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Determination of the Incommensurately Modulated Structure of (Perylene)Co(mnt)₂-(CH₂Cl₂)_{0.5} by Direct Methods

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Abstract

For the organic conductor (perylene)Co(mnt)₂-(CH₂Cl₂)_{0.5}, where mnt is maleonitriledithiolate, the incommensurate displacive modulation is determined using X-ray diffraction data for main reflections and first- and second-order satellites, collected at a temperature of 283 K. The lattice parameters of the unit cell of the average structure are: $a = 6.5441$ (13), $b = 11.7173$ (15), $c = 16.4251$ (17) Å, $\alpha = 92.092$ (11), $\beta = 95.343$ (16), $\gamma = 94.67$ (2)°, with $V = 1248.6$ (3) Å³ and $Z = 2$. The components of the modulation wavevector are given by: $q_1 = 0.211$ (13), $q_2 = -0.1374$ (5), $q_3 = -0.368$ (2). The symmetry of the modulated structure is given by the (3+1)-dimensional superspace group $P\bar{1}(q_1, q_2, q_3)$. Direct methods were used to obtain a starting model for the modulation. The subsequent refinement converged to $R = 0.126$ for 2835 observed ($I/\sigma > 2.5$) reflections. Partial R factors are 0.111 for 1450 main reflections, 0.143 for 1188 first-order satellites and 0.263 for 197 second-order satellites. The modulation is described by sawtooth-shaped functions for the Co and S atoms and by rigid-body

modulations, up to third-order harmonics, for the perylene units and parts of the mnt fragments. The largest amplitudes were found for the Co (0.77 Å) and S atoms (0.48–0.63 Å) and were mainly directed along the a axis. The four equatorial Co—S distances are only slightly affected by the modulation, but the two apical Co—S distances show large variations with distances ranging from 2.05 to 3.86 Å. These variations are out of phase. This causes the coordination of the Co atom to vary from a distorted octahedral coordination by six S atoms to a region with fivefold coordination and *vice versa*. The valence of the Co atom, as calculated by the bond-valence method, varies between 2.92 and 3.57. The stacking of the Co(mnt)₂ units can be described by oligomeric packages of four or five dimerized Co(mnt)₂ units.

1. Introduction

(Perylene)Co(mnt)₂(CH₂Cl₂)_{0.5} (denoted PECO) belongs to a series of molecular conductors based on perylene (Fig. 1a) and metal bis(dithiolenes) of the type $M(\text{mnt})_2$ (Fig. 1b) with the general formula (perylene) _{n} $M(\text{mnt})_2$, where M is a metal atom, mnt is maleonitriledithiolate and $n = 1, 2$. The average structure of PECO at room temperature is triclinic, space group $P\bar{1}$ with two formula units in the unit cell (Gama *et al.*, 1992). The structure contains polymeric chains of Co(mnt)₂ units, alternated

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by almost uniform stacks of perylene molecules along the *a* axis. The dichloromethane molecules are situated at centers of symmetry and are therefore disordered. Each Co atom appears to be octahedrally coordinated by S atoms. The four equatorial S atoms [*e.g.* atoms S(1–4), see Fig. 2] and the Co atom all belong to the same Co(mnt)₂ unit, but each apical S atom [*e.g.* S(1') or S(4'), see Fig. 2] is an equatorial S atom in a neighboring Co(mnt)₂ unit. Thus, each Co(mnt)₂ unit shares two Co—S bonds with each of the two neighbouring units. As a result, stacks are formed of Co—S octahedra sharing a single S_{apical}—S_{equatorial} edge with each neighbor. The two S atoms along this common edge are related to one another by a center of symmetry. Differences in inter-Co(mnt)₂ contacts suggest that the polymeric chain of Co(mnt)₂ units can also be described as a chain of dimerized Co(mnt)₂ units (Gama *et al.*, 1992).

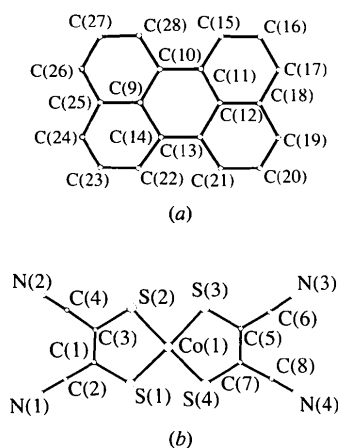


Fig. 1. Geometry of the molecular units: (a) perylene molecule (H atoms not shown); (b) Co(mnt)₂ unit.

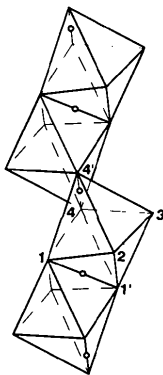


Fig. 2. Part of the chain of Co—S octahedra along the *a* axis. The two octahedra at the bottom of the figure form one dimer and the two octahedra at the top of the figure form the other dimer. The viewing direction is along *c** on the (*a*,*b*) plane. Small circles represent centers of symmetry. Numbers *n* represent atoms S(*n*).

The present paper is concerned with the determination of the incommensurately modulated structure of PECO.* A starting model for the refinement of the modulation was obtained from a multidimensional direct-methods procedure (Hao, Liu & Fan, 1987; Fu & Fan, 1994), where, for both main reflections and first-order satellites, normalized structure factors were used instead of common structure factors (Lam, Beuskens & van Smaalen, 1992, 1993, 1994). The modulation is found to be large (amplitudes of 0.77 Å for cobalt and 0.48–0.63 Å for sulfur) and is related to a mixed valence state of the Co atoms (valence fluctuations ranging from 2.92 to 3.57). Therefore, not all Co atoms are octahedrally coordinated, as suggested by the average structure.

2. X-ray diffraction experiment

The diffraction pattern of crystals with an incommensurate one-dimensional modulation is characterized by the presence of strong main reflections at the nodes of the reciprocal lattice {*a**, *b**, *c**} of the average structure, accompanied by satellite reflections that are usually weaker (Janssen, Janner, Looijenga-Vos & de Wolff, 1992; van Smaalen, 1994, and references therein). The complete diffraction pattern can be indexed by four integers (*hklm*), according to $\mathbf{S} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}$, where $\mathbf{q} = q_1\mathbf{a}^* + q_2\mathbf{b}^* + q_3\mathbf{c}^*$ is the modulation wave-vector.

The average structure, given by the main reflections (*m* = 0), was determined by Gama *et al.* (1992), using 6039 main reflections, of which 3948 were observed.† On the same crystal, hereafter termed crystal (1), intensities of first-order satellites (*|m|* = 1) were also measured, in a hemisphere up to $\theta = 20^\circ$ for MoK α radiation. A total of 4773 unique satellite reflections were obtained, of which 1640 reflections were denoted as observed (*I*/ σ > 2.5). Lattice parameters were reported as *a* = 6.551 (1), *b* = 11.732 (2), *c* = 16.481 (2) Å,

*For readers who may have limited experience in the area of incommensurately modulated structures, the following notes may be useful. (1) Such a structure cannot be described as a periodic assembly of identical units, but it can be approximated by an 'average' structure with translational symmetry. (2) The deviation from this hypothetical 'average' structure can be described by periodic variations in the unit cells (*e.g.* of atomic positions). (3) This periodic variation defines a long-range order of the true structure, thereby causing satellite Bragg reflections to occur around the positions in reciprocal space of the Bragg reflections caused by the periodic average structure. (4) The term incommensurate implies that the periodicity of the modulation (variation) is not an integral multiple of the unit cell, *i.e.* the structure at hand is not a classical 'superstructure'. (5) The higher-dimensional description of three-dimensional reciprocal space is geometrically defined in the next section. See, for example, Janssen, Janner, Looijenga-Vos & de Wolff (1992) for more details.

† Refinement of the average structure, using main reflections only, allowed the positioning of a disordered C atom [denoted C(29) with occupancy factor 1/2], which was not given in the list of coordinates by Gama *et al.* (1992).

$\alpha = 92.08$ (1), $\beta = 95.30$ (1) and $\gamma = 94.62$ (1) $^\circ$. The modulation wavevector was reported as $\mathbf{q} = (0.224, -0.132, -0.359)$. Crystal (1) appeared to be twinned, with the twinning matrix given by

$$\begin{pmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{pmatrix}_{\text{II}} = \begin{pmatrix} -1.004 & -0.005 & -0.001 \\ 0.310 & 0.310 & 0.695 \\ 0.319 & 1.314 & -0.306 \end{pmatrix} \cdot \begin{pmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{pmatrix}_{\text{I}},$$

where the subscripts I and II denote the two domains. It follows that the domains have a common a axis, but no definite relationship (twinning law) could be found in other directions, either in direct space or in reciprocal space. Because the unit cell is triclinic, overlap between reflections of the two domains will only occur at special points. Analysis of the final refinement did not show any systematic influence of the twinning. Therefore, the intensities of domain I were used in the refinements without any correction.

Motivated by the relatively large R factors for the main reflections after the final refinement and the unsatisfactory geometry of the model (§4), a second crystal was selected for data collection (crystal 2). This crystal was four times smaller than crystal (1), making it more difficult to measure the weak satellites. On the other hand, crystal (2) was not twinned, thus excluding contamination of the intensities by a second domain. Nevertheless, the fit to the main reflections did not improve and the relatively high R factors must be ascribed to intrinsic effects.

For crystal (2), X-ray diffraction experiments were performed at 283 K on an Enraf-Nonius CAD-4F diffractometer employing $\text{Mo } K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Dimensions of the unit cell of the average structure were determined from a least-squares treatment of the setting angles of 25 main reflections with $6 < \theta < 17^\circ$. Similarly, the components of the modulation wavevector were determined from eight first-order satellites with $7 < \theta < 16^\circ$. As satellite reflections were very weak and required about 10 min measuring time each, it was decided to measure only those reflections which could be expected to be 'observable'. All main reflections and first-order satellites measured on crystal (1), which satisfied the condition $I/\sigma > 1.5$, were measured for crystal (2). Also, 3000 second-order satellites having the largest calculated intensities were measured: these intensities were calculated using the parameters of the model which was refined with the data measured for crystal (1), where first- and second-order harmonics were used to describe the modulations. Reflections within a hemisphere were measured. Crystal and instrumental stability were checked throughout the data collection by monitoring the intensities of three main reflections. Variations in these intensities were corrected by a smoothed curve. On all reflections, profile analysis was performed using a local program which combines the methods of Lehman & Larsen (1974) and

Table 1. Summary of X-ray diffraction data for crystal (2)

Crystal	Black, $0.05 \times 0.16 \times 0.42$		
Color, dimensions (mm ³)	Black, $0.05 \times 0.16 \times 0.42$		
$\mu(\text{Mo } K\alpha)$ (cm ⁻¹)	11.429		
D_{calc} (g cm ⁻³)	1.687		
Intensity measurements			
Reflection order ($ m $)	0	1	2
Scan method	ω	ω	ω
Scan width ($^\circ$)	1.95	1.95	1.95
Max. scan time (s)	300	300	600
θ_{max} ($^\circ$)	29	21	29
h range	0, 8	0, 6	0, 9
k range	-15, 15	-11, 11	-15, 15
l range	-21, 21	-15, 15	-20, 20
Intensity control reflections	1, -1, -6, 0	1, -1, -6, 0	1, -1, -6, 0
	1, 4, -2, 0	1, 4, -2, 0	1, 4, -2, 0
	-2, 1, -2, 0	-2, 1, -2, 0	-2, 1, -2, 0
Monitoring interval (h)	1	1	2
Drift correction (%)	2.1	3.3	7.5
Min./max. absorption correction factors	0.773/1.226	0.774/1.226	0.773/1.224
No. of unique reflections	2677	2107	3000
No. of unique reflections with $I/\sigma > 2.5$	1450	1188	197
Average structure			
a, b, c (\AA)	6.5441 (13), 11.7173 (15), 16.4251 (17)		
α, β, γ ($^\circ$)	92.092 (11), 95.343 (16), 94.67 (2)		
Z, V (\AA^3)	2, 1248.6 (3)		
Space group	$P1$ (No. 2)		
Modulated structure			
q_1, q_2, q_3	0.211 (13), -0.1374 (5), -0.368 (2)		
Superspace group	$P1(q_1, q_2, q_3)$ (No. 2)		

Grant & Gabe (1978). Reflection profiles appeared to be elongated along the a^* direction, which caused a relatively large standard deviation in this component of the modulation wavevector. An *ab initio* empirical absorption correction was applied using the local program *EMPABS*, based on the method of North, Philips & Mathews (1968). After Lorentz and polarization corrections, the data were reduced to $|F_{\text{obs}}|$ values (see Table 1 for details).*

Comparison of observed structure factors for both crystals led to conventional disagreement factors $R = 0.133$, $R = 0.124$ and $R = 0.150$ for all reflections, main reflections and first-order satellites respectively.

3. Direct-methods solution

Data measured on crystal (1) were used to determine the phases of the satellite reflections by a direct-methods procedure. Estimates of the scale factor (K), the overall isotropic temperature parameter (B) and the overall modulation parameter (U_1) were obtained by a statistical procedure (Lam, Beurskens & van Smaalen, 1992, 1994). With only main reflections and first-order satellites available, the modulation parameter (U_1) represents a weighted average, over all atoms, of the

* A list of structure factors has been deposited with the IUCr (Reference: JS0010). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

first-order harmonic components of the modulation functions. Since a lack of stoichiometry is unlikely to occur in this structure, only displacive modulations are considered here. The average intensities are plotted in Fig. 3. The fitted parameters, $K = 1.081$, $B = 1.96 \text{ \AA}^2$ and $U_1 = 0.421 \text{ \AA}$, were used for the calculation of normalized structure factors (Lam, Beurskens & van Smaalen, 1993).

The phases of the main reflections calculated from the known average structure can be used as good approximations for the phases of the main reflections of the modulated structure. It has been shown that these phases, together with the measured intensities of the main reflections and satellites, can be used to determine the phases of the satellites (Hao, Liu & Fan, 1987). This method is employed in the computer program *DIMS* (Fu & Fan, 1994).

Initially, structure factors (F) were used in a default run of *DIMS*. The 1000 strongest main reflections with calculated phases were kept fixed in the procedure. Starting phases for the 1000 strongest satellite reflections were assigned at random, creating 20 different phase sets. These phases were refined in ten cycles by use of the four-dimensional Sayre equation. Not more than 300 triplet relations were allowed to contribute to a single satellite phase. The best set of satellite phases was selected with the default combined figure-of-merit. It appeared that all 20 refined phase sets were almost identical, all corresponding to a successful solution of the phase problem.

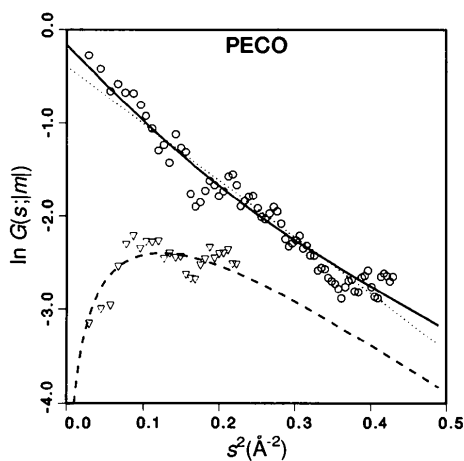


Fig. 3. Natural logarithm of the seminormalized average intensities $G(s; |m|)$ as a function of s^2 , where $s = (\sin \theta)\lambda$. Circles (main reflections) and triangles (first-order satellites) represent experimental values obtained as $G(s; |m|) = (I / \sum_{\mu} f_{\mu}(s))_{s, |m|}$, where the summation extends over all atoms μ in the unit cell of the average structure. The average $(\dots)_{s, |m|}$ is taken in intervals of s at constant $|m|$. The dotted line represents a conventional Wilson plot ($K = 1.217$ and $B = 3.05 \text{ \AA}^2$) against main reflections only. The solid and dashed lines describe the fits against main reflections and first-order satellites, respectively, and were obtained in a single-fit procedure (Lam, Beurskens & van Smaalen, 1992, 1994).

In a restart of the direct-methods procedure, normalized structure factors (E) were used. All reflections having $|E| \geq 1.25$ (925 main reflections and 642 first-order satellites) were input to the program *DIMS*, in an otherwise default run (as above). All 20 solutions generated by *DIMS* were identical and contained 46 satellites with incorrect phases. A similar default run using the same number of strongest $|F|$ values gave 20 almost identical phase sets with the best solution having 54 incorrect phases. This is in agreement with de Gelder *et al.* (1995), who found that the use of $|E|$ values generally results in a slightly better convergence of the refinement of the Sayre equation.

Four-dimensional electron-density maps were calculated from the phased structure factors (F) using the program *FOURIER* (Petříček, 1993). These maps clearly reveal the displacements of the Co and S atoms: large displacements along the a axis and much smaller displacements along the b and c axes. The displacements of the Co and S atoms in one Co(mnt)₂ unit are approximately in phase. Electron-density maps for atoms Co and S(1) are given in Fig. 4(a) and (b), respectively. The following estimates were obtained for the first-order harmonics of the modulation functions of the Co and S atoms

$$\begin{aligned} \text{Co, } a_{1,x}^{\mu,s} &= -0.07; \\ \text{S(1-4), } a_{1,x}^{\mu,s} &= -0.05. \end{aligned}$$

Initial values for the other amplitudes of these atoms are taken as zero (see §1 for definition). Note that these large displacements along the a axis could also be inferred from the large values of the temperature parameter U_{11} of these atoms in the average structure (Gama *et al.*, 1992), but their numerical values and their relative phases only follow from the direct-methods procedure.

From the electron-density maps, it can be seen that the displacements of the Co atom and the S(1-4) atoms look more like 'sawtooth' functions rather than the simple sine waves assumed above. This implies that higher-order harmonics have important contributions to the atomic displacements, as was confirmed by further analysis.

4. Refinement of the modulated structure

A model for the incommensurately modulated structure of *PECO* can be presented by specifying for each atom its average position, occupancy factor, temperature parameters and displacive modulation functions. A full-matrix least-squares refinement on $|F_{\text{obs}}|$ values of the structural parameters was performed using the program *JANA* (Petříček & Coppens, 1988; Petříček, 1993), minimizing the function wR

$$wR = \left[\frac{\sum w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2}{\sum w|F_{\text{obs}}|^2} \right]^{1/2},$$

using the weighting scheme $w = (\sigma^2 + 0.02|F_{\text{obs}}|^2)^{-1}$.

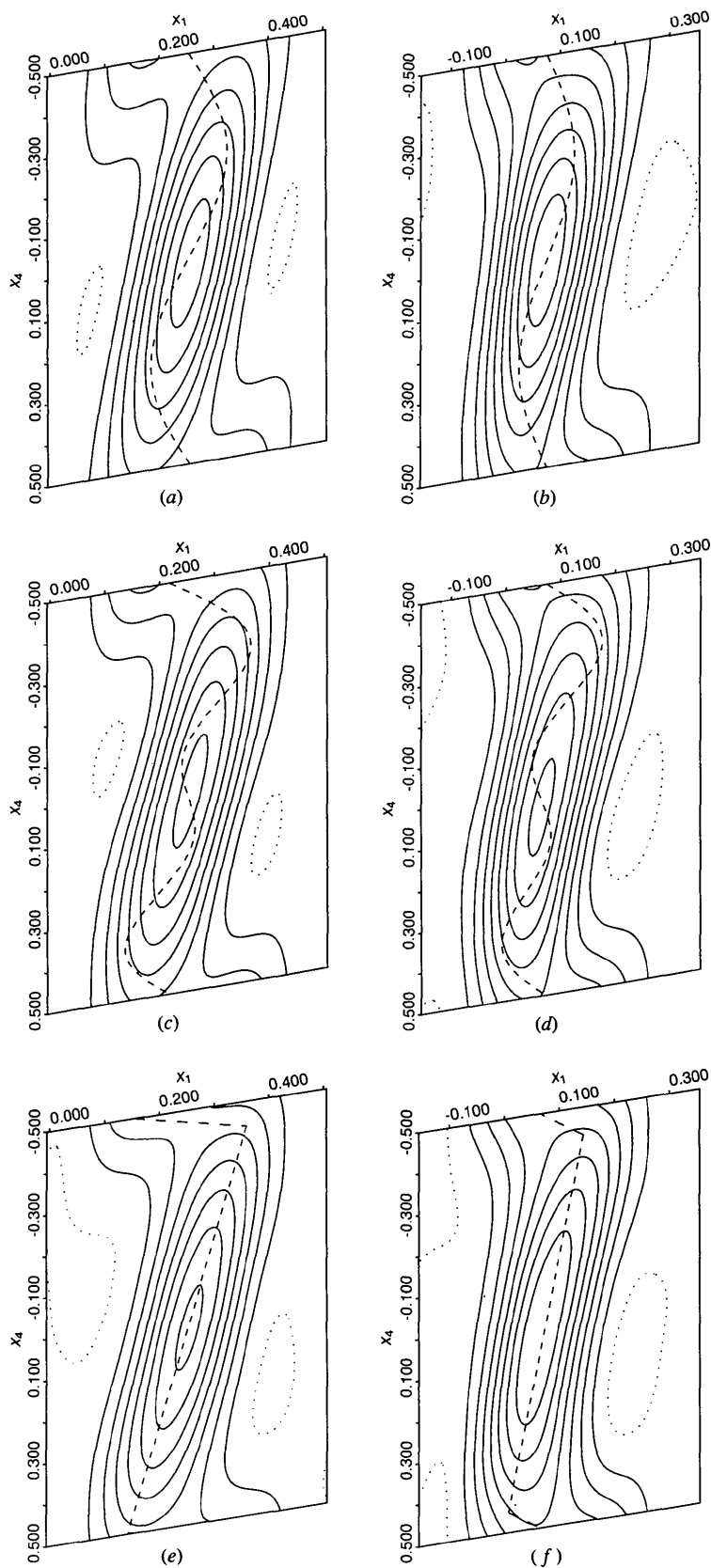


Fig. 4. Electron-density contours in the (x_1, x_4) plane, through the atoms Co and S(1), calculated from phased F_{obs} values. Contours of positive electron density are denoted by solid lines. Contours of zero and negative electron density are denoted by dotted lines. In addition, the x_1 components of the atomic modulation functions are indicated by dashed lines. Contour intervals are $8 \text{ e} \text{ \AA}^{-3}$ for the Co atom and $4 \text{ e} \text{ \AA}^{-3}$ for the S(1) atom. (a) Co atom, for main reflections, phases were calculated from the average structure (Gama *et al.*, 1992), for satellite reflections, phases were obtained from the direct-methods procedure. The modulation function (first-order harmonics) was calculated from the estimated modulation parameters. (b) S(1) atom, see (a) for explanation. (c) Co atom, phases and modulation function (first- and second-order harmonics) were calculated using parameters obtained from the final refinement on crystal 1. (d) S(1) atom, see (c) for explanation. (e) Co atom, phases and modulation function (sawtooth-shaped) were calculated using parameters obtained from the final refinement on crystal (2). (f) S(1) atom, see (e) for explanation.

The modulation functions

The position of an atom μ in an incommensurately modulated structure is given by $\mathbf{r}(\mu, \mathbf{L}_\mu) = \mathbf{r}_0^\mu + \mathbf{L}_\mu + \mathbf{u}^\mu$, where $\mathbf{r}_0^\mu = (x_0^\mu, y_0^\mu, z_0^\mu)$ is the average position of the atom relative to the origin in the unit cell of the average structure, \mathbf{L}_μ is a lattice vector of the average structure and $\mathbf{u}^\mu = (u_x^\mu, u_y^\mu, u_z^\mu)$ describes the atomic displacement functions. The latter are periodic functions, with period 1, of the four-dimensional coordinate $\bar{x}_4^\mu = \mathbf{q} \cdot (\mathbf{r}_0^\mu + \mathbf{L}_\mu) + t$, where t is the internal parameter (de Wolff, 1974). With the program *JANA*, the following displacive modulation functions can be used. [Note, all vectors are described with respect to the basis (a,b,c) of the average structure with the subscript $i = x, y, z$ denoting the various components, respectively.]

(1) For individual atoms, the most general form of a displacement function is given by a truncated Fourier series

$$u_i^\mu(\bar{x}_4^\mu) = \sum_n [a_{n,i}^{\mu,s} \sin(2\pi n \bar{x}_4^\mu) + a_{n,i}^{\mu,c} \cos(2\pi n \bar{x}_4^\mu)], \quad (1)$$

where $a_{n,i}^{\mu,s}$ and $a_{n,i}^{\mu,c}$ are the amplitudes of the sine and cosine part, respectively, of the n th-order harmonic component and the summation extends over all harmonics with $n \geq 1$.

(2) Displacements of individual atoms can also be described by 'sawtooth' functions

$$u_i^\mu(\bar{x}_4^\mu) = (2u_{0,i}^\mu/\Delta_\mu)(\bar{x}_4^\mu - \bar{x}_{4,0}^\mu), \quad (2)$$

where $u_{0,i}^\mu$, $\bar{x}_{4,0}^\mu$ and Δ_μ are, respectively, the amplitude, the center and the width of the sawtooth function. This definition (2) applies within the interval $\bar{x}_{4,0}^\mu - \Delta_\mu/2 < \bar{x}_4^\mu \leq \bar{x}_{4,0}^\mu + \Delta_\mu/2$. The modulation function is defined as periodic, *i.e.* $u_i^\mu(\bar{x}_4^\mu + 1) = u_i^\mu(\bar{x}_4^\mu)$, and is discontinuous at the interval boundaries. For $\Delta_\mu \neq 1$, the sawtooth function leads to occupancy factor modulation (Petříček, Gao, Lee & Coppens, 1990).

(3) The atomic displacement can also be described by a 'triangle' function, *i.e.* a combination of two sawtooth functions

$$u_i^\mu(\bar{x}_4^\mu) = \begin{cases} (2u_{0,i}^\mu/\Delta_\mu)(\bar{x}_4^\mu - \bar{x}_{4,0}^\mu) & (\bar{x}_{4,0}^\mu - \Delta_\mu/2 < \bar{x}_4^\mu \leq \bar{x}_{4,0}^\mu + \Delta_\mu/2) \\ (-2u_{0,i}^\mu/1 - \Delta_\mu)(\bar{x}_4^\mu - \bar{x}_{4,0}^\mu - 1/2) & (\bar{x}_{4,0}^\mu + \Delta_\mu/2 < \bar{x}_4^\mu \leq \bar{x}_{4,0}^\mu - \Delta_\mu/2 + 1), \end{cases}$$

again with a periodic continuation beyond the indicated intervals. In the program *JANA*, this type of modulation can be mimicked by substitutional modulation on two atoms (μ and ν), both of the same type and both having the same average position (which implies $\bar{x}_4^\mu = \bar{x}_4^\nu$), occupancy factor and thermal parameters. The displacement of the first atom (μ) is described by a sawtooth function (2), with parameters $u_{0,i}^\mu$, $\bar{x}_{4,0}^\mu$ and Δ_μ ($0 < \Delta_\mu < 1$). The displacement of the second atom (ν) is also described by a sawtooth function (2), but with

parameters $u_{0,i}^\nu$, $\bar{x}_{4,0}^\nu$ and Δ_ν ($0 < \Delta_\nu < 1$) which are related to the modulation parameters of the first atom as

$$u_{0,i}^\nu = -u_{0,i}^\mu, \quad \bar{x}_{4,0}^\nu = \bar{x}_{4,0}^\mu + 1/2, \quad \Delta_\nu = 1 - \Delta_\mu. \quad (4)$$

Note that, in contrast to the sawtooth function [(2)], with the triangle function [(3)], the occupancy factor of the combined atom, as a function of \bar{x}_4^μ , is always equal to 1. As a result, no occupancy-factor modulation exists for the combined atom.

Rigid-body modulation

For atoms forming a specific group or molecule, the displacements of the individual atoms can be restricted in such a way that the geometry of the group is preserved ('rigid-body' modulation). The displacement of each atom is still described by (1), but with \bar{x}_4^μ replaced by $\bar{X}_4^k = \mathbf{q} \cdot \mathbf{R}^k + t$, where \mathbf{R}^k is the phase-reference point of the k th rigid body, chosen as the center of mass of the rigid body. The atomic modulation parameters in (1) are expressed in terms of the translational and rotational displacements of the k th rigid group

$$a_{n,i}^{\mu,s} = [\mathbf{T}_n^{k,s} + \mathbf{W}_n^{k,s} \times (\mathbf{r}_0^\mu + \mathbf{L}_\mu - \mathbf{R}^k)]_i \quad (5)$$

and

$$a_{n,i}^{\mu,c} = [\mathbf{T}_n^{k,c} + \mathbf{W}_n^{k,c} \times (\mathbf{r}_0^\mu + \mathbf{L}_\mu - \mathbf{R}^k)]_i. \quad (6)$$

Here, $\mathbf{T}_n^{k,s} = (t_{n,x}^{k,s}, t_{n,y}^{k,s}, t_{n,z}^{k,s})$ and $\mathbf{T}_n^{k,c} = (t_{n,x}^{k,c}, t_{n,y}^{k,c}, t_{n,z}^{k,c})$ represent, respectively, the sine and cosine parts of the n th-order harmonic components of the translation of the rigid body. Similarly, the rotation of the rigid body, around the center of mass \mathbf{R}^k , is given by $\mathbf{W}_n^{k,s} = (w_{n,x}^{k,s}, w_{n,y}^{k,s}, w_{n,z}^{k,s})$ and $\mathbf{W}_n^{k,c} = (w_{n,x}^{k,c}, w_{n,y}^{k,c}, w_{n,z}^{k,c})$, respectively. Note that the rotational terms in (5) and (6) are rectilinear approximations to a true rotation and, therefore, are only valid with reasonable precision for rotations up to $\sim 10^\circ$.

During structure refinement, the following groups were treated as rigid bodies: NCN(1) and NCN(2), which

$$\begin{aligned} & (\bar{x}_{4,0}^\mu - \Delta_\mu/2 < \bar{x}_4^\mu \leq \bar{x}_{4,0}^\mu + \Delta_\mu/2) \\ & (\bar{x}_{4,0}^\mu + \Delta_\mu/2 < \bar{x}_4^\mu \leq \bar{x}_{4,0}^\mu - \Delta_\mu/2 + 1), \end{aligned} \quad (3)$$

are mnt groups without the S atoms, and PERYLENE, *i.e.* the perylene molecule, with H atoms at calculated positions. All atoms in these groups were assigned displacements given by (1), with the amplitudes defined by (5) and (6). Further, for each group, a single overall anisotropic temperature tensor has been used for all atoms of the group, except for the H atoms of the perylene molecule for which an overall isotropic temperature factor has been used. No rigid-body

constraints were imposed upon the average positions of the atoms of the groups.

Introduction of rigid bodies was necessary because there happened to be a large number of rigid chemical bonds in the mnt fragments and the perylene molecule, causing the thermal parameters of atoms connected by these bonds to be highly correlated. Further, there were not enough second- and higher-order satellites to determine unambiguously the modulation parameters of harmonics of order higher than 1; it is known that thermal vibration and displacive modulation are highly correlated (Lam, Beurskens & van Smaalen, 1994). The introduction of rigid bodies greatly reduces the number of parameters needed to describe the modulated structure. As a result, the standard deviations of the temperature parameters and the modulation parameters of harmonics of order higher than 1 were significantly reduced. However, a slight increase in *R* factors was observed.

Initial refinement on data from crystal (1)

Refinement of the modulated structure started from the average structure (Gama *et al.*, 1992), with estimates for the modulations of the Co and S atoms obtained as described above. The anisotropic temperature parameters of these atoms in the average structure were reduced accordingly (Lam, Beurskens & van Smaalen, 1994). Initial values for the modulation parameters of the other atoms were taken as zero. The dichloromethane molecule was included in the refinement with no modulation for the disordered C(29) atom. During the initial refinements, average positions of all atoms were kept fixed and only the perylene molecule was treated as a rigid body.

Refinement, allowing only first-order harmonics, converged smoothly to $R \simeq 0.17$ and $R \simeq 0.32$ for main reflections and first-order satellites, respectively. With allowance for second-order harmonics, these *R* factors decreased to $R \simeq 0.13$ and $R \simeq 0.16$, respectively. The large decrease in the *R* factor for the satellites indicates that second-order harmonics, having atomic modulation amplitudes of 0.29 Å for the Co atom and 0.46–0.49 Å for the S atoms, are indeed very important for the atomic displacements (see §3). The final refinement on crystal (1) was performed using three rigid bodies: NCN(1), NCN(2) and PERYLENE. Temperature tensors and modulation parameters (harmonics with $n \leq 2$) of all individual atoms and of the three rigid bodies were included in the refinement. In addition, the average positions of all non-H atoms were also allowed to vary. The H atoms of perylene were refined riding on their parent C atoms with isotropic temperature parameters that were initially fixed at $U_{\text{iso}} = 0.06 \text{ \AA}^2$. *R* factors are 0.13 and 0.14 for main reflections and first-order satellites, respectively.

Unfortunately, the model at hand proved not to be very satisfactory. For the Co and S atoms, atomic displacements were not in good agreement with the electron-

Table 2. Fractional coordinates of the average atomic positions

These results are obtained from the final refinement against data collected from crystal (2). The standard deviations of the coordinates are given in parentheses.

	x_a^0	y_a^0	z_a^0
Co	0.2509 (9)	0.5577 (3)	0.02520 (19)
S(1)	0.0756 (13)	0.3892 (5)	0.0376 (3)
S(2)	0.1739 (14)	0.6177 (5)	0.1480 (3)
S(3)	0.3913 (14)	0.7359 (5)	0.0155 (4)
S(4)	0.3820 (14)	0.5006 (5)	-0.0875 (3)
C(1)	0.058 (4)	0.387 (2)	0.1432 (12)
C(2)	0.015 (4)	0.283 (2)	0.1791 (13)
C(3)	0.096 (4)	0.487 (2)	0.1885 (12)
C(4)	0.074 (4)	0.495 (2)	0.2745 (12)
N(1)	-0.032 (4)	0.1975 (18)	0.2075 (12)
N(2)	0.064 (3)	0.496 (2)	0.3433 (11)
C(5)	0.453 (4)	0.7356 (19)	-0.0837 (13)
C(6)	0.513 (4)	0.837 (2)	-0.1178 (14)
C(7)	0.442 (4)	0.6301 (18)	-0.1286 (12)
C(8)	0.487 (4)	0.634 (2)	-0.2128 (13)
N(3)	0.553 (4)	0.9243 (18)	-0.1441 (14)
N(4)	0.511 (4)	0.6340 (18)	-0.2789 (11)
C(9)	0.295 (4)	0.184 (2)	0.5850 (13)
C(10)	0.288 (4)	0.079 (2)	0.6243 (13)
C(11)	0.264 (4)	-0.031 (2)	0.5757 (13)
C(12)	0.246 (4)	-0.027 (2)	0.4899 (13)
C(13)	0.248 (4)	0.080 (2)	0.4493 (13)
C(14)	0.282 (4)	0.184 (2)	0.4959 (13)
C(15)	0.252 (4)	-0.136 (2)	0.6126 (15)
C(16)	0.228 (4)	-0.239 (2)	0.5650 (14)
C(17)	0.206 (4)	-0.235 (2)	0.4814 (15)
C(18)	0.218 (4)	-0.131 (2)	0.4415 (14)
C(19)	0.198 (4)	-0.127 (2)	0.3552 (14)
C(20)	0.203 (4)	-0.028 (2)	0.3180 (14)
C(21)	0.228 (4)	0.077 (2)	0.3645 (13)
C(22)	0.279 (4)	0.294 (2)	0.4627 (15)
C(23)	0.305 (4)	0.394 (2)	0.5094 (16)
C(24)	0.331 (4)	0.393 (2)	0.5903 (16)
C(25)	0.320 (4)	0.290 (2)	0.6326 (14)
C(26)	0.350 (4)	0.287 (2)	0.7176 (15)
C(27)	0.336 (4)	0.187 (2)	0.7558 (15)
C(28)	0.311 (4)	0.081 (2)	0.7117 (13)
H(15)	0.264 (6)	-0.137 (3)	0.674 (2)
H(16)	0.222 (6)	-0.314 (3)	0.592 (2)
H(17)	0.185 (6)	-0.308 (3)	0.448 (2)
H(19)	0.180 (6)	-0.201 (3)	0.3214 (19)
H(20)	0.188 (6)	-0.029 (3)	0.256 (2)
H(21)	0.232 (6)	0.151 (3)	0.3369 (18)
H(22)	0.264 (6)	0.295 (3)	0.402 (2)
H(23)	0.309 (6)	0.469 (3)	0.482 (2)
H(24)	0.348 (6)	0.468 (3)	0.624 (2)
H(26)	0.373 (6)	0.361 (3)	0.751 (2)
H(27)	0.351 (6)	0.188 (3)	0.817 (2)
H(28)	0.307 (6)	0.006 (3)	0.7401 (19)
Cl	0.910 (3)	0.9306 (13)	0.0594 (9)
C(29)	0.046 (14)	-0.029 (7)	-0.024 (5)

density maps of these atoms (Figs. 4c and d). In addition, ranges of *t* values were found with too short Co—S distances, *e.g.* less than 1.8 Å. Also, because of the high *R* factors, the reflection data were suspected to suffer from overlap caused by twinning (§2), although tests could not provide convincing evidence for such influence. Further, because of the large modulation amplitudes of the first- and second-order harmonics of the displacements of the Co and S atoms, it was expected that second-order satellites might be strong. For these reasons, it was decided to measure new X-ray data on crystal (2).

Table 3. *Temperature parameters for individual atoms and rigid groups*

These results are obtained from the final refinement against data collected from crystal (2). The standard deviations of the temperature parameters are given between parentheses. The correction to the atomic form factor because of thermal vibration is given by $\exp(-2\pi^2 \sum_{i,j=1}^3 U_{ij} S_i S_j a_i^* a_j^*)$ for the anisotropic case and by $\exp[-8\pi^2 U(\sin \theta)^2/\lambda^2]$ for the isotropic case. The isotropic temperature parameter for the H atoms of the perylene molecule is equal to $U = 0.05(2) \text{ \AA}^2$. The temperature tensors of the groups NCN(1) and NCN(2) are not positive definite.

	$U_{11} (\text{\AA}^2)$	$U_{22} (\text{\AA}^2)$	$U_{33} (\text{\AA}^2)$	$U_{12} (\text{\AA}^2)$	$U_{13} (\text{\AA}^2)$	$U_{23} (\text{\AA}^2)$
Co	0.035 (2)	0.0144 (16)	0.0192 (13)	-0.0007 (15)	0.0031 (12)	0.0088 (11)
S(1)	0.041 (5)	0.029 (4)	0.023 (3)	0.001 (4)	0.009 (3)	0.006 (3)
S(2)	0.046 (4)	0.032 (4)	0.026 (3)	-0.007 (3)	0.007 (3)	0.001 (3)
S(3)	0.047 (5)	0.023 (3)	0.034 (3)	-0.005 (3)	0.008 (3)	0.005 (3)
S(4)	0.036 (4)	0.022 (4)	0.029 (3)	-0.001 (3)	-0.003 (3)	0.011 (3)
Cl	0.22 (2)	0.039 (17)	0.11 (2)	-0.049 (15)	0.050 (16)	0.019 (16)
C(29)	0.12 (8)	0.08 (6)	0.10 (6)	0.02 (6)	-0.01 (6)	-0.07 (5)
Group						
NCN(1)	-0.002 (8)	0.008 (12)	0.020 (5)	0.005 (8)	-0.002 (6)	0.008 (7)
NCN(2)	0.020 (9)	0.013 (8)	0.016 (8)	0.016 (8)	0.014 (7)	0.015 (7)
PERYLENE	0.014 (4)	0.035 (4)	0.031 (4)	0.003 (3)	0.012 (3)	0.013 (3)

Table 4. *Modulation parameters for individual atoms and rigid groups*

These results are obtained from the final refinement against data collected from crystal (2). The standard deviations of the modulation parameters are in parentheses. Parameter symbols used are the elements of the vectors defined in equations (1) – (6).

		$u_{0,x}^{\mu}$	$u_{0,y}^{\mu}$	$u_{0,z}^{\mu}$	$\bar{x}_{4,0}^{\mu}$	Δ_{μ}	
Co		-0.1082 (9)	0.0201 (5)	-0.0094 (3)	0.028 (3)	0.938 (12)	
S(1)		-0.069 (2)	0.0113 (12)	-0.0008 (7)	0.009 (6)	0.89 (4)	
S(2)		-0.072 (2)	0.0159 (12)	-0.0040 (7)	-0.062 (6)	0.95 (4)	
S(3)		-0.091 (2)	0.0083 (11)	-0.0093 (8)	0.058 (5)	0.86 (3)	
S(4)		-0.096 (2)	0.0035 (11)	-0.0004 (7)	0.107 (5)	0.90 (3)	
Cl	n	$a_{n,x}^{\mu,s}$	$a_{n,y}^{\mu,s}$	$a_{n,z}^{\mu,s}$	$a_{n,x}^{\mu,c}$	$a_{n,y}^{\mu,c}$	$a_{n,z}^{\mu,c}$
	1	-0.029 (4)	-0.0242 (19)	-0.0004 (14)	0.006 (4)	0.014 (2)	0.0044 (15)
	2	0.024 (7)	-0.014 (4)	0.002 (2)	0.033 (6)	-0.014 (3)	0.006 (2)
	3	0.004 (10)	0.022 (4)	0.011 (4)	-0.007 (11)	0.001 (5)	-0.016 (4)
Group	n	$w_{n,x}^{k,s}$	$w_{n,y}^{k,s}$	$w_{n,z}^{k,s}$	$w_{n,x}^{k,c}$	$w_{n,y}^{k,c}$	$w_{n,z}^{k,c}$
NCN (1)	1	-0.022 (2)	0.0070 (15)	-0.0001 (8)	-0.010 (2)	0.0127 (16)	-0.0009 (10)
	2	0.020 (4)	0.010 (3)	0.0011 (16)	0.015 (4)	0.002 (3)	-0.0015 (4)
	3	-0.012 (5)	-0.011 (4)	-0.003 (4)	-0.021 (6)	0.016 (4)	0.003 (2)
NCN(2)	1	-0.035 (2)	0.0032 (16)	-0.0077 (10)	0.009 (2)	0.0042 (15)	-0.0018 (9)
	2	-0.012 (4)	-0.004 (3)	0.0013 (15)	0.001 (4)	-0.011 (3)	0.0053 (16)
	3	-0.006 (8)	0.000 (4)	-0.002 (3)	0.024 (6)	-0.006 (3)	-0.010 (2)
PERYLENE	1	-0.0068 (10)	0.0056 (8)	-0.0052 (5)	0.0021 (14)	0.0022 (9)	-0.0009 (5)
	2	-0.003 (2)	0.0005 (18)	0.0060 (10)	-0.001 (3)	-0.002 (2)	0.0012 (11)
	3	0.006 (5)	-0.004 (2)	-0.0038 (13)	0.008 (4)	-0.002 (3)	-0.0009 (18)
Group	n	$w_{n,x}^{k,s}$	$w_{n,y}^{k,s}$	$w_{n,z}^{k,s}$	$w_{n,x}^{k,c}$	$w_{n,y}^{k,c}$	$w_{n,z}^{k,c}$
NCN(1)	1	0.0032 (14)	0.0029 (12)	0.0013 (7)	-0.0011 (16)	0.0075 (14)	-0.0001 (8)
	2	-0.001 (3)	0.006 (2)	-0.005 (12)	0.000 (2)	-0.0045 (19)	-0.0021 (11)
	3	0.004 (4)	-0.001 (3)	-0.0059 (14)	-0.006 (3)	0.006 (2)	0.0017 (17)
NCN(2)	1	-0.0008 (16)	0.0008 (13)	0.0009 (8)	0.0079 (15)	0.0081 (14)	0.0021 (8)
	2	-0.010 (2)	-0.002 (2)	-0.0009 (11)	-0.001 (2)	-0.009 (2)	-0.0014 (13)
	3	-0.003 (4)	0.007 (4)	0.003 (2)	-0.007 (2)	-0.002 (3)	-0.0044 (13)
PERYLENE	1	-0.0015 (6)	-0.0014 (4)	-0.0004 (3)	0.0007 (5)	0.0028 (3)	-0.0004 (2)
	2	0.0073 (8)	0.0008 (8)	0.0026 (5)	-0.0019 (11)	0.0013 (5)	0.0007 (4)
	3	0.0059 (11)	-0.0011 (13)	0.0002 (6)	0.0022 (17)	0.0050 (10)	0.0012 (7)

Refinement on data from crystal (2)

Refinement of the model, having only first- and second-order harmonics for the modulation functions of individual atoms and the rigid bodies, still resulted in relatively large R factors and Co—S bonds that were too short. Alternatively, sawtooth functions (2) without occupancy-factor modulation ($\Delta_{\mu} = 1$) were used to describe the displacements of the Co and S atoms. Considering the anharmonicity and the magnitudes of the displacements of the Co and S atoms, it is very likely that

higher-order harmonics are also important for the modulations of the rigid bodies. Therefore, the modulation functions of the rigid bodies and the Cl atom were allowed to include all harmonics up to $n = 3$. Although the R factors were only slightly lower ($R = 0.11$, $R = 0.15$ and $R = 0.34$, respectively, for main reflections, first- and second-order satellites), the sawtooth-shaped modulation function did give a much better description of the electron density and now only chemically reasonable values were found for the Co—S distances.

Further improvement of the fit (especially to the second-order satellites) was obtained by triangle functions (3) describing the modulations of the Co and S atoms (Fig. 4e and f). The final R factor on a total of 330 structural parameters is 0.126 for 2835 observed ($I/\sigma \geq 2.5$) reflections. Partial R factors are 0.111, 0.143 and 0.263, respectively, for 1450 main reflections, 1188 first-order satellites and 197 second-order satellites; corresponding wR values are 0.120, 0.185 and 0.279. Final values for the parameters describing average positions, thermal vibration and displacive modulations are given in Tables 2, 3 and 4, respectively.

5. Description of the modulated structure

Most of the Co atoms are octahedrally coordinated by S atoms. The four equatorial S atoms [S(1–4)] belong to the same $\text{Co}(\text{mnt})_2$ unit and the two apical S atoms [S(1') and S(4')] belong to different neighboring $\text{Co}(\text{mnt})_2$ units. Coordinates and the modulation function of S(1') are related to those of S(1) by a center of symmetry at $(0, \frac{1}{2}, 0, 0)$ in four-dimensional space. Similarly, coordinates and the modulation function of S(4') are related to those of S(4) through a center of symmetry at $(\frac{1}{2}, \frac{1}{2}, 0, 0)$.

Displacive modulations for the Co (amplitude 0.77 Å) and S atoms (amplitudes ranging from 0.48 to 0.63 Å) are mainly directed along the a axis. The displacements of the Co atom and its four equatorial S atoms are approximately in phase, causing the corresponding Co—S bonds to vary only slightly (between 2.14 and 2.34 Å) as a function of the internal parameter t (Table 5 and Fig. 5). Because of the symmetry relation between S(1') and S(1) and, similarly, between S(4') and S(4), the displacement of the Co atom is approximately 180° out of phase with the displacements of S(1') and S(4'). As a

Table 5. Minimum, average and maximum Co—S distances (Å)

Bond	Minimum distance	Average distance	Maximum distance	Distance by Gama <i>et al.</i> (1992)
Co—S(1)	2.22	2.23	2.33	2.23
Co—S(2)	2.14	2.23	2.27	2.23
Co—S(3)	2.15	2.23	2.34	2.23
Co—S(4)	2.15	2.22	2.33	2.23
Co—S(1')	2.05	2.42	3.06	2.44
Co—S(4')	2.27	2.68	3.86	2.62

result, the Co—S distances for the two apical S atoms show large variations, with distances ranging from 2.05 to 3.86 Å (Table 5 and Fig. 5). For S(4'), there appears to be a region with relatively short Co—S distances (less than 2.5 Å) and a region where there is no bonding left (distances larger than 3.0 Å). The Co—S(1') distance varies less than the Co—S(4') distance, such that S(1') is considered to be bonded to the Co atom for all values of t (despite the rather large distances around $t = 0.6$, see comments below). The picture emerges of a coordination of the Co atom which is either six- or fivefold. The ratio of the number of Co atoms in each type of coordination can be obtained from the width of the t interval corresponding to that type of coordination. For a distance of 3.0 Å, this width is equal to $\Delta t_{\text{exp}} = 0.213$ (Fig. 5). For chemical reasons (see below), it is inferred that this width is $\Delta t_{\text{th}} = 0.211$, which means that 21.1% of all Co atoms are fivefold coordinated.

For incommensurate crystals, the bond-valence method due to Brown (1981) can be used to calculate valences of atoms as a function of the internal parameter t (van Smaalen, 1992). The valence of the Co atom as a function of t is given in Fig. 6, together with the

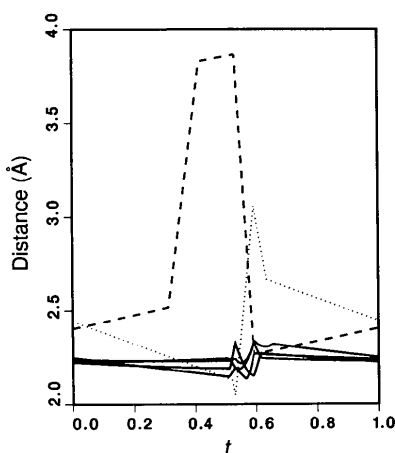


Fig. 5. Distances between the Co atom and its coordinating S atoms as a function of the internal parameter t . The continuous lines represent Co—S distances in the same $\text{Co}(\text{mnt})_2$ unit, the dotted line represents the Co—S(1') distances and the dashed line represents the Co—S(4') distances.

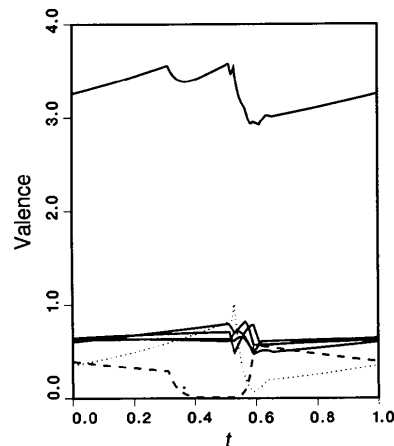


Fig. 6. Valences for the Co—S bonds as a function of the internal parameter t . The continuous lines in the lower half of the figure represent valences for Co—S bonds in the same $\text{Co}(\text{mnt})_2$ unit, the dotted line represents the valence for the Co—S(1') bond and the dashed line represents the valence for the Co—S(4') bond. The continuous line in the top half of this figure is the total valence of the Co atom.

individual bond valences of its six coordinating S atoms [$R_0 = 2.06 \text{ \AA}$, from Brese & O'Keeffe (1991)]. The picture of a varying cobalt coordination is confirmed, as the bond valence of the Co—S(4') bond is virtually zero for $0.40 < t < 0.55$, *i.e.* for these values of t the Co atom is only bonded to five S atoms. The valence of the Co atom varies between 2.92 and 3.57 and is indicative of a varying valence state of cobalt in this compound. The interpretation of relative values of the (bond) valences, as has been done here, is certainly meaningful, but one should be cautious to use the absolute values because the employed bond-valence parameter was derived for inorganic salts and not for organometallic compounds.

For a chemical interpretation of the modulation in the bonding of the Co(mnt)₂ units, consider stepping along the a axis, *i.e.* along the chains of Co(mnt)₂ units, with stepsize $a = |a|$. Each step is equivalent to a change $\Delta t_{\text{th}} = q_1 = 0.211$ in the internal parameter t , corresponding to a periodicity of the modulation along the a axis of $4.74a$. Fig. 5 then shows that after four or five steps along the a axis, the Co—S(4') distance changes from bonding to nonbonding. The nonbonding state is restricted to this one step and changes to bonding again at the next step [the peak width Δt_{exp} in the Co—S(4') distance plot corresponds well to one along the a axis]. Note that the Co(mnt)₂ units are always dimerized through S(1) and S(1') (*i.e.* one dimer per average unit cell). These dimers form chains along the a axis connected through S(4) and S(4'). However, after four or five dimers, a gap in the chain occurs in the region where the Co—S(4') bond becomes nonbonding. As a result the chains of Co(mnt)₂ units actually consist of oligomeric packages of four or five dimerized Co(mnt)₂ units and the Co atoms at the ends of each package only show fivefold coordination.*

Furthermore, the chain of packages must make chemical sense: if after five dimers the strain in a package (embedded in the perylene moiety of the structure) is released by one broken Co—S(4') bond, the next package again is likely to consist of five dimers, and so on. However, as the modulation is not commensurate, at some point a package may consist of only four dimers when the next Co—S(4') bond is broken. The long-range order which exists in the structure makes it unlikely that some of the packages *by chance* consist of three or six dimers. If the chain of packages is considered to consist of N packages containing five dimers relative to one package containing four dimers, then the ratio x of the number of broken connections relative to the number of dimers can be

written as $x = (N + 1)/(5N + 4) = \Delta t_{\text{th}} = 0.211$, from which it follows that $N = 2.84$. Thus, in first approximation, the chains consist of three packages containing five dimers alternated by one package containing four dimers, but at some point there are not three but just two packages containing five dimers, which prevents the modulation from being commensurate along the a axis.

One should realize that the description of the displacements of the Co and S atoms by triangle functions is an approximation to the true modulation of these atoms, introduced to restrict the number of variable parameters in the refinement to a manageable number. If higher-order harmonics could be refined properly, the variations in the Co—S distances are expected to become smoother. Therefore, the rather wild, but small, variations in the Co—S distances around $t = 0.55$ for atoms S(1–4) and S(1') should not be taken too seriously. The same is true for the sharp maximum Co—S(1') distance at $t = 0.6$. This also means that the differences between the minimum and maximum distances given in Table 5 should be narrowed.

Minimum values for the distances between Co and its coordinating S atoms are thus in good agreement with the Co—S single-bond distance of 2.20 \AA (Pauling, 1960). Also, the average distances (Table 5) between Co and its coordinating S atoms are in good agreement with distances found for the same bonds in the average structure (Gama *et al.*, 1992).

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* Note. The packages of four or five dimerized Co(mnt)₂ units are the result of releasing the strain in the hypothetical chain of uninterrupted connected dimers. It is unlikely that a 'statistical' distribution of packages of four and five dimers is alternated by one package of one dimer ($\Delta t_{\text{exp}} > \Delta t_{\text{th}}$) or by one package of nine dimers ($\Delta t_{\text{exp}} < \Delta t_{\text{th}}$). Therefore, it is inferred that $\Delta t_{\text{exp}} = \Delta t_{\text{th}}$, which agrees very well within the experimental uncertainty.

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Anion Disorder in the 115–118 K Structures of the Organic Superconductors κ_L -(BEDT-TTF)₂Cu(CF₃)₄(C₂H₃Cl₃) and κ_L -(BEDT-TTF)₂Ag(CF₃)₄(C₂H₃Cl₃) [BEDT-TTF = 3,4;3',4'-Bis(ethylenedithio)-2,2',5,5'-tetrathiafulvalene]

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Abstract

The low-temperature structures of the isostructural organic superconductors κ_L -(BEDT-TTF)₂-Cu(CF₃)₄TCE, 5,5',6,6'-tetrahydro-2,2'-bis{1,3-dithiolo[4,5-*b*][1,4]dithiin}ylidene tetra(trifluoromethyl)copper trichloroethane (1) (transition temperature, $T_c = 4$ K), and κ_L -(BEDT-TTF)₂Ag(CF₃)₄TCE, 5,5',6,6'-tetrahydro-2,2'-bis{1,3-dithiolo[4,5-*b*][1,4]dithiin}ylidene tetra(trifluoromethyl)silver trichloroethane (2) ($T_c = 2.6$ K), contain crystallographically disordered anions and 1,1,2-trichloroethane (TCE) solvent molecules. Each entity is described as a mirror-symmetric superposition of two asymmetric components. The extent of anion disorder is extraordinary for an organic superconductor. Crystal data: (1) 2C₁₀H₈S₈.CuC₄F₁₂.C₂H₃Cl₃, $M_r = 1242.28$, orthorhombic, $T = 118$ K, $a = 12.918$ (4), $b = 37.899$ (7), $c = 8.487$ (2) Å, $V = 4155.1$ (18) Å³, $Pnma$ (D_{2h}^{16} , No. 62), $Z = 4$, $F(000) = 2486$, $D_x = 1.986$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 15.74$ cm⁻¹, $R = 0.051$, $wR = 0.039$ for 3572 independent reflections with $I > 2\sigma(I)$; (2) 2C₁₀H₈S₈.AgC₄F₁₂.C₂H₃Cl₃, $M_r = 1286.61$, orthorhombic, $T = 115$ K, $a = 12.936$ (4), $b = 37.976$ (8), $c = 8.526$ (2) Å, $V = 4188.4$ (18) Å³, $Pnma$ (D_{2h}^{16} , No. 62), $Z = 4$, $F(000) = 2553$, $D_x = 2.040$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 15.16$ cm⁻¹, $R = 0.050$, $wR = 0.048$ for 4022 independent reflections with $I > 2\sigma(I)$.

1. Introduction

Organic superconductors based on the organic electron-donor molecule BEDT-TTF [3,4;3',4'-

bis(ethylenedithio)-2,2',5,5'-tetrathiafulvalene, abbreviated ET] now number over 40 (Ishiguro & Yamaji, 1990; Williams, Ferraro, Thorn, Carlson, Geiser, Wang, Kini & Whangbo, 1992), with superconducting transition temperatures (T_c) as high as 12.8 K (at 0.5 kbar pressure) in κ -(ET)₂Cu[N(CN)₂]Cl (Williams, Kini, Wang, Carlson, Geiser, Montgomery, Pyrka, Watkins, Kommers, Boryschuk, Strieby Crouch, Kwok, Schirber, Overmyer, Jung & Whangbo, 1990). It was recognized many years ago that in cation radical salts, crystallographic disorder in the charge-compensating anion was detrimental to the occurrence of superconductivity. In most cases, superconductivity is totally suppressed by the random electrostatic potentials generated by the disordered anions, e.g. in the related salt (TMTSF)₂ClO₄ (TMTSF = 3,4,3',4'-tetramethyl-2,2',5,5'-tetraselenafulvalene) the noncentrosymmetric anions are disordered on a site with inversion symmetry at room temperature (Bechgaard, Carneiro, Rasmussen, Olsen, Rindorf, Jacobsen, Pedersen & Scott, 1981). Upon slowly lowering the temperature through a first-order crystallographic phase transition at 24 K, the unit cell doubles and the anions form a crystallographically ordered arrangement (Gubser, Fuller, Poehler, Stokes, Cowan, Lee & Bloch, 1982; Pouget, Shirane, Bechgaard & Fabre, 1983). Upon further cooling, the salt becomes superconducting at 1.4 K (Bechgaard, Carneiro, Olsen, Rasmussen & Jacobsen, 1981). However, if the cooling is carried out too rapidly, the phase transition is suppressed and the metastable room-temperature structure is locked in at low temperature (Pouget,