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The Crystal and Molecular Structure of Tris(ethylthioxanthato)cobalt(III), Co(C₂H₅SCS₂)₃

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The crystal and molecular structure of tris(ethylthioxanthato)cobalt(III), $Co(C_2H_5SCS_2)_3$, has been determined by a three-dimensional X-ray analysis, using data collected by an 'on-line' automated diffractometer (Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å). The structure was determined by Patterson and Fourier methods and refined by means of anisotropic least-squares methods down to a conventional $R = 4.6\%$. All the hydrogen atoms have been located. Crystal data are as follows: $a = 10.23(1)$, $b = 17.56(1)$, $c = 11.71(1)$ Å; $\alpha = 91.1(1)$, $\beta = 115.5(1)$, $\gamma = 94.6(1)°$; $Z = 4$. Space group: $P\bar{1}$. There are two independent molecules in the asymmetric unit; in both of them the cobalt is surrounded by six sulphur atoms from three ligand ions, which are arranged at the corners of an octahedron distorted to D_3 symmetry. The Co–S distances (mean value: 2.398(1) Å) are longer than those found in tris(diethyldithiocarbamato)-Co(III) (mean value: 2.258(1) Å) and in tris-(O-ethylxanthato)Co(III) (mean value 2.277(3) Å). The two non-equivalent molecules are identical stereochemically, apart from a distortion of the ethyl groups. Packing is determined by van der Waals contacts.

Introduction

Recent research concerning the chemical, magnetic and spectroscopic properties of metal alkylthioxanthates has been published by Corazza & Pelizzi (1970). The crystal structure determination of the product obtained by recrystallizing (from chloroform and ethanol) bis(ethylthioxanthato)nickel(II), Ni(ETX)₂, (ETX = ethylthioxanthato), showed that, during this operation, parts of the ligands decompose and dimers are formed

by ethylthiolato bridges (Chiesi Villa, Gaetani Manfredotti, Nardelli & Pelizzi, 1970). On the other hand, no change is observed on recrystallizing Co(ETX)₃, as shown by the X-ray structure determination reported in the present paper. The interest in this analysis was due to the fact that there is no exhaustive information concerning the sulphur coordination sphere in Co(III) complexes, particularly from the structural point of view. Hitherto, only two structures of Co(III) compounds with ligands containing sulphur have been

studied, *viz.* tris(diethyldithiocarbamato)Co(III), Co(DTC)$_3$, (Merlino, 1968) and tris-(O-ethylxanthato)-Co-(III), Co(EX)$_3$, (Merlino, 1969).

Experimental

The crystals of Co(ETX)$_3$ examined in the present work were prepared by Corazza & Pelizzi (1970). They were dark-green flattened prisms elongated along [001], showing pleochroic effects: on observation along a direction normal to the flattened faces, they appeared bottle-green when the electric vector vibrated parallel to [001] and black-green when the electric vector was perpendicular to [001]. The unit-cell dimensions, determined from rotation and Weissenberg photographs and refined by an 'on-line' single-crystal automated Siemens diffractometer using Mo $K\alpha$ radiation ($\bar{\lambda} = 0.7107$ Å), are as follows:

Co(C$_2$H$_5$SCS$_2$)$_3$, $M = 470.8$
$a = 10.23$ (1), $b = 17.56$ (1), $c = 11.71$ (1) Å

$\alpha = 91.1$ (1), $\beta = 115.5$ (1), $\gamma = 94.6$ (1)°
$V = 1890$ Å^3, $Z = 4$, $D_x = 1.96$, $D_m = 1.97$ g.cm^{-3}
$\mu = 18.7$ cm^{-1} (Mo $K\alpha$), $F(000) = 960$
Space group: $P\bar{1}$ (from structural analysis).

Three-dimensional intensity data were collected on the same diffractometer using the $\omega/2\theta$ scan technique ($2\theta_{max} = 58°$) and Mo $K\alpha$ radiation. Intensities of 9991 reflexions were measured; of these 5257, having $I > 2\sigma(I)$, were used in the refinement.

The structure amplitudes were obtained after the usual Lorentz and polarization reduction and the absolute scale was established by successive comparison with the calculated values. No correction for absorption was applied as the sample used to collect data was very small. (It was roughly a cylinder with a mean radius of 0.007 cm.)

Determination of the structure and refinement

The structure was solved by the heavy-atom technique,

Table 1. *Final atomic fractional coordinates* ($\times 10^4$), *thermal parameters* ($\times 10^2 \times 8\pi^2$Å^2) *and e.s.d.'s for non-hydrogen atoms*

The anisotropic temperature factor is:
$$\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)].$$

	$x/a(\sigma)$	$y/b(\sigma)$	$z/c(\sigma)$	$B_{11}(\sigma)$	$B_{22}(\sigma)$	$B_{33}(\sigma)$	$B_{12}(\sigma)$	$B_{13}(\sigma)$	$B_{23}(\sigma)$
Co(1)	535 (1)	2313 (1)	1640 (1)	343 (3)	299 (3)	307 (3)	30 (2)	157 (3)	−4 (2)
Co(2)	485 (1)	2767 (1)	6650 (1)	296 (3)	313 (3)	324 (3)	44 (2)	142 (2)	53 (2)
S(1)	2325 (1)	2746 (1)	911 (1)	271 (5)	302 (5)	295 (5)	35 (4)	133 (4)	63 (4)
S(2)	2709 (2)	1762 (1)	2955 (1)	341 (5)	316 (5)	270 (5)	68 (4)	121 (4)	68 (4)
S(3)	5255 (2)	2159 (1)	2482 (2)	238 (5)	482 (7)	439 (7)	54 (5)	88 (5)	80 (6)
S(4)	−953 (2)	1577 (1)	2416 (1)	389 (6)	312 (5)	302 (5)	10 (4)	226 (5)	−4 (4)
S(5)	−586 (1)	1228 (1)	153 (1)	314 (5)	273 (5)	299 (5)	−20 (4)	182 (4)	−48 (4)
S(6)	−2508 (2)	169 (1)	925 (1)	408 (6)	312 (6)	435 (7)	−61 (5)	227 (5)	26 (5)
S(7)	−1257 (1)	3127 (1)	389 (1)	280 (5)	278 (5)	234 (4)	48 (4)	91 (4)	−5 (4)
S(8)	884 (2)	3427 (1)	2990 (1)	396 (6)	270 (5)	227 (5)	73 (4)	69 (4)	−24 (4)
S(9)	−1240 (2)	4547 (1)	1899 (1)	519 (7)	319 (6)	339 (6)	166 (5)	111 (5)	−40 (5)
S(11)	2128 (1)	2428 (1)	5808 (1)	227 (4)	303 (5)	280 (5)	5 (4)	110 (4)	−29 (4)
S(12)	2760 (1)	3519 (1)	7901 (1)	324 (5)	278 (5)	334 (5)	5 (4)	146 (4)	−52 (4)
S(13)	5102 (1)	3314 (1)	7150 (1)	250 (5)	346 (6)	402 (6)	−51 (4)	129 (4)	−33 (5)
S(14)	−878 (1)	3420 (1)	7509 (1)	341 (5)	313 (5)	277 (5)	77 (4)	177 (4)	62 (4)
S(15)	−622 (1)	3727 (1)	5189 (1)	340 (5)	342 (6)	307 (5)	118 (4)	191 (4)	129 (4)
S(16)	−2555 (2)	4601 (1)	5990 (2)	397 (6)	307 (6)	456 (7)	147 (5)	214 (5)	66 (5)
S(17)	−1381 (1)	1782 (1)	5409 (1)	248 (5)	300 (5)	230 (4)	14 (4)	60 (4)	51 (4)
S(18)	834 (1)	1699 (1)	7964 (1)	308 (5)	261 (5)	228 (4)	8 (4)	50 (4)	47 (4)
S(19)	−1225 (2)	337 (1)	6817 (1)	458 (7)	288 (6)	322 (6)	−61 (5)	99 (5)	55 (4)
C(1)	3443 (5)	2237 (3)	2081 (5)	325 (21)	247 (19)	271 (19)	6 (16)	113 (16)	−15 (15)
C(2)	5590 (6)	2634 (4)	1264 (7)	314 (24)	399 (27)	644 (34)	43 (20)	283 (24)	101 (24)
C(3)	5169 (7)	2106 (4)	80 (6)	376 (26)	599 (35)	435 (28)	119 (24)	191 (23)	85 (24)
C(4)	−1359 (5)	986 (3)	1126 (4)	243 (17)	228 (18)	266 (18)	47 (14)	116 (15)	21 (14)
C(5)	−2767 (6)	−289 (3)	−566 (6)	366 (24)	278 (22)	416 (25)	−24 (18)	128 (20)	−49 (18)
C(6)	−3959 (7)	17 (4)	−1691 (6)	350 (26)	657 (39)	440 (30)	63 (25)	88 (23)	57 (26)
C(7)	−560 (5)	3712 (3)	1722 (4)	311 (20)	224 (18)	250 (18)	30 (15)	118 (16)	11 (14)
C(8)	−2692 (7)	4668 (4)	336 (6)	399 (27)	469 (30)	414 (27)	198 (23)	27 (22)	−25 (22)
C(9)	−2094 (9)	5037 (5)	−530 (7)	743 (45)	569 (39)	461 (33)	135 (34)	169 (31)	188 (29)
C(11)	3346 (5)	3073 (3)	6940 (4)	252 (18)	235 (18)	259 (18)	22 (14)	92 (15)	65 (14)
C(12)	5323 (6)	2650 (3)	6052 (6)	321 (23)	394 (26)	475 (27)	16 (19)	215 (21)	−53 (21)
C(13)	5703 (8)	1872 (4)	6610 (8)	504 (33)	402 (30)	873 (47)	122 (25)	375 (34)	42 (30)
C(14)	−1359 (5)	3919 (3)	6182 (5)	263 (18)	185 (17)	344 (20)	45 (14)	158 (16)	26 (14)
C(15)	−2910 (7)	4975 (3)	4459 (6)	468 (29)	347 (25)	407 (26)	159 (22)	132 (22)	138 (20)
C(16)	−4113 (8)	4479 (5)	3363 (7)	463 (34)	762 (46)	475 (34)	153 (32)	48 (27)	26 (31)
C(17)	−616 (5)	1261 (3)	6692 (4)	287 (19)	223 (17)	248 (17)	34 (14)	140 (15)	28 (13)
C(18)	−2667 (6)	54 (3)	5247 (6)	362 (24)	332 (24)	383 (25)	−80 (19)	41 (20)	3 (19)
C(19)	−2074 (8)	−229 (4)	4345 (7)	577 (37)	553 (36)	466 (32)	−51 (29)	136 (28)	−159 (27)

starting from the analysis of the three-dimensional Patterson function. Because $Z=4$, it was assumed that the $P\bar{1}$ space group was the most probable one, with two non-equivalent molecules in the unit cell. This assumption proved correct and only one Fourier synthesis, calculated with the contributions of Co(1) and Co(2) only, was sufficient to locate all non-hydrogen atoms. Refining by block-diagonal least squares (the minimized function was $\sum w(\Delta F)^2$ with unit weights) gave $R=5\cdot2\%$. A very small improvement (to $R=5\cdot1$ %) was obtained by using weighting coefficients, derived from the $\langle|\Delta F|\rangle$ versus $\langle F_o\rangle$ distribution (Stout & Jensen, 1968). All the hydrogen atoms were subsequently located by an F_o-F_c synthesis and the complete least-squares refinement (isotropic for H's) led to a final R index of $4\cdot6\%$. The final atomic parameters with e.s.d.'s are given in Tables 1 and 2. The list of observed and calculated structure factors is available from the authors on request.

Table 2. *Coordinates* ($\times 10^3$), *thermal parameters* ($\times 10 \times 8\pi^2\text{Å}^2$) *and e.s.d.'s for the hydrogen atoms*

	$x/a(\sigma)$	$y/b(\sigma)$	$z/c(\sigma)$	$B(\sigma)$
H(2·1)	654 (6)	280 (3)	171 (5)	45 (12)
H(2·2)	522 (6)	309 (3)	112 (5)	38 (11)
H(3·1)	424 (6)	210 (3)	−35 (5)	47 (13)
H(3·2)	532 (6)	234 (3)	−48 (5)	50 (13)
H(3·3)	564 (6)	167 (3)	41 (5)	59 (14)
H(12·1)	618 (5)	292 (3)	600 (5)	35 (11)
H(12·2)	430 (6)	265 (3)	503 (5)	40 (11)
H(13·1)	675 (7)	203 (4)	736 (6)	64 (15)
H(13·2)	578 (6)	166 (4)	585 (6)	59 (14)
H(13·3)	484 (6)	168 (3)	664 (5)	51 (13)
H(5·1)	−176 (6)	−27 (3)	−56 (5)	45 (12)
H(5·2)	−303 (6)	−89 (3)	−41 (5)	47 (12)
H(6·1)	−386 (6)	51 (3)	−174 (5)	55 (14)
H(6·2)	−397 (6)	−23 (4)	−240 (6)	59 (14)
H(6·3)	−455 (7)	−22 (4)	−153 (6)	65 (15)
H(18·1)	−332 (6)	−30 (3)	530 (5)	41 (12)
H(18·2)	−325 (6)	51 (3)	499 (5)	41 (12)
H(19·1)	−138 (6)	27 (3)	415 (5)	53 (14)
H(19·2)	−145 (6)	−71 (3)	458 (5)	55 (14)
H(19·3)	−289 (6)	−52 (3)	359 (6)	53 (14)
H(8·1)	−342 (6)	500 (3)	39 (5)	49 (13)
H(8·2)	−303 (6)	416 (3)	7 (5)	52 (13)
H(9·1)	−144 (6)	547 (3)	−10 (6)	55 (14)
H(9·2)	−273 (7)	529 (4)	−115 (6)	69 (16)
H(9·3)	−163 (7)	463 (4)	−84 (6)	63 (15)
H(15·1)	−322 (6)	537 (3)	453 (5)	48 (12)
H(15·2)	−196 (6)	495 (3)	441 (5)	48 (13)
H(16·1)	−374 (7)	402 (4)	326 (6)	62 (15)
H(16·2)	−409 (6)	481 (4)	270 (6)	54 (14)
H(16·3)	−503 (7)	444 (4)	328 (6)	68 (15)

The atomic scattering factors used throughout the calculations were those of Cromer & Mann (1968) for Co, S and C and those of Stewart, Davidson & Simpson (1965) for H.

All calculations were performed on the C.D.C. 6600 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale (Bologna) using programs written by Immirzi (1967).

Description of the structure and discussion

The crystal structure consists of two crystallographically independent molecules in which each cobalt atom is surrounded by three ethylthioxanthato groups arranged at the vertices of a distorted octahedron (Fig. 1), and with each ethylthioxanthato group behaving as a bidentate ligand through two sulphur atoms. The two coordination octahedra are equivalent as far as the bond distances and angles on Co are concerned, as can be seen from Table 3, in which the relevant distances and angles are quoted.

The Co–S distances are not significantly different in both octahedra; their mean value [$2\cdot398$ (1) Å] is greater than the sum of the Pauling covalent radii ($2\cdot26$ Å) and greater than the distances found in other Co(III) complexes with ligands containing sulphur, e.g. in Co(DTC)_3 (mean value $2\cdot258$ (1) Å; Merlino, 1968) and in Co(EX)_3 (mean value $2\cdot277$ (3) Å; Merlino, 1969). (The parameters of these complexes are compared in Fig. 2.) These differences cannot be justified by steric hindrance in the coordination spheres, as the values found for the $\text{S}\cdots\text{S}$ contacts, involving different ligands, are larger in Co(ETX)_3 ($3\cdot48$–$3\cdot64$ Å) than in Co(DTC)_3 ($3\cdot31$–$3\cdot37$ Å) and in Co(EX)_3 ($3\cdot34$–$3\cdot44$ Å).

All these compounds are diamagnetic, so that the observed differences in the metal–sulphur distances are not related to any spin effects. The trend of the Co–S distances in these complexes does not agree with the ligand field strengths determined by Kanekar, Dhingra, Marathe & Nagarajan (1967) using the nuclear magnetic resonance of ^{59}Co and spectroscopic data, as can be seen from the values for the paramagnetic contributions to the chemical shifts (σ_{para}) and for the energy separation (E) between $^1A_{1g}$ and $^1T_{1g}$ states quoted in Table 4. Neither can the differences be accounted for by considering the distortion of the coordination sphere from the theoretical octahedron, as the distortion is of the same kind in the three compounds. In fact, all three compounds give stereographic projections which are coincident within 2–3° (Fig. 3). It is worthy of notice that the distortion approximately maintains D_3 symmetry for the ligand field in all these compounds. The observed discrepancies between Co–S distances and spectroscopic properties indicate the need for further work.

The values of the angles S–C–S in the coordination rings increase from Co(DTC)_3 to Co(EX)_3 and to Co(ETX)_3, and this trend can be related to the increasing of the π delocalization on the C–S bonds. On the other hand, the angles S–Co–S, which are nearly equal in Co(DTC)_3 and Co(EX)_3, become smaller in Co(ETX)_3, and this is connected with the larger Co–S distances.

The three coordination rings are not mutually per-

Table 3. *Distances and angles*

(*a*) In the two coordination polyhedra

Co(1)–S(1)	2·410 (3) Å	Co(2)–S(11)	2·391 (3) Å	S(1)Co(1)S(2)	73·9 (1)°	S(11)Co(2)S(12)	74·0 (1)°
Co(1)–S(2)	2·389 (4)	Co(2)–S(12)	2·409 (4)	S(1)Co(1)S(5)	97·6 (1)	S(11)Co(2)S(15)	97·3 (1)
Co(1)–S(4)	2·395 (3)	Co(2)–S(14)	2·386 (3)	S(1)Co(1)S(7)	95·9 (1)	S(11)Co(2)S(17)	94·1 (1)
Co(1)–S(5)	2·404 (4)	Co(2)–S(15)	2·408 (4)	S(1)Co(1)S(8)	96·2 (1)	S(11)Co(2)S(18)	95·1 (1)
Co(1)–S(7)	2·396 (4)	Co(2)–S(17)	2·394 (4)	S(1)Co(1)S(4)	165·0 (1)	S(11)Co(2)S(14)	165·7 (1)
Co(1)–S(8)	2·395 (3)	Co(2)–S(18)	2·400 (3)	S(2)Co(1)S(4)	94·3 (1)	S(12)Co(2)S(14)	95·1 (1)
				S(2)Co(1)S(5)	96·9 (1)	S(12)Co(2)S(15)	96·8 (1)
Co(1)S(1)C(1)	84·5 (2)°	Co2)S(11)C(11)	84·7 (2)°	S(2)Co(1)S(8)	97·7 (1)	S(12)Co(2)S(18)	98·3 (1)
Co(1)S(2)C(1)	84·9 (2)	Co(2)S(12)C(11)	84·3 (2)	S(2)Co(1)S(7)	166·5 (1)	S(12)Co(2)S(17)	165·5 (1)
Co(1)S(4)C(4)	84·1 (2)	Co(2)S(14)C(14)	83·9 (2)	S(4)Co(1)S(5)	74·2 (1)	S(14)Co(2)S(15)	74·3 (1)
Co(1)S(5)C(4)	83·9 (2)	Co(2)S(15)C(14)	83·6 (2)	S(4)Co(1)S(7)	97·1 (1)	S(14)Co(2)S(17)	97·9 (1)
Co(1)S(7)C(7)	84·5 (2)	Co(2)S(17)C(17)	84·6 (2)	S(4)Co(1)S(8)	94·6 (1)	S(14)Co(2)S(18)	95·7 (1)
Co(1)S(8)C(7)	84·3 (2)	Co(2)S(18)C(17)	84·4 (2)	S(5)Co(1)S(7)	93·2 (1)	S(15)Co(2)S(17)	92·9 (1)
				S(5)Co(1)S(8)	162·2 (1)	S(15)Co(2)S(18)	162·6 (1)
				S(7)Co(1)S(8)	74·3 (1)	S(17)Co(2)S(18)	74·1 (1)

(*b*) In the ligands

C(1)–S(1)	1·687 (6) Å	C(11)–S(11)	1·699 (5) Å	S(1)C(1)S(2)	116·7 (3)°	S(11)C(11)S(12)	116·9 (3)°
C(1)–S(2)	1·703 (7)	C(11)–S(12)	1·692 (6)	S(1)C(1)S(3)	126·2 (3)	S(11)C(11)S(13)	124·7 (3)
C(1)–S(3)	1·723 (6)	C(11)–S(13)	1·721 (6)	S(2)C(1)S(3)	117·1 (3)	S(12)C(11)S(13)	118·3 (3)
C(2)–S(3)	1·808 (9)	C(12)–S(13)	1·816 (7)	C(1)S(3)C(2)	104·7 (3)	C(11)S(13)C(12)	103·8 (3)
C(2)–C(3)	1·530 (10)	C(12)–C(13)	1·531 (9)	S(3)C(2)C(3)	112·3 (5)	S(13)C(12)C(13)	111·8 (5)
C(4)–S(4)	1·692 (5)	C(14)–S(14)	1·699 (6)	S(4)C(4)S(5)	117·8 (3)	S(14)C(14)S(15)	118·1 (3)
C(4)–S(5)	1·687 (6)	C(14)–S(15)	1·678 (7)	S(4)C(4)S(6)	117·2 (3)	S(14)C(14)S(16)	116·4 (3)
C(4)–S(6)	1·724 (6)	C(14)–S(16)	1·729 (6)	S(5)C(4)S(6)	124·9 (3)	S(15)C(14)S(16)	125·5 (3)
C(5)–S(6)	1·811 (7)	C(15)–S(16)	1·817 (8)	C(4)S(6)C(5)	105·0 (3)	C(14)S(16)C(15)	104·7 (3)
C(5)–C(6)	1·503 (8)	C(15)–C(16)	1·532 (9)	S(6)C(5)C(6)	112·8 (4)	S(16)C(15)C(16)	112·2 (5)
C(7)–S(7)	1·692 (5)	C(17)–S(17)	1·692 (5)	S(7)C(7)S(8)	116·9 (3)	S(17)C(17)S(18)	116·9 (3)
C(7)–S(8)	1·702 (5)	C(17)–S(18)	1·697 (5)	S(7)C(7)S(9)	124·9 (3)	S(17)C(17)S(19)	125·1 (3)
C(7)–S(9)	1·718 (6)	C(17)–S(19)	1·723 (6)	S(8)C(7)S(9)	118·2 (3)	S(18)C(17)S(19)	118·0 (3)
C(8)–S(9)	1·824 (6)	C(18)–S(19)	1·821 (6)	C(7)S(9)C(8)	104·5 (3)	C(17)S(19)C(18)	104·5 (2)
C(8)–C(9)	1·523 (13)	C(18)–C(19)	1·520 (12)	S(9)C(8)C(9)	111·4 (5)	S(19)C(18)C(19)	112·1 (5)
S(1)–S(2)	2·836 (4)	S(11)–S(12)	2·890 (4)				
S(1)–S(3)	3·042 (5)	S(11)–S(13)	3·029 (5)				
S(2)–S(3)	2·923 (4)	S(12)–S(13)	2·930 (3)				
S(4)–S(5)	2·893 (3)	S(14)–S(15)	2·896 (3)				
S(4)–S(6)	2·916 (5)	S(14)–S(16)	2·914 (4)				
S(5)–S(6)	3·025 (4)	S(15)–S(16)	3·029 (4)				
S(7)–S(8)	2·892 (5)	S(17)–S(18)	2·888 (4)				
S(7)–S(9)	3·024 (4)	S(17)–S(19)	3·030 (4)				
S(8)–S(9)	2·935 (4)	S(18)–S(19)	2·932 (5)				

(*c*) Involving hydrogen atoms

C(2)–H(21)	0·90 (5) Å	C(12)–H(12·1)	0·99 (6) Å	C(6)–H(62)	0·93 (7) Å	C(16)–H(16·2)	0·99 (7) Å
C(2)–H(22)	0·91 (6)	C(12)–H(12·2)	1·21 (5)	C(6)–H(63)	0·80 (8)	C(16)–H(16·3)	0·90 (8)
C(3)–H(31)	0·86 (5)	C(13)–H(13·1)	1·06 (5)	C(8)–H(81)	1·00 (6)	C(18)–H(18·1)	0·90 (6)
C(3)–H(32)	0·84 (6)	C(13)–H(13·2)	1·00 (8)	C(8)–H(82)	0·93 (5)	C(18)–H(18·2)	1·01 (6)
C(3)–H(33)	0·94 (5)	C(13)–H(13·3)	0·93 (7)	C(9)–H(91)	0·94 (5)	C(19)–H(19·1)	1·17 (6)
C(5)–H(51)	1·03 (7)	C(15)–H(15·1)	0·81 (6)	C(9)–H(92)	0·89 (6)	C(19)–H(19·2)	1·06 (6)
C(5)–H(52)	1·10 (5)	C(15)–H(15·2)	1·01 (7)	C(9)–H(93)	1·03 (8)	C(19)–H(19·3)	1·01 (5)
C(6)–H(61)	0·87 (5)	C(16)–H(16·1)	0·94 (8)				

(*d*) S···S contacts involving adjacent ligands

S(1)–S(5)	3·622 (5) Å	S(11)–S(15)	3·603 (5) Å	S(2)–S(8)	3·602 (4) Å	S(12)–S(18)	3·637 (4) Å
S(1)–S(7)	3·568 (4)	S(11)–S(17)	3·503 (4)	S(4)–S(7)	3·590 (4)	S(14)–S(17)	3·604 (5)
S(1)–S(8)	3·576 (4)	S(11)–S(18)	3·535 (4)	S(4)–S(8)	3·519 (4)	S(14)–S(18)	3·548 (4)
S(2)–S(4)	3·507 (5)	S(12)–S(14)	3·538 (4)	S(5)–S(7)	3·488 (3)	S(15)–S(17)	3·481 (3)
S(2)–S(5)	3·586 (6)	S(12)–S(15)	3·602 (6)				

Table 4. ^{59}Co *n.m.r. chemical-shift data, energy separation between* $^1A_{1g}$ *and* $^1T_{1g}$ *and bond distances (average values) in the crystals*

Compound	σ_{para}(%)	(Ecm^{-1})	Co–S(Å)	Reference
Tris-(O-ethylxanthato)Co(III) Co[C$_2$H$_5$OCS$_2$]$_3$	−3·06	16100	2·277 (3)	Merlino (1969)
Tris(ethylthioxanthato)Co(III) Co[C$_2$H$_5$SCS$_2$]$_3$	−3·08	16000	2·398 (1)	Present work
Tris(diethydithiocarbamato)Co(III) Co[(C$_2$H$_5$)$_2$NCS$_2$]$_3$	−3·23	15300	2·258 (1)	Merlino (1968)

pendicular. The dihedral angles they form are:

Co(1)S(1)C(1)S(2) ∧ Co(1)S(4)C(4)S(5)   83·4°
Co(1)S(1)C(1)S(2) ∧ Co(1)S(7)C(7)S(8)   84·0
Co(1)S(4)C(4)S(5) ∧ Co(1)S(7)C(7)S(8)   83·1
Co(2)S(11)C(11)S(12) ∧ Co(2)S(14)C(14)S(15) 83·6
Co(2)S(11)C(11)S(12) ∧ Co(2)S(17)C(17)S(18) 85·3
Co(2)S(14)C(14)S(15) ∧ Co(2)S(17)C(17)S(18) 82·4

The sulphur atoms are slightly displaced along tetrahedral directions with respect to the mean coordination planes in the octahedra, as can be seen from the data in Table 5.

All the CS_3 groups are planar and their corresponding bond distances are not significantly different. The C–S bonds involving the coordinated sulphur
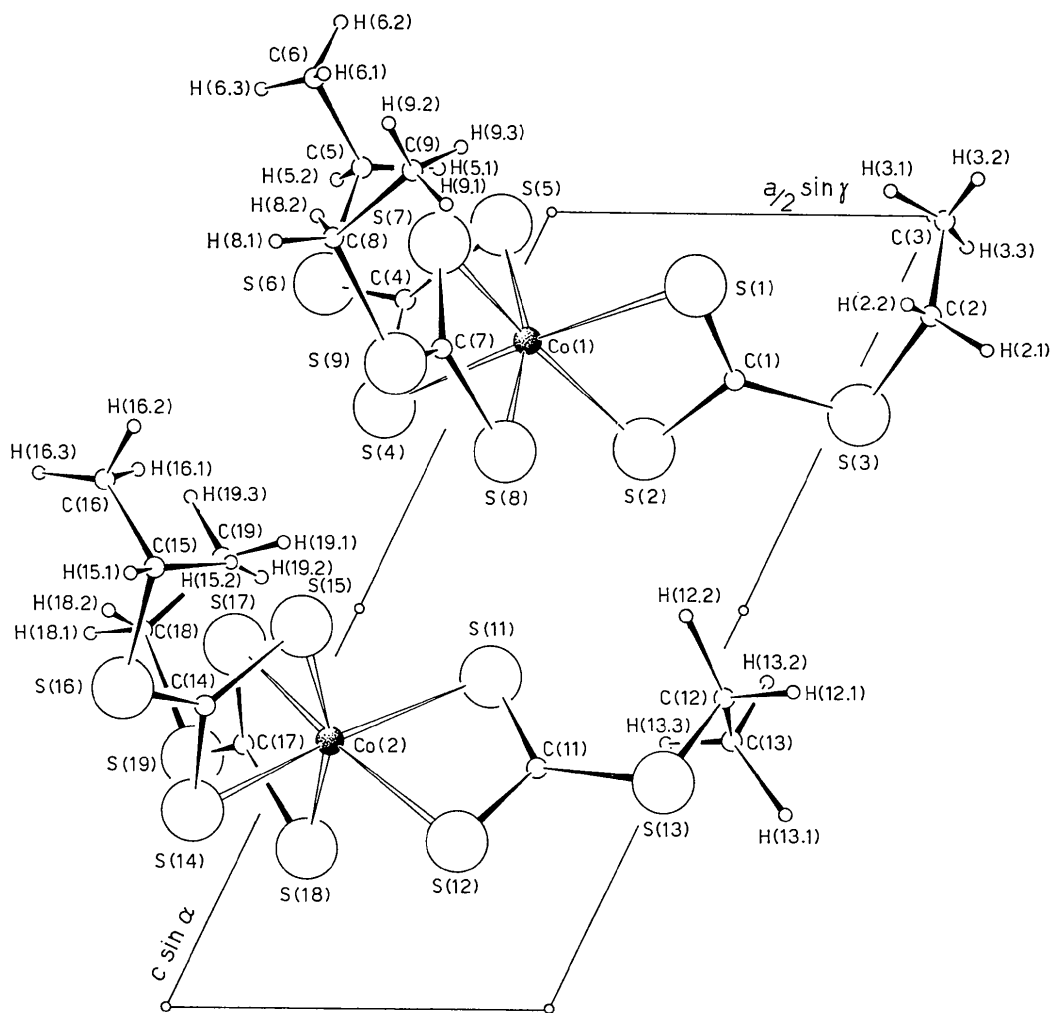

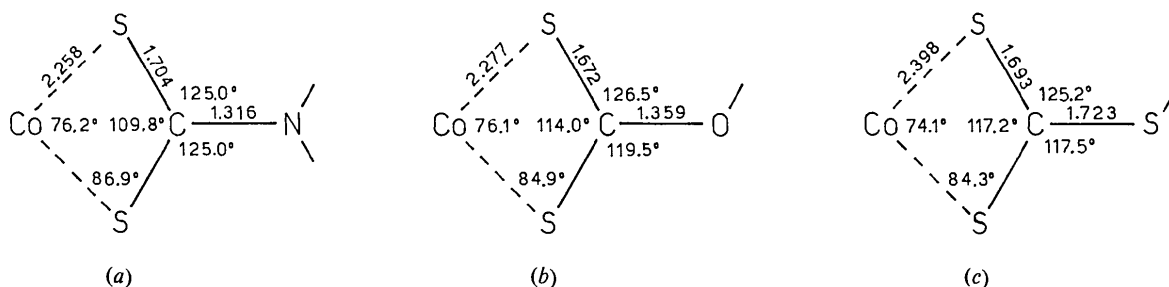Fig. 1. Projection of the structure on (010).

(a)   (b)   (c)

Fig. 2. Comparison of bond distances and angles (mean value) in: (a) tris(diethyldithiocarbamato)Co(III); (b) tris-(O-ethylxanthato)Co(III); (c) tris(ethylthioxanthato)Co(III).

Table 5. *Distances of the sulphur and cobalt atoms from the mean coordination planes in the two octahedra*

	Δ(Å)		Δ(Å)		Δ(Å)
S(1)	0·232	S(2)	0·186	S(1)	−0·259
S(2)	−0·184	S(5)	−0·200	S(4)	−0·238
S(4)	0·106	S(7)	0·247	S(5)	0·276
S(7)	−0·149	S(8)	−0·245	S(8)	0·229
Co(1)	−0·005	Co(1)	0·012	Co(1)	−0·009
S(11)	0·230	S(12)	0·194	S(11)	−0·210
S(12)	−0·174	S(15)	−0·197	S(14)	−0·269
S(14)	0·101	S(17)	0·258	S(15)	0·276
S(17)	−0·144	S(18)	−0·242	S(18)	0·226
Co(2)	−0·012	Co(2)	−0·013	Co(2)	−0·022

Table 6. *Comparison between the coordinates of molecule* 1, [Co(1)S(1)···S(9)C(1)···C(9)] *and those of molecule* 2, [Co(2)S(11)···S(19)C(11)···C(19)]

$$r'_1 = Ar_1 + t \text{ with } A = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{pmatrix} \text{ and } t = 0, \tfrac{1}{2}, \tfrac{1}{4}.$$

Molecule 1	Molecule 2	$(x_2-x'_1)/a$	$(y_2-y'_1)/b$	$(z_2-z'_1)/c$
Co(1)	Co(2)	−0·0050	0·0080	0·0010
S(1)	S(11)	−0·0197	0·0174	−0·0103
S(2)	S(12)	0·0051	0·0281	−0·0054
S(3)	S(13)	−0·0153	0·0473	−0·0332
S(4)	S(14)	0·0075	−0·0003	0·0093
S(5)	S(15)	0·0036	−0·0045	0·0065
S(6)	S(16)	0·0047	−0·0230	0·0036
S(7)	S(17)	−0·0124	−0·0091	0·0020
S(8)	S(18)	−0·0050	0·0126	−0·0026
S(9)	S(19)	0·0015	−0·0116	−0·0082
C(1)	C(11)	−0·0097	0·0310	−0·0141
C(2)	C(12)	−0·0267	0·0284	−0·0212
C(3)	C(13)	0·0534	−0·1022	0·1530
C(4)	C(14)	0·0000	−0·0095	0·0036
C(5)	C(15)	−0·0143	−0·0314	0·0025
C(6)	C(16)	−0·0154	−0·0504	0·0054
C(7)	C(17)	−0·0056	−0·0027	−0·0030
C(8)	C(18)	0·0025	−0·0278	−0·0089
C(9)	C(19)	0·0020	−0·0192	−0·0125

atoms are a little shorter than the C–S bonds with the uncoordinated sulphur, although the differences are not always statistically significant. These bond distances are consistent with a π delocalization in the CS_3 systems. The S–C distances involving the ethyl carbon atoms are all longer than the previous ones, and their mean value, 1·82 Å, corresponds to that expected for a single $S-C(sp^3)$ bond. Owing to the asymmetric situation of the C_2H_5 group with respect to the CS_3 group, the two SCS angles external to the coordination ring are rather different (Table 3).

In the asymmetric unit, there are two independent molecules which are equivalent from the chemical point of view only so far as the coordination around
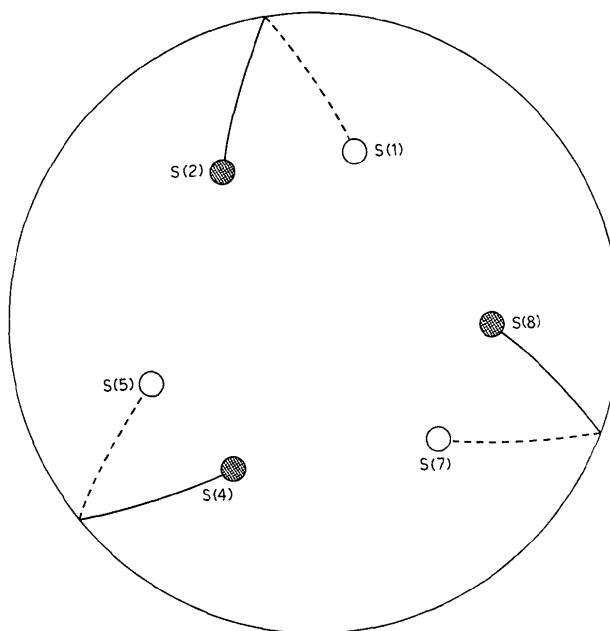

Fig. 3. Stereographic projection of a coordination polyhedron viewed along its threefold axis.

the metal and the dimensions of the ligands are concerned, but are different as regards the orientation of their ethyl groups. Indeed the analysis of the reciprocal orientation of the two independent molecules shows that applying a c glide at $\tfrac{1}{4}b$, they almost superimpose, as can be seen from Table 6. The most important discrepancies are for the methyl carbon atoms C(13) and C(3), and it is significant that if these two atoms were in the exactly symmetry-related positions, they would give packing distances which are too short.

All the packing distances are consistent with the van der Waals contacts.

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