4290 *Inorg. Chem.* **1994,** *33,* 4290−4294

Electronic Structure of the 1:1 Mixed Molecular and Polymeric Conductor (perylene)Co(mnt)$_2$(CH$_2$Cl$_2$)$_{0.5}$ and Comparison with the 2:1 α-(perylene)$_2$M(mnt)$_2$ Phases

Luis F. Veiros and Maria José Calhorda*

Centro de Química Estrutural, Departamento de Engenharia Química, Instituto Superior Técnico,
P-1096 Lisboa Codex, Portugal

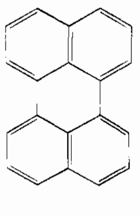
Enric Canadell*

Laboratoire de Chimie Théorique (CNRS URA 506), Université de Paris-Sud,
91405 Orsay Cedex, France

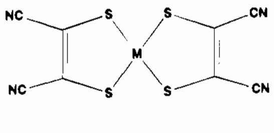
Received April 8, 1994®

A tight binding band structure study of the 1:1 mixed molecular and polymeric conductor (perylene)Co(mnt)$_2$(CH$_2$Cl$_2$)$_{0.5}$ is reported. It is found that this salt should be a strongly 1D metal with the conductivity originating from the perylene chains. The electron count needed to stabilize the polymeric chain present in this salt is shown to correspond to Co(mnt)$_2^-$, and the dimerization gap induced in the HOMO band of the perylene chains is found to be very small. On the basis of these results and by comparison with the known thermopower and transport properties of this salt, it is proposed that the charge transfer from perylene to Co(mnt)$_2$ should be somewhat smaller than one. A comparison of these results with those for the related 2:1 α-(perylene)$_2$M(mnt)$_2$ phases is also reported.

Molecular conductors based on perylene (Per, **1**) and M(mnt)$_2$ (**2**, where M = Fe, Co, Ni, Pt, Pd, Cu, and Au and mnt = maleonitriledithiolate) have been known for a long time,[1] yet the interesting physics exhibited by these systems is not fully understood.[2] Most of them have a 2:1 stoichiometry (i.e. (Per)$_2$M(mnt)$_2$) and their crystal structures are such that the M(mnt)$_2$ chains are surrounded by six chains of perylene whereas the perylene chains are surrounded by three M(mnt)$_2$ and three perylene chains.[3] These are the so-called α-phases and the interesting physics of most of them stems from the existence of both delocalized electrons in the perylene stacks and localized electrons in the M(mnt)$_2$ stacks.[1,2,4] Recently, several new charge transfer salts with different stoichiometries and structures have been reported.[5−7] One of the more interesting ones is PerCo(mnt)$_2$(CH$_2$Cl$_2$)$_{0.5}$[5] which is the first mixed molecular and polymeric charge transfer salt among the perylene−M(mnt)$_2$ systems.



1



2

PerCo(mnt)$_2$(CH$_2$Cl$_2$)$_{0.5}$ is metallic at room temperature and exhibits two types of transitions: a metal to semiconductor transition around 277 K and a semiconductor to semiconductor transition at 190−170 K.[5] Magnetic susceptibility and thermopower measurements as a function of temperature also show anomalies related to these transitions. Since PerCo(mnt)$_2$(CH$_2$Cl$_2$)$_{0.5}$ has an incommensurately modulated room temperature structure in which the solvent molecules could not be completely determined, it was suggested that the low temperature transition can be related to the ordering of the CH$_2$Cl$_2$ solvent molecules.[5] The origin of the first transition is however quite unclear. One of the more serious problems when trying to unravel the origin of the anomalies in the transport properties of this system is the lack of information concerning the charge transfer from perylene to M(mnt)$_2$. In the present work, we report our extended Hückel tight binding band structure calculations[8] for PerCo(mnt)$_2$(CH$_2$Cl$_2$)$_{0.5}$ and use them to discuss the following questions. First, what is the more likely charge transfer from

---

® Abstract published in *Advance ACS Abstracts,* August 1, 1994.

(1) Alcácer, L.; Maki, A. H. *J. Phys. Chem.* **1974**, *78*, 215.

(2) (a) Alcácer, L. *Mol. Cryst. Liq. Cryst.* **1985**, *120*, 221. (b) Gama, V. P.; Henriques, R. T.; Almeida, M. *NATO-ASI Lower Dimensional Systems and Molecular Electronics*; Metzger, R. M., Day, P., Papavassiliou, G., Eds.; Plenum Press: New York, 1991; p 205. (c) Almeida, M.; Gama, V.; Henriques, R. T.; Alcácer, L. in *Inorganic and Organometallic Polymers with Special Properties*; Laine, R. M., Ed.; Kluwer Acad. Publ.: Dordrecht, The Netherlands, 1992; p 163.

(3) Alcácer, L.; Novais, H.; Pedroso, F.; Flandrois, S.; Coulon, C.; Chasseau, D.; Gaultier, J. *Solid State Commun.* **1980**, *35*, 945.

(4) (a) Alcácer, L.; Maki, A. H. *J. Phys. Chem.* **1976**, *80*, 1912. (b) Henriques, R. T.; Alcácer, L.; Pouget, J. P.; Jérome, D. *J. Phys. C: Solid State Phys.* **1984**, *17*, 5197. (c) Henriques, R. T.; Alcácer, L.; Almeida, M.; Tomic, S. *Mol. Cryst. Liq. Cryst.* **1985**, *120*, 237. (d) Bourbonnais, C.; Henriques, R. T.; Wzietek, P.; Köngeter, D.; Jérome, D.; Voiron, J. *Phys. Rev. B* **1991**, *44*, 641. (e) Gama, V.; Henriques, R. T.; Bonfait, G.; Almeida, M.; Ravy, S.; Pouget, J. P.; Alcácer, L. *Mol. Cryst. Liq. Cryst.* **1993**, *234*, 171. (f) Henriques, R. T.; Gama, V.; Bonfait, G.; Santos, I. C.; Matos, M. J.; Almeida, M.; Duarte, M. T.; Alcácer, L. *Synth. Met.* **1993**, *55−57*, 1846.

(5) Gama, V.; Henriques, R. T.; Bonfait, G.; Almeida, M.; Meetsma, A.; van Smaalen, S.; de Boer, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 1986.

(6) Gama, V.; Henriques, R. T.; Almeida, M.; Veiros, L. F.; Calhorda, M. J.; Meetsma, A.; de Boer, J. L. *Inorg. Chem.* **1993**, *32*, 3705.

(7) Gama, V.; Henriques, R. T.; Bonfait, G.; Pereira, L.; Waerenborgh, J. C.; Santos, I. C.; Duarte, M. T.; Cabral, J. M. P.; Almeida, M. *Inorg. Chem.* **1992**, *31*, 2598.

(8) Whangbo, M.-H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 6093. A modified Wolfsberg−Helmholz formula (Ammeter, J.; Bürgi, H.-B.; Thibeault, J.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686) was used to evaluate the nondiagonal $H_{\mu\nu}$ values. The exponents and parameters used are those of Table 1.

0020-1669/94/1333-4290$04.50/0

Table 1. Exponents and Parameters Used in the Calculations

atom	orbital	$H_{\mu\mu}$ (eV)	ζ_1	$c_1{}^a$	ζ_2	$c_2{}^a$
Co	4s	−9.21	2.00			
	4p	−5.29	2.00			
	3d	−13.18	5.55	0.5679	2.10	0.6059
S	3s	−20.00	1.817			
	3p	−13.30	1.817			
C	2s	−21.40	1.625			
	2p	−11.40	1.625			
N	2s	−26.00	1.95			
	2p	−13.40	1.95			
H	1s	−13.60	1.30			

[a] Contraction coefficients used in the double-ζ expansion.

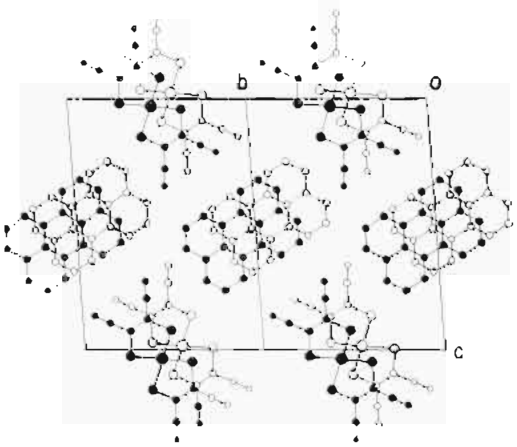
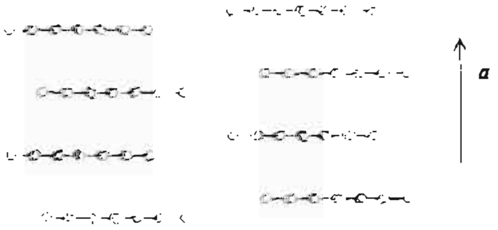


Figure 1. Projection along the *a* axis of the PerCo(mnt)$_2$(CH$_2$Cl$_2$)$_{0.5}$ crystal structure.

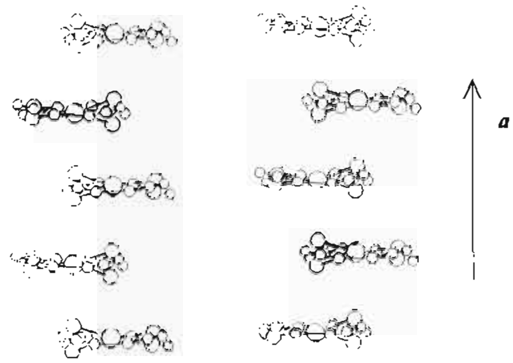
perylene to M(mnt)$_2$? Second, what is the respective role of the perylene stacks and M(mnt)$_2$ polymeric chains in the transport properties? Third, why only for M = Co the acceptors have been found as a polymeric chain? Finally, we would like to compare the electronic structure of the title salt with those of the α-phases.



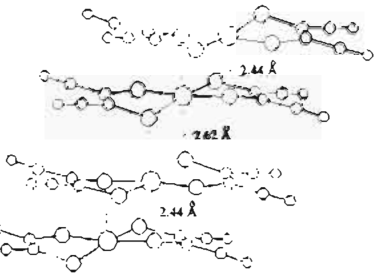
3

Crystal Structure

As also found in the well-known α-phases, the crystal structure of PerCo(mnt)$_2$ (CH$_2$Cl$_2$)$_{0.5}$ (see Figure 1) is built from chains of perylene and Co(mnt)$_2$. However because of the different stoichiometry these chains are arranged in a different way. In the present case it would be more appropriate to describe the structure as made up of slabs of perylene and Co(mnt)$_2$(CH$_2$Cl$_2$)$_{0.5}$ alternating along the *c*-direction. The perylene molecules are slipped in such a way as to form zigzag chains (**3**) along the *a*-direction with slightly alternating interplanar distances (i.e., 3.27–3.28 Å), although this small difference lies within the accuracy limits of the structure. The Co(mnt)$_2$ chains also have a zigzag shape, and as shown in **4**, which is a view perpendicular to the Co(mnt)$_2$ slabs, they are arranged in such a way as to create empty cavities every two units along *a*. It is inside these cavities that the CH$_2$Cl$_2$ solvent molecules are located. It is important to point out that the room temperature structure is modulated with an incommensurate wave vector $\mathbf{q} = 0.22a^* - 0.13b^* - 0.36c^*$.[5] However, the structure was solved without taking into account this modulation so that it is an average structure. The CH$_2$Cl$_2$ solvent molecules are located at inversion centers of the structure which means that, at least in the average structure, they are disordered. Actually, the Co atoms of the Co(mnt)$_2$ units are octahedrally coordinated (see **5**) by four sulfur atoms of the monomer unit (Co–S = 2.31 Å) and two sulfur atoms of the Co(mnt)$_2$ units above and below (Co–S = 2.44 and 2.62 Å). Thus, the Co(mnt)$_2$ chain is a real polymeric chain. The apical Co–S bonds are arranged in such a way (see **5**) that the polymeric chain is strongly dimerized.



4



5

Electronic Structure

A detailed study of the different types of interactions in the crystal structure of PerCo(mnt)$_2$(CH$_2$Cl$_2$)$_{0.5}$ shows that there are three different perylene···perylene interactions and seven different perylene···Co(mnt)$_2$ interactions. The latter are associated with an S···C contact of 3.74 Å and several N···C contacts between 3.20 and 3.59 Å. In order to see if these contacts could play any role in determining the shape of the bands near the Fermi level (i.e., those which will be responsible for the physical properties of the solid), we calculated the β_{ij} interaction energies[9] associated with the HOMO of perylene and the HOMO and LUMO of the Co(mnt)$_2$ units. It turns out that they are all very small, i.e., around 2 orders of magnitude smaller than the perylene···perylene interactions along the stacks. Consequently,

---

(9) Williams, J. M.; Wang, H.-H.; Emge, T. J.; Geiser, U.; Beno, M. A.; Leung, P. C. W.; Carlson, K. D.; Thorn, R. J.; Schultz, A. J.; Whangbo, M.-H. *Prog. Inorg. Chem.* **1987**, *35*, 51. (b) Since overlap is explicitely included in extended Hückel calculations, these interaction energies (β) should not be confused with the conventional transfer integrals (*t*). Although the two quantities are obviously related and have the same physical meaning, the absolute values of β are somewhat greater than those of *t*.

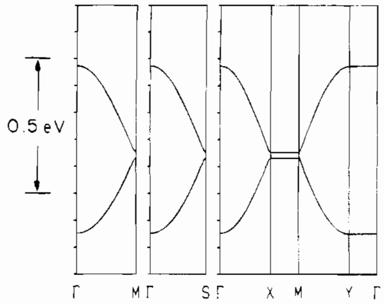
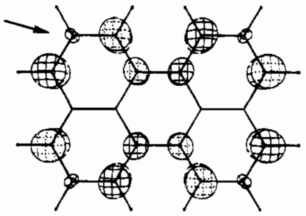


Figure 2. Dispersion relations of the two perylene HOMO bands in PerCo(mnt)$_2$ (CH$_2$Cl$_2$)$_{0.5}$. Γ, *X*, *Y*, *M*, and *S* refer to the wave vectors (0, 0), (a*/2, 0), (0, b*/2), (a*/2, b*/2), and ($-a$*/2, b*/2), respectively, where *a* is the chain direction.

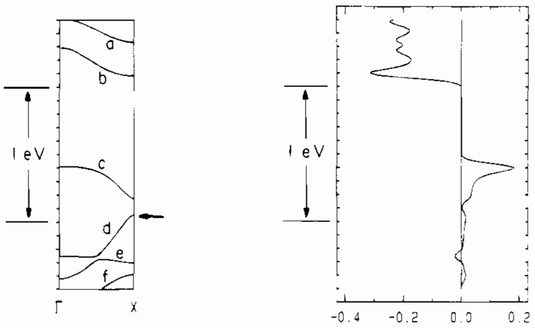
since we are mainly interested in the charge transfer and the transport properties of the system, we can consider separately the electronic structure of the perylene slabs and the Co(mnt)$_2$ chains.

A. Perylene Slabs. There are three different perylene···perylene intermolecular contacts: two of them are along the chains and one involves perylenes of different chains. Although the two intermolecular interactions along the chain are different as far as the C···C contacts are concerned (3.25, 3.33 Å *vs* 3.14, 3.30 Å), the corresponding $\beta_{\text{HOMO-HOMO}}$ interaction energies are very similar (0.388 *vs* 0.364 eV). The third intermolecular contact is associated with a quite long C···C contact (3.46 Å). In addition, the corresponding carbon atoms (marked with an arrow in **6**) are associated with practically zero coefficients in the HOMO of perylene (**6**) so that this interchain interaction is very small ($\beta_{\text{HOMO-HOMO}}$ = 0.001 eV). On the basis of these results, a very strong one-dimensional (1D) character for the HOMO bands of perylene is expected. This is substantiated by the calculated dispersion relations shown in Figure 2. It is worth pointing out that the dimerization gap (i.e., the energy gap between the two bands) is very small (~0.02 eV). The total width of the HOMO bands is 0.60 eV which, as will be shown later, is very similar to the width of the HOMO band of the uniform perylene chains in the α-phases.



6

B. Co(mnt)$_2$ Chains. The calculated band structure of the Co(mnt)$_2$ chain in PerCo(mnt)$_2$(CH$_2$Cl$_2$)$_{0.5}$ is reported in Figure 3a. Bands a and b are built from the Co z^2 orbital strongly destabilized through interaction with the *z* orbitals of the associated apical S atoms. The four bands c−f have as the main character the HOMO and LUMO of the two Co(mnt)$_2$ units. These two orbitals are essentially the in-phase and out-of-phase combinations of the LUMO of mnt^{2-}. The highest occupied level of the chain before the electron transfer from perylene is marked with an arrow in Figure 3a. Thus, three of the four HOMO- and LUMO-based bands are filled whereas only one electron occupies the HOMO of the isolated unit. Since the unit cell of the Co(mnt)$_2$ chain contains two Co(mnt)$_2$ units, this means that three electrons per Co(mnt)$_2$ occupy the HOMO/LUMO levels of the chain but only one those of the molecular unit. This is easy to understand. As found for related metal bis(dithiolenes)[10] the energy splitting between the HOMO and LUMO of Co(mnt)$_2$ is relatively small.[6] These orbitals have strong contributions from the S *z* orbitals and lie not far from the filled d-block levels. When going from the isolated Co(mnt)$_2$ unit to the Co(mnt)$_2$ chain, the ligand environment of Co changes from square planar to octahedral because of the relatively short Co−S distances noted in **5**. Thus, the z^2 level of each of the two Co(mnt)$_2$ units is strongly raised in energy and generates one of the empty antibonding e$_g$ bands of the chain (a and b in Figure 3a). Consequently two electrons per Co(mnt)$_2$ unit are formally transferred from the Co to the ligands and the metal becomes Co(III), as it should be in a local octahedral environment. Thus, both structurally and electronically, the Co(mnt)$_2$ units in PerCo(mnt)$_2$(CH$_2$Cl$_2$)$_{0.5}$ form a real polymeric chain.



(a) (b)

Figure 3. (a) Dispersion relations of the bands near the Fermi level for the Co(mnt)$_2$ chain in PerCo(mnt)$_2$(CH$_2$Cl$_2$)$_{0.5}$. The arrow refers to the highest occupied level of this chain before the charge transfer from perylene. (b) Average COOP curve for the apical Co−S bonds of the chain (the scale and energy levels are identical to those in part a.

The important result of Figure 3a is that there is quite a large energy gap between bands c and b. As shown in figure 3b, which is the average COOP (crystal orbital overlap population)[11] of the apical Co−S bonds, band c is Co−S bonding. In fact, around 10% of the average Co−S overlap population between adjacent Co(mnt)$_2$ units originates from band c. Thus the system will have a strong tendency to fill this band with two electrons suggesting that each perylene transfers one electron to the chain. It is important to note that whereas there is a large band gap between bands c and b, there is only a small band gap between bands c and d, so that it is clear that the number of electrons needed to confer stability to this chain is that corresponding to Co(mnt)$_2^-$. This explains why Co(mnt)$_2$ is the only M(mnt)$_2$ system leading to this polymeric chain in charge transfer salts with perylene. For M = Fe, the charge transfer from perylene should be too large. For M = Ni, band c is already filled and the electrons from perylene should fill the antibonding band b. In both cases the system will choose to have another type of structure and/or stoichiometry.

C. Comparison with the α-Phases. Before discussing the relationship between the electronic structure and the transport properties of PerCo(mnt)$_2$(CH$_2$Cl$_2$)$_{0.5}$, it is important to consider the electronic structure of the α-(Per)$_2$M(mnt)$_2$ phases. A typical projection of their crystal structure along the *b* axis is shown in Figure 4.[2,3] The overlapping mode between two successive

---

(10) (a) Canadell, E.; Ravy, S.; Pouget, J. P.; Brossard, L. *Solid State Commun.* **1990**, *75*, 633. (b) Doublet, M. L.; Canadell, E.; Pouget, J. P.; Yagubskii, E. B.; Ren, J.; Whangbo, M.-H. *Solid State Commun.* **1993**, *88*, 699. (c) Schultz, A.; Wang, H.-H.; Soderholm, L. C.; Sifter, T. L.; Williams, J. M.; Bechgaard, K.; Whangbo, M.-H. *Inorg. Chem.* **1987**, *26*, 3757.

(11) Hughbanks, T.; Hoffmann, R. *J. Am. Chem. Soc.* **1983**, *105*, 3528.

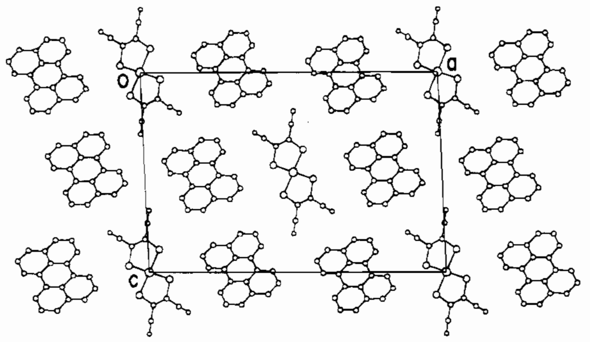


Figure 4. Projection along the *b* axis of the crystal structure of the α-(Per)$_2$M(mnt)$_2$ phases.

perylene molecules is almost identical to that in PerCo(mnt)$_2$(CH$_2$Cl$_2$)$_{0.5}$. However, in contrast with the zigzag chains (**3**) of PerCo(mnt)$_2$(CH$_2$Cl$_2$)$_{0.5}$, the perylene chains are now uniform. The M(mnt)$_2$ chains are uniform for M = Ni, Pt, Pd, Cu, and Au but dimerized for M = Fe and Co.[7] There is experimental evidence in all these salts for perylene occurring as Per$^{+1/2}$.

Analysis of the crystal structure of the α-(Per)$_2$Pd(mnt)$_2$ phase reveals that there are the following intermolecular interactions: one perylene••perylene intrachain interaction, three perylene••perylene interchain interactions, one Pd(mnt)$_2$••Pd(mnt)$_2$ intrachain interaction and five perylene••Pd(mnt)$_2$ interactions. As found for PerCo(mnt)$_2$ (CH$_2$Cl$_2$)$_{0.5}$, all the interchain perylene••perylene and perylene••Pd(mnt)$_2$ interactions are extremely small compared with the intrachain perylene••perylene, according to their β interaction energies. The $\beta_{\text{HOMO-HOMO}}$ for the perylene intrachain interaction is very similar (0.3508 eV) to those of the slightly dimerized chains of PerCo(mnt)$_2$ (CH$_2$Cl$_2$)$_{0.5}$. The $\beta_{\text{LUMO-LUMO}}$ of the intrachain Pd(mnt)$_2$ interaction is smaller but is however nonnegligible (0.1885 eV). The calculated width of the perylene HOMO band is 0.59 eV. This value is in excellent agreement with the bandwidth proposed on the basis of thermopower measurements (0.5−0.65 eV depending on M). The bandwidth of the Pd(mnt)$_2$ LUMO band is 0.38 eV. Very similar results are obtained for the M = Pt and Au phases. With perylene as Per$^{+1/2}$ and negligible perylene••perylene and perylene••Pd(mnt)$_2$ interchain interactions, the perylene HOMO bands will be independent and three-fourths filled each.

On the basis of these results we can propose the following conclusions. First, α-(Per)$_2$M(mnt)$_2$ should be very strongly 1D metals. This is in agreement with the fact that the conductivity along the directions perpendicular to the chain are smaller than the conductivity along the chain by a factor of 500−1000.[4b,7] Second, the metallic properties are associated with the perylene chains and consequently, the low temperature metal to insulator transitions should be Peierls transitions associated with a tetramerization of the perylene chains. This has been recently established for M = Cu and Ni by X-ray diffuse scattering experiments.[12] Third, it should be pointed out that although the calculated bandwidths of the M(mnt)$_2$ bands are not large enough to lead to metallic properties when these levels are partially filled and thus, the electrons transfered to the M(mnt)$_2$ units will be localized, they certainly implicate quite sizeable interactions among these localized electrons. As a consequence, the M(mnt)$_2$ chains should be susceptible to spin-Peierls type transitions leading to nonmagnetic ground states, when the M(mnt)$_2^-$ units have unpaired electrons (i.e., M = Ni, Pd, Pt). Evidence for a doubling of the periodicity of the M(mnt)$_2$ chains coexisting with the tetramerization of the perylene chains has been recently reported for M = Ni.[12] This doubling was previously noticed in the Pt and Pd compounds[4b] and in the first case is responsible for a specific heat anomaly.[13]

It should be noted that the M(mnt)$_2$ chains are dimerized for M = Fe and Co. However, this structural feature can not be attributed to some kind of electronic instability of the M(mnt)$_2$ chains because the overlap mode between adjacent M(mnt)$_2$ units in the average structure of the Fe salt, is not the same as in other α-phases, presenting a metal-over-sulfur type overlap, as found in the polymeric chain of PerCo(mnt)$_2$(CH$_2$Cl$_2$)$_{0.5}$. The electronic reasons behind the tendency to form metal-over-sulfur dimers for iron and cobalt bis(dithiolenes) have been analyzed by Alvarez, Vicente, and Hoffmann[14] and will not be repeated here. The metal to insulator transition in these phases has been shown[12] to be associated with a doubling of the already doubled unit cell, i.e., there is a tetramerization of the perylene chains exactly as in all other α-phases. It should be pointed out that the thermopower of these dimerized phases, is very similar to those of the other α-phases, which suggests that the dimerization gap felt by the electrons at the Fermi level in the perylene stacks is very small, i.e., effectively these systems behave also as having a three-fourths-filled perylene HOMO band.

D. Electronic Structure, Charge Transfer, and Transport Properties in PerCo(mnt)$_2$(CH$_2$Cl$_2$)$_{0.5}$. Our calculations for the α-(Per)$_2$M(mnt)$_2$ phases seem to describe very well the bandwidth and other characteristics of these salts. Thus, in this section, we will try to correlate our calculations for PerCo(mnt)$_2$(CH$_2$Cl$_2$)$_{0.5}$ with the available physical measurements on this salt in order to provide some answers to the questions raised in the introduction. In both the α-(Per)$_2$M(mnt)$_2$ and PerCo(mnt)$_2$(CH$_2$Cl$_2$)$_{0.5}$ salts we found that the coupling between the perylene and the M(mnt)$_2$ chains is very weak. In addition, although the M(mnt)$_2$ chains in the average structure of PerCo(mnt)$_2$(CH$_2$Cl$_2$)$_{0.5}$ are strongly dimerized, the dimerization gap we calculate for the perylene chains (see Figure 2) is extremely weak (~0.02 eV). This means that, except at very low temperatures, this gap will be of the same order as the thermal energy, and for all practical purposes, it will be ignored by the electrons of the perylene chains. Since the total width of the perylene HOMO bands in PerCo(mnt)$_2$(CH$_2$Cl$_2$)$_{0.5}$ and α-(Per)$_2$M(mnt)$_2$ is practically identical, and since we know that as far as the perylene electrons are concerned, the dimerized and nondimerized α-phases behave equivalently, we conclude that except for the filling of the perylene band, there is no reason to believe that the perylene chains are electronically different in the two types of salts. Thus, from now on and except when otherwise stated, we will consider that there is a single perylene HOMO band.

Now we can try to answer the question of the electron transfer. If, as in the α-phases, the perylene molecules were found in average as Per$^{+1/2}$, the perylene band would be three-fourths-filled and band c of the M(mnt)$_2$ polymeric chain (see Figure 3) would be half-filled (remember that the unit cell of the M(mnt)$_2$ polymeric chain contains two formula units). The latter is quite flat (much more than the LUMO band of the M(mnt)$_2$ chains in the α-phases) so that the electrons in this band will most certainly be localized. Thus the metallic type conductivity of PerCo(mnt)$_2$(CH$_2$Cl$_2$)$_{0.5}$ must be due to the perylene band. However, if this band was three-fourths-filled, the thermopower should be quite similar to those of the α-phases

---

(12) Gama, V.; Henriques, R. T.; Almeida, M.; Pouget, J. P. *Synth. Met.* **1993**, *55−57*, 1677.

(13) Bonfait, G.; Matos, M. J.; Henriques, R. T.; Almeida, M. *J. Phys. IV-C2* **1993**, *3*, 251.

(14) Alvarez, S.; Vicente, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 6253.

and not very small as reported for this salt. In fact, the thermopower measurements would be more consistent with a nearly half-filled perylene band. This suggests that perylenes are found as Per^+ and consequently, that the perylene band is half-filled and band c of Figure 3 is full. As discussed before, the filling of band c is essential for the stabilization of the chain **5**. However, a half-filled perylene band would lead to a Mott–Hubbard insulating state (or, if the dimerization gap was significant, to a forbidden band gap semiconductor),[15] in contradiction to the reported metallic properties of this salt. Thus, at least momentarily, we are led to the conclusion that the average electron transfer for perylene is somewhat smaller than 1.

At this point we should slightly digress and consider an apparent unrelated problem: why is the $Co(mnt)_2$ chain **5** found to be strongly dimerized in the average structure? We note that both n-$Bu_4NCo(S_2C_6Cl_4)_2$[16] and $Co[S_2C_2(CF_3)_2]$[17] contain dimeric cobalt units. The Co–S distances in these systems are 2.404 and 2.38 Å, respectively. Several $Fe(SC_2R_2)_2^-$ species are also known to exist as dimers.[18] Thus, the available structural information suggests that for the electron counts corresponding to $Co(mnt)_2$ and $Co(mnt)_2^-$ the dimeric form is the preferred alternative. A rational for this observation has been presented by Alvarez, Vicente, and Hoffmann.[14] Our analysis of the electronic structure of the chain **5** reveals that this type of chain should be stable for the electron count of $Co(mnt)_2^-$. Consequently, for $Co(mnt)_2^-$ both the chain and the dimers are possible but for one electron less per formula unit, only the dimers are possible. This is in excellent agreement with the observation of dimerized $M(mnt)_2^-$ stacks in the α-phases of Fe and Co[7] but a polymeric chain **5** only for Co.[5] Two remarks are in order at this point. First, the short Co–S distance in the polymeric chain **5** is practically identical to those found in the above mentioned dimeric species. Second, according to our discussion of the correlation between the transport properties and the electronic structure of the perylene chains, the charge transfer from perylene to the $M(mnt)_2$ species should be somewhat smaller than needed to really form the chain. In plain chemical language this means that we have electrons enough to form many of the interdimer bonds of the polymer but not all. In this case, a possible structural alternative is a polymeric chain of dimers with modulated interdimer bonds so that the average interdimer distance is longer than the intradimer one. In the language of solid state physics, it would be said that the polymeric chain is the result of an incommensurate charge density wave on a chain of dimers, already present at room temperature. We conclude that, in order to have a consistent picture of the conductivity, thermopower, and structural properties of $PerCo(mnt)_2(CH_2Cl_2)_{0.5}$, a charge transfer from perylene somewhat smaller than one has to be assumed.

What can be said about the possible origin of the two transitions? We first note that our analysis suggests that, except for the electron filling, there is no essential difference between the perylene chains in the α-phases and the title compound. The smaller conductivity of the later is most likely a consequence of the random potential created by the disordered CH_2Cl_2 solvent molecules. Since the metal to insulator transition in the α-phases is a Peierls transition,[12] we do not see any reason why this should not be the case here also. Although the diffuse X-ray scattering measurements gave no evidence for a Peierls distortion,[5] we note that more than 10 years elapsed until the Peierls type mechanism could be proven for the α-phases by this technique, because of the weakness of the superlattice reflections which make their detection difficult.[12] In the present case, the existence of the additional incommensurate modulation and the solvent disorder can complicate even more the situation. The alternative explanation based on a localization of the carriers in the perylene chain is unlikely because in this case the transition would be broader. As previously proposed, the second transition, which is associated with a large hysteresis, is probably due to an ordering of the CH_2Cl_2 solvent molecules.[5]

Concluding Remarks

$PerCo(mnt)_2(CH_2Cl_2)_{0.5}$ is a mixed molecular and polymeric conductor having a room temperature incommensurately modulated structure. From a comparison between the conductivity, thermopower, crystal structure, and electronic band structure calculations, it seems that the charge transfer from perylene should be somewhat smaller than one. We propose that the room temperature structural modulation originates from the polymeric chain because the number of electrons per $Co(mnt)_2$ unit is slightly smaller than needed to stabilize the chain. According to our calculations, the metallic properties of $PerCo(mnt)_2(CH_2Cl_2)_{0.5}$ are due to the perylene chains and the metal to insulator transition is most likely due to a Peierls transition. According to the proposed charge transfer, there should also be localized electrons in the polymeric chain. Thus, further magnetic and diffuse X-ray scattering measurements as well as resolution of the modulated structure are clearly needed in order to test the results of our study and to better understand the origin of the rich and interesting physics exhibited by the perylene–$M(mnt)_2$ charge transfer salts.

Acknowledgment. We are greatly indebted to Dr. M. Almeida for his interest in this work and for invaluable discussions. E.C. thanks Dr. J. P. Pouget for many interesting discussions concerning the α-phases. This work was partially supported by the JNICT (PMCT/C/CEN/367/90). L.F.V. thanks Fundaçao Calouste Gulbenkian for a travel grant.

---

(15) Torrance, J. B. *Acc. Chem. Res.* **1979**, *12*, 79.

(16) Baker-Hawkes, M. J.; Dori, Z.; Eisenberg, R.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 4253.

(17) Enemark, J. H.; Lipscomb, W. N. *Inorg. Chem.* **1965**, *4*, 1729.

(18) (a) Kanatzidis, M. G.; Coucouvanis, D. *Inorg. Chem.* **1984**, *23*, 403. (b) Snow, M. R.; Ibers, J. *Inorg. Chem.* **1973**, *12*, 249.