) from the thiooxalate complex and is consistent with the opposite signs of the spectroscopic trigonal splitting parameter that have been assigned to the two complexes (Piper & Karipides, 1964; Hidaka & Douglas, 1964).

The authors thank Dr M. R. Taylor of the Flinders University of South Australia for diffractometer facilities and the Australian Research Grants Committee for financial support.

## References

- ALCOCK, N. W. (1970). In *Crystallographic Computing*, edited by F. R. AHMED, pp. 272–278. Copenhagen: Munksgaard.
- BUTLER, K. R. & SNOW, M. R. (1971a). *Inorg. Chem.* **10**, 1838–1840.
- BUTLER, K. R. & SNOW, M. R. (1971b). *J. Chem. Soc. (D)*, pp. 550–551.
- BUTLER, K. R. & SNOW, M. R. (1971c). *J. Chem. Soc. (A)*, pp. 565–569.
- BUTLER, K. R. & SNOW, M. R. (1972). *Inorg. Nucl. Chem. Lett.* **8**, 541–545.
- CORFIELD, P. W. R., DOEDENS, R. J. & IBERS, J. A. (1967). *Inorg. Chem.* **6**, 197–204.
- CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
- CRUICKSHANK, D. W. J., PILLING, D. E., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, edited by R. PEPINSKY. London: Pergamon Press.
- DALZELL, B. C. & ERIKS, K. (1971). *J. Amer. Chem. Soc.* **93**, 4298–4380.
- DE MEULENAER, J. & TOMPA, H. (1965). *Acta Cryst.* **19**, 1014–1018.
- DWYER, F. P. & SARGESON, A. M. (1959). *J. Amer. Chem. Soc.* **81**, 2335–2336.
- FREEMAN, H. C., GUSS, J. M., NOCKOLDS, C. E., PAGE, R. & WEBSTER, A. (1970). *Acta Cryst.* **A26**, 149–152.
- GUSS, J. M., NOCKOLDS, C. E. & WOOD, A. M. (1970). *User Manual for a Computer-Controlled Diffractometer*. Univ. of Sydney, School of Chemistry.
- HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.
- HELMHOLZ, L. (1939). *J. Amer. Chem. Soc.* **61**, 1544–1550.
- HIDAKA, J. & DOUGLAS, B. E. (1964). *Inorg. Chem.* **3**, 1724–1728.
- HOLLANDER, F. J. & COUCOUVANIS, D. (1974). *Inorg. Chem.* **13**, 2381–2386.
- International Tables for X-ray Crystallography* (1968). Vol. III. Birmingham: Kynoch Press.
- LEWIS, D. F., LIPPARD, S. J. & ZUBIETA, J. A. (1972). *J. Amer. Chem. Soc.* **94**, 1563–1575.
- MCCAFFERY, A. J., MASON, S. F. & BALLARD, R. E. (1965). *J. Chem. Soc.* pp. 2883–2892.
- MASON, S. F. (1963). *Quart. Rev.* **17**, 20–66.
- MERLINO, S. (1968). *Acta Cryst.* **B24**, 1441–1448.
- MUETTERTIES, E. L. & WRIGHT, C. H. (1967). *Quart. Rev.* **21**, 109–194.
- OKAYA, Y. & PEPINSKY, R. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, edited by R. PEPINSKY. London: Pergamon Press.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
- PIPER, T. S. & KARIPIDES, A. G. (1962). *Mol. Phys.* **5**, 475–483.
- PIPER, T. S. & KARIPIDES, A. G. (1964). *J. Chem. Phys.* **40**, 674–682.
- RAE, A. D. (1965). *Acta Cryst.* **19**, 683–684.
- RAMACHANDRAN, G. N. & RAMACHANDRA AYYAR, R. (1963). In *Crystallography and Crystal Perfection*, edited by G. N. RAMACHANDRAN, pp. 25–41. London: Academic Press.
- SNOW, M. R. (1972). *J. Chem. Soc. Dalton*, pp. 1627–1634.
- SNOW, M. R. (1974). *Acta Cryst.* **B30**, 1850–1856.