Magnetic Properties of the Low-Dimensional Systems $(Per)_2M(mnt)_2$ (M = Cu and Ni)

Vasco da Gama, Rui T. Henriques, and Manuel Almeida*

Departamento de Química, ICEN-INETI, P-2686 Sacavém Codex, Portugal

Luís Alcácer

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

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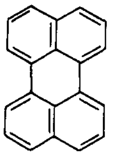
The magnetic properties of the two-chain compounds based on perylene (Per) and metal–bis(maleonitriledithiolate) ($M(mnt)_2$) with general formula $(Per)_2M(mnt)_2$, M = Cu and Ni, either α or β polymorphs, were studied by EPR and static magnetic susceptibility in the range 4–300 K. The EPR spectra of single crystals of the Cu compounds show a relatively narrow line (0.3 and 4 G at room temperature for the α and β phases, respectively) with g values close to those of perylene, consistent with a full charge transfer $(Per)_2^+[M(mnt)_2]^-$ and a diamagnetic organometallic species. The EPR spectra of the Ni compounds show wider (300 and 180 G at room temperature for the α and β phases, respectively) and anisotropic lines with temperature-dependent g values, denoting spin exchange between the electrons on the perylene cations and the $Ni(mnt)_2^-$ units. The highly conducting α-Cu phase has a magnetic susceptibility due to a small and almost temperature-independent contribution of the perylene conduction electrons that vanishes at the metal to insulator transition at 33 K. The α-Ni compound, in addition to a similar Pauli-like contribution, has its magnetic susceptibility dominated by a larger term due to the chains of $Ni(mnt)_2^-$ spins, also vanishing at the metal to insulator transition (25 K). The magnetic susceptibility of the semiconducting β-phases of the Cu and Ni compounds shows a distinct behavior with a continuous increase of susceptibility upon cooling following a $T^{-\alpha}$ law, with $\alpha \simeq 0.8$, indicative of disorder. These results are compared with those of the other members of this family of compounds, and for the α-compounds, they are discussed in terms of the instabilities occurring in the conduction perylene chains (Peierls) and in the $Ni(mnt)_2$ spin chains (spin-Peierls).

Introduction

The molecular conductors $(Per)_2M(mnt)_2$, with M = Cu and Ni (Per = perylene, (I) and mnt = maleonitriledithiolate or *cis*-2,3-dimercapto-2,3-butenedinitrile, (II)),are members of a large and unique family of molecular compounds that, depending on the transition metal M, can have in the same solid conduction chains of perylene molecules and chains of $M(mnt)_2^-$ units with localized magnetic moments.[1-3] These two types of stacks are prone to the instabilities typical of one-dimensional conducting (Peierls) or magnetic (Spin-Peierls) systems, and the role of each type of instability in the observed low-temperature phase transitions has remained open to discussion.[1,4,5] The magnetic properties of these compounds are one of their more interesting aspects that, until the moment, has been only partially addressed.[3,6-8]



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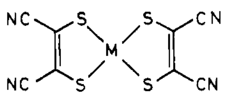

II

The Cu and Ni compounds are known to exist in two polymorphs: α and β.[2] The α phases, characterized by segregated stacks of Per and $M(mnt)_2^-$ units, are quasi-one-dimensional metals at high temperatures, undergoing metal–insulator (M–I) transitions at 25 and 33 K for M = Ni and Cu, respectively,[1-4] which are accompanied by lattice distortions,[5] while the β phases have a disordered structure with lower conductivity.[2] In these compounds the paramagnetic susceptibility is expected to be due only to the perylene cations for the Cu compound, and in case of the Ni one, due both to the perylene cations and the paramagnetic $Ni(mnt)_2^-$ units.

In spite of the importance of the magnetic properties, namely to further understand the nature of the low-temperature phase transitions, this study has been hampered with difficulties associated with both the small dimensions of the single crystals and occurrence, in an uncontrolled way, of the α and β polymorphs in the same preparation. In this paper we report results of a study using both EPR and static magnetic susceptibility measurements. By the combination of these techniques, we aim at not only obtaining the susceptibility of each compound and phase but also at the separation of the contributions of each type of chain to the total susceptibility, thus providing a better understanding of the properties of this family of compounds and the role of the magnetic chains in the low-temperature phase transitions.

Experimental Section

Polycrystalline samples of $(Per)_2M(mnt)_2$, with M = Cu and Ni, were prepared by electrocrystallization as previously described.[2] By this procedure α and β phase crystals ($\cong 2 \times 0.01 \times 0.01$ mm^3), hardly distinguishable one from each other by eye, and in variable amounts, are obtained in each batch.

Single-crystal EPR spectra were obtained with samples previously identified as α or β phase based on their different thermopower measured at room temperature (22–23 μV/K in the β phases compared to 35–38 μV/K in the α phases)[2] and after removal of the electrical contacts. The sample needle axis, b, was placed perpendicular to the static magnetic field, H, without any specific orientation of the a and b axes. A conventional X-band spectrometer (Brucker ESP 300) equipped with a helium flow cryostat (Oxford Instruments ESR-900) was used. The temperature was measured with a gold (0.07 at % Fe)-chromel thermocouple with an accuracy of 2 K, but the temperature was

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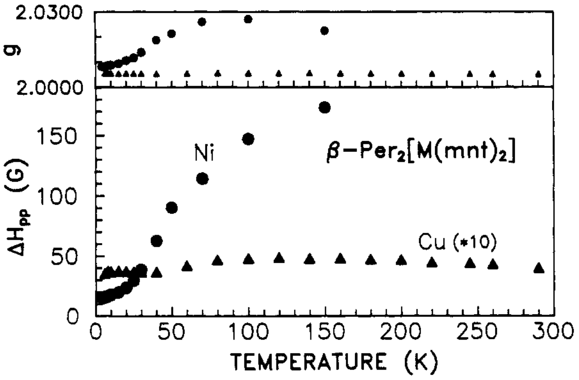

Figure 1. Line width, ΔH_{pp}, and g values of the EPR spectra of β-$Per_2M(mnt)_2$ single crystals ($H \perp b$) as a function of temperature: (▲) M = Cu, line width values multiplied by 10, (●) M = Ni.

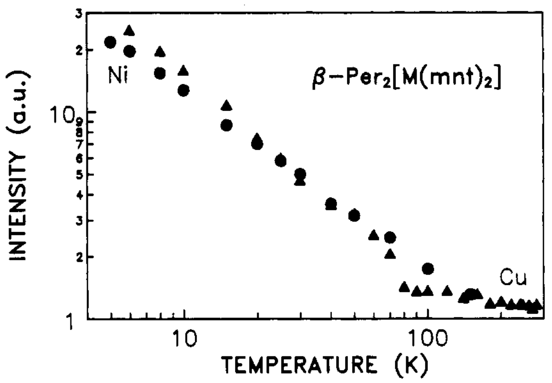

Figure 2. Integrated intensity of the EPR spectra of β-$Per_2M(mnt)_2$ single crystals ($H \perp b$) as a function of temperature: (▲) M = Cu, (●) M = Ni.

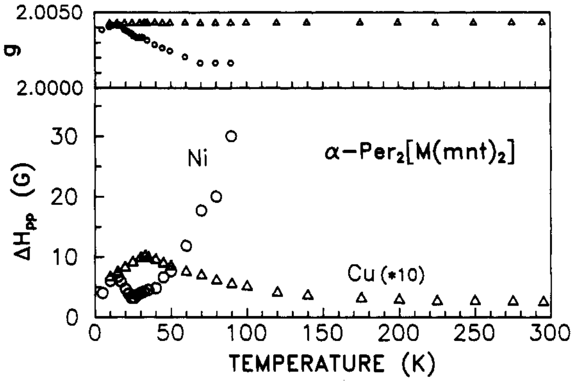

Figure 3. Line width, ΔH_{pp}, and g values of the EPR spectra of α-$Per_2M(mnt)_2$ single crystals ($H \perp b$) as a function of temperature: (△) M = Cu, line width values multiplied by 10, (○) M = Ni.

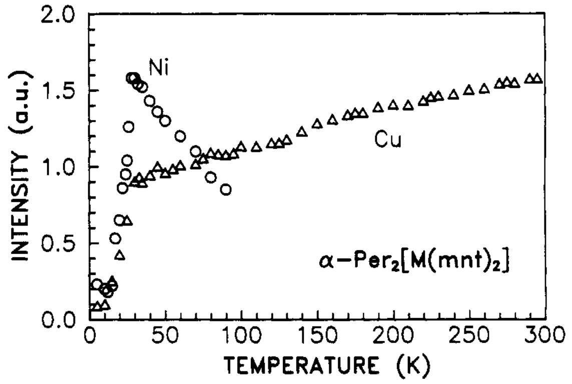

Figure 4. Integrated intensity, of the EPR spectra of α-$Per_2M(mnt)_2$ single crystals ($H \perp b$) as a function of temperature: (△) M = Cu, (○) M = Ni.

stabilized within 0.2 K. g factors were determined by simultaneously measuring the magnetic field (NMR Gaussmeter ER035M, Brucker) and the microwave frequency (HP-5350B frequency counter).

Magnetic susceptibility measurements were performed in the range 4–300 K using a longitudinal Faraday system (Oxford Instruments) with a 7-T superconducting magnet. Polycrystalline samples of ≃5–20 mg were placed inside a thin wall Teflon bucket previously calibrated. Force was measured with a microbalance (Sartorius S3D-V) applying downward and reverse gradients of 5 T/m, under fields of 2 and 5 T. Under these conditions the magnetization was found to the proportional to the applied magnetic field.

Results

EPR. The EPR spectra observed with single crystals consisted of a single line, for which line widths, g values, and integrated intensities are represented in Figures 1–4.

The β-Ni crystals present a significantly larger line width (180 G at 150 K decreasing to 15 G at 4 K) than the β-Cu analogue (4 G almost temperature independent in the range 4–300 K), but both with an integrated intensity that increases smoothly upon cooling. The broadening of the EPR line and the decrease of its intensity on heating precluded the accurate determination of the integrated intensity of the EPR signal of β-Ni above 150 K. As shown in Figure 2, for both β-Ni and β-Cu compounds the EPR signal intensities at low temperatures follow the same temperature dependence as the static magnetic susceptibility (see the next section), close to $T^{-\alpha}$, with $\alpha \simeq 0.8$.

The α-Cu crystals present an almost isotropic line at a temperature-independent $g = 2.0043$, very close to that of the perylene cation in solutions,[9] as in the β-polymorph, but with a line width even smaller (Figure 3). At room temperature the line width is ≃0.3 G, increasing slightly upon cooling until close to 35 K where it reaches a maximum of ≃1 G and then decreases again for lower temperatures. As shown in Figure 4, the temperature dependence of the intensity of this line is small at high temperatures and similar to those found in the Co and Fe compounds.[8] Upon cooling from room temperature there is a small decrease until ≃35 K, and then, at the metal to insulator transition (32 K), there is a fast vanishing of the intensity.

In α-Ni, due to reasons similar those above referred for β-Ni, the observation of the EPR signal became limited to temperature lower than 100 K, where a relatively narrow line with temperature-dependent g values was visible. This line appeared at g values increasing continuously upon cooling from 2.0010 at 100 K to 2.0045 at 4 K (Figure 3), while its intensity was strongly temperature dependent with a maximum at ≃30 K (Figure 4). As the signal to noise ratio prevented the observation of an EPR spectrum in a single crystal above 100 K, we used an α-Ni polycrystalline sample in order to get a more intense signal. The spectra of the polycrystalline sample consisted of a broad line (≃300 G), unobserved in a single crystal, that dominates at higher temperatures (Figure 5). At lower temperatures a new narrow line develops, becoming clearly observed below 100 K. This new line appears superimposed to the broad line and corresponds to that observed in the single-crystal experiments. Simultaneously with the development of this new narrow line upon cooling for $T < 100$ K, the broad line is significantly shifted to higher g values ($g \simeq 2.8$ at 50 K), well above those of the $Ni(mnt)_2^-$ species ($g = 2.161$, $g_2 = 2.042$, and $g_3 = 1.998$[10]). As a consequence of this broad line, the temperature dependence of the signal intensity in the polycrystalline sample is different from that of the narrow line observed in single-crystal experiments and in general agreement with that of the static magnetic susceptibility (see next section).

Static Magnetic Susceptibility. Paramagnetic susceptibility results were obtained after subtracting, from the experimentally

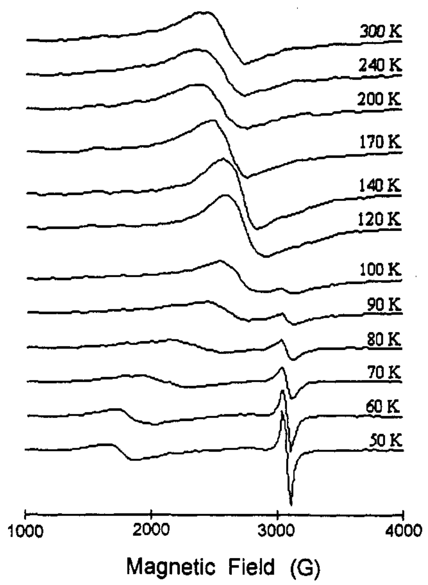

Figure 5. EPR spectra of a polycrystalline sample of α-$(Per)_2Ni(mnt)_2$ at different temperatures indicated.

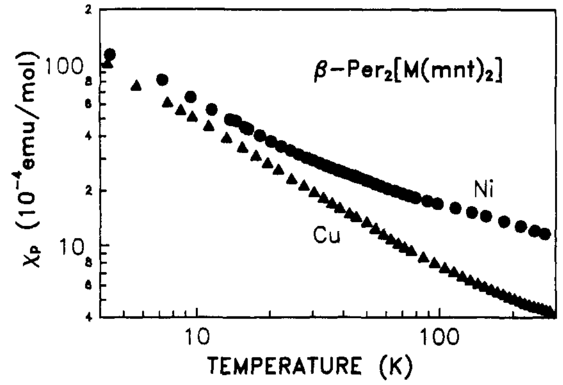

Figure 6. Paramagnetic susceptibility, χ_P, of β-$(Per)_2M(mnt)_2$, M = Ni (●) and Cu (▲), as a function of temperature.

determined values, the diamagnetic contribution, estimated from tabulated Pascal constants as 4.23×10^{-4} emu·mol^{-1} for both the Ni and Cu compounds.

The static magnetic susceptibility measurements were made in polycrystalline samples that, as explained before, have variable amounts of the α and β polymorphs. The susceptibility of the β phase is significantly larger than that of the α phase, and therefore it could be easily obtained from measurements in sampels coming from batches containing almost 100% of the β phase, as judged, by room temperature thermopower measured in many single crystals sampled from these preparations. The paramagnetic susceptibility obtained in this way for β-Ni and β-Cu (Figure 6) have a temperature dependence in reasonable agreement with those of the EPR signal intensity. At low temperatures, the paramagnetic susceptibility, χ_P, follows approximately $\chi_P = CT^{-\alpha}$, with $\alpha = 0.8$ for M = Cu and $\alpha = 0.75$ for M = Ni.

The susceptibility of the α-Ni and α-Cu compounds was obtained from measurements in batches with small but never negligible amounts of β phase crystals. The results shown in Figures 7 and 8 were obtained in α-rich samples after removing a term corresponding to the paramagnetic susceptibility of 12.5% of β phase for the M = Cu and 5% of β phase for the M = Ni compound. In case of the M = Cu compound an additional temperature-independent term ($\simeq 0.4 \times 10^{-4}$ emu/mol) was also removed in order to obtain a magnetization close to zero well below the metal to insulator transition. The paramagnetic susceptibility of α-Cu obtained in this way has a temperature dependence very close to that of the EPR signal intensity. Similar results were obtained in samples with different amounts of β phases. The reproducibility of the results obtained in different preparations and the general good agreement with the EPR intensity confirms the validity of the procedure followed in the decomposition of the static susceptibility results.

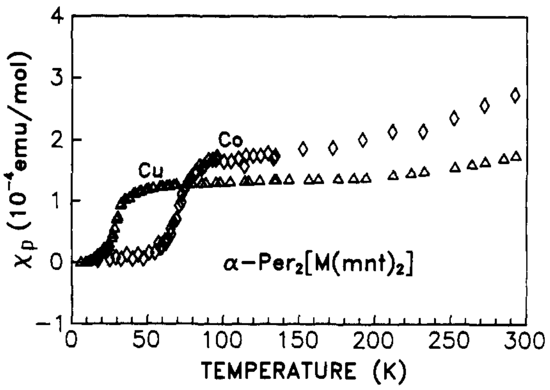

Figure 7. Paramagnetic susceptibility, χ_P, of α-$(Per)_2M(mnt)_2$, M = Cu (△) and Co (◇),[3] as a function of temperature.

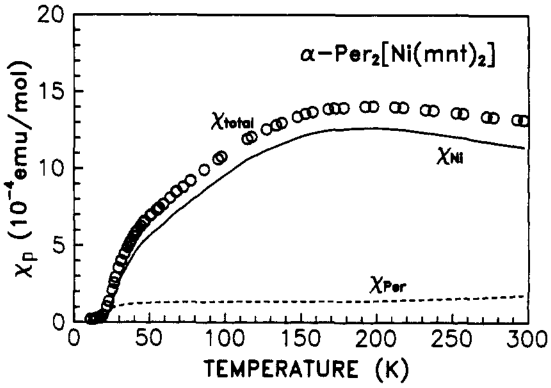

Figure 8. Paramagnetic susceptibility, χ_P, of α-$(Per)_2Ni(mnt)_2$ as a function of temperature. The solid line represents the $Ni(mnt)_2^-$ chain's contribution and the dashed line is the perylene Pauli contribution estimated from the α-Cu compound susceptibility with rescaled transition temperature (see text).

Discussion

The paramagnetic susceptibility, χ_P, of these compounds can be considered as the sum of two contributions:

$$\chi_P = \chi_{Per} + \chi_{M(mnt)_2} \qquad (1)$$

one due to the perylene cations (forming regular chains in the α phase), χ_{Per}, and one other contribution of the $M(mnt)_2^-$ species, $\chi_{M(mnt)_2}$. The last contribution is zero in case of diamagnetic $M(mnt)_2^-$ species, as for M = Cu,[10,11] giving an important additional contribution to the susceptibility. The paramagnetic $Ni(mnt)_2^-$ units are responsible for the observed enhanced magnetic susceptibility of the Ni compounds (either α or β) when compared with the Cu analogs. The diamagnetic nature of the $Cu(mnt)_2$ units is further confirmed by the almost isotropic and temperature-independent g values of the EPR line of the Cu compounds, very close to those of the perylene cation in solutions,[9] in contrast to those of the compounds with Ni.

The β phase crystals have a magnetic susceptibility with a clearly different temperature dependence from the α phases, increasing smoothly upon cooling. The behavior clearly observed in β phases at low temperatures, both the EPR and by static magnetic susceptibility, where $\chi_P = CT^{-\alpha}$, with the exponent α significantly smaller than 1, is typical of disordered systems and has been observed also in many other disordered 1D systems with random exchange antiferromagnetic interactions.[12-14] The discussion of the properties of the β phases is limited by the lack of detailed structural information. However, it is clear that this type of behavior of the magnetic susceptibility must be ascribed to localized spins, probably as a consequence of the structural disorder that is known to exist in the β phases associated with an one-dimensional 6b superstructure.[2]

It is worth refering that, assuming an equal χ_{Per} contribution in these two β-compounds, it is possible to estimate $\chi_{\mathrm{Ni(mnt)_2}}$ by subtraction of the susceptibility of the β-Cu compound from that of the β-Ni. This gives a contribution of $\chi_{\mathrm{Ni(mnt)_2}} \simeq 7 \times 10^{-4}$ emu/mol at 300 K, increasing smoothly to $\simeq 9 \times 10^{-4}$ emu/mol at 20 K. This almost temperature-independent $\chi_{\mathrm{Ni(mnt)_2}}$ contribution suggests that the disorder is associated mainly with the perylene spins.

The small Pauli-like paramagnetic susceptibility of the α-Cu compound, vanishing at the metal to insulator transition, strongly suggests that it is due to delocalized conduction electrons. The temperature dependence of the EPR signal intensity in α-Cu agrees very well with the temperature dependence of the static susceptibility measurements, both vanishing at the metal to insulator transition temperature $T_{\mathrm{M-I}} \simeq 25$ K, and the narrow line widths observed are indicative of delocalized and highly mobile conduction electrons. The g values further confirm that the conduction electrons responsible for this susceptibility are in the perylene chains in agreement with previous thermopower results.[2]

For a regular chain of partially oxidized molecules like those of perylene in these compounds, the tight binding model, neglecting the Coulomb correlations, predicts for the Pauli paramagnetic susceptibility:[15]

$$\chi_{\mathrm{Po}} = N\mu_{\mathrm{B}}^2/\pi t \sin(\pi\rho/2) \qquad (2)$$

where N is the Avogadro's number, μ_{B} the Bohr magneton, $4t$ the bandwidth, and ρ the number of electrons per molecule. In the presence of Coulomb correlations, the susceptibility is enhanced approximately as[15,16]

$$\chi_{\mathrm{P}} = \chi_{\mathrm{Po}}/\{1 - U_{\mathrm{ef}}/[2\pi t \sin(\pi\rho/2)]\} \qquad (3)$$

where χ_{Po} is the uncorrelated spin susceptibility given by eq 2 and U_{ef} is the effective on-site Coulomb correlation parameter. The stoichiometry imposes in these compounds $\rho = {}^3/_2$, i.e. a ${}^3/_4$-filled band. Using the bandwidth derived from thermopower measurements as $4t \simeq 0.6$ eV,[2] and from the room temperature value of $\chi_{\mathrm{Po}} = 1.8 \times 10^{-4}$ emu/mol, one obtains $U_{\mathrm{ef}}/4t \simeq 0.5$, confirming the previous indications that the correlation effects are relatively small in this family of compounds. As shown in Figure 7, the paramagnetic susceptibility of the α-Cu compound is comparable to that of the Co analogue (taken from ref 3 after removing a small temperature-independent contribution $\simeq 0.7 \times 10^{-4}$ emu/mol to ensure, as done for the Cu compound, a magnetization close to zero below the metal to insulator transition) that, apart from a higher transition temperature, presents a slightly higher paramagnetic susceptibility but with a similar temperature dependence. The higher susceptibility in the Co compound correlates well with its higher thermopower,[3] both indicating that, most probably as a consequence of different interplanar perylene spacing distances, the bandwidth is slightly larger in the Cu than in the Co compound.

In view of the great similarity of the transport properties of the isostructural α-Ni and α-Cu compounds, the $\chi_{\mathrm{Ni(mnt)_2}}$ contribution can be estimated assuming that χ_{Per} is the same in the Ni and Cu compounds, just with a correction for the slightly different metal to insulator transition temperatures. The result of such decomposition procedure is shown in Figure 8, where $\chi_{\mathrm{Ni(mnt)_2}}$ is represented by the continuous line and χ_{Per}, estimated from the previously obtained susceptibility of the α-Cu compound, by the dashed line. In spite of all possible errors involved in the decomposition process, it becomes clear that $\chi_{\mathrm{Ni(mnt)_2}}$ has a maximum around 190 K, then decreases upon cooling, with a faster decrease toward zero close to the metal to insulator transition at 25 K. This decrease, with a maximum slope around $T_{\mathrm{M-I}}$, differs from the case of the compound with M = Pt where a sharper knee is observed exactly at $T_{\mathrm{M-I}}$ without such a large decrease above $T_{\mathrm{M-I}}$.[17]

It is tempting to fit the $\chi_{\mathrm{Ni(mnt)_2}}$ at high temperatures ($T > 100$ K) to the calculations of Bonner and Fischer (B–F) for an antiferromagnetic Heisenberg linear chain,[18] according to which the broad maximum of the susceptibility around 190 K would indicate an antiferromagnetic coupling constant $J \simeq 150$ K. However the experimental data cannot be fitted to the B–F calculations which for $J = 150$ K would predict a significantly smaller susceptibility, by a factor of $\simeq 0.6$, well beyond the experimental uncertainty estimated as $\simeq 10\%$. In any case it is clear that, even at higher temperatures, there are antiferromagnetic interactions between the $\mathrm{Ni(mnt)_2^-}$ spins in each chain. It is not yet clear the nature of this coupling that could be partially direct and partially indirect, mediated through the conduction electrons in the perylene chains.

In the case of the analogue with M = Pt, EPR and ^{1}H NMR studies showed the existence of such an indirect coupling between the localized spins and conduction electrons in the form of a Kondo-like interstack exchange coupling and possible RKKY interactions between the $\mathrm{M(mnt)_2}$ spins.[17] The temperature dependence of the g value of the narrow EPR line emerging in the spectra of the polycrystalline M = Ni sample at temperatures below 100 K and the shift of the broad line to higher g values suggest a temperature-dependent coupling of the $\mathrm{Ni(mnt)_2}$ spins with the perylene chains. The two types of chains appear progressively decoupled below 100 K, where the two lines are observed in the EPR spectra, while above 100 K up to room temperature, due to spin-exchange interactions between the two chains, only one broad line is observed. The different temperature dependencies of the direct and indirect contributions can explain the difficulties in adjusting the experimental data with a B–F model with a temperature independent J. In this respect it is worth referring that an unexplained increase of g values was also observed, although in a more sudden and sharper fashion, in copper phtalocyanine iodide $\mathrm{Cu(Pc)(I_3)_{1/3}}$,[19] a solid also presenting two types of one-dimensional systems (conduction electrons and localized spins) but in the same chain.

It is important to note that the final decrease of the susceptibility toward zero at lower temperatures denotes the approach to a final three-dimensional ordering of the spin chains, which requires an indirect coupling mechanism. In fact, due to the structure of these α-compounds,[2] this coupling, as any $\mathrm{Ni(mnt)_2}$ interchain coupling, can occur only if mediated through the perylene chains that completely surround and isolate, one from each other, the $\mathrm{Ni(mnt)_2}$ chains.

The large decrease of the susceptibility below 100 K can be associated with the one-dimensional precursor effects of the lattice dimerization observed by X-ray diffuse scattering in the range 25–100 K.[5] This lattice dimerization was ascribed to the pairing of the $\mathrm{Ni(mnt)_2}$ units,[5] and therefore the faster susceptibility decrease upon cooling above 25 K is associated with this $\mathrm{Ni(mnt)_2^-}$ chains distortion, denoting the existence of a magnetoelastic coupling as in a spin-Peierls transition.

One-dimensional diffuse scattering, as precursor effects of a lattice dimerization, have been also observed in the analogues with M = Pt and Pd, for which the $\mathrm{M(mnt)_2^-}$ units are also paramagnetic. However, in these cases the intensity of the $b^*/2$ susceptibility diverges at the critical temperature $T_{\mathrm{M-I}}$,[20] where a fast and sharp decrease of the magnetic susceptibility is also observed.[17] This is different from the α-Ni compound where the intensity of the $b^*/2$ scattering, although increasing upon cooling, as well as the associated coherence length, never condenses in sharp Bragg spots at low temperatures,[5] in a behavior indicative of an incomplete long-range three-dimensional ordering.

In conclusion we were able to identify the different magnetic susceptibility behaviors of the α and β polymorphs of the $\mathrm{(Per)_2M}$-

$(mnt)_2$ compounds with M = Cu and Ni. The lower conducting β phases which are known to have structural disorder[2] present a magnetic susceptibility increasing continuously upon cooling. In the metallic α phases, the paramagnetic susceptibility is due to a Pauli contribution of the conducting perylene chains that vanishes at the metal to insulator transition T_{M-I}, and in the cases of M = Ni is also due to a contribution of the $Ni(mnt)_2$ spin chains, also decreasing around T_{M-I} as in a spin-Peierls transition.

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