

- OZEKI, K., SAKABE, N. & TANAKA, J. (1969). *Acta Cryst.* **B25**, 1038–1045.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 255. Ithaca: Cornell Univ. Press.
- SAKURAI, T. & OKUNUKI, M. (1971). *Acta Cryst.* **B27**, 1445–1453.
- SHELDRIK, G. M. (1976). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.
- SINGH, C. (1965). *Acta Cryst.* **19**, 861–864.
- STEWART, J. M. (1976). The XRAY 76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- WIERZCHOWSKI, K. L., LITONSKA, E. & SHUGAR, D. (1965). *J. Am. Chem. Soc.* **87**, 4621–4629.
- WITTENBERG, E. (1966). *Chem. Ber.* **99**, 2391–2398.

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The Crystal Structures of the Room- and Low-Temperature Modifications of Tris(η -cyclopentadienyl)-di- μ_3 -thio-tricobalt, $[\text{Co}_3(\eta\text{-C}_5\text{H}_5)_3\text{S}_2]$

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Abstract

The crystal structures of the title compound at room temperature and at 130 K are determined. The room-temperature modification is hexagonal, $P6_3/m$, with $a = 9.413(2)$, $c = 10.094(4)$ Å and $Z = 2$, and is isostructural with $[\text{Ni}_3(\eta\text{-C}_5\text{H}_5)_3\text{S}_2]$ [(Vahrenkamp, Vernon, Uchtman & Dahl (1968). *J. Am. Chem. Soc.* **90**, 3272–3273)], except for the mode of statistical distribution of the η -cyclopentadienyl rings. The Co–Co distance is 2.691 Å which is definitely longer than those of most of the other trinuclear cobalt complexes, and this difference is explained by the Cotton–Haas theory of metal–metal bonding. The low-temperature modification is also hexagonal with $a = 16.080(2)$, $c = 29.886(2)$ Å and $Z = 18$; this is a superstructure of the room-temperature modification and the symmetry can be given by the *Mischgruppe* $P6_1 \cup p3^\circ$. The trigonal bipyramid comprising Co_3S_2 is no longer regular and the three η -cyclopentadienyl rings take three definite orientations.

Introduction

Tris(η -cyclopentadienyl)-di- μ_3 -thio-tricobalt, $[\text{Co}_3(\eta\text{-C}_5\text{H}_5)_3\text{S}_2]$, was first prepared by Otsuka, Nakamura & Yoshida (1968). They also found that this complex is paramagnetic at room temperature and becomes dia-

magnetic below 192.5 K. Sorai, Kosaki, Suga, Seki, Yoshida & Otsuka (1971) interpreted the mechanism of the phase transition in terms of the cooperative coupling between the orientational motion of the η -cyclopentadienyl rings (hereafter Cp rings) and the electronic states of the molecule. In this paper, the crystal structures of the title compound at room temperature and at 130 K are reported.

Determination of the crystal structure of the room-temperature modification

Crystals of tris(η -cyclopentadienyl)-di- μ_3 -thio-tricobalt were kindly provided by Professor Otsuka. They are hexagonal platelets or slender needles, dark brown in color. Weissenberg and oscillation photographs showed the dihexagonal symmetry $6/mmm$. The systematic extinctions were observed only for $00l$ with l odd, corresponding to the space group $P6_322$, but it was soon found that the crystal consisted of twins, as will be described later. A crystal approximately $0.2 \times 0.2 \times 0.3$ mm was used for X-ray data collection on a Rigaku four-circle diffractometer. The crystal data are given in Table 1. The cell parameters were determined with Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) by a least-squares fit of 15 reflexions in the range $40^\circ \leq 2\theta \leq 50^\circ$. The estimated standard deviations of the cell parameters are those from the least-squares calculations.

The integrated intensities were obtained for $2\theta \leq 58^\circ$ by the ω - 2θ scanning method (scan speed 2° min^{-1}) using Mo $K\alpha$ radiation monochromatized with pyrolytic graphite at a take-off angle of 5° . The scan width in ω was $(1.0 + 0.4 \tan \theta)^\circ$ with background counts of 3s on either side of the peak. To check instrument and crystal stability, the intensities of three reflexions were measured after every 50 reflexions. Altogether 324 independent reflexions with $|F_o| \geq 3\sigma(|F|)$ were measured. The usual Lorentz and polarization corrections were applied, but no absorption or extinction corrections were made.

A three-dimensional Patterson function computed from the observed data did not give any clue to a plausible structure. It was found, however, that the diffraction feature of the crystal appeared exactly the same as that reported for the crystal of its Ni congener (Vahrenkamp, Vernon, Uchtman & Dahl, 1968). It follows that the crystal consists of twins, each of the two component crystals having the symmetry $P6_3/m$, the c axis in common and (100) as the twinning plane. On the assumption that the crystal structure is isostructural with its Ni congener and that the ratio of the two component crystals is 1:1, the structure factor calculations were carried out, ignoring the Cp rings; from these, approximate coordinates of the Co and S atoms were obtained.

The three Co atoms and two S atoms of the molecule form a trigonal bipyramid. A three-dimensional Fourier synthesis phased by these atoms showed the Cp groups as circular haloes with several lumps perpendicular to the lines connecting the center of the molecule and the Co atoms and symmetrically disposed with respect to the plane of the Co_3 cluster. Thus, it is concluded that the Cp rings are arranged statistically within their planes so as to give the molecule $\bar{6}$ symmetry. There are a number of possibilities for the statistical arrangement of the Cp rings, but a structure having more than four orientations can be regarded as almost the same as free rotation with respect to the diffraction effect so that this was not considered further. Two types of model, structure (a) and structure (b), were considered. Structure (a) is a model in which the Cp rings take two orientations statistically in the ring plane

with a mutual angle of 180° . Structure (b) is a model in which the Cp rings take three orientations statistically in the ring plane with mutual angles of 120° . A regular pentagon 1.43 \AA on an edge was assumed for the Cp ring; x and y for the Co, z for the S atom, x and y for the centroid of the Cp ring, B (isotropic temperature factors) for the C atoms, B_{ij} (anisotropic temperature factors) for the Co and S atoms and m (the fraction of one of the component crystals of the twin) were subjected to least-squares refinement for the two structures. In the least-squares calculations the function $\sum w[|F_o(hkl)|^2 - s^2|F_c(hkl)|^2]^2$ was minimized using the methods of Vahrenkamp, Vernon, Uchtman & Dahl (1968) and Wei, Wilkes & Dahl (1967), where s is an adjusting factor. The following formulas were used for the diffraction intensity of the twinned composite:

$$|F_o(hkl)|^2 = m|F'_o(hkl)|^2 + (1-m)|F'_o(khl)|^2, (1a)$$

$$|F_c(hkl)|^2 = m|F'_c(hkl)|^2 + (1-m)|F'_c(khl)|^2. (1b)$$

The weighting scheme $w = 1$ if $0 \leq \sqrt{|F_o|^2} \leq 20.0$, otherwise $w = 1.0/[1.0 + (\sqrt{|F_o|^2} - 20.0) \times 0.836]$, was used. The coordinates of the Co and S atoms obtained by these two models both agree to within 0.0002. With 324 independent intensity data $R_1(F^2)$ was 0.104 for structure (a) and 0.103 for structure (b), where $R_1(F^2)$ is defined as

$$R_1(F^2) = \frac{\sum ||F_o(hkl)|^2 - s^2|F_c(hkl)|^2|}{\sum |F_o(hkl)|^2}. (2)$$

It was impossible to choose between the two structures from the intensity data alone. This is chiefly because of the overlapping of reflexions hkl and khl , which is inherent in the crystal. However, from the structure analysis of the low-temperature modification which will be described in the following section it is concluded that structure (b) is the more plausible structure. The coordinates of the Co and S atoms and of the centroid of the Cp ring are given in Table 2.*

Table 1. *Crystal data of the room-temperature modification*

Formula	$[\text{Co}_3(\eta\text{-C}_5\text{H}_5)_3\text{S}_2]$
M_r	436.22
Space group	$P6_3/m$
Unit-cell dimensions (\AA)	$a = 9.413 (2)$ $c = 10.094 (4)$
Z	2
D_m (Mg m^{-3})	1.86
D_x (Mg m^{-3})	1.870
μ for Mo $K\alpha$ (mm^{-1})	3.46
Observed reflexions	648
Independent reflexions	324

* The list of structure factors obtained at room temperature and Table 4 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34540 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Positional and thermal parameters (\AA^2), with standard deviations in parentheses, for the room-temperature modification*

	x	y	z	B	B_{11}	B_{33}
Co	0.4973 (2)	0.1730 (2)	$\frac{1}{2}$		0.0130 (3)	0.00840 (15)
S		$\frac{1}{2}$	0.3997 (2)		0.0130 (2)	0.00970 (16)
Cp*	0.305 (2)	-0.018 (2)	$\frac{1}{2}$	6.0 (5)		

* The centroid of the Cp ring. Each Cp ring takes statistically three orientations given by structure (b).

Determination of the crystal structure of the low-temperature modification

For the low-temperature X-ray study, an evaporated-liquid-nitrogen gas gun was used that directed a steady stream of cold gas on to the crystal and its immediate environment. A number of superstructure reflexions were found when the crystal was cooled to the low-temperature phase. When the crystal was brought back to room temperature all the superstructure reflexions disappeared, so that the transition is confirmed to be reversible. On repeating the cooling and heating, however, it was found that the crystals became ill defined so that it was necessary to replace one crystal by another until sufficient diffraction data to carry out the analysis had been collected. All the data were obtained with Co $K\alpha$ radiation, maintaining the crystal at 130 ± 5 K. Fig. 1 shows examples of oscillation photographs taken about the c axis at room temperature and at 130 ± 5 K. In the low-temperature modification the dimensions of the a , b and c axes are approximately three times as large as those of the room-temperature modification. Weissenberg and oscillation photographs showed $6/mmm$ symmetry. As has been mentioned above, the crystal consists of twins and it is most likely that the transition only occurs within the component crystals so that the crystal below the transition temperature also consists of the same type of twin as that of the room-temperature modification. The unit-cell dimensions obtained in the same way as for the room-temperature modification are $a' = b' = 27.852$ (2), $c' = 29.886$ (2) Å. [Compare with $3 \times a(\text{room temperature}) = 28.239$ Å, $3 \times c(\text{room temperature}) = 30.282$ Å.] The unit cell, therefore, contains $2 \times 3 \times 3 \times 3 = 54$ molecules.

Since all reflexions $h'k'l'$, for $-h' + k' \neq 3n$ are missing, the lattice can be reduced to $a = (\frac{2}{3})a' + (\frac{1}{3})b'$, $b = -(\frac{1}{3})a' + (\frac{2}{3})b'$, $c = c'$. The lattice constants of the reduced cell are now $a = b = 16.080$ (2), $c = 29.886$ (2) Å and $Z = 18$. The crystal data are shown in Table 3. Fig. 2 shows the sections of the reciprocal lattice constructed from the observed reflexions shown in open circles, where the dotted lines are axes of the reciprocal lattice of the large unit cell. Open circles in Fig. 2 (a) and (b) appear on the same reciprocal-lattice points of the room-temperature modification and they are the fundamental reflexions. Open circles in Fig. 2(c)

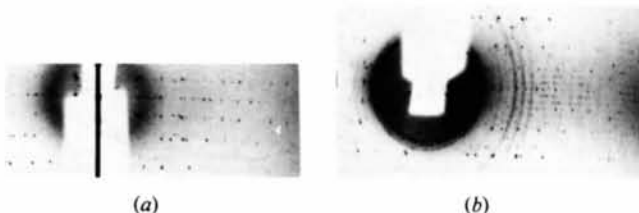


Fig. 1. Oscillation photographs with rotation about the c axis (a) at room temperature and (b) at 130 ± 5 K.

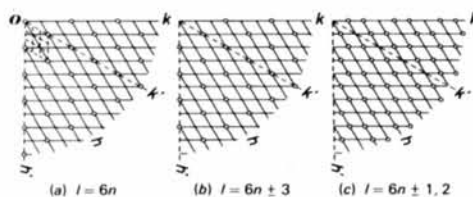


Fig. 2. Reciprocal-lattice diagrams for the low-temperature modification.

are the superstructure reflexions, where unusual extinction rules are observed; these can be summarized as follows:

$$\begin{aligned} hkl: & -h + k \neq 3n \quad \text{if } l = 3n \\ & -h + k = 3n \quad \text{if } l \neq 3n \\ 00l: & l \neq 6n. \end{aligned} \quad (3)$$

The only space group which is compatible with these extinction rules is $P6_1$ ($P6_3$), which arises from $l = 6n$ for $00l$. The extinction rules for the superstructure reflexions suggest that there must be some kind of regularity in the atomic arrangement in addition to the space-group symmetry operations. Suppose we place a scalene, as an exaggerated model for the Co_3 cluster, upon a plane. If we produce scalenes by rotations of the scalene around its center, followed by translations,

$$\text{Rot}(n\alpha).T(n_1a'/3 + n_2b'/3), \quad (4)$$

where $\alpha = 2\pi/3$ and $n = n_1 + n_2$, we obtain an arrangement of the scalenes which has the required translational symmetry parallel to the XY plane, as shown in Fig. 3. It can be shown that the combined operations, (4), are identical with a set of threefold point operations at those points indicated by small hollow triangles in Fig. 3. The set of these threefold point operations make a plane group, $p3^\circ$.*

It is assumed that each atom of the molecule is related by the symmetry $p3^\circ$ with the corresponding atoms of other molecules in the same plane. If we add a 6_1 axis perpendicular to the molecular layer at the origin indicated in Fig. 3, we obtain an atomic

* The notation $p3^\circ$ instead of $p3$ is used to avoid confusion arising from 3 and 3° . The notation 3° does not mean the threefold rotational symmetry axis, but it is effective only within a plane.

Table 3. Crystal data for the low-temperature modification

Unit-cell dimensions (Å)	$a = b = 16.080$ (2) $c = 29.886$ (2)
Z	18
D_x (Mg m^{-3})	1.948
Symmetry	$P6_1 \cup p3^\circ$
Observed reflexions	216
Fundamental reflexions	150
Superstructure reflexions	66
Temperature of experiment	130 ± 5 K

arrangement which satisfies all the extinction rules given in (3), as will be explained in the following.

Consider any atom of the molecule in the reduced cell. The atom lies on a plane which has the symmetry $p3^\circ$. This requires that there are two other atoms which are the corresponding atoms of the two other molecules in the asymmetric unit. The coordinates of these atoms can be given by

$$x, y, z; -\frac{1}{3} - y, \frac{1}{3} + x - y, z; \frac{1}{3} - x + y, -\frac{1}{3} - x, z. \quad (5)$$

Now, from the 6_1 operations passing through the origin perpendicular to the plane of these three positions, one obtains the following eighteen positions:

$$\begin{aligned} &x, y, z; -\frac{1}{3} - y, \frac{1}{3} + x - y, z; \frac{1}{3} + y - x, -\frac{1}{3} - x, z; \\ &\bar{y}, x - y, \frac{1}{3} + z; -\frac{1}{3} - x + y, -\frac{2}{3} - x, \frac{1}{3} + z; \\ &\frac{1}{3} + x, \frac{2}{3} + y, \frac{1}{3} + z; y - x, \bar{x}, \frac{2}{3} + z; \frac{2}{3} + x, \frac{1}{3} + y, \frac{2}{3} + z; \\ &-\frac{2}{3} - y, -\frac{1}{3} - y + x, \frac{2}{3} + z; \bar{x}, \bar{y}, \frac{1}{2} + z; \\ &\frac{1}{3} + y, -\frac{1}{3} - x + y, \frac{1}{2} + z; -\frac{1}{3} - y + x, \frac{1}{3} + x, \frac{1}{2} + z; \\ &y, y - x, \frac{5}{6} + z; \frac{1}{3} + x - y, \frac{2}{3} + x, \frac{5}{6} + z; \\ &-\frac{1}{3} - x, -\frac{2}{3} - y, \frac{5}{6} + z; x - y, x, \frac{1}{6} + z; \\ &-\frac{2}{3} - x, -\frac{1}{3} - y, \frac{1}{6} + z; \frac{2}{3} + y, \frac{1}{3} + y - x, \frac{1}{6} + z. \quad (6) \end{aligned}$$

These positions are shown in Fig. 4. They comprise three sets of the general equivalent positions of $P6_1$. The geometrical structure factors for these eighteen positions clearly show all of the extinction rules of (3), as shown in Table 4.*

The structure is now characterized by the positional and thermal parameters of the 20 non-hydrogen atoms (3Co, 2S, 15C). The intensities of the superstructure reflexions were measured by the visual method using Weissenberg photographs taken with Co $K\alpha$ radiation. Since it was impossible to obtain quantitative intensity data, we had to resort to the trial-and-error method. The three Cp rings of the molecule are no longer equivalent and take three independent orientations. It is most likely that there are three orientations within their planes for these Cp rings in which they are trapped in the low-temperature modification, while in the room-temperature modification each Cp ring will take any

* See deposition footnote.

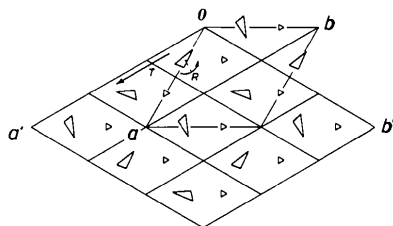


Fig. 3. Arrangement of a scalene satisfying the plane-group symmetry $p3^\circ$. Small regular triangles indicate the points of threefold point operations, $p3^\circ$.

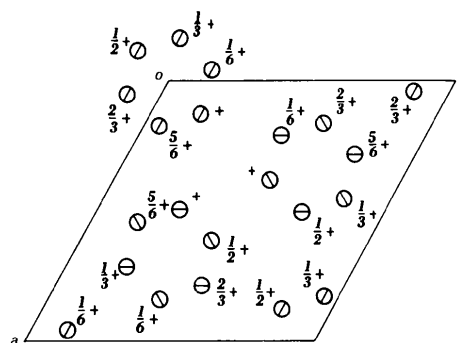


Fig. 4. Eighteen general positions generated by the 6_1 axis and $p3^\circ$ as mentioned in the text. Fractions in the figure represent the heights of the general positions along the c axis.

one of these orientations. It is assumed that the three Cp rings are oriented in their planes with the same angle, 120° (see α , β , and γ in Fig. 7). A fairly good agreement between the observed and calculated intensities of the superstructure reflexions (Fig. 5) was obtained for the parameter values given in Table 5. Here, (1) was used for the expression of intensities of the twin composite. m was assumed to be $\frac{1}{2}$, since it was found to be close to this value in the room-temperature modification. The coordinates of the Co and S atoms are fairly approximate, but not much weight can be placed on those of the C atoms. Mean standard deviations of the coordinates of the Co and S atoms and those of the centroids of the Cp rings are 0.009, 0.008 and 0.006.

Results and discussion

The room-temperature modification

The projection of the structure on to [001] is shown in Fig. 6. It is isostructural with tris(η -cyclopentadienyl)-di- μ_3 -thio-trinickel (Vahrenkamp, Vernon, Uchtman & Dahl, 1968), though a reservation is made for the statistical distribution of the Cp rings of the molecule. The $[\text{Co}_3(\eta\text{-C}_5\text{H}_5)_3\text{S}_2]$ molecule has symmetry 6, and hence the Co_3S_2 cluster forms a regular trigonal bipyramid, and the three Cp rings are bound to

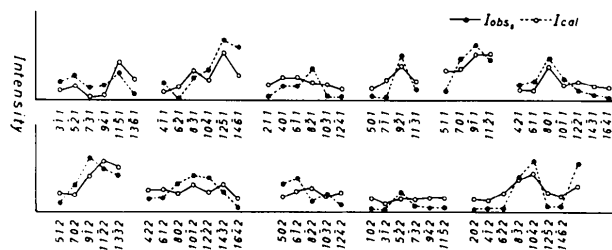


Fig. 5. Observed and calculated intensities for the low-temperature modification.

Table 5. *Positional and isotropic thermal parameters for the low-temperature modification*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Co(1)	0.391	0.110	0.081	2.5
Co(2)	0.223	-0.049	0.084	2.5
Co(3)	0.375	-0.069	0.079	2.2
S(1)	0.333	0	0.134	2.5
S(2)	0.333	0	0.032	2.2
Cp(α)*	0.457	0.238	0.083	6.0
Cp(β)*	0.096	-0.120	0.083	6.0
Cp(γ)*	0.425	-0.131	0.083	6.0

* The coordinates of the centroids.

the cluster perpendicularly to the lines connecting the center of the molecule and the Co atoms with their centroids. These Cp rings are statistically distributed within their planes and prefer three orientations with a mutual angle of 120° (shown as α, β, and γ in Fig. 7), so as to have a horizontal plane of symmetry. Significant interatomic distances and bond angles are shown in Table 6. The Co—Co distance, 2.691 Å, found in this complex is longer than that found in [Co₃(CO)₉S], 2.64 Å (Wei & Dahl, 1967), and is much longer than those reported in many similar trinuclear cobalt complexes, which lie between 2.46 and 2.50 Å {Co₃(CO)₁₀BH₂N(C₂H₅)₃, Klanberg, Askew & Guggenberger, 1968; [Co₃(CO)₉C₂]₂, Dellaca, Penfold, Robinson, Robinson & Spencer, 1970; CH₃CCo₃(CO)₉, Sutton & Dahl, 1967; CH₃CCo₃(CO)₈P(C₂H₅)₃, Brice, Penfold, Robinson & Taylor, 1970}. These differences can well be accounted for by the number of electrons occupying the antibonding orbitals of the Co₃ cluster, based on Cotton & Haas's (1964) approximation. The two complexes [Co₃(η-C₅H₅)₃S₂] and [Co₃(CO)₉S] supply 8 and 7 electrons, respectively, and all the other complexes mentioned above only supply 6 electrons to the antibonding orbitals. The Co—S distance, 2.168 Å, can be compared to that reported for [Co₃(CO)₉S]. The shortest intermolecular atomic distance, 3.59 Å, is found between a S atom and a C atom of a neighboring molecule.

The low-temperature modification

The low-temperature modification is a superstructure of that of the room-temperature modification. The symmetry of the molecule is now 1, and the Co₃S₂ cluster becomes a scalene bipyramid and the three Cp rings are no longer equivalent but take three definite orientations, with a mutual angle of 120°, shown as α, β, and γ in Fig. 7. There are three molecules in the asymmetric unit. These three molecules are 'equivalent', this being imposed not by the space-group symmetry but by the plane-group symmetry imposed on the three corresponding atoms of the three

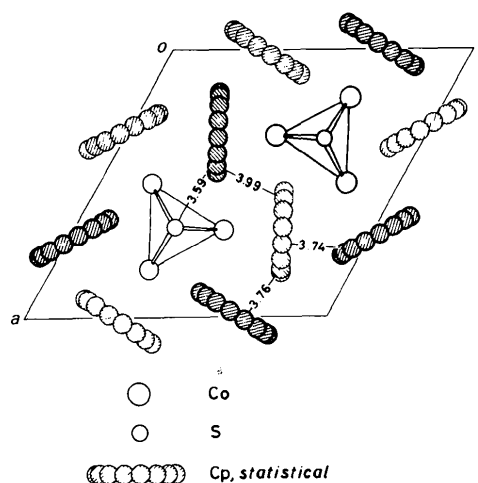


Fig. 6. The crystal structure for the room-temperature modification, projected along the *c* axis.

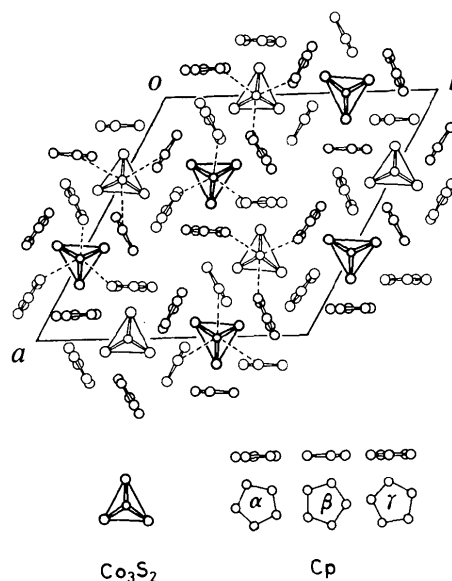


Fig. 7. Bounded projection of the crystal structure for the low-temperature modification along the *c* axis, $z = 0 - \frac{1}{3}$, based on the coordinates in Table 5.

Table 6. *Interatomic distances (Å) and angles (°) within the molecule, with standard deviations in parentheses, for the room-temperature modification*

Co—Co	2.691 (4)	Co—S—Co	79.3 (4)
Co—S	2.168 (4)	S—Co—Co	51.4 (4)
S...S	3.022 (4)	S—Co—S	88.8 (4)
Co...centroid of the Cp ring	1.80		

molecules. A bounded projection of the structure on to [001] for *z* from 0 to $\frac{1}{3}$ is shown in Fig. 7, where the Co₃S₂ clusters and the Cp rings drawn in thick lines lie on adjacent layers *c*/6 above those of the rest. Interatomic distances and angles are given in Table 7. It is

Table 7. *Interatomic distances (Å) and angles (°) within the molecule, with standard deviations in parentheses, for the low-temperature modification*

Co(1)—Co(2)	2.63 (1)	Co—S—Co	75.2 (9) ~ 81.7 (9)
Co(2)—Co(3)	2.62 (1)	Mean	77.7
Co(3)—Co(1)	2.76 (1)		
Mean	2.67	S—Co—Co	47.9 (9) ~ 56.9 (9)
		Mean	51.5
Co(1)—S(1)	2.20 (1)		
Co(2)—S(1)	2.05 (1)		
Co(3)—S(1)	2.27 (1)		
Co(1)—S(2)	2.12 (1)		
Co(2)—S(2)	2.05 (1)		
Co(3)—S(2)	2.10 (1)		
Mean	2.13		

interesting to see that though the molecular axis connecting the two S atoms, which was the threefold rotational symmetry axis in the room-temperature modification, has now lost its symmetry properties, each of the two S atoms still has three 'equivalent' C atoms at distances of ~ 3.6 Å as its immediate neighbors, which are shown by broken lines.

The symmetry of the low-temperature modification

In the crystal structure of the low-temperature modification, additional local symmetries are found which are exact, as far as the observed extinctions show. These symmetries are closely related to, but do not belong to, the space group of the crystal. The generating symmetry operations of space group $P6_1$, on which the whole atomic arrangement is based, are t_{10} , t_{01} and 6_1 , where t_{10} and t_{01} are the unit translational symmetries along the x and y axes. Further, the corresponding atoms of the molecules lying on the same layer perpendicular to the z axis form the plane group $p3^\circ$, whose generating symmetry operations are t_{10} , t_{01} and 3° . Thus, the set of the whole symmetry operations does not form any group, but can be represented by the *Mischgruppe* $P6_1 \cup p3^\circ$, as is shown schematically in Fig. 8. The existence of crystal structures based on a *Mischgruppe* has been discussed (Sadanaga, 1963), but the crystal structure of the low-temperature modifi-

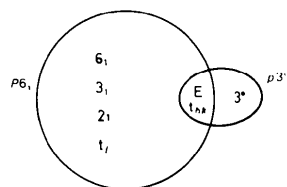


Fig. 8. *Mischgruppe* $P6_1 \cup p3^\circ$.

cation presented in this paper is the first example of this kind ever reported.

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References

- BRICE, M. D., PENFOLD, B. R., ROBINSON, W. T. & TAYLOR, S. R. (1970). *Inorg. Chem.* **9**, 362–367.
- COTTON, F. A. & HAAS, T. E. (1964). *Inorg. Chem.* **3**, 10–17.
- DELLACA, R. J., PENFOLD, B. R., ROBINSON, B. H., ROBINSON, W. T. & SPENCER, J. L. (1970). *Inorg. Chem.* **9**, 2204–2211.
- KLANBERG, F., ASKEW, W. B. & GUGGENBERGER, L. J. (1968). *Inorg. Chem.* **7**, 2265–2271.
- OTSUKA, S., NAKAMURA, A. & YOSHIDA, T. (1968). *Justus Liebigs Ann. Chem.* **719**, 54–60.
- SADANAGA, R. (1963). *J. Crystallogr. Soc. Jpn.* **5**(2), 10–20 (in Japanese).
- SORAI, M., KOSAKI, A., SUGA, H., SEKI, S., YOSHIDA, T. & OTSUKA, S. (1971). *Bull. Chem. Soc. Jpn.* **44**, 2364–2371.
- SUTTON, P. W. & DAHL, L. F. (1967). *J. Am. Chem. Soc.* **89**, 261–268.
- VAHRENKAMP, H., VERNON, A. UCHTMAN, V. A. & DAHL, L. F. (1968). *J. Am. Chem. Soc.* **90**, 3272–3273.
- WEI, C. H. & DAHL, L. F. (1967). *Inorg. Chem.* **6**, 1229–1236.
- WEI, C. H., WILKES, G. R. & DAHL, L. F. (1967). *J. Am. Chem. Soc.* **89**, 4792–4793.