loss of one water molecule; this also is well explained by the crystal structure.

All the programs used throughout the work, apart from the *SORTE* program, are collected in the *X-ray '63 System*. The computations were carried out at the Centro Nazionale Universitario di Calcolo Elettronico (Pisa).

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The Crystal and Molecular Structure of Cobalt(III) Tris(*O*-ethylxanthate)

BY STEFANO MERLINO

Istituto di Mineralogia dell'Università di Pisa, IV Sezione del Centro Nazionale di Cristallografia del C.N.R., Italy

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Cobalt(III) tris(*O*-ethylxanthate) crystallizes in the rhombohedral space group $R\bar{3}$, with two molecules in the unit cell, $a=9{\cdot}65$ Å, $\alpha=100°48'$. The crystal structure has been determined by two-dimensional Patterson and Fourier syntheses and refined with three-dimensional data by anisotropic least-squares methods, with a final agreement index for the observed reflexions, $R_1=0{\cdot}090$. Each molecule is made up of three ethylxanthic ligands coordinated to a cobalt atom through the sulphur atoms; the molecule has trigonal symmetry C_3–3. The intermolecular interactions are of the van der Waals type. Mean bond lengths: Co–S, 2·277; S–C, 1·673; C–O, 1·359 Å. The $\cdots S_2C{=}OR$ form makes only a minor contribution to the structure of the xanthic radical.

Introduction

Recently the refinement of the structure of cobalt(III) tris(*N,N*-diethyldithiocarbamate) (Merlino, 1968) has been completed in our laboratory, as part of a research programme developed with the aim of gaining information on metal–sulphur bonds and on the structure of xanthic and dithiocarbamic ligands.

The results obtained confirm that the resonance form $\cdots S_2C{=}NR_2$ makes an important contribution to the molecular structure. Chatt, Duncanson & Venanzi (1956*a*,*b*) explained the importance of this resonance form by the strong electron releasing effect of the $-NR_2$ group and the ability of the sulphur atoms to accept electrons; they observe that the resonance form $\cdots S_2C{=}OR$ would make only a minor contribution to the structure of the xanthates, because of the smaller mesomeric effect of the –OR group relative to the $-NR_2$ group.

An indication of this is given by the comparison of the C–N = 1·33 Å distance in nickel diethyldithiocarbamate (Bonamico, Dessy, Mariani, Vaciago & Zambonelli, 1965), nickel di-n-propyldithiocarbamate (Peyronel & Pignedoli, 1967) and zinc diethyldithiocarbamate (Bonamico, Mazzone, Vaciago & Zambonelli, 1965), with the distance C–O = 1·38 Å found in nickel ethylxanthate, whose structure was determined from two-dimensional data (Franzini, 1963) and the distances C–O = 1·33 and 1·42 Å (average 1·38 Å) found in zinc ethylxanthate (Ikeda & Hagihara, 1966). However these comparisons are not conclusive and it seemed useful to investigate the Co^{III} ethylxanthate crystal structure, the determination of which is the subject of this paper.

Experimental

The X-ray crystallography of cobalt(III) tris(*O*-ethylxanthate) was studied by Derenzini (1938); he

found it to be rhombohedral with the following unit-cell dimensions:

$a_{rh}=9{\cdot}52$ kX$=9{\cdot}54$ Å, $a_{hex}=14{\cdot}62$ kX$=14{\cdot}64$ Å,
$\alpha_{rh}=100°\,18'$, $c_{hex}=13{\cdot}23$ kX$=13{\cdot}25$ Å.

$D_m=1{\cdot}63$, $D_c=1{\cdot}72$ g.cm^{-3}, with two molecules in the rhombohedral unit cell. From the possible space groups Derenzini proposed $R\bar{3}$, as the iron ethylxanthate crystals, isomorphous with those of cobalt ethylxanthate, develop as a third-order rhombohedron.

Buerger precession photographs were taken around the ternary axis and around the edge of the rhombohedron. The following constants were obtained:

$a_{rh} = 9{\cdot}65 \pm 0{\cdot}01$ Å, $a_{hex}=14{\cdot}87$ Å,
$\alpha_{rh} = 100°48' \pm 10'$, $c_{hex}=13{\cdot}22$ Å;
$U_{rh}=843{\cdot}9$ Å;
$D_c=1{\cdot}662$ g.cm^{-3}.

In this paper rhombohedral (obverse setting) indices and coordinates are used throughout.

Multiple-level precession photographs were compatible with a Laue symmetry $\bar{3}$; considering the absence of systematic extinctions, the possible space groups are then $R3$ and $R\bar{3}$. The observed density of 1·63 g.cm^{-3} requires two molecules per rhombohedral cell. The most probable space group, therefore, is $R\bar{3}$, in accordance with Derenzini's choice; this was subsequently confirmed by the structure determination.

The intensity data were collected with zirconium-filtered Mo $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å) by means of Buerger precession photographs with the multiple-exposure technique and integration process. A crystal of the compound was reduced to a nearly spherical shape with a mean diameter of 0·76 mm ($\mu R=0{\cdot}66$ for Mo $K\alpha$ radiation). Photographs of six layers with [010] as the precession axis ($k=0$ through 5) and an equatorial layer with [111] as precession axis were taken. A total of 1012 independent reflexions were observed. The intensities, measured with a Nonius microdensitometer, were processed by a program written by Catani & Zanazzi (1965). Corrections were made for Lorentz and polarization factors and for the absorption factor by the three-constant formula for spherical crystals of Palm (1964).

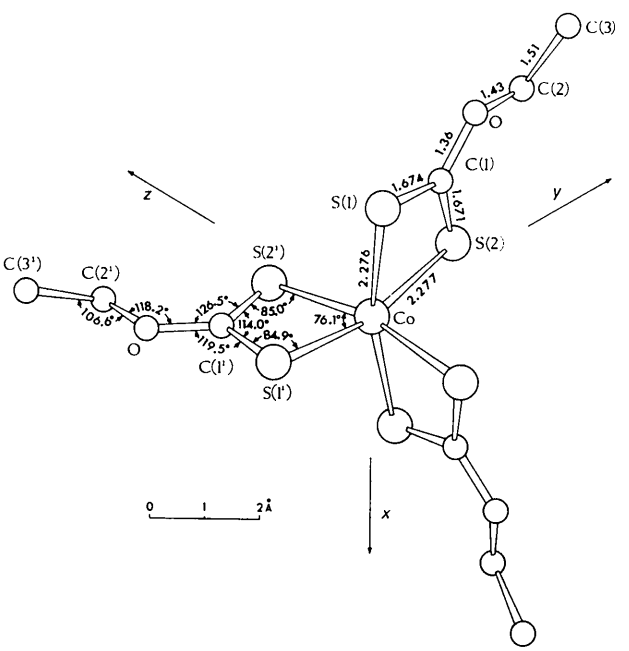


Fig. 1. The molecular structure of cobalt(III) tris(*O*-ethylxanthate).

Determination of the structure

The structure was determined with two-dimensional data, from only the $h0l$ reflexions; indeed, for the structure determination of a rhombohedral crystal just one electron density projection is sufficient, as it is equal to two other (symmetry-equivalent) projections. The cobalt atom is in special position 2(*c*) with coordinates (x,x,x). By means of the [010] Patterson projection it was easy to obtain the value of x for the cobalt atom. The first electron density map, calculated with the signs determined by the cobalt atom, revealed the positions of the two sulphur atoms of the asymmetric unit. A second Fourier synthesis revealed the positions of the remaining heavy atoms.

After two cycles of least-squares refinement with isotropic temperature factors, the reliability index R_1, defined as $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ was 0·13.

The refinement

The atomic coordinates obtained in the previous stage were refined by a full-matrix least-squares program (Busing, Martin & Levy, 1962) from three-dimensional data; the various layers were initially placed on the same scale by comparison of common reflexions; the six scale factors were subsequently included among the refined parameters. Individual isotropic temperature factors were assigned to all the heavy atoms. Three refinement cycles with unit weights for all the observed reflexions reduced the reliability index from $R_1=0{\cdot}210$ to $R_1=0{\cdot}122$.

Anisotropic temperature factors were then introduced, in the form:

$$\exp\{-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\}$$

for non-hydrogen atoms. The hydrogen atom positions were calculated assuming: (1) C–H bond lengths of 1·08 Å; (2) tetrahedral hybridization of the carbon atoms; (3) staggered conformation of the ethyl groups. The positional and isotropic thermal parameters (5 Å^2) of the hydrogen atoms were maintained constant.

Further least-squares cycles reduced the reliability index to $R_1=0{\cdot}090$, whereas $R_2=w[\Sigma||F_o|-|F_c||^2/$

$\Sigma w|F_o|^2]^{1/2}$ was 0·088. In these cycles the 101 reflexion was assigned zero weight, because it was apparently affected by extinction; the weighting scheme applied to the remaining reflexions was:

$$w = \frac{1}{1+[(|F_o|-8|F_{min}|)/5|F_{min}|]^2},$$

where $|F_{min}|$ was the minimum observable value of

Table 1. *Observed and calculated structure factors*

Reflexions for which FO is listed as 0 were not recorded. That marked with an asterisk was probably affected by extinction

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
0	0	1	47.1	-49.3	6	-11		7.8	-8.4	2	1	-8	35.7	-37.9	6	1	4	14.2	-13.4	-10	1	7	14.6	-15.3
0	0	2	37.2	-35.5	6	-12		16.3	17.1	2	1	-9	21.3	23.4	6	1	5	16.8	-16.5	-10	1	8	17.4	-17.1
0	0	3	23.9	-18.8	7	0	1	38.3	-37.2	2	1	-10	23.1	25.8	6	1	6	12.3	9.7	-10	1	9	15.9	17.2
0	0	4	19.4	18.6	7	0	2	11.7	-10.7	2	1	-12	18.2	-22.0	6	1	7	29.5	29.5	-10	1	-2	11.7	8.2
0	0	5	59.1	-56.6	7	0	3	39.9	37.3	-2	1	2	54.8	-58.0	6	1	8	9.9	-7.4	-10	1	-3	22.4	-18.4
0	0	7	24.7	23.6	7	0	4	7.8	-5.7	-2	1	3	63.6	-59.5	6	1	-2	8.8	8.3	-10	1	-4	12.2	10.7
0	0	8	16.8	-15.2	7	0	5	16.1	-17.1	-2	1	4	33.4	29.2	6	1	-3	17.4	-15.9	-10	1	-6	16.6	-14.8
0	0	9	22.4	19.7	7	0	6	10.6	10.7	-2	1	5	38.3	38.4	6	1	-4	32.4	33.5	-10	1	-7	9.2	6.6
0	0	10	7.2	-5.8	7	0	7	9.8	8.0	-2	1	6	23.8	19.3	6	1	-5	26.3	-28.0	-10	1	-8	11.6	11..
0	0	11	12.3	10.3	7	0	8	11.7	11.4	-2	1	7	8.9	7.5	6	1	-6	18.2	23.0	11	1	2	12.9	11.7
0	0	12	8.9	-7.9	7	0	9	6.1	-7.2	-2	1	9	29.4	-27.7	6	1	-7	12.4	-13.1	11	1	-2	19..	24.5
1	0	1*	85.4	-109.8	7	0	-2	20.4	-24.1	-2	1	10	15.2	-15.3	6	1	-8	24.6	-28.8	11	1	-4	24..	-25.
1	0	2	43.6	-38.6	7	0	-3	20.8	20.1	-2	1	11	13.4	8.9	6	1	-9	8.4	-10.9	11	1	-9	9.2	14.5
1	0	4	63.7	-65.5	7	0	-4	38..	37.0	-2	1	13	11.4	-11.0	6	1-11		11.7	13.7	11	1-10		7.9	-13.5
1	0	5	27.0	23.5	7	0	-5	6.3	-7.2	-2	1	-2	78.9	89.2	6	1-12		7.5	-15.2	-11	1	7	12.9	12.6
1	0	6	76.9	81.1	7	0	-6	24.8	20.9	-2	1	-3	34.7	30.9	-6	1	2	64.7	60.7	-11	1	9	11.2	-11.4
1	0	7	17.3	-14.4	7	0	-8	28.1	-24.2	-2	1	-4	63.8	-59.4	-6	1	3	44.4	-40.6	-11	1	-4	11.7	10.9
1	0	8	1.2	-8.7	7	0	-9	7.8	-6.5	-2	1	-5	34.9	33.1	-6	1	4	49.8	-47.9	-11	1	-5	11.8	-9.2
1	0	9	11.3	-10.3	7	0	-11	7.2	7.5	-2	1	15	29.4	29.7	-6	1	5	29.1	26.3	-11	1	-7	1.2	9.1
1	0	11	11.6	-9.4	7	0	-12	8.2	-9.4	-2	1	-7	12.5	12.0	-6	1	6	7.9	-5.8	12	1	2	13.5	-13.5
1	0	-1	67.3	75.7	8	0	2	28.8	27.6	-2	1	-8	9.9	-9.9	-6	1	7	9.6	-6.7	12	1	-3	19.7	21.4
1	0	-2	55.2	-58.8	8	0	3	10.8	10.9	-2	1	-9	8.4	9.4	-6	1	8	27.4	26.1	12	1	-7	10.1	-15.6
1	0	-3	46.3	45.6	8	0	4	32.6	-33.4	-2	1-10		17.3	-18.4	-6	1	9	21.3	19.9	-12	1	2	9..	-9.9
1	0	-4	12.7	-9.8	8	0	5	17.8	18.8	3	1	2	9.7	9.5	-6	1	-9	8.6	-8.1	-12	1	3	7.8	-7.3
1	0	-5	13.8	12.5	8	0	6	6.6	-5.7	3	1	4	8.7	5.6	-6	1	12	6.7	-5.7	-12	1	5	17.1	16.1
1	0	-6	16.7	-15.4	8	0	7	7.0	-6.1	3	1	5	27.1	-26.5	-6	1	13	7.4	-5.7	-12	1	6	13.9	-12.8
1	0	-7	19.5	-19.7	8	0	8	5.4	-6.5	3	1	7	13.4	14.6	-6	1	-2	21.5	21.2	-12	1	-5	17.8	-16.3
1	0	-8	19.2	-18.2	8	0	-1	12.6	9.5	3	1	9	21.6	21..	-6	1	-3	8.2	8.5	-12	1	-6	11.5	9.8
1	0	-9	11.4	-11.7	8	0	-2	41..	-42.3	3	1	11	12.7	12.5	-6	1	-4	18.6	-19.9	-13	1	2	7.5	8.4
1	0	-10	21.5	-21.3	8	0	-3	22.9	-20.8	3	1	11	15.1	-12.5	-6	1	-5	17.1	16.4	-13	1	6	12.7	13.3
1	0	-12	7.5	8.3	8	0	-4	15.9	16.5	3	1	12	14.5	-13.1	-6	1	-7	8.2	-7.0	-13	1	7	11.4	-10.4
1	0	-13	5.2	-7.1	8	0	-5	7.4	-7.2	3	1	-2	6.8	-6.7	-6	1	-8	17.8	-15.6	-13	1	8	5.9	7.2
2	0	1	79.0	81.1	8	0	-7	9.3	7.4	3	1	-3	15.9	16.4	-6	1	-9	11.5	11.4	-13	1	-1	12.3	10.8
2	0	2	36.4	-34.4	8	0	-8	15.5	13.6	3	1	-4	58.9	61.8	-6	1-11		8.4	-7.9	-13	1	-4	12.9	-10.7
2	0	3	36.9	-34.4	8	0	-9	8.2	-6.7	3	1	-5	16.2	16.1	-6	1-11		8.8	7.0	2	2	2	9.7	-8.2
2	0	4	15.2	13.6	8	0-11		9.6	-8.0	3	1	-6	67.6	-66.4	7	1	2	25.5	28.2	2	2	4	19.2	-19.1
2	0	5	61.4	63..	8	0-12		7.4	8.9	3	1	-7	12.2	12.5	7	1	3	12.4	-13.2	2	2	5	21.9	-21.9
2	0	6	19.7	-17.3	9	0	2	22.5	19.9	3	1	-9	20.7	-23.0	7	1	4	18.4	-18.0	2	2	6	33.6	32.3
2	0	7	41.0	-44.8	9	0	3	38.3	-38.2	3	1-11		18.0	18.9	7	1	5	22.7	21.3	2	2	10	18.8	19.1
2	0	8	9.1	7.9	9	0	4	11.4	10.7	-3	1	2	17.7	-17.2	7	1	6	22.1	23.8	2	2	11	11.7	-19.4
2	0	9	8.4	-8.2	9	0	5	5.9	-6.1	-3	1	3	59.4	-58.9	7	1	7	18.3	-18.3	2	2	-2	1..	-122.7
2	0	10	5.4	-7.7	9	0	7	6.1	6.4	-3	1	4	41.0	-38.4	7	1	-2	29.1	-30.5	2	2	-4	32.7	29.9
2	0	11	8.3	7.4	9	0	-2	25.3	24.2	-3	1	5	34.6	33.7	7	1	-3	12.1	-11.3	2	2	-6	55.6	-54.6
2	0	12	11.5	12.6	9	0	-3	12.9	-13.2	-3	1	6	10.3	-15.5	7	1	-5	20.6	23.0	2	2	-7	30.9	37.8
2	0	-1	38.1	28.3	9	0	-4	7.7	-7.6	-3	1	7	15.5	13.4	7	1	-6	9.2	8.5	2	2	-8	34..	-32.9
2	0	-2	30.8	-31.9	9	0	-5	13.0	13.6	-3	1	9	29.9	29.5	7	1	-7	32.6	36.1	2	2-10		9.5	9.1
2	0	-3	1.6	-9.4	9	0	-8	30.5	-29.7	-3	1	11	13.7	-13.5	7	1	-8	9..	11.3	-2	2	3	111.9	121.2
2	0	-5	15.7	-14.6	9	0	-9	20.6	18.9	-3	1	11	11.7	-11.1	7	1-11		26.4	-33.4	-2	2	4	31..	26.6
2	0	-6	31.6	28.4	1	1	1	16.6	17.1	-3	1	12	16.2	16.1	-7	1	2	37.2	34.5	-2	2	5	17.7	-15.8
2	0	-7	7.5	-8.8	10	0	2	19.4	-19.6	-3	1	-2	34.6	40.7	-7	1	3	41.3	39.0	-2	2	6	10.7	-15.2
2	0	-8	42.4	43.5	11	0	4	6.1	8.1	-3	1	-3	121.1	-126.8	-7	1	4	11..	-5.7	-2	2	7	14.1	-12.2
2	0	-9	13.7	16.9	11	0	6	5.9	6.7	-3	1	-4	36.3	34..	-7	1	5	27.4	-26.4	-2	2	8	13.9	-13.9
2	0	-11	32.3	-33.3	10	0	-2	20.8	-19.4	-3	1	-5	8.6	9.6	-7	1	7	19.6	-19.1	-2	2	10	14.9	14.0
2	0	-12	14..	14.5	10	0	-3	15.5	17.3	-3	1	-6	13.9	-18.6	-7	1	8	9.7	-7.9	-2	2	11	11.3	-11.1
3	0	2	3..	-3..	11	0	-6	5..	5.4	-3	1	-7	29.4	-28.2	-7	1	9	13.2	12.1	-2	2	-3	69.7	72.5
3	0	5	12.1	-12.1	12	0	-7	29.2	28.8	-3	1	-8	32.3	29.8	-7	1	-2	18.5	-16.2	-2	2	-5	24.4	-23.6
3	0	6	13.1	-15.2	12	0	-8	13.1	-13..	-3	1-12		12.2	-11.9	-7	1	-3	32..	-32.2	-2	2	-6	14.2	14.6
3	0	7	29.5	28.1	12	0	-9	22.6	-21.6	4	1	2	17.5	18.9	-7	1	-4	24.1	22.3	-2	2	-8	19.1	23.4
3	0	9	19.9	-20.7	11	0	3	8.5	1.2	4	1	3	6.7	-5.4	-7	1	-5	7.2	6.4	-2	2	-9	15.6	-14.8
3	0	10	19.7	20.9	11	0	-1	18..	17.8	4	1	4	12.3	13.4	-7	1	-7	11.7	-9.6	-2	2-10		13.3	14.2
3	0	11	11.3	9.7	11	0	-3	25.9	-27.2	4	1	5	19.2	-19.0	-7	1	-8	9.3	7.2	-2	2-11		15.9	-18.8
3	0	-1	31.6	29.5	11	0	-4	8.2	8.0	4	1	6	19.6	19.0	-7	1-11		11.0	11.5	3	2	3	14.8	-16.9
3	0	-2	27.1	24.8	11	0	-6	7.2	-6.9	4	1	7	10.2	-8.8	8	1	3	21.3	-22.0	3	2	4	41.3	-41.0
3	0	-3	37.8	32.6	11	0	-8	22.7	23.5	4	1	8	16.3	16.3	8	1	5	8.8	9.2	3	2	5	23.6	22.1
3	0	-4	23.1	-22.5	12	0	-2	14.5	14.7	4	1	10	5.6	-6.4	8	1	6	8.7	-11.5	3	2	7	11.7	12.7
3	0	-5	64.8	-63.6	12	0	-4	11..	-11.6	4	1	11	12.1	-13.5	8	1	8	8.5	9.8	3	2	10	15.5	-16.1
3	0	-6	3.6	-4.9	12	0	-7	8.1	-7.7	4	1	-2	9.3	9.4	8	1	-2	13.5	14.0	3	2	-3	65..	-88.1
3	0	-7	27.8	25.4	12	0	-8	15.5	-15.0	4	1	-3	63.4	-64.2	8	1	-3	14.7	-17.7	3	2	-4	16.8	15.7
3	0	-8	35.2	-29.7	12	0	-9	6.2	-6.9	4	1	-4	28.7	-26.9	8	1	-4	25.5	-27.1	3	2	-5	32.6	33.2
3	0	-10	27..	26.1	1	1	1	55.2	56.7	4	1	-5	74.5	83.9	8	1	-6	6.2	8.4	3	2	-6	15.8	15.2
3	0	-11	8.5	-7.7	1	1	2	17..	-15.2	4	1	-6	9.2	8.3	8	1	-7	14.1	-15.4	3	2	-7	40..	-43.6
3	0	-12	14.1	-16.2	1	1	3	13.5	9.1	4	1	-7	33.1	-33.1	8	1	-9	10.7	11.5	3	2	-8	22.7	24.4
4	0	-13	9.1	10.2	1	1	5	109.6	104.3	4	1	-9	9.6	-8.7	8	1-10		7.4	11.6	3	2	-9	13.9	-17.6
4	0	1	63.4	-60.3	1	1	6	22.2	-24.2	4	1-10		9.6	-9.8	8	1-11		16.3	-22.8	-3	2	3	51.4	-51.3
4	0	2	11.7	-12.7	1	1	7	6.7	-8.4	-4	1	2	24.9	22.5	-8	1	2	57.5	-55.4	-3	2	4	55.4	58.9
4	0	3	28.8	26.2	1	1	8	16..	16.1	-4	1	3	47.6	43.4	-8	1	3	41.3	38.6	-3	2	5	22.4	-20.0
4	0	7	10.1	8.4	1	1	10	11.1	-10.2	-4	1	4	23.9	-20.0	-8	1	5	13.3	12.3	-3	2	6	23.7	18.2
4	0	8	36..	-36.2	1	1	-1	9..	-21.5	-4	1	5	23.5	-20.4	-8	1	7	20.5	20.3	-3	2	8	22.3	21.7
4	0	9	21.8	21.8	1	1	-2	44.1	42.2	-4	1	6	23.8	22.5	-8	1	10	15.1	15.2	-3	2	11	11.6	10.6
4	0	-1	12.1	-11.6	1	1	-3	12.6	8.3	-4	1	7	14.3	15.7	-8	1	12	10..	-9.9	-3	2	12	11.1	11.9
4	0	-2	21.5	18.5	1	1	-4	41.3	38.7	-4	1	8	28.5	-28.1	-8	1	13	7.8	-7.1	-3	2	13	14.1	-15.0
4	0	-3	18.3	-17.7	1	1	-5	17.1	-15.6	-4	1	9	24.9	-24.8	-8	1	-3	42.2	40.0	-3	2	-3	78.9	79.6
4	0	-4	8..	8.5	1	1	-6	33.6	33.9	-4	1	10	28.9	28.9	-8	1	-4	14.7	12.4	-3	2	-4	46.6	-44.4
4	0	-5	35.8	-32.8	1	1	-7	44.4	-42.5	-4	1	11	11.8	-12.3	-8	1	-5	17.2	-15.0	-3	2	-5	10.0	11.0
4	0	-6	40.5	-40.4	1	1	-8	20.1	15.8	-4	1	13	9.7	9.2	-8	1	-6	8.4	8.2	-3	2	-6	12.0	-10.8
4	0	-7	25.6	22.6	1	1	-9	10.5	11.6	-4	1	-2	73.8	-69.5	-8	1	-7	9.6	-10.1	-3	2	-8	29.5	-29.2
4	0	-8	29.9	30.6	1	1-11		13.2	-11.9	-4	1	-3	9.7	-6.7	-8	1	-9	17.1	-15.3	-3	2	-9	23.2	19.6
4	0	-9	14.6	-14.3	1	1-11		21.8	-23.5	-4	1	-4	17.3	14.3	-8	1-10		8.7	10.0	4	2	3	13.1	-13.1
4	0	-11	13.1	12.4	1	1-12		11.3	10.8	-4	1	-7	44.1	41.2	9	1	2	18.4	-21.1	4	2	4	22.1	21.7
4	0	-12	13.8	-13.2	-1	2	2	25.4	-25.9	-4	1	-9	31.8	-31.6	9	1	3	7.4	-5.2	4	2	5	23.9	23.8
5	0	1	23..	-18.9	-1	1	3	27.9	23.4	-5	1-10		16.5	16.1	9	1	4	11.6	12.1	4	2	9	14.9	-7.8
5	0	2	54.3	52.7	-1	1	4	62.4	60.9	5	1	2	42.1	-45.3	9	1	-3	24.8	29.5	4	2	-3	29.6	24.2
5	0	3	15.5	14.2	-1	1	5	15.1	-13.4	5	1	3	6.8	6.1	9	1	-5	16.6	-19.1	4	2	-4	29.	-25.0
5	0	4	24..	22.7	-1	1	7	14.8	-15.2	5	1	6	23.7	-23.2	9	1	-6	8.7	-10.6	4	2	-6	24..	22.8
5	0	5	23.1	-21.9	-1	1	8	22.1	-21.3	5	1	-2	24.4	-22.6	9	1	-7	17.8	22.0	4	2	-7	25.4	26.7
5	0	6	15.5	15.3	-1	1-11		21.6	19.9	5	1	-3	34.9	45.4	9	1	-8	7.5	11.4	4	2	-10	25.5	27.2
5	0	7	20.5	-27.2	-1	1	-2	66.2	-65.7	5	1	-4	47.2	-46.9	9	1	-9	10.5	-13.7	-4	2	5	24.4	24.2
5	0	8	8.3	6.8	-1	1	-3	31.9	28.7	5	1	-6	34.1	34.1	9	1-10		7.7	9.8	-4	2	6	36.8	-35.8
5	0	-2	34.8	34.3	-1	1	-4	9.5	-9.6	5	1	-7	10.7	-9.9	-9	1	3	23.1	-22.1	-4	2	7	31.5	-30.8
5	0	-4	49.6	-48.1	-1	1	-5	33.8	-33.7	5	1	-8	12.8	11.9	-9	1	4	26.5	25.4	-4	2	8	35.4	-29.2
5	0	-5	77.7	67.4	-1	1	-6	26.4	-24.4	5	1-11		11.2	11.3	-9	1	5	22.4	-20.9	-4	2	9	31.9	31.6
5	0	-6	33.7	-26.7	-1	1	-7	18.7	17.9	5	1-12		12.2	11.3	-9	1	6	17.5	17.4	-4	2	10	12.4	-13.4
5	0	-7	10.3	-15.4	-1	1	-8	32..	34.9	-5	1	2	27.8	-24.5	-9	1	7	16.8	-15.7	-4	2	12	12.9	12.2
5	0	-9	24.4	25.2	-1	1-11		11.5	-12.0	-5	1	3	47.6	-44.3	-9	1	8	25.2	25.2	-4	2	-3	73.9	-68.1
5	0	-10	12.3	-11.3	-1	1-12		8.5	-7.9	-5	1	4	48.2	46.2	-9	1	9	7.5	-6.4	-4	2	-6	42.7	-39.8
5	0	-12	6.3	-6.6	2	1	2	33.1	35.5	-5	1	5	11.3	-11.7	-9	1	12	7.4	8.3	-4	2	-8	37.2	36.3
5	0	-13	12.2	-13.1	2	1	3	6.5	6.8	-5	1	6	18.5	-15.5	-9	1	13	15.5	-11.7	-4	2	-9	13.3	13.6
6	0	1	40.9	46.3	2	1	4	51..	56.3	-5	1	7	21.7	19.4	-9	1	-2	28.8	25.6	5	2	3	23..	20.6
6	0	2	24.3	-23.5	2	1	5	45..	-45.2	-5	1	8	37.3	34.7	-9	1	-4	27.3	-24.1	5	2	4	13.8	-13.9
6	0	6	26.1	-25.3	2	1	6	48.9	-52.3	-5	1	9	31.3	-30.7	-9	1	-5	16.6	16.2	5	2	5	24.9	-24.7
6	0	8	13.3	12.9	2	1	7	24.1	22.9	-5	1	10	16.6	-15.6	-9	1	-6	16.8	-15.0	5	2	7	8.5	8.9
6	0	9	1.2	9.2	2	1	8	19.3	-18.6	-5	1	12	12.1	-12.4	-9	1	-7	13.4	11.7	5	2	8	12.2	-13.7
6	0	-1	54.1	-53.3	2	1	10	12.3	9.8	-5	1	13	7.1	6.5	10	1	3	17.4	19.6	5	2	-4	24.3	-22.7
6	0	-3	44.7	44.3	2	1	11	18.3	18.8	-5	1	-2	38.7	-33.8	10	1	-2	11.0	10.3	5	2	-5	48.4	-49.2
6	0	-4	27.1	-26.3	2	1	-2	63.5	59.6	-5	1	-4	7.4	8.0	10	1	-3	23.5	-28.0	5	2	-6	13.1	-11.8
6	0	-5	18.9	-17.5	2	1	-3	11.5	-10.5	-5	1	-6	21.9	21.9	10	1	-4	19.6	22.0	5	2	-7	11.6	12.2
6	0	-6	23.9	19.2	2	1	-4	32.7	-29.6	-5	1	-8	32.5	-30.3	10	1	-8	15.6	21.8	5	2	-8	6.1	7.8
6	0	-7	32.9	-32.3	2	1	-5	39.9	-42.8	-5	1-11		12.2	-10.4	-10	1	2	31.6	30.6	5	2-10		14.6	14.6
6	0	-9	8.3	7.8	2	1	-6	16.8	17.8	6	1	2	17.4	-16.5	-10	1	3	9.9	-10.9	-5	2	3	27.6	24.3
6	0	-10	15.3	13.8	2	1	-7	11.9	11.8	6	1	3	7.9	6.9	-10	1	5	21.6	21.8	-5	2	4	9.	-8.2

Table 1 (*cont.*)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-5	2	5	22.4	18.4	-9	2	11	10.4	-10.6	-5	3	11	9.9	-12.4	4	4	4	74.5	-73.2	10	4	-6	13.5	-12.5
-5	2	6	44.8	43.4	-9	2	12	6.8	-9.2	-5	3	-4	6.9	6.9	4	4	5	18.1	14.8	10	4	-7	11.4	11.0
-5	2	7	22.5	19.9	-9	2	13	13.9	7.4	-5	3	-5	41.5	53.0	4	4	9	22.2	22.9	10	4	-10	12.5	8.1
-5	2	8	28.3	-25.6	-9	2	-3	25.3	21.9	-5	3	-6	28.1	-35.9	4	4	-4	21.5	21.1	10	4	-13	14.1	-9.4
-5	2	9	20.1	-19.3	-9	2	-8	12.3	-10.9	-5	3	-8	12.1	16.1	4	4	-5	33.5	-34.8	-10	4	5	11.6	-12.8
-5	2	10	15.7	15.3	10	2	-4	12.7	-12.9	6	3	4	7.6	7.8	4	4	-7	36.4	-41.0	-10	4	6	10.8	11.1
-5	2	-4	36.4	33.5	10	2	-5	17.4	14.9	6	3	5	12.5	13.9	4	4	-8	29.5	30.9	-10	4	7	10.8	-7.0
-5	2	-5	31.2	-30.3	-10	2	4	23.4	22.9	6	3	6	27.3	-24.8	4	4	-9	13.9	-14.4	-10	4	-6	9.4	-16.3
-5	2	-7	30.4	34.3	-10	2	5	12.9	-14.8	6	3	-5	30.9	26.2	4	4	-11	21.5	22.5	11	4	-7	17.4	-15.1
-5	2	-9	16.3	-15.7	-10	2	6	24.3	-24.3	6	3	-6	29.4	23.6	4	4	-12	12.4	12.5	-11	4	5	15.4	-20.6
6	2	3	16.2	-17.2	-10	2	8	11.1	13.4	6	3	-7	15.1	-10.6	4	4	-13	14.0	-13.3	12	4	-6	16.7	9.9
6	2	5	18.0	18.0	-10	2	-3	14.0	-13.7	6	3	-8	30.9	-27.8	-4	4	5	24.3	-27.5	12	4	-8	11.4	-10.8
6	2	6	33.1	35.4	-10	2	-5	10.7	8.5	6	3	-9	38.1	34.8	-4	4	6	25.7	30.8	12	4	-9	12.4	12.9
6	2	7	25.3	-27.3	-10	2	-6	7.8	8.9	6	3	-11	18.2	-14.8	-4	4	7	24.3	29.0	-12	4	5	14.4	15.7
6	2	-3	36.9	35.5	-10	2	-7	14.3	-12.7	-6	3	4	12.1	14.4	-4	4	-6	16.6	-16.5	-12	4	6	11.3	-14.2
6	2	-4	15.4	15.6	11	2	-3	15.9	19.5	-6	3	5	4.6	-6.2	-4	4	-7	23.7	24.8	-13	4	5	11.5	10.7
6	2	-5	11.8	11.7	11	2	-4	11.4	-12.7	-6	3	7	14.1	15.7	-4	4	-8	14.6	-14.6	5	5	9	15.1	-17.1
6	2	-6	27.1	-27.2	-11	2	5	14.6	11.9	-6	3	8	18.3	-22.6	-4	4	-9	7.6	-9.0	5	5	-5	28.8	-30.7
6	2	-7	15.5	17.8	-11	2	6	7.4	7.1	-6	3	10	8.8	16.3	-4	4	-10	13.5	-12.8	5	5	-6	17.2	15.8
6	2	-10	24.1	-28.2	-11	2	7	10.3	-11.2	-6	3	12	14.1	-21.3	-4	4	-11	19.2	15.7	5	5	-7	28.9	29.0
-6	2	3	9.1	-6.9	-11	2	11	13.1	-14.1	-6	3	-4	36.7	39.1	5	4	5	10.2	9.0	5	5	-8	14.4	-11.9
-6	2	5	8.1	7.3	-11	2	-5	13.7	11.0	-6	3	-5	23.4	-27.5	5	4	8	20.7	22.6	5	5	-9	14.4	-10.4
-6	2	6	36.2	-33.4	-11	2	-6	11.7	-9.0	-6	3	-6	10.3	-15.2	5	4	10	13.7	-17.0	5	5-10		14.3	12.6
-6	2	7	19.4	15.8	12	2	-4	15.0	15.8	-6	3	-7	12.7	16.7	5	4	-5	57.2	54.1	5	5-11		17.5	-17.7
-6	2	8	22.8	22.3	12	2	-5	13.9	-15.0	-6	3	-8	10.1	-14.8	5	4	-6	17.8	15.0	-5	5	7	6.2	8.7
-6	2	9	21.3	-18.6	-12	2	5	24.0	-22.0	7	3	5	11.4	-11.5	5	4	-7	11.4	-10.8	-5	5	8	11.5	-13.4
-6	2	-3	17.6	16.6	-12	2	5	12.4	12.7	7	3	6	9.1	-11.1	5	4	-8	37.0	-31.0	-5	5	9	7.4	5.3
-6	2	-5	25.5	-27.1	-13	2	6	16.9	-18.9	7	3	7	15.6	14.8	5	4	-9	28.8	23.9	-5	5	10	12.5	14.0
-6	2	-6	29.7	27.1	-14	2	5	8.4	7.2	7	3	-4	24.2	21.5	5	4	10	24.8	-20.8	-5	5	11	9.6	8.0
-6	2	10	9.4	10.7	3	3	3	47.4	-44.3	7	3	-5	40.7	-41.1	5	4	11	7.6	-5.5	-5	5	-6	17.5	-15.3
-6	2	11	18.4	-18.1	3	3	4	28.1	23.1	7	3	-6	16.5	13.6	5	4	13	15.1	13.7	-5	5	-7	9.2	8.2
7	2	3	18.8	18.0	3	3	5	43.1	43.4	7	3	-7	22.5	17.9	-5	4	5	7.7	-5.8	-5	5	-8	9.3	6.6
7	2	5	23.2	24.8	3	3	-4	42.6	-46.0	7	3	-8	28.5	-22.6	-5	4	6	33.1	-38.9	6	5	8	13.6	-11.2
7	2	6	33.0	-33.7	3	3	-7	6.6	8.4	7	3	-10	21.9	20.3	-5	4	7	16.6	17.8	6	5	-6	21.6	-18.5
7	2	-3	18.4	-18.7	3	3	-8	12.8	-13.9	7	3	-12	9.8	-7.4	-5	4	11	10.3	12.5	6	5	-8	26.3	22.7
7	2	-4	17.3	-20.1	3	3	-9	18.9	18.6	-7	3	4	18.3	20.3	-5	4	-5	23.5	-21.6	6	5	12	13.7	-7.3
7	2	-5	9.3	-9.0	3	3	12	23.2	-26.5	-7	3	6	18.5	23.9	-5	4	-6	39.4	41.8	-6	5	7	23.2	-25.3
7	2	-6	24.9	27.5	-4	3	5	15.8	18.5	-7	3	-6	37.0	-48.3	-5	4	-7	12.7	-10.1	-6	5	8	21.5	24.3
7	2	-7	24.4	-27.7	-3	3	7	17.5	21.9	-7	3	7	9.8	12.6	-5	4	-8	7.6	6.9	-6	5	8	15.1	-13.3
7	2	-9	21.3	22.0	-3	3	11	19.4	-24.8	-7	3	8	13.5	15.7	-5	4	12	15.3	17.8	-6	5	9	21.3	-23.4
7	2	10	9.4	10.4	-3	3	-4	44.6	43.9	-7	3	11	12.8	14.7	6	4	-5	24.7	-27.4	-6	5	11	12.6	13.5
7	2	11	24.4	-29.6	-3	3	-5	16.5	14.3	-7	3	-7	26.9	-26.6	6	4	-6	10.2	5.9	-6	5	-6	24.5	28.2
-7	2	3	35.5	-36.1	-3	3	-6	15.2	-12.9	-7	3	-6	9.7	13.7	6	4	-7	54.1	47.5	-6	5	-7	12.7	14.7
-7	2	4	19.4	-18.4	-3	3	-9	16.5	-16.8	8	3	5	15.1	-16.5	6	4	-8	18.9	-13.7	7	5	-6	22.4	-19.8
-7	2	5	8.4	7.9	-3	3	11	11.2	11.9	8	3	6	15.2	12.2	6	4	-9	23.3	-16.7	7	5	-8	15.4	-12.4
-7	2	6	39.7	37.2	-3	3	12	8.8	-8.3	8	3	-4	16.6	14.3	6	4	10	14.6	11.8	7	5	-9	9.7	6.8
-7	2	7	36.6	-34.7	4	3	5	42.4	-38.9	8	3	-5	57.9	53.5	6	4	11	13.4	-11.6	7	5	11	9.1	8.3
-7	2	8	14.9	12.5	4	3	10	13.5	14.0	8	3	-6	42.8	-35.4	-6	4	5	30.4	32.0	-7	5	8	9.6	11.2
-7	2	12	11.3	12.2	4	3	-4	41.1	-32.1	8	3	-9	18.5	-14.8	-6	4	6	19.5	25.2	-7	5	11	8.2	-10.0
-7	2	-3	16.4	16.7	4	3	-8	16.3	15.0	-8	3	4	8.2	-10.3	-6	4	7	15.8	-19.1	-7	5	-6	6.8	-5.5
-7	2	-4	52.5	-48.5	4	3	-10	29.8	27.5	-8	3	5	17.5	21.9	-6	4	8	14.5	17.8	-7	5	-10	11.8	-14.2
-7	2	-5	16.6	14.7	4	3	12	10.8	-7.9	-8	3	6	8.0	7.9	-6	4	11	20.7	-25.2	8	5	-6	11.7	11.1
-7	2	13	12.3	-11.1	4	3	13	15.3	-15.7	-8	3	7	25.5	-34.8	-6	4	12	9.1	12.0	8	5	11	13.6	-11.8
8	2	3	8.0	-9.2	4	3	14	15.5	13.7	-8	3	-4	20.0	-25.6	-6	4	-5	31.2	37.8	-8	5	6	11.3	13.0
8	2	5	8.0	-8.2	-4	3	4	10.7	10.7	-8	3	-5	12.1	14.9	-6	4	-6	13.4	-16.2	-8	5	7	7.9	8.3
8	2	-3	18.6	18.6	-4	3	5	27.3	-31.5	9	3	5	14.4	9.6	7	4	-6	33.4	-25.0	-8	5	9	12.2	-12.1
8	2	-4	20.9	22.7	-4	3	6	11.4	-13.5	9	3	-4	13.9	-8.8	7	4	-7	12.3	9.1	-8	5	10	12.3	13.3
8	2	-5	34.3	-39.3	-4	3	7	13.7	16.3	9	3	-5	22.1	18.6	7	4	-8	21.9	16.3	-8	5	-7	8.9	11.7
8	2	-7	13.2	10.9	-4	3	8	15.5	19.2	9	3	-6	20.3	17.4	-7	4	5	29.3	-36.3	-8	5	-9	12.9	-15.0
8	2	-8	12.0	-12.5	-4	3	14	33.3	-41.2	9	3	-8	23.1	21.8	-7	4	9	14.5	17.3	9	5	-6	11.2	-8.7
8	2	-10	17.3	18.7	-4	3	-6	6.5	8.4	9	3	-9	22.1	-16.8	-7	4	7	11.3	12.3	9	5	11	17.2	13.6
-8	2	3	32.3	29.3	-4	3	-7	22.3	-28.2	-9	3	6	17.3	21.9	-7	4	12	13.4	-18.3	9	5	12	11.4	-9.9
-8	2	4	22.8	-19.9	-4	3	-8	7.2	-8.3	10	3	-4	23.1	-19.2	-7	4	-5	14.7	-18.4	9	5	13	11.2	-10.0
-8	2	5	12.7	-12.1	-4	3	10	21.3	23.3	10	3	-9	16.2	12.2	-7	4	-6	9.7	-14.1	-9	5	8	15.6	16.0
-8	2	6	27.5	26.7	5	3	4	26.5	-29.3	-10	3	4	13.8	12.7	-7	4	8	11.4	-16.1	-9	5	9	11.5	-12.7
-8	2	8	21.8	-20.6	5	3	5	10.1	7.0	-10	3	5	24.5	-27.2	8	4	5	21.6	18.6	-9	5	10	11.7	-11.5
-8	2	9	17.4	16.0	5	3	6	16.3	16.0	-10	3	6	9.5	12.2	8	4	-5	11.0	8.4	-9	5	-8	12.2	-11.9
-8	2	10	22.0	-21.3	5	3	7	10.8	-13.5	-10	3	-4	14.4	-15.7	8	4	-6	9.3	8.6	10	5	-7	27.6	-24.0
-8	2	13	12.8	13.8	5	3	9	14.9	16.2	-10	3	-7	13.1	19.1	8	4	-7	15.1	-13.5	10	5	-8	13.5	14.6
-8	2	14	8.5	-6.5	5	3	-4	30.4	28.1	11	3	4	6.8	-9.8	8	4	-8	17.7	13.2	10	5	-9	8.5	-6.5
-8	2	-3	32.7	-26.7	5	3	-5	14.2	-11.9	11	3	-5	12.7	-11.9	8	4	-9	13.5	-9.8	10	5	-10	9.0	5.9
-8	2	-4	23.8	22.7	5	3	-6	7.8	-8.2	11	3	-7	12.2	-9.4	-8	4	6	21.4	-27.3	10	5	12	19.1	15.8
-8	2	-5	9.2	8.1	5	3	-7	40.4	-35.7	-11	3	5	12.5	15.9	-8	4	7	8.3	-9.2	-10	5	9	14.2	15.1
-8	2	-6	13.1	9.6	5	3	-8	15.0	13.9	-11	3	6	10.9	-17.3	-8	4	8	10.5	12.7	-10	5	10	12.4	-12.3
9	2	3	11.0	13.1	5	3	-9	16.2	-17.3	-11	3	7	11.6	16.1	-8	4	-8	14.4	-18.4	-10	5	-7	13.1	-12.7
9	2	-3	12.3	-12.4	5	3	11	15.1	13.6	-11	3	11	13.3	-16.2	-8	4	-9	12.3	20.2	-11	5	9	13.4	11.6
9	2	-4	22.2	24.5	5	3	12	13.2	13.5	-11	3	-6	9.5	14.1	9	4	-9	22.0	14.8	-11	5	-6	11.2	-13.6
9	2	-5	21.5	25.1	5	3	-13	16.3	-13.4	12	3	-9	12.9	10.5	9	4	12	14.7	-7.9	-12	5	7	8.3	10.1
9	2	-6	24.4	-30.2	-5	3	4	23.5	27.6	12	3	-10	21.8	-18.8	9	4	13	10.5	13.8	-12	5	8	8.5	-11.7
-9	2	4	15.1	-15.4	-5	3	5	9.5	8.6	-12	3	4	16.8	-22.6	-9	4	5	21.3	26.6	-12	5	9	9.1	-5.9
-9	2	5	17.1	-17.3	-5	3	6	18.8	-22.1	-12	3	5	11.1	10.4	-9	4	9	10.5	11.9	-12	5	10	9.8	8.5
-9	2	7	27.1	26.4	-5	3	7	31.4	-36.5	-12	3	11	12.6	-15.4	-9	4	-6	14.3	18.9	-13	5	8	13.2	14.4

$|F_o|$, in this case 7·0. With such a weighting scheme no trends were apparent when the average values of $w(F_o-F_c)^2$ were plotted *versus* $|F_o|$. In the last refinement cycle no parameter shifted by more than 0·1 of the estimated standard deviation.

The atomic scattering factors used in the structure factor calculations were obtained from *International Tables for X-ray Crystallography* (1962).

The observed and calculated structure factors are compared in Table 1. The atomic parameters used

Table 2. *Positional parameters of the heavy atoms in fractional coordinates and, in parentheses, the significant figures of their standard deviations*

	x	*y*	*z*
Co	0·2934 (2)	*x*	*x*
S(1)	0·2359 (3)	0·4688 (3)	0·4504 (3)
S(2)	0·1004 (3)	0·3482 (3)	0·1574 (3)
O	0·0193 (9)	0·5636 (9)	0·3235 (9)
C(1)	0·1055 (12)	0·4682 (13)	0·3087 (12)
C(2)	−0·0976 (16)	0·5537 (16)	0·2038 (15)
C(3)	−0·1456 (15)	0·6950 (15)	0·2313 (13)

Table 3. *Thermal parameters of the heavy atoms and, in parentheses, the significant figures of their standard deviations*

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0·0055 (2)	β_{11}	β_{11}	0·0015 (2)	β_{12}	β_{12}
S(1)	0·0073 (4)	0·0078 (4)	0·0056 (3)	0·0028 (3)	0·0008 (3)	0·0013 (3)
S(2)	0·0080 (4)	0·0082 (4)	0·0057 (3)	0·0026 (3)	0·0009 (3)	0·0010 (3)
O	0·0097 (12)	0·0115 (13)	0·0088 (12)	0·0070 (10)	0·0013 (10)	0·0011 (10)
C(1)	0·0071 (14)	0·0087 (15)	0·0053 (13)	0·0029 (12)	0·0029 (11)	0·0010 (11)
C(2)	0·0136 (21)	0·0145 (22)	0·0110 (19)	0·0083 (18)	0·0010 (17)	0·0065 (18)
C(3)	0·0159 (23)	0·0148 (22)	0·0101 (19)	0·0118 (19)	0·0026 (17)	0·0058 (17)

in the final structure factor calculations are given in Tables 2–4.

Table 4. *Calculated parameters for the hydrogen atoms*

	x	*y*	*z*
H(1)	−0·064	0·536	0·103
H(2)	−0·187	0·462	0·198
H(3)	−0·237	0·693	0·143
H(4)	−0·058	0·784	0·237
H(5)	−0·182	0·710	0·332

Description and discussion of the structure

The structure consists of enantiomorphous molecules $Co(S_2COC_2H_5)_3$ (Fig. 1); their crystal packing (Fig. 2) is governed by normal van der Waals interactions.

The interatomic distances and bond angles were calculated by means of the *ORFFE* program of Busing, Martin & Levy (1964). The closest intermolecular distances (less than 4·0 Å) are reported in Table 9. The atoms of the different asymmetric units are related to the symmetry equivalent atoms of the fundamental unit as follows:

i	atom at	z	x	y
ii	atom at	$-x$	$1-y$	$1-z$
iii	atom at	$1-z$	$1-x$	$1-y$
iv	atom at	$1-y$	$1-z$	$1-x$
v	atom at	z	$1+x$	y
vi	atom at	$-x$	$1-y$	$-z$

Intramolecular distances and bond angles are reported in Tables 5, 6 and 7 and in Fig. 1.

The molecule has symmetry C_3–3, with three ethylxanthic ligands coordinated to cobalt through the sulphur atoms; distances and angles in the cobalt coordination sphere are given in Table 7.

Among the crystal structures of metal xanthates so far determined, the most similar to that of Co^{III} ethylxanthate are those of arsenious (Carrai & Gottardi, 1960) and antimonious xanthates (Gottardi, 1961); in these compounds the molecules have trigonal symmetry with three xanthic ligands coordinated to the metal atom, so that the six sulphur atoms form a distorted octahedron around it. There are only three sulphur atoms at a bonding distance, however, so that the two S–C bonds in each ligand are not equivalent, which is

Table 5. *Bond distances with their standard deviations*

	Distance	e.s.d.	Mean	Calculated
Co—S(1)	2·276 Å	0·004 Å	2·277 Å	
Co—S(2)	2·277	0·004		
S(1)–C(1)	1·674	0·012	1·673	1·669 Å
S(2)–C(1)	1·671	0·012		
C(1)–O	1·359	0·017	1·359	1·359
O—C(2)	1·431	0·017		
C(2)–C(3)	1·514	0·022		

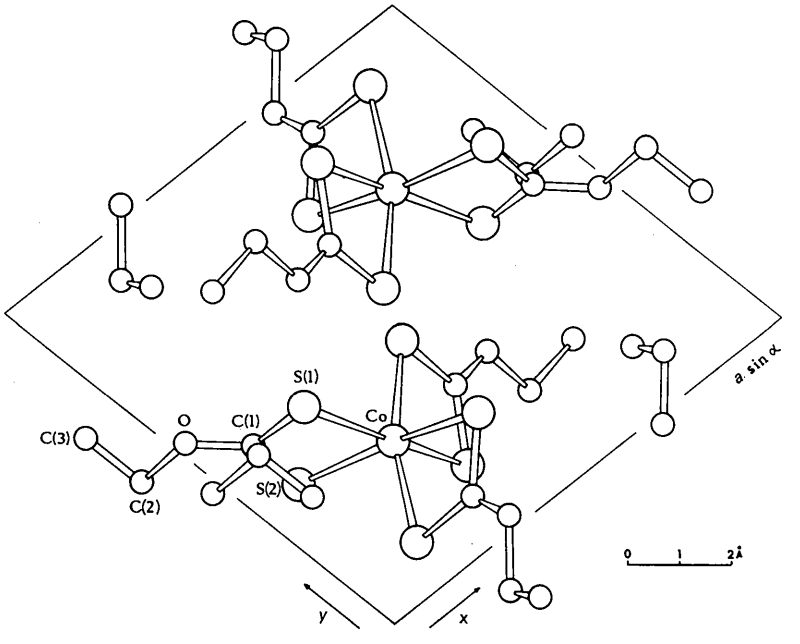


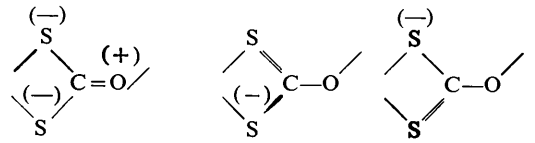
Fig. 2. [001] projection of the unit cell.

Table 6. *Bond angles with standard deviations*

	Angle	e.s.d.
S(1)–Co—S(2)	76° 6′	9′
Co—S(1)–C(1)	84 56	27
Co—S(2)–C(1)	84 58	27
S(1)–C(1)–S(2)	114 1	48
S(1)–C(1)–O	119 28	48
S(2)–C(1)–O	126 29	50
C(1)–O—C(2)	118 9	57
O—C(2)–C(3)	106 38	1° 1′

particularly evident in the more precisely determined structure of antimonious xanthate. In the present structure, on the other hand, the ethylxanthic group has two chemically equivalent sulphur atoms. All the atoms of each ligand, apart from the terminal carbon atom, lie in a plane with the cobalt atom (Table 8).

The mean values of the S–C and C–O bond lengths are 1·673 Å and 1·359 Å respectively (see Table 5); the bond distances calculated in terms of the valence-bond theory agree very well with these values, assuming the following contributions of the resonance structures:



(I) 13% (II) 43·5% (III) 43·5%

Bond order – bond length curves were derived with the use of the Pauling relation:

$$r_x = r_1 - (r_1 - r_2)\frac{3x}{2x+1}.$$

It was assumed that for the S–C bond $r_1 = 1{\cdot}812$ Å and $r_2 = 1{\cdot}607$ Å (Pauling, 1960); for the C–O bond $r_1 = 1{\cdot}437$ Å and $r_2 = 1{\cdot}185$ Å (Cox & Jeffrey, 1951). The corresponding resonance structures in Co^{III} diethyldithiocarbamate gave the contributions: 42%, 29%, 29%. The calculated values are reported in Table 5 for comparison with the observed values.

The hypothesis of Chatt, Duncanson & Venanzi, reported in the introduction, on the minor contribution of the resonance form of the type (I) in xanthates relative to that in the dithiocarbamates, is fully confirmed.

Chatt, Duncanson & Venanzi (1956*a*,*b*) also emphasize that the dithiocarbamic ligand, owing to the greater electron drift into the sulphur atoms, should form stronger complexes than the xanthic ligand; this explains the longer Co–S bond length (2·277 Å) found in Co^{III} ethylxanthate as compared with the value (2·258 Å) found in Co^{III} diethyldithiocarbamate.

As regards bond angles, the difference between S(1)–C(1)–O (119·5°) and S(2)–C(1)–O (126·5°) is noteworthy; this difference is the result of the steric interaction S(2)···C(2) (3·03 Å). In fact in Co^{III} diethyldithiocarbamate where both the sulphur atoms, of the ligand are subject to similar steric interactions, the corresponding angles are: S(1)–C(4)–N(2), 124·0°, S(3)–C(4)–N(2), 126·0°; S(2)–C(1)–N(1), 125·1°. Moreover the bond angles S(1)–C(4)–S(3) and S(2)–C(1)–$S(2^i)$ are reduced to 110° compared with the value of 114° found in Co^{III} ethylxanthate.

The two-dimensional Patterson and Fourier syntheses were calculated on the Calcolatrice Elettronica Pisana (C.E.P.). All the other calculations were performed on the IBM 7090 computer of the Centro Nazionale Universitario di Calcolo Elettronico (Pisa).

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Table 7. *Distances and angles in the cobalt coordination sphere*

Co—S(1)	2·276 Å	S(1)–Co–S(2)	76° 6′
Co—S(2)	2·277	S(1)–Co–$S(1^i)$	94 17
S(1)–S(2)	2·806	S(1)–Co–$S(2^i)$	96 47
S(1)–$S(1^i)$	3·337	S(2)–Co–$S(1^i)$	165 49
S(1)–$S(2^i)$	3·404	S(2)–Co–$S(2^i)$	94 28
S(2)–$S(2^i)$	3·344		

Table 8. *Mean-plane parameters and deviations of atoms from the plane*

The equation of the plane is in the form $Ax + By + Cz = D$, where x, y and z are fractional coordinates, calculated after Schomaker, Waser, Marsh & Bergman (1959).

A	*B*	*C*	*D*	Atoms defining the plane
5·5026	6·3176	−5·2388	1·9241	Co, S(1), S(2), C(1), O, C(2)

	Deviation		Deviation
Co	0·007 Å	C(1)	−0·003 Å
S(1)	−0·024	O	0·048
S(2)	0·004	C(2)	−0·031
		C(3)	0·454

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Table 9. *Shortest intermolecular distances*

S(1)···S(1^{iii})	3·60 Å
S(1)···O^{ii}	3·59
S(1)···C(2^{ii})	3·85
S(1)···C(3^{ii})	3·86
S(2)···C(2^{vi})	3·78
S(2)···C(3^{vi})	3·81
O ····O^{ii}	3·89
O ····C(2^{v})	3·52
O ····C(3^{iv})	3·94
C(1)···C(3^{iv})	3·92

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On the Crystal Structure of Pumpellyite

BY E. GALLI AND A. ALBERTI

Istituto di Mineralogia dell'Università di Modena, Italy

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Pumpellyite, $Ca_8Al_8(Mg, Fe^{II}, Fe^{III}, Al)_4$ $[(SiO_4)_4/(Si_2O_7)_4/(OH)_8(H_2O, OH)_4]$ is a mixed-group silicate, like epidote, which crystallizes in the monoclinic system, space group $A2/m$, with $a=8·83$, $b=5·90$, $c=19·17$ Å, $\beta=97°7'$ and $Z=1$. The structure was refined, with isotropic thermal parameters, by the least-squares method to an R value of 12·3% for observed reflexions. Pumpellyite is characterized by the presence of two types of symmetrically independent chains of octahedra. The first type, through the point ($a/2$, $c/4$), is made up of Al (50%), Mg (35%), Fe (15%), the second of Al only. Both types of chain are united by isolated tetrahedra, SiO_4, and double tetrahedra, Si_2O_7. Finally, in the crystal structure there are two independent calcium atoms in sevenfold coordination. An interesting feature is the distorted coordination of one tetrahedron of the group Si_2O_7. All other bond distances are within the limits given in the literature.

Introduction

The silicate mineral pumpellyite, like epidote, is characteristic of low grade metamorphic rocks. Pumpellyite probably occurs in nature more frequently than is usually believed; it is easily mistaken for epidote.

This is a report of the refinement of the crystal structure of the mineral. A description of the unrefined structure has been given by Gottardi (1965).

Experimental

The pumpellyite studied was from Hicks Ranch, Sonoma County, California, U.S.A.

The unit-cell data, $a=8·83\pm0·01$, $b=5·90\pm0·01$, $c=19·17\pm0·02$, $\beta=97°7'\pm5'$ were determined, and are similar to those given by Coombs (1953). These data were obtained by a least-squares method starting from the lattice spacings measured on a Guinier–De Wolff powder diagram (Cu radiation) calibrated with 10% silicon powder. The space group was confirmed as $A2/m$.

The density was measured, on small splinters weighing a few milligrams, with a torsion microbalance; the result was $D_{exp}=3·18\pm0·03$ g.cm^{-3}.

A chemical analysis was performed by A. Alietti; the results of this analysis allows the calculation of the following formula, on the basis of 56 oxygen atoms:

$(Ca_{7·60}Mg_{0·40})_{tot=8·00}(Mg_{1·20}Fe^{II}_{0·77}Fe^{III}_{0·18}Al_{10·00})_{tot=11·97}[Si_{11·20}Al_{0·80})_{tot=12·00}O_{44}/\{(OH)_{9·29}(H_2O)_{2·71}\}_{tot=12·00}]$,
$Z=1$.

The above formula and unit-cell constants lead to a calculated density of $D_{calc}=3·20$.

The different atoms are grouped following the crystallochemical rules, to reach totals of atomic coefficients near to multiples of 4 (positions with a multipli-