

(Perylene)Co(mnt)₂(CH₂Cl₂)_{0.5}: A Mixed Molecular and Polymeric Conductor

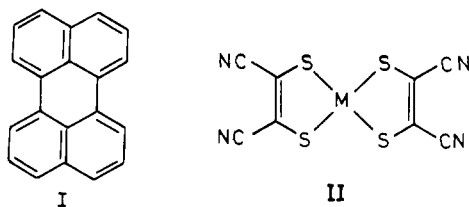
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Abstract: Single crystals of the quasi-one-dimensional conductor (perylene)Co-bis(maleonitriledithiolate)(CH₂Cl₂)_{0.5} were prepared by electrocrystallization. The structure at room temperature is incommensurate with modulation wave vector (0.22a*, -0.13b*, -0.36c*). At T = 295 K it crystallizes in space group P $\bar{1}$ with Z = 2 and lattice parameters a = 6.551 (2) Å, b = 11.732 (2) Å, c = 16.481 (2) Å, α = 92.08 (1)°, β = 95.30 (1)°, γ = 94.62 (1)°, and V = 1251.1 (5) Å³. The structure consists of almost regular perylene stacks and polymeric chains of dimerized Co-bis(dithiolate) units along the a axis, with the solvent molecules disordered in the free spaces. At room temperature, electrical conductivity ($\sigma_{RT} \approx 60 \Omega^{-1} \text{cm}^{-1}$) and absolute thermoelectric power ($S_{RT} = -8 \mu\text{V K}^{-1}$) approach metallic behavior at high temperatures. These transport properties and magnetic susceptibility measurements show a metal to insulator transition at 272–277 K and a second semiconductor to semiconductor phase transition at ca. 170–190 K, both with a remarkable hysteresis.

Introduction

Several molecular conductors based on perylene (Per, I) and metal bis(dithiolenes) of the type M(mnt)₂ (mnt = maleonitriledithiolate or *cis*-2,3-dimercapto-2-butenedinitrile, II) with



general formula (Per)₂M(mnt)₂ (M = Pt, Pd, Au, Cu, Ni) have been reported in the past.^{1–5} In all these cases, metallic properties are associated with perylene regular stacks packed around half the number of M(mnt)₂ stacks. Depending on the metal (M) some members of this family (e.g., for M = Pt, Pd, or Ni) have localized magnetic momenta in the M(mnt)₂ units,^{6–8} but these, as a consequence of relatively large spacing, do not contribute significantly to the electrical conductivity. In this paper we report the synthesis, the structure, and the electrical and magnetic properties of the first member of this family with a 1:1 stoichiometry and segregated stacks, PerCo(mnt)₂(CH₂Cl₂)_{0.5}, which, in addition to high electrical conductivity, displays an unusual polymeric arrangement of the Co(mnt)₂ units. Preliminary data on the transport properties of this compound were recently reported.⁹

Experimental Section

Electrocrystallization. PerCo(mnt)₂(CH₂Cl₂)_{0.5} single crystals were prepared by electrochemical oxidation of dichloromethane solutions of perylene and (n-C₄H₉)₄N[Co(mnt)₂] ($\approx 10^{-2}$ M) by a procedure identical to those previously described for other compounds of this family.^{2,5} Special care was taken with the previous purification of the starting reagents; perylene (Sigma) was gradient sublimed (10⁻² Torr, 110 °C) several times after pentane recrystallization and alumina–silica chromatography,¹⁰ and (n-C₄H₉)₄N[Co(mnt)₂], prepared as previously described,¹¹ was recrystallized from acetone–isobutanol. Dichloromethane (Merck p.a.) was previously distilled, dried with molecular sieves, and passed through an alumina column just before use, and the solutions were deaerated with argon. The electrocrystallization was performed in a two-compartment cell on platinum electrodes through a galvanostatic technique,¹² using current densities in the range 2–10 $\mu\text{A}/\text{cm}^2$. The crystals were harvested after ≈ 5 days and washed with dichloromethane. The crystals obtained by this procedure are black, with metallic shine, but present two types of habit; most of them (>95%) are relatively thick

($\approx 3 \times 0.2 \times 0.2 \text{ mm}^3$) with only a minor amount of thinner and distinct needle-shaped crystals ($\approx 5 \times 0.05 \times 0.02 \text{ mm}^3$). Physical and structural properties of the thin needles indicate that they correspond to the 2:1 stoichiometry as the compounds of this family previously studied and their properties will be reported elsewhere.¹³ Elemental analyses of selected thicker crystals gave the following results. Anal. Found: C, 53.50; H, 1.96; N, 8.76; S, 20.35. Calcd for CoClS₄N₄C_{28.5}H₁₃: C, 53.99; H, 2.07; N, 8.84; and S, 20.23. The presence of chlorine in the thick crystals resulting from dichloromethane molecules incorporated in the crystal structure (approximately 0.5 for each Co) was confirmed by SEM-EDS.

X-ray Diffraction: Crystal and Molecular Structure. A black crystal having approximate dimensions of 0.20 \times 0.20 \times 0.45 mm³ was glued on top of a glass fiber and transferred to the goniometer mounted on an Enraf-Nonius CAD-4F diffractometer, with graphite-monochromatized Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Unit cell parameters were determined from a least-squares treatment of the SET4¹⁴ setting angles of 20 reflections with 18.12° < θ < 19.86°. The unit cell was identified as triclinic. The crystal structure is at room temperature modulated with an incommensurate wave vector $\mathbf{q} = 0.22a^*, -0.13b^*, -0.36c^*$ as shown by the presence of satellite reflections. The modulated structure solution is under way and will be reported elsewhere.¹⁵ In the present paper, the satellites are neglected, and therefore only the average structure is reported as determined by the main reflections. Choice of space group P $\bar{1}$ was confirmed by the solution and the successful refinement of the structure. Reduced cell calculations did not indicate any higher metrical

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Table I. Crystal Data and Structure Analysis Results

chemical formula	C ₂₈ H ₁₂ CoS ₄ N ₄ (CH ₂ Cl ₂) _{0.5}
formula weight	634.07
crystal system	triclinic
space group, no. ²⁶	P $\bar{1}$, 2
a, Å	6.551 (2)
b, Å	11.732 (2)
c, Å	16.481 (2)
α , deg	92.08 (1)
β , deg	95.30 (1)
γ , deg	94.62 (1)
V, Å ³	1251.1 (5)
Z	2
D _{calc} , g·cm ⁻³	1.683
F(000), electrons	640
μ (Mo K α), cm ⁻¹	11.4
temperature, K	295
θ range; min, max, deg	1.25, 28.00
reference reflections; rms dev, %	025; 1.2 123; 1.1 131; 1.4
total no. of data	6561
unique no. of data	6039
observed data ($I \geq 2.5\sigma(I)$)	2079
no. of refined parameters	344
final agreement factors	
$R_F = \sum(F_o - F_c) / \sum F_o $	0.127
$wR = [\sum(w(F_o - F_c)^2) / \sum w F_o ^2]^{1/2}$	0.130
weighting scheme	1
$S = [\sum w(F_o - F_c)^2 / (m - n)]^{1/2}$	3.717

^a m = number of observations; n = number of variables.

lattice symmetry,¹⁶ and examination of the final atomic coordinates of the structure did not yield extra symmetry elements.¹⁷ The data set was collected at room temperature in ω - 2θ scan mode ($\Delta\omega = 0.95 + 0.35 \tan \theta$). Crystal and/or instrumental instability was monitored by measurement of the intensities of three reference reflections that were collected after every 2 h of X-ray exposure time; these reflections exhibit a linear decay of 17% during the 94.4 h of X-ray exposure time. The intensity data were corrected for the decay, for the Lorentz and polarization effects, but not for absorption. Standard deviations on the intensities based on counting statistics were increased according to an analysis of the excess variance¹⁸ of the three reference reflections: $\sigma^2(I) = \sigma_{\text{ca}}^2(I) + (0.019I)^2$. Equivalent reflections were averaged ($\Sigma\sigma/\Sigma I = 0.034$), resulting in 6039 unique reflections and 2079 reflections satisfying the $I > 2.5\sigma(I)$ criterion of observability.

The structure was solved by direct methods (SHELXS86)¹⁹ with the "brute force" approach. The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms of the two major residues of the compound were refined with block-diagonal least-squares procedures (CRYLSQ)²⁰ minimizing the function $Q = \sum_k [w(|F_o| - |F_c|)^2]$. Subsequent Fourier summations showed some density in the vicinity of the inversion center at the origin of the unit cell, which could be correlated to a chlorine position of the solvent molecule of dichloromethane. Following the inclusion of the positional parameters of the chlorine atom, the remainder of the structure refined smoothly. A high thermal displacement had to be attributed to the chlorine of the dichloromethane residue (the overall geometry (distance Cl(1)-Cl(1a) = 2.72 Å; symmetry code (a) 2 - x, 2 - y, -z) of the methylene chloride molecule appeared rather distorted, suggesting some degree of disorder, but no resolvable disorder could be stated). The hydrogen atoms were included in the final refinement riding on their carrier atoms with their positions calculated by using sp² hybridization at the C atom as appropriate with a fixed C-H distance of 0.98 Å. Final refinement on F_o by full-matrix least-squares techniques with anisotropic thermal displacement parameters for the non-hydrogen atoms and one overall temperature factor for the hydrogen atoms converged at $R_F = 0.127$ ($wR = 0.130$, $w = 1$, $S = 3.717$). A final difference Fourier synthesis reveals residual densities between -0.66 and +2.11 e/Å³. Crystal data and

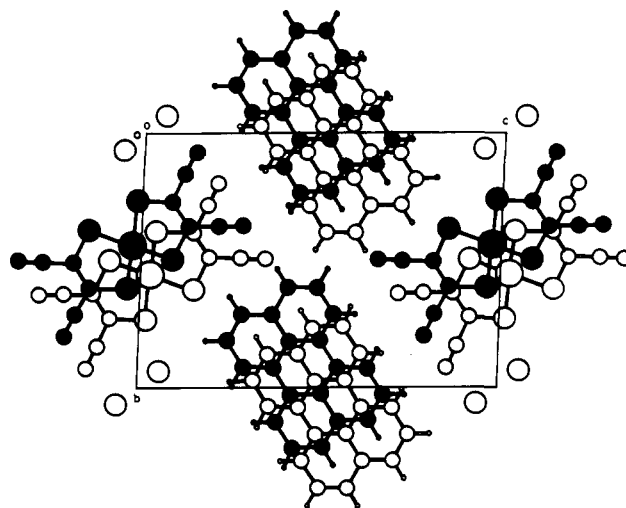
Figure 1. Projection along the a axis of the PerCo(mnt)₂(CH₂Cl₂)_{0.5} crystal structure.

Table II. Co-S Bond Lengths (Å) in Different Co-Dithiolenes Compounds

	Co ₂ ⁻ (S ₂ C ₂ Cl ₄) ₄ ²⁻	Co ₂ ⁻ (S ₂ C ₂ (CF ₃) ₂) ₄ ⁰	PerCo(mnt) ₂ ⁻ (CH ₂ Cl ₂) _{0.5}
ref	30	31	this work
equatorial	2.185 (7)	2.16 (2)	2.23
apical	2.404 (7)	2.38 (2)	2.443 (9)/2.62 (1)

experimental details of the structure determination are compiled in Table I. Scattering factors were those given by Cromer and Mann,²¹ and anomalous dispersion factors taken from Cromer and Liberman²² were included in F_c . All calculations were carried out on the CDC-Cyber 962-31 computer of the University of Groningen with the program packages XTAL,²³ PLATON²⁴ (calculation of geometric data), and an extended version of the program PLUTO²⁵ (preparation of illustrations).

Electrical Transport Measurements. The electrical conductivity measurements along the a axis of the needles were made in the temperature range 80–300 K using an in-line four-probe configuration and dc current of 1 μ A. Electrical contacts on the sample were made with platinum paint (Demetron 308A) to 25- μ m gold wires. Special care was taken to select samples with low ($\leq 1\%$) unnested/nested voltage ratio as defined by Schaffer et al.²⁷ The sample was placed inside a liquid nitrogen cryostat chamber with helium as exchange gas, and the temperature monitored by a calibrated copper-constantan thermocouple placed close to the sample.

The thermopower was measured, along the needle axis a, relative to gold, in the range 350–100 K, by a slow ac technique (10⁻² Hz) in an apparatus similar to the one described by Chaikin et al.²⁸ placed in a vacuum chamber ($<10^{-4}$ Torr) inside a liquid nitrogen cryostat. The thermal gradients used were ≤ 1 K, and they were monitored by a copper-constantan thermocouple. Absolute thermopower was obtained after correction for the small absolute thermopower of gold using the data of Huebner.²⁹

Magnetic Susceptibility. Magnetic susceptibility measurements were performed in the range 4–320 K with a Faraday system (Oxford Instruments) with a 7-T superconducting magnet in a polycrystalline sample of 23 mg placed inside a thin-wall Teflon sample holder previously

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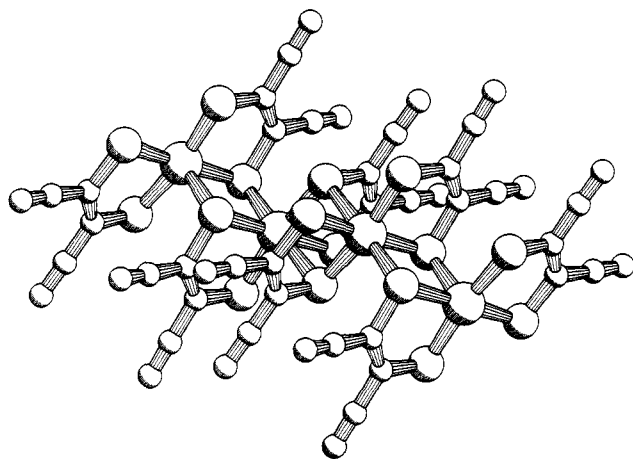


Figure 2. View of the polymeric arrangement of the $\text{Co}(\text{mnt})_2$ units in $\text{PerCo}(\text{mnt})_2(\text{CH}_2\text{Cl}_2)_{0.5}$, each unit being connected with two Co-S bonds to each neighbor.

measured empty and under the same conditions. The magnetic fields used were of 2 and 5 T, and force was measured with a microbalance (Sartorius S3D-V) applying forward and reversed gradients of 5 T m^{-1} . In these conditions the magnetization was found to be proportional to applied magnetic field.

Results

Related by centers of symmetry, the unit cell contains two perylene and two $\text{Co}(\text{mnt})_2$ molecules, both at a general position. The CH_2Cl_2 group is situated at a center of symmetry and is, therefore, at least in the average structure in disorder: Only the one independent chlorine atom could be located. Refinement of the occupation of the Cl position gave no reason to assume that there is not a full CH_2Cl_2 molecule per unit cell. The average crystal structure for $\text{PerCo}(\text{mnt})_2$, ignoring the incommensurate modulation, clearly shows almost uniform stacks of perylene molecules and dimerized polymeric chains of $\text{Co}(\text{mnt})_2$. The Co atoms have octahedral coordination by four sulfur atoms of two mnt units at 2.23 Å in an almost square-planar configuration and two apical sulfur atoms of the $\text{Co}(\text{mnt})_2$ units above or below (see Figure 2) at distances of 2.443 (9) and 2.62 (1) Å. As indicated in Table II, both the equatorial and apical Co-S distances are slightly larger than those observed in other dimerized Co-dithiolene complexes^{30,31} and also larger than the Co-S single-bond distance 2.20 Å.³² Each $\text{Co}(\text{mnt})_2$ unit has two Co-S bonds with each neighbor unit, making a dimerized polymer of $\text{Co}(\text{mnt})_2$. Stacks of perylene molecules, arranged in sheets parallel to the a, b plane, alternate with the polymer chains. The dichloromethane molecules, one per each unit cell, are disordered in the free space between the chains.

The distance between successive perylene units is alternatively 3.27 and 3.28 Å with a superposition mode shown in Figure 2 of the projection of the structure along a , since the perylene molecules are planar and almost perpendicular to the a axis ($0.35 (50)^\circ$). This mode is essentially the same as the one observed in the $(\text{Per})_2\text{M}(\text{mnt})_2$ compounds with $\text{M} = \text{Pt}, \text{Pd}, \text{Au},$ and Ni , where larger intermolecular spacings in the range 3.32–3.36 Å have been observed.^{2,4,5} In view of the relatively large standard deviations of the distances between perylene molecules (0.005 Å) the perylene stacks can be considered as uniform within experimental error. The dihedral angle of the perylene molecules with the $\text{Co}(\text{mnt})_2$ units is $23.10 (30)^\circ$. Similar polymeric organometallic structures are known for bis(oxalato)cuprate(II) complexes,³³ but to the best of our knowledge, this is the first polymeric structure with metal

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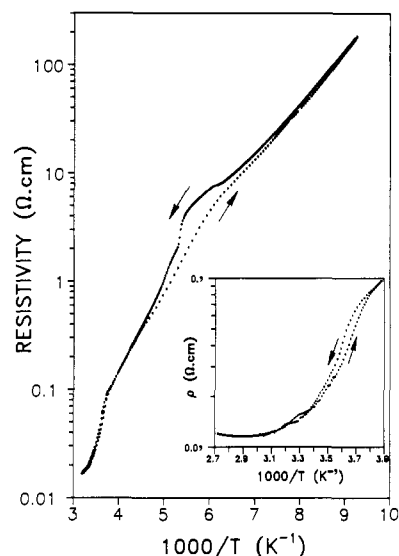


Figure 3. Electrical resistivity measured along the needle axis a of $\text{PerCo}(\text{mnt})_2(\text{CH}_2\text{Cl}_2)_{0.5}$ as a function of temperature T .

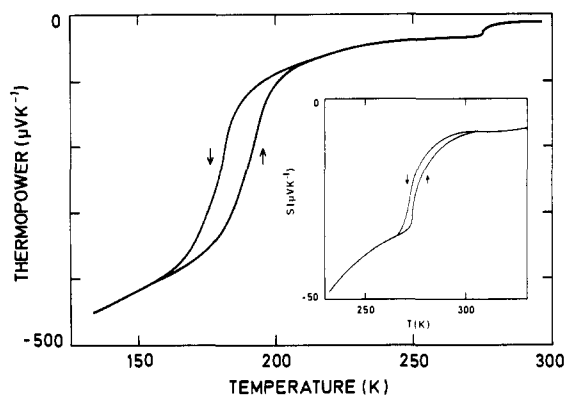


Figure 4. Absolute thermoelectric power measured along the needle axis a of $\text{PerCo}(\text{mnt})_2(\text{CH}_2\text{Cl}_2)_{0.5}$ as a function of temperature.

over sulfur in a bis(dithiolene) complex.

$\text{PerCo}(\text{mnt})_2(\text{CH}_2\text{Cl}_2)_{0.5}$ single crystals show rather different transport properties when compared with the 2:1 compounds. At room temperature the electrical conductivity (Figure 3) is $\approx 60 \pm 20 \Omega^{-1} \text{ cm}^{-1}$ having a broad maximum at $\approx 340 \text{ K}$, and a metal insulator transition is evident at 272 K upon cooling and at 277 K on heating. Below this transition the conductivity is activated with an activation energy of 0.15 eV, until approximately 166 K on cooling or at 188 K on heating, where a second transition is observed as a continuous increase of resistivity and a change to an activation energy of 0.10 eV below this phase transition. The actual place of this anomaly and the amplitude of the hysteresis are dependent on the heating or cooling rates used.

Both transitions are also seen in thermopower measurements (Figure 4). Above room temperature, the thermopower approaches a metal-like behavior, with a small, negative, and nearly temperature-independent value, $-8 \mu\text{V K}^{-1}$. At lower temperatures it drops, approaching a semiconducting behavior with strong anomalies at the transitions referred before. Both thermopower and resistivity show a significant hysteresis of 5 and 10–20 K at the higher and lower phase transitions, respectively. The slightly smaller hysteresis in the thermopower measurements ($\approx 10 \text{ K}$ compared with $\approx 20 \text{ K}$ in resistivity) is probably due to the much smaller heating and cooling rates used ($\approx 0.1 \text{ K/min}$) than in resistivity measurements ($\approx 0.3 \text{ K/min}$). This hysteresis is clearly observed but with a continuous variation of the transport parameters without noticeable discontinuities, and therefore it is not clear that the transitions are of first order.

The paramagnetic susceptibility results, calculated from magnetization measurements after correction for a diamagnetic contribution estimated as $3.01 \times 10^{-4} \text{ emu/mol}$ using tabulated

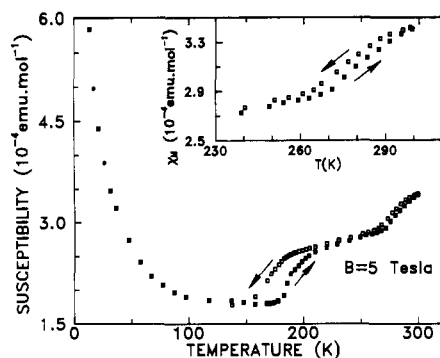


Figure 5. Paramagnetic susceptibility of PerCo(mnt)₂(CH₂Cl₂)_{0.5} as a function of temperature.

Pascal constants, are shown in Figure 5. At room temperature the paramagnetism is rather small, corresponding to 3.4×10^{-4} emu/mol, a value of the same order of magnitude of the Pauli paramagnetism of (Per)₂Au(mnt)₂, 2×10^{-4} emu/mol.³⁴ The two phase transitions are seen as a decrease of magnetization upon cooling and both with hysteresis. In this case the larger hysteresis at the low-temperature phase transition may result from a relatively faster cooling or heating rate during the magnetization measurements. At low temperature ($T < 100$ K) a Curie tail corresponding to approximately 2.5% of 1/2 spins per formula unit is observed. However, a detailed analysis shows that this tail is proportional to $1/T^{0.6}$, a power law typical of disordered systems with random exchange antiferromagnetic interactions³⁵ as experimentally found in systems like Ad(TCNQ)₂³⁶ and Qn(TCNQ)₂.³⁷

Discussion

The two phase transitions in this compound have probably different origins. The low-temperature phase transition with the large hysteresis and quite sensitive to the cooling or heating rate is probably due to the ordering or freezing of the solvent molecules incorporated in the structure. The high-temperature phase transition can have an electronic nature, but for a clear assignment and in order to explain the properties of this compound, it is essential to know the degree of charge transfer between the perylene and the Co(mnt)₂ chains. Cyclic voltammetry studies performed in perylene and in (*n*-C₄H₉)₄NCo(mnt)₂, in the same conditions as those used for the electrocrystallization, showed that the oxidation potential of perylene (0.92 V vs SCE) lies very close to the one for the oxidation of Co(mnt)₂⁻ to [Co(mnt)₂]₂⁻ (0.88 V vs SCE), and therefore it is not clear from these studies whether in this solid we have Per⁺ and Co(mnt)₂⁻ or (Per)₂⁺ and [Co(mnt)₂]₂⁻ or any intermediate degree of charge transfer. Several efforts to detect any EPR signal in these crystals at different

temperatures in the range 80–300 K were unsuccessful. In the case of Co(III) in an octahedral coordination, as in this case, a diamagnetic organometallic species could occur with no EPR signal, but in all cases, a signal from the oxidized perylene species is expected. One possible explanation for the EPR-silent behavior could be on the lattice distortion and/or an unusual line-broadening mechanism.

In view of the structure, charge transport can in principle occur both through the perylene stacks and/or through the Co–S chains. The regular stacks of perylene molecules at short distances are expected to generate electronic bands with widths significantly larger than those of (Per)₂M(mnt)₂ systems with M = Pt, Pd, Au, and Ni, estimated in ca. 0.6 eV.³⁸ However, in this case, these bands will be perturbed by the dimerization of the neighbor Co(mnt)₂ chains. The width of the band associated with the HOMO of the Co(mnt)₂ units is also expected not to be negligible in spite of the Co–S distance alternation with Co–S distances slightly larger than the Co–S single bond. The contribution of the two chains for the electrical transport will depend on the structure of the bands associated with the donor or acceptor chains whose filling will depend on the unknown degree of charge transfer. This is further complicated by the incommensurate modulation of the structure that most probably is induced by an incommensurate charge transfer. It should be noted that the satellite reflections corresponding to the incommensurate structure do exist at room temperature, i.e., 20 °C above $T_c \approx 272$ –275 K, and therefore cannot be associated with the observed transitions. Diffuse X-ray scattering investigations at room temperature³⁹ apart from the satellites did not show any diffuse lines as expected for 1D precursor effects of a Peierls transition. Clearly, without knowing the degree of charge transfer, it is not possible to further conclude in this unusual and interesting problem. Further crystallographic studies in the vicinity of the high-temperature phase transition taking into account the modulation of the structure and detailed band structure calculations, presently in progress, are expected to clarify this situation.

In conclusion, we have demonstrated that PerCo(mnt)₂(CH₂Cl₂)_{0.5} is a unique compound with coexistence of molecular stacks and polymeric chains in a structure that provides relatively high electrical conductivity.

Acknowledgment. We acknowledge Prof. L. Alcácer for stimulating discussions and continuous encouragement. Thanks are due to J. P. Pouget and S. Ravy for the first observation of the incommensurate satellites. This work was partially supported by EEC under ESPRIT Basic Research Action 3121 and by Junta Nacional de Investigação Científica e Tecnológica under Contract 798/90/MPF. The stay of G. B. in LNETI was supported by CNRS.

Supplementary Material Available: Tables listing atomic coordinates, thermal displacement parameters, and bond distances and angles (8 pages); tables of F_o , F_c , and $\sigma(F)$ (28 pages). Ordering information is given on any current masthead page.

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