# Counterion dimerisation effects in the two-chain compound (Per)<sub>2</sub>[Co(mnt)<sub>2</sub>]: structure and anomalous pressure dependence of the electrical transport properties<sup>†</sup>

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The crystal structure of  $(Per)_2[Co(mnt)_2]$ , was investigated by single crystal X-ray diffraction. Its refinement shows a strong chemical dimerization of the anions  $[Co(mnt)_2]_2^{2-}$ . This is responsible for a unit cell doubling along the staking axis *b* when compared with other members of the  $\alpha$ -  $(Per)_2[M(mnt)_2]$  family of the low dimensional molecular conductors, with M = Ni, Cu, Au, Pt or Pd. The dimerized  $[Co(mnt)_2]_2^{2-}$  stacks appear however as poorly correlated in the *ac* plane. The electrical conductivity of this compound measured in single crystals exhibits anomalous pressure dependence, where under increasing hydrostatic pressure the conductivity decreases while the metal insulator transition temperature is enhanced. This effect is ascribed to the dimeric nature of the counterions which imposes a sliding of the stacked perylene molecules along alternated directions in their planes.

# Introduction

The family of compounds  $(Per)_2[M(mnt)_2]$  remain rather unique among solid state materials because they provide examples of low dimensional systems presenting two types of chains (conducting and magnetic) in the same solid.<sup>1</sup> In these solids regular stacks of partially oxidised perylene molecules  $(Per)^{0.5+}$  are responsible for metallic properties at high temperatures and coexist side by side with stacks of  $M(mnt)_2^-$  anions which, depending on the metal M, can be diamagnetic (M = Au, Cu, Co) or bear localized spins (S = 1/2 for M = Ni, Pt, Pd or S = 3/2 for M = Fe). These systems are quite interesting because both chains interact and are subject to the instabilities of low dimensional conducting and magnetic systems. The unusual properties of these compounds have attracted continued research interest for more than 30 years, recently renewed by the discovery of field induced transitions.<sup>2</sup>

The  $(\text{Per})_2[\text{Co}(\text{mnt})_2]$  compound, as well as the Fe analogue, is a special member of this quasi-isostructural family of two chain compounds where there is a lattice doubling along the stacking axis b ( $b \approx 8.2$  Å)<sup>3</sup> when compared with undimerised anion members such as M = Cu, Ni, Au or Pt, which are all isostructural and present a unit cell with a stacking parameter  $b \approx$ 4.1 Å.<sup>1,4</sup> This unit cell doubling in the Fe and Co compounds was clearly seen in an early Weisenberg and Laue X-ray work,<sup>5</sup> and has been considered as a consequence of the well known chemical dimerisation of the anion.<sup>6</sup> However the full crystal structure refinement of the compounds with dimerised anions has never been reported.

† CCDC reference number 710242. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b820995m Early work,<sup>7</sup> recently confirmed in more detailed studies, showed that with the application of pressure to the M = Au and Pt compounds, there is an enhancement of electrical conductivity and the low temperature CDW transitions (at 12 and 8 K, respectively) are not only decreased<sup>8</sup> but at moderate pressures of the order of 4–6 kbar metallic features, such as magnetoresistance oscillations from quantum interference are observed down to the lowest temperatures.<sup>9</sup>

These results have led us to explore the pressure effects in the Co analogue which are reported in this paper. We found that, at variance with the Au analogue and the general behaviour of most, if not all molecular materials, the electrical conductivity of the Co compound decreases under increasing hydrostatic pressure, while the metal to insulator transition temperature is enhanced. This effect is ascribed to the dimeric nature of the couterions and their interaction with donor stacks, and discussed in terms of the crystal structure which was also reinvestigated and analyzed.

# Experimental

(Per)<sub>2</sub>[Co(mnt)<sub>2</sub>] crystals were obtained by electrocrystallization under general conditions previously reported.<sup>3</sup> Using galvanostatic conditions (1  $\mu$ A cm<sup>-2</sup>) for *ca*. 8 d, crystals with typical dimensions, 3 × 0.05 × 0.02 mm<sup>3</sup> were obtained on platinum electrodes from a dichloromethane solution of perylene and (*n*-Bu<sub>4</sub>N)[Co(mnt)<sub>2</sub>].

## Crystallography

Crystallographic data for (Per)<sub>2</sub>[Co(mnt)<sub>2</sub>] were collected on a Bruker AXS-KAPPA APEX II area detector diffractometer equipped with an Oxford Cryosystem open-flow nitrogen cryostat at 150 K using graphite-monochromated Mo K $\alpha$  ( $\lambda =$ 0.71073 Å) in the  $\varphi$ - and  $\omega$ -scan techniques. Cell parameters were retrieved using Bruker SMART software and refined using

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Bruker SAINT<sup>10</sup> on all observed reflections. Empirical absorption corrections were applied using SADABS.<sup>11</sup> The structures were solved by direct methods using SIR 97<sup>12</sup> and refined using full-matrix least-squares refinement against  $F^2$  using SHELXL-97.<sup>13</sup> All programs are included in the package of programs WINGX.<sup>14</sup> All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were inserted in idealized positions riding on the parent C atom. The molecular structures were done with ORTEP3 for Windows,<sup>15</sup> included in the software package. Details for the X-ray data collection and refinement of this compound can be found in Table 1 Selected bond lengths and bond angles are given in Table 2.<sup>†</sup>

#### **Electrical transport measurements**

Electrical resistivity measurements were performed along the long axis (crystallographic *b*-axis) of the needle-shaped crystals using a four probe *ac* lock-in method. Pressure was applied using a He gas compressor unit connected *via* capillaries to a BeCu clamped cell. Two samples were measured simultaneously in the cell, yielding nearly identical results. By warming the cell above the solid-gas phase boundary between measurements, the pressure could be changed *in situ*. A third sample was used for the room temperature pressure sweep data shown below.

### **Results and discussion**

#### Crystal structure

Several single crystal X-ray diffraction tests, in different instruments both with Cu and Mo K $\alpha$  radiation, have led to different but related unit cells. Often results are consistent with a monoclinic unit cell *P*21/*n* with parameters a = 17.5429(4) Å, b =4.0659(1) Å, c = 25.0320(5) Å,  $\beta = 92.016(1)^{\circ}$  at 150 K (see Table 1), similar to the unit cell of the  $\alpha$ -phases of the compounds of this family with undimerised anions. In addition, centered unit cells with a doubling of two parameters a = 50.0762(13) Å, b =8.1357(5) Å, c = 17.5463(5) Å,  $\beta = 91.986(1)^{\circ}$  have also been

 Table 1
 Crystal data for (Per)<sub>2</sub>[Co(mnt)<sub>2</sub>]

150(2)
C <sub>48</sub> H <sub>24</sub> N <sub>4</sub> S <sub>4</sub> Co
843.88
Monoclinic, $P2_1/n$
17.5429(4)
4.0659(1)
25.0320(5)
92.016(1)
1784.37(7)
2, 1.571
$0.60 \times 0.06 \times 0.05$
0.760
862
3.26-28.41
-23/23, -5/4, -33/33
3576/0/272
$12212/3576 (R_{int} = 0.0636)$
Semi-empirical from equivalents
0.9630, 0.6583
0.822
R = 0.0440, wR = 0.0799
0.250, -0.461

**Table 2** Selected bond lengths (Å) for  $(Per)_2[Co(mnt)_2]^a$ 

$C_{2} = S(2) \# 2$	2 405(2)	Co. Co#2	2 2162(1)
$C_0 - S(3) + 2$	2.403(3) 2.1046(0)	$C_0 = C_0 + 2$	3.2102(1) 2.2122(0)
$C_0 = S(1)$	2.1040(9)	$C_0 = S(1) \# 1$	2.5155(9)
Co-S(3)	2.1841(15)	Co-S(2)#1	2.1796(15)
S(2)-C(2)	1.834(3)	S(1) - C(1)	1.719(3)
S(3)-C(2)	1.668(3)	C(1)-C(2)	1.364(3)
C(1)–C(3)	1.435(4)	C(2)-C(4)	1.431(3)
C(3)-N(1)	1.147(4)	C(4)–N(2)	1.134(3)
<sup><i>a</i></sup> Symmetry ope	erations: $\#1 - x + 1$ , -	-y+1, -z+1 # 2 - x	+1, -y, -z+1

obtained in agreement with the parameter  $b \approx 8.2$  Å found also in Weisenberg and Laue exposures.<sup>6</sup> However, either due to weak diffraction intensities or poor crystal quality, the data collected with the larger unit cells has never led to a consistent structural refinement, which was only possible with the reduced unit cell leading to an average structure, as previously reported for the Fe compound with a lower quality of refinement.<sup>3</sup>

The refinement of data obtained with the monoclinic unit cell *P*21/*n* with parameters a = 17.5429(4) Å, b = 4.0659(1) Å, c = 25.0320(5) Å,  $\beta = 92.016(1)^{\circ}$  converged to an average structure with a crystal packing typical of  $\alpha$ -(Per)<sub>2</sub>[M(mnt)<sub>2</sub>] phases as show in Fig. 1 with donor and acceptor units as depicted in the ORTEP views of Fig. 2 also showing the atomic numbering scheme.

Perylene molecules are tilted 56.67° towards *b* and they stack along this axis in the usual graphite-like overlapping mode separated by 3.31(1) Å. The [Co(mnt)<sub>2</sub>] units are tilted by 77.21° towards the *b*-axis. The main feature of this average structure is the presence of the Co atom in a general position near an inversion center, implying two equally populated nearby positions, and anomalously large displacement parameters observed for one of the sulfur atoms. This was interpreted as resulting from disorder among two almost equally populated (50.5 and 49.5%) positions (S2 and S3) (Fig. 2 and 3). If one takes alternatively any of the two disordered positions along one anion stack, the lattice parameter *b* becomes doubled and these stacks are now formed by dimers of neighbouring [Co(mnt)<sub>2</sub>]<sup>-</sup> anions which are virtually identical to the well known [Co(mnt)<sub>2</sub>]<sub>2</sub><sup>2-</sup> occurring in many salts (Fig. 3).<sup>6</sup>

These dimers are made by connecting nearby  $Co(mnt)_2$  units through two Co–S3\* bonds at 2.405(3) Å (Fig. 3). This Co–S3 bond length is comparable to the apical Co–S bonds in other dimersised Co bisdithiolene complexes such as  $[Co(S_2C_2(CF_3)_2],$ HPyr $[Co(mnt)_2]$  and *n*-Bu<sub>4</sub>N $[Co(mnt)_2]$  with bond lengths of 2.382(4) Å,<sup>16</sup> 2.43 Å<sup>17</sup> and 2.40 Å<sup>6</sup> respectively. The Co atom lays 0.24 Å above the average S<sub>4</sub> plane, a typical distance observed in other Co dimers ( $\approx 0.24$  Å). All other bond lengths of the anion assume values typical of Co(mnt)<sub>2</sub> complexes (Table 2). Therefore this small unit cell refers to an average structure of a situation where nearby anion chains are incoherently dimerised.

There are several short contacts between the anions and the perylene donors which are listed in Table 3. A significant number of these contacts depend on the position of disordered S atoms, S2 or S3. The position S2 has two shorter contacts S2…H26–C26 at 2.950 Å and S2…H27–C27 at 2.961 Å, while the other position has only one slightly larger contact S3…H26–C26 at 2.983 Å. This means that the anion dimerisation, which corresponds to an alternation of the two disordered positions S2 and S3, imposes an alternation of contacts between anionic and donor chains,



Fig. 1 (a) View of the  $(Per)_2[Co(mnt)_2]$  average crystal structure along b. (b) Partial view of anion stacks I, II and III along a + c.

making effective in the perylene conducting chains the lattice doubling of the  $[Co(mnt)_{2}]_{2}$  chains (Fig. 4).

There are different ways in which nearby dimerised chains can be arranged. In one extreme situation the anion chains can be completely uncorrelated and this disordered situation leads to the small unit cell of the average structure described above. However a weak correlation is expected between anion chains, especially along c trough the donor acceptor contacts shown in Fig. 4. As a result, other ordered or partially ordered situations are also expected to occur, thus explaining the difficulties in having a convergent refinement of structural data collected with larger unit cells. Although the correlation between nearby anionic chains is expected to be weak, the large unit cells can be understood as resulting from a specific ordered arrangement of nearby dimerised chains as in the one shown in Fig. 5.

In summary, different degrees of anionic interchain correlation are possible in  $(Per)_2[Co(mnt)_2]$  and the small unit cell corresponds to a situation of incoherently dimerised nearby anionic



**Fig. 2** ORTEP diagrams and atomic numbering scheme for perylene and  $[Co(mnt)_2]$  units. The  $[Co(mnt)_2]_2$  dimer shown is obtained by the appropriated choice of one position for the Co and S atoms, S2 and S3. Symmetry operations: \* (1 - x, 1 - y, 1 - z), \*\* (1 - x, -y, 1 - z).



**Fig. 3** (a) Stacks of disordered  $[Co(mnt)_2]^-$  anions with Co and S2/(S3) atoms in two positions. (b) Chain of dimerised  $[Co(mnt)_2]_2^{2-}$  anions obtained by an alternated choice of any of the two positions of disordered Co and S2/S3 atoms. (c) Chain of dimerised  $[Co(mnt)_2]_2^{2-}$  anions obtained by an alternative choice of the two positions mentioned in the previous example. The dashed line represents Co–S(3) apical bonds at 2.405(3) Å.

chains, while larger unit cells correspond to other ordered arrangements of nearby dimerised anionic chains.

#### Electrical conductivity under pressure

The room temperature pressure dependent electrical conductivity of  $(Per)_2[Co(mnt)_2]$  measured along the *b*-axis, is plotted in Fig. 6. For low pressures below 1 kbar there is a very small linear increase of conductivity upon increasing pressure of *ca* 0.9% kbar<sup>-1</sup>, soon followed by maximum and a turnover towards a fast exponential decrease of conductivity reaching *ca* 5% kbar<sup>-1</sup> at 8 kbar. This behaviour contrasts with the regular increase of conductivity observed in most molecular materials, including the analogous compound (Per)<sub>2</sub>[Au(mnt)<sub>2</sub>] also shown in Fig. 6. The present results for the Au(mnt)<sub>2</sub> compound are similar to those previously reported<sup>7</sup> and they correspond to an initial linear increase of conductivity of *ca*. 14% kbar<sup>-1</sup>. It should be noted that this increase is however significantly smaller than that



Fig. 4 View of one stack of dimerised  $[Co(mnt)_2]_2^{2-}$  anions surrounded by two perylene stacks, showing by dashed lines the alternation of donor acceptor short contacts.



Fig. 5 Schematic representation of a possible combination in the *ac* plane of the two choices of dimerised anionic chains, leading to a cell with parameters: a' = a, b' = 2b, c' = 2c. The two differently patterned bricks represent anionic stacks corresponding to choices (b) and (c) of Fig. 3.

observed in many other organic conductors, namely the Fabre  $(TMTTF)_2X$  and Bechgaard  $(TMTSF)_2X$  salts, where increases of *ca* 50% kbar<sup>-1</sup> and 25% kbar<sup>-1</sup>, respectivel, y have been observed.<sup>18</sup>

The temperature dependence of the electrical resistivity measured in  $(Per)_2[Co(mnt)_2]$  single crystals under different pressures is shown in Fig. 7. Above 1 kbar the transition

 Table 3
 Short contacts and hydrogen bonds in the crystal structure of (Per)<sub>2</sub>[Co(mnt)<sub>2</sub>]

Atoms	d/Å	$d - \Sigma R_{ m vdW}$ /Å	Symmetry operator
C10…C29	3.351	-0.049	x, 1 + y, z
C12···C27	3.342	-0.058	x, 1 + y, z
C14…C11	3.319	-0.081	x, 1 + y, z
C16…C19	3.366	-0.034	x, 1 + y, z
C20…C23	3.346	-0.054	x, 1 + y, z
C28…C25	3.338	-0.062	x, 1 + y, z
C23…H25	2.872	-0.028	1/2 - x, $1/2 + y$ , $1/2 - z$
C25…H23	2.780	-0.120	1/2 - x, $1/2 + y$ , $1/2 - z$
	D…A/Å	$D-H\cdots A/^{\circ}$	
S2…H26-C26	2.950	130.88	1 - x, -y, 1 - z
S2…H27–C27	2.961	140.29	1-x, 1-y, 1-z
S3…H26-C26	2.983	133.59	1 - x, -y, 1 - z
N2…H13-C13	2.682	134.60	1-x, 1-y, 1-z
N1…H21–C21	2.605	143.04	1/2 - x, $1/2 + y$ , $1/2 - z$



**Fig. 6** Room temperature pressure dependence of the normalized electrical resistivity of  $(Per)_2[Co(mnt)_2]$  and  $(Per)_2[Au(mnt)_2]$ , measured along the *b*-axis. The inset shows in detail the low pressure regime.

temperature, as denoted by a maximum in the derivative  $d\ln\rho/d(1/T)$  shown in the inset of Fig. 7, increases regularly and becomes more sharply defined under increasing pressure. The transition temperature under 1 kbar was found to be 71.5(5) K, a value already smaller than 73.0(5) found previously at ambient pressure.<sup>1</sup> This difference correlates well with the increase of conductivity at room temperature up to 1 kbar. Under 8 kbar, the highest pressure measured, the transition temperature reaches 131 K (Fig. 8). A similar pressure trend is also observed in the energy gap estimated from the activation energy of the electrical resistivity in a range well below the transition temperature, as also shown in Fig. 8.

These results suggest two competing pressure effects taking place in  $(Per)_2[Co(mnt)_2]$ . Besides the usual decrease of resistivity and  $T_c$  due to bandwidth increase under pressure there is an anomalous exponential increase of resistivity and  $T_c$ , which



Fig. 7 Logarithmic sample resistance R of  $(Per)_2[Co(mnt)_2]$  as a function of the reciprocal temperature under the different pressures indicated. The inset shows the derivative of  $\ln(R)$  versus inverse temperature for selected pressures.



**Fig. 8** The transition temperature (circles, right axis) of  $(Per)_2[Co(mnt)_2]$  and energy gap (triangles, left axis) as found by fitting the low temperature portion of the data, between the dashed lines in Fig. 5. Data at 1 bar (open symbols) from ref. 3.

becomes dominating above 1 kbar. Since the homogenous decrease of intermolecular distances leads to an increase of bandwidth this observed anomalous behaviour cannot result from a simple isotropic and homogenous decrease of intermolecular distances and must result from changes of intermolecular overlap, possibly due to a sliding and tilting of stacked molecules under pressure. To the best of our knowledge this is the first time such anomalous behavior has been found in molecular materials under hydrostatic pressure. In the few cases previously reported where an increase of resistivity was observed by applying pressure, such as  $\theta$ -(BEDTTTF)<sub>2</sub>CsZn(SCN)<sub>4</sub><sup>19</sup> or  $\beta'$ -(Me<sub>4</sub>–As)[Pd(dmit)<sub>2</sub>]<sub>2</sub>,<sup>20</sup> uniaxial strain conditions lead to a change in intermolecular contact geometry due to molecular slipping.<sup>21</sup>

A fuller understanding of the pressure effects in (Per)2- $[Co(mnt)_2]$  waits for detailed structural analysis under pressure. However, in view of the alternation of short donor acceptor interchain contacts depicted in fig. 4, a likely mechanism of the response of the  $(Per)_2[M(mnt)_2]$  compounds under pressure is the sliding of the perylene molecules in alternated directions along their planes in response to the alternation of stronger and weaker donor acceptor contacts. In addition, the alternation of contacts can be further enhanced under pressure by the possible change of the tilting of the rigid [Co(mnt)<sub>2</sub>]<sub>2</sub> anions. This side slipping of perylene molecules simultaneously enhances the dimerisation effect on the conducting chains and reduces the bandwidth. In fact, the side motion of the perylene molecules changing their overlap mode is expected to decrease the bandwidth much faster and more drastically than the increase of bandwidth due to a decrease of perylene interplane distance.

## Conclusions

In conclusion, the (Per)<sub>2</sub>[Co(mnt)<sub>2</sub>] compound presents a structure with the crystal packing typical of the  $\alpha$ -(Per)<sub>2</sub>[M(mnt)<sub>2</sub>] phases but with the anionic chains being chemically dimerised. However the phase of dimerisation in nearby anionic chains is poorly correlated leading to situations that can easily range from ordered to incoherent arrangements depending on the crystallization conditions and crystal quality. The application of increasing hydrostatic pressure in  $(Per)_2[Co(mnt)_2]$  above 1 kbar leads to an unusual situation where the electrical conductivity is decreased while the associated transition temperature is increased. This anomalous behaviour can be understood as a consequence of a change of the perylene molecule overlap due to a transverse sliding of molecules along alternated directions of their planes imposed by the dimerised anion stacks.

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