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Synthesis of Designed Conductive One-Dimensional Coordination Polymers of Ni(II) with 6-Mercaptopurine and 6-Thioguanine

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Calculations performed with the goal of designing suitable electrical conductive $[M(6\text{-MP})_2]_n$ (M = transition metal, 6-MP = 6-mercaptopurinato) one-dimensional coordination polymers suggested that metal ions such as Ni(II) could provide suitable materials. In this work, direct hydrothermal reactions between 6-mercaptopurine (6-MPH) and the analogous 6-thioguanine (6-ThioGH) with $NiSO_4 \cdot 6H_2O$ yield the compounds $[Ni(6\text{-MP})_2]_n \cdot 2nH_2O$ [**1**] and $[Ni(6\text{-ThioG})_2]_n \cdot 2nH_2O$ [**2**]. The X-ray structures confirm that both compounds present similar structures based on one-dimensional chains in which the deprotonated nucleobases act as the bridging ligands connecting the metal ions by short distances. Electrical measurements at room temperature confirm the conductor character of both coordination polymers. The small differences found in these measurements have been rationalized with the help of density functional theory calculations. Preliminary adsorption studies on surfaces for **1** have allowed characterization of single chains on mica and graphite. The results obtained suggest the potential use of coordination polymers on nanomaterials for molecular electronics.

Introduction

Two approaches can be followed to generate nanocomponents: (i) *top-down* and (ii) *bottom-up* strategies.[1] In the latter, the self-assembly of molecules makes it possible to organize materials in the range from a few nanometers to several micrometers. Self-assembly *bottom-up* processes are expected to be the base of molecular electronics for the construction of nanocircuits. Supramolecular chemistry holds together, by means of non-covalent bonds, suitable building blocks to create larger aggregates. In this context, coordination bonds play a central role in creating supramolecules of different dimensionality, called coordination polymers. The suitable selection of the building blocks, either the metal ions or the metal complexes and the organic fragments, may allow the generation of a wide range of architectures with different properties.

Recently, coordination polymers have attracted attention because of their potential applications in several areas such as catalysis, electronics, photochemistry, and magnetochemistry.[2] Despite the importance of electrical conductivity in material science only a few studies have addressed this property in coordination polymers.[3] Therefore, empirical and theoretical studies are required in the search for conductive coordination polymers. This is an essential aspect from the perspective of their potential use as molecular conductive wires for nanoelectronics.[4,5] For this purpose, we have recently studied the one-dimensional (1D) coordination polymer $[Cd(6\text{-MP})_2]_n$ (6-MP = 6-mercaptopurinato).[4,6] Initially, this particular coordination polymer was selected because its basic structural aspects resemble those expected for M-DNA.[4] We have previously found several ways to organize this polymer on surfaces, but its final electrical characterization has demonstrated insulator behavior.[4]

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Additional theoretical calculations on similar systems but with several transition metal ions, $[M(6\text{-MP})_2]_n$ (M = divalent transition metal ion), have shown that coordination polymers with Cu(II) should be of a metallic character, and those with Fe(II) and Ni(II) should present a lower HOMO–LUMO gap and, in comparison with the Cd(II) polymer, thus presenting better electrical conductivity.[7]

Now we have focused on the synthesis and empirical electrical characterization of the previously designed coordination polymer $[Ni(6\text{-MP})_2]_n \cdot 2nH_2O$ [**1**]. Additionally, we have prepared a new analogous system with a related nucleobase $[Ni(6\text{-ThioG})_2]_n \cdot 2nH_2O$ [**2**], to compare the influence of this small change on the ligand (one amino group at the C2 position) in the electrical conductivity. Finally, we present initial studies carried out on surfaces to address the potential use of the new materials as conductive nanowires.

Experimental Section

Materials. All chemicals were of reagent grade and were used as commercially obtained. FTIR spectra (KBr pellets) were recorded on a Perkin-Elmer 1650 spectrophotometer. Elemental analyses were performed by the Microanalysis Service of the University Autónoma of Madrid on a LECO CHNS-932 microanalyzer.

Synthesis of $[Ni(6\text{-MP})_2]_n \cdot 2nH_2O$ (1). A mixture of $NiSO_4 \cdot 6H_2O$ (0.15 g, 0.57 mmol) and 6-mercaptopurine (0.17 g, 0.99 mmol) in a buffer acetic acid/sodium acetate solution (8 mL) was fully stirred at room temperature, sealed in a 23 mL Teflon-lined autoclave, and heated at 160 °C for 120 h. Then, the autoclave was slowly cooled (0.3 °C/min.) to ambient temperature. The resulting prismatic red crystals were washed with water and dried in air. Yield 0.042 g (18.6%, based on Ni). Anal. Calcd (found) for $C_{10}H_{10}N_8O_2S_2Ni$: C, 30.24 (29.71); H, 2.52 (2.38); N, 28.23 (27.62); S, 16.13 (16.56). IR selected data (KBr, cm^{-1}): 3300(s), 2395(s), 1842(m), 1594(s), 1439(m), 1396(s), 1331(s), 1217(s), 1173(m), 1147(m), 1024(m), 951(m), 854(m), 682(w), 622(m).

Synthesis of $[Ni(6\text{-ThioG})_2 \cdot 2H_2O]_n$ (2). The reaction was carried out as mentioned above for compound **1**, using 6-thioguanine (0.16 g, 0.94 mmol) instead of 6-MPH. Yield 0.035 g (15.0%, based on Ni). Anal. Calcd (found) for $C_{10}H_{12}N_{10}O_2S_2Ni$: C, 29.36 (30.10); H, 2.44 (2.11); N, 34.25 (34.90); S, 15.66 (16.10). IR selected data (KBr, cm^{-1}): 3437(s), 3304(s), 3126(s), 2947(m), 2773(m), 2695(m), 1648(s), 1628 (s), 1585(s), 1500(s), 1366(s), 1312(m), 1253(m), 1194(m), 1137(w), 1026(w), 967(w), 933(m), 857(m), 824(m), 639(m), 575(m).

The purity of the crystal samples of **1** and **2** has been checked by IR spectroscopy, powder X-ray diffraction, and ICO-AES analyses.

Preparation of the Surfaces. To obtain reproducible results, very flat surfaces with precisely controlled chemical functionalities, freshly prepared just before the chemical deposition, were used. Two different commercially available supports were used: Muscovite Mica and Highly Oriented Pyrolitic Graphite (HOPG). Both of them were cleaved with adhesive tape. The surface of freshly exfoliated mica was modified by immersion on a poly-L-lysine solution (0.01% solution; from Sigma) for 15 min and then intensively washed with water.

Sample Preparation for AFM. One milligram of crystals of compound **1** were suspended in 1 mL of ethanol and sonicated (680 W, 40 kHz) for 2 h. The resulting solution was centrifuged at 40000 rpm for 10 min, and the supernatant diluted up to a concentration of 10^{-5} and 10^{-6} g/L. Then, 10 μL of this solution were deposited on HOPG and modified mica substrates. Finally, the samples were left in air allowing the complete solvent evaporation.

Table 1. Single-Crystal Data and Structure Refinement Details

	1	**2**
formula	$C_{10}H_{10}N_8NiO_2S_2$	$C_{10}H_{12}N_{10}NiO_2S_2$
w (g mol^{-1})	397.09	427.13
shape	prismatic	prismatic
dimensions (mm)	$0.05 \times 0.01 \times 0.01$	$0.06 \times 0.03 \times 0.02$
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	3.6770(5)	3.646(2)
b (Å)	9.1056(11)	9.715(6)
c (Å)	11.121(2)	11.298(6)
α (deg)	111.25(1)	110.28(5)
β (deg)	95.74(1)	96.95(4)
γ (deg)	99.95(1)	100.66(4)
V (Å^3)	336.41(9)	361.4(4)
Z	1	1
μ (mm^{-1})	1.777	1.665
D_{calc} (g cm^{-3})	1.567	1.962
independent reflns	2888	1042
reflns $[I > 2\sigma(I)]$	1228	374
R_{int}	0.0532	0.0941
params	107	115
$\Delta\rho_{max,min}$ (e Å^{-3})	0.931, −0.491	0.507, −0.469
final R^a indexes $[I > 2\sigma(I)]$	R1 = 0.0477 wR2 = 0.0804	R1 = 0.0532 wR2 = 0.0982
R indexes all data	R1 = 0.1292 wR2 = 0.0897	R1 = 0.1628 wR2 = 0.1227

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = [\sum w(||F_o| - |F_c||)^2/\sum w|F_o|^2]^{1/2}$.

X-ray Data Collection and Structure Determination. Data collections were carried out at 293 K with an Xcalibur diffractometer equipped with an area detector and graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The data reduction was done with the CrysAlis RED program.[8] Information concerning data collection is summarized in Table 1. Only non single-crystal specimens were found both for compounds **1** and **2**, therefore the X-ray diffraction measurements were performed on twinned specimens. The *hkl* file corresponding to the major domain of these non-merohedral twins was processed to avoid reflections with significant contribution from the minor domains. The structures were solved by direct methods using the SIR97 program.[9] Full matrix least-squares refinements were performed on F^2 using SHELXL97.[10] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the purine bases were positioned geometrically and allowed to ride on their parent atoms with $U_{iso} = 1.2U_{iso}$(parent). The hydrogen atoms of the crystallization water oxygen atoms were not found in the difference Fourier map. All calculations were performed using the WinGX crystallographic software package.[11] Summaries of crystal data collection and refinement parameters are given in Table 1. Selected bond lengths and angles are listed in Table 2.

AFM measurements. AFM images were acquired in dynamic mode at room temperature and ambient pressure using a Nanotec Electronica system (www.nanotec.es) processed with the WSxM v2.2 software.[12] Olympus cantilevers were used with a nominal force constant of 0.75 N/m and a resonance frequency of about 70 kHz.

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Table 2. Selected Bond Lengths (Å) and Angles (deg) in Compounds **1** and **2**^{a}

compound **1**		compound **2**	
Ni−N7	2.023(3)	Ni−N7	2.045(9)
Ni−S6	2.5111(11)	Ni−S6	2.510(3)
Ni−S6^{i}	2.6229(11)	Ni−S6^{i}	2.595(3)
N7−Ni−N7^{ii}	180(-)	N7−Ni−N7^{ii}	180(-)
N7−Ni−S6	85.62(10)	N7−Ni−S6	85.0(3)
N7−Ni−S6^{ii}	94.38(10)	N7−Ni−S6^{ii}	95.0(3)
N7−Ni−S6^{iii}	87.17(9)	N7−Ni−S6^{iii}	88.0(2)
N7−Ni−S6^{i}	92.83(9)	N7−Ni−S6^{i}	92.0(2)
S6−Ni−S6^{i}	91.46(3)	S6−Ni−S6^{i}	91.14(10)
S6−Ni−S6^{ii}	180(-)	S6−Ni−S6^{ii}	180(-)
S6−Ni−S6^{iii}	88.54(3)	S6−Ni−S6^{iii}	88.86(10)

^{a} Symmetry codes for compound **1**: (i) $x+1, y, z$; (ii) $-x+2, -y, -z+1$; (iii) $-x+1, -y, -z+1$; and for compound **2**: (i) $x-1, y, z$ (ii) $-x, -y+1, -z+1$; (iii) $-x+1, -y+1, -z+1$.

Conductivity Measurements. The direct current (DC) electrical conductivity measurements were performed on two different single crystals of compound **1** and **2** at 300 K with two contacts. The contacts were made with platinum wires (25 μm diameter). The samples were measured at 300 K applying an electrical current with voltages from +10 to −10 V. The measurements were performed, in both compounds, along the crystallographic *a* axis.

Computational Methods. Our calculations were based on the density functional theory[13] (DFT) as implemented in the SIESTA code,[14,15] within the spin-polarized generalized gradient approximation (GGA),[16] with core electrons represented by separable[17] norm-conserving pseudopotentials. Several convergence tests were performed to ensure that the standard double-ς basis set, with polarization orbitals (DZP), provided a good description of the systems in the present work. Our study addresses infinitely long polymer chains simulated using periodic boundary conditions in a supercell, which included large vacuum regions in the two directions perpendicular to the chains to minimize the interaction between the wire in the supercell and its periodic images (atoms in neighboring molecules were at least 15 Å apart). This methodology[14,15] has been successfully applied to many different biomolecular systems in previous studies.[18]

Results and Discussion

A wide range of properties and potential applications have been reported for coordination polymers. However, electrical conductivity, one of the major keys in material science, has not been properly examined for these polymers. In principle, 1D coordination polymers showing electrical conductivity in bulk may be considered potential candidates for molecular wires. Because of several chemical (i.e., versatility as ligands[19]) and biochemical (i.e., model compounds[20,21]) reasons, nucleobases as ligands have attracted major attention in coordination chemistry. Besides, the use of nucleobases as building blocks for the construction of 1D coordination polymers may give structures resembling some forms of DNA.[4,22] However, despite general interest in metal-nucleobase chemistry, a recent revision has indicated a small number of coordination polymers with nucleobases as ligands.[22]

6-Mercaptopurine (6-MPH) is a synthetic purine nucleobase which is the thio analogue of natural hypoxanthine, while 6-thioguanine is the thio analogue of guanine. Coordination chemistry of nucleobase thio-derivatives has been well established,[23] in part because some of these ligands present interesting biological activity. Few X-ray structures have been reported for both 6-MPH and 6-ThioGH with metal ions, with most of the samples being either monomeric or dimeric complexes, besides just three coordination polymers.[23]

The direct self-assembling reaction between Cd(II) and 6-MPH, at buffered pH under heat, has been proven to be a suitable method for generating the 1D coordination polymer $[\mathrm{Cd(6\text{-}MP)_2}]_n$, both in the solid state and on surfaces.[6] However, similar reactions carried out with a large variety of metal ions and in particular with Ni(II) under a wide range of conditions (pHs and temperatures) have failed. Similar procedures also were fruitless for 6-thioguanine. Solvo- and hydrothermal methods have been proven to be suitable for synthesizing a large variety of coordination polymers under higher temperature and pressure conditions.[2] Thus, by reacting 6-MPH or 6-ThioGH with $\mathrm{NiSO_4 \cdot 6H_2O}$ under hydrothermal conditions, single crystals of $[\mathrm{Ni(6\text{-}MP)_2}]_n \cdot 2n\mathrm{H_2O}$ (**1**) and $[\mathrm{Ni(6\text{-}ThioG)_2}]_n \cdot 2n\mathrm{H_2O}$ (**2**) were obtained.

The crystal structures of compounds **1** and **2** are similar to that previously reported for the cadmium mercaptopurine analogue.[24] Their crystal structures consist of parallel neutral chains of $[\mathrm{Ni(L)_2}]_n$ (L being 6-mercaptopurinate and 6-thioguaninate for compounds **1** and **2**, respectively) and crystallization water molecules which are joined together by means of hydrogen bonds (Figure 1). The 1D complex is based on stacked centrosymmetric $[\mathrm{Ni(L)_2}]$ entities, which are linked together through axial Ni−S bonds, forming a linear 1D chain along the crystallographic *a* axis. The deprotonated mercaptopurine or thioguanine ligand chelates the metal center through the N(7) and S(6) atoms and binds the nickel atom from the upper entity through the S(6) atom. Structural parameters of the metal center coordination sphere remain essentially the same for compounds **1** and **2**. The main differences with the cadmium analogue are due to the smaller size of the nickel atom that leads to shorter metal−ligand distances: M−N7: 2.283(Cd) and 2.023−2.045(Ni), M−S6: 2.689(Cd) and 2.510−2.511(Ni), M−S6^{i}: 2.868(Cd) and 2.595−2.623(Ni). As a consequence of the shortening of the coordinate bonds, closer contact between the metal atoms of two alternate $[\mathrm{Ni(L)_2}]$ entities is obtained: Cd···Cd^{i}: 3.918 Å and Ni···Ni^{i}: 3.677 and 3.646 Å for compounds **1** and **2**, respectively. A characteristic of these compounds is that the two purine bases chelated to the same metal center are parallel but not coplanar, probably because of steric hindrance between the S6 and H8 atoms. The interplanar distance ranges from 1.161 to 1.419 Å, the larger value corresponding to compound **2**. The stacking of the centrosymmetric $[\mathrm{Ni(L)_2}]$ entities is also ensured by

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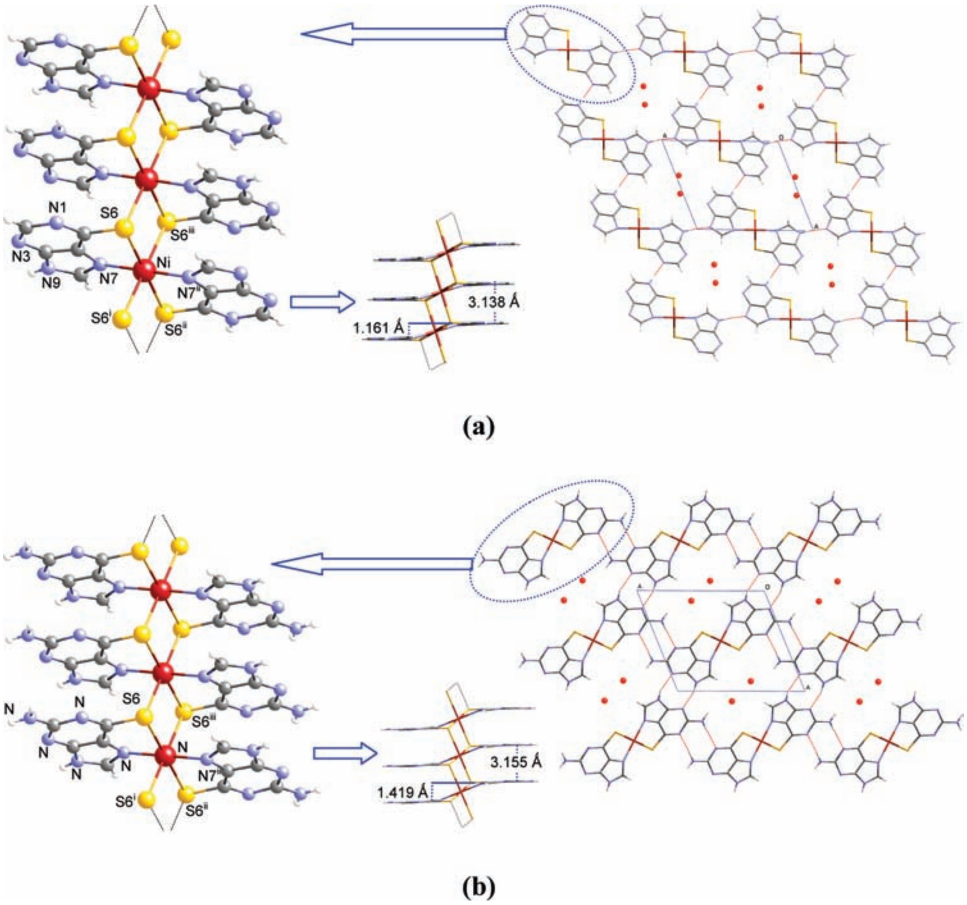

Figure 1. Fragment of the polymeric chain and crystal packing of compounds (a) $[Ni(\mu\text{-}6\text{-}MP^{-})_2]_n\cdot 2nH_2O$ (**1**) and (b) $[Ni(\mu\text{-}6\text{-}TG^{-})_2]_n\cdot 2nH_2O$ (**2**). The disorder of compound **1** has been removed for clarity. Red dashed lines represent hydrogen bonds.

parallel-displaced face-to-face aromatic interactions established between the purine bases placed on the same side of the chain. The maximum approach takes place between the imidazolic ring and the pyrimidinic rings of adjacent purine derivatives. The geometrical parameters are well within the typically accepted ranges for these non-covalent interactions (centroid···centroid distance: 3.199(2) and 3.254(6) Å; dihedral angle between rings: 2.3(2) and 2.8(2)°; lateral offset: 0.47 and 0.84 Å for compounds **1** and **2**, respectively).[25]

With respect to thione/thiol tautomerism, the analysis of the corresponding C−S bond distances, which are in the range of 1.66−1.75 Å, support the thione tautomers in compounds **1** and **2**. The major effect of the deprotonation of a ring nitrogen atom in the purine derivates is the narrowing of the corresponding C−N−C angle by about 3−7°.[23] In a previous paper we reported the angles around N1 and N9 for neutral *1H*,*9H*-6-mercaptopurine (6-MPH) and doubly deprotonated 6-mercaptopurinato ($6\text{-}MP^{2-}$) ligands with the same coordination mode.[6] The values for the neutral *1H*,*9H*-6-mercaptopurine are 123.8−124.7° around N1 and 107.2−107.5 around N9. In compound $[Cd(6\text{-}MP^{2-})_2]_n[Ca(H_2O)_6]_n$ the angles are 117.8(2) and 102.6(2)° around N1 and N9, respectively. In compound **1**, the measured angles around N1 and N9: 120.3(4) and 104.9(3)° are between the previous ones. This seems to indicate that the hydrogen atom is disordered over N1 and N9 with half occupation factors ($1H\text{-}6\text{-}MP^{-}/9H\text{-}6\text{-}MP^{-}$), instead of being fully placed on N1 ($1H\text{-}6\text{-}MP^{-}$) or N9 ($9H\text{-}6\text{-}MP^{-}$). On the other hand, the analysis of the crystal structure presents two common hydrogen bond distances of 2.787 Å for N1···N1 and 2.771 Å for N9···N9. These hydrogen bonds are only possible if we assume, as we have done, the presence of both $1H\text{-}6\text{-}MP^{-}$ and $9H\text{-}6\text{-}MP^{-}$ tautomers within the structure. The attempt to obtain an ordered model by solving the crystal structure at *P1* was unsuccessful. In the case of compound **2**, the Difference Fourier Map, the angles around the N9 and N1 nitrogen atoms and the hydrogen bond scheme are in agreement with the hydrogen atom fully placed on N9 ($9H\text{-}6\text{-}ThioG^{-}$).

The overall cohesiveness of the crystal structures is ensured in both compounds by means of hydrogen bonding interactions that every complex polymeric chain establishes with four adjacent chains. In compound **1**, mercaptopurinato ligand has only one hydrogen bond donor position and, as a consequence, every ligand only establishes two hydrogen bonds with other ligands: one as the donor and the other as the acceptor (N1···N1: 2.787(7) Å and N9···N9: 2.771(6) Å). This means that the interaction between ligands belonging to adjacent chains involves only one hydrogen bond. On the contrary, in compound **2**, the two additional hydrogen bond donor positions of the exocyclic amino group make it possible for every 6-thioguaninato ligand to establish four hydrogen bonds in its interactions with itself. This leads to a hydrogen bond scheme in which the non-covalent interaction between two adjacent chains involves two hydrogen bonds per thioguaninato ligand. The hydrogen bond

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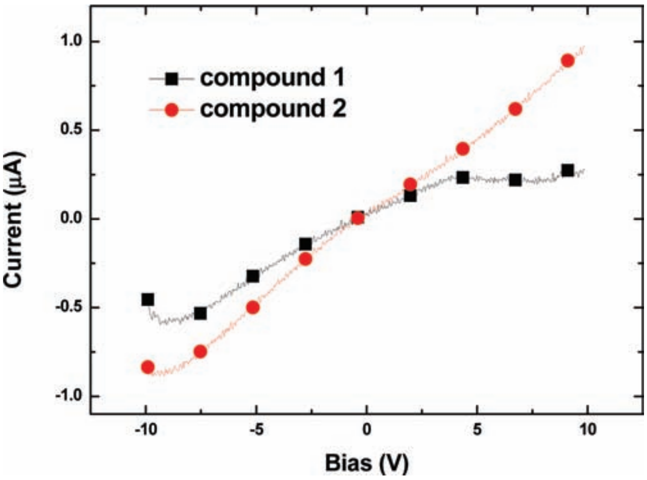

Figure 2. Two probe electrical measurements for compounds **1** and **2** at 300 K.

interaction takes place both through the Watson–Crick edge (N2···N1: 3.008(12) Å, N2–H···N1: 177°) or through the Hoogsteen face (N9···N3: 2.871(12) Å, N9–H···N3: 159°). In both cases the packing of the chains gives rise to channels parallel to the crystallographic *a* axis (16.3% of the unit cell volume with 5.7 × 7.1 Å approximate dimensions for compound **1** and 12.8% of the unit cell volume with 6.2 × 6.3 Å approximate dimensions for compound **2**) that are occupied by crystallization water molecules that, based on the presence of short potential donor···acceptor atom distances, seems to be tightly hydrogen bonded among them and to the complex polymeric chains.

Despite the major interest of the chemistry and material science community in the study of several properties associated to coordination polymers, electrical conductivity is still a poorly developed property.[2,3] Recent studies have shown the potential interest[26] and feasible applications[27] that may arise from conductive coordination polymers. Two probe DC electrical conductivity measurements at 300 K carried out in several monocrystals of **1** and **2** show ohmic behavior, with conductivity values of 1.10×10^{-5} and 1.34×10^{-4} S cm^{-1}, of the crystals of **1** and **2**, respectively (Figure 2). These conductivity values are probably underestimated because of crystal-electrode electrical contacts. The conductivity values obtained are high in comparison with those reported for similar coordination polymers.[27,28] In view of the X-ray structures of **1** and **2**, this result is in some way unexpected. To rationalize it, DFT theoretical calculations were carried out.

Previous DFT calculations that we have reported[7] addressed the electronic properties of the fully relaxed $[Ni(6\text{-}MP)_2 \cdot 2H_2O]_n$ theoretical structure obtained by replacing the Cd(II) with Ni(II) atoms in the $[Cd(6\text{-}MP)_2 \cdot 2H_2O]_n$ structure (previously solved by X-ray diffraction).[7] For comparison, in the present work we compute the DFT-GGA electronic structure of $[Ni(6\text{-}MP)_2 \cdot 2H_2O]_n$ using the experimental X-ray crystal structure to validate the data. In addition, we calculate the electronic structure for the new compound **2**, also in the atomic geometry determined by the new X-ray diffraction analysis.

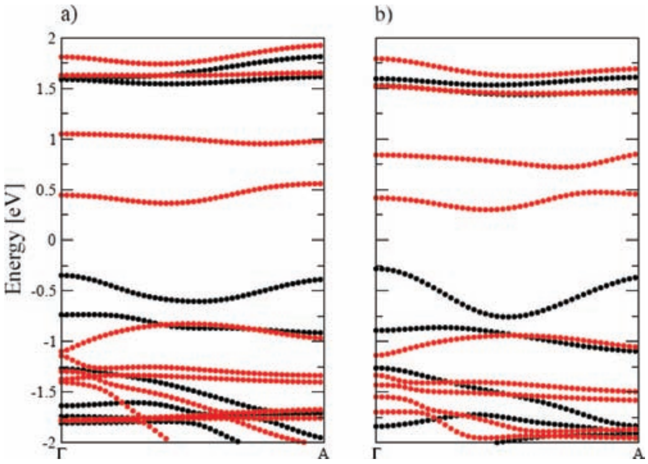

Figure 3. Band structure of the geometries obtained by X-ray of $[Ni(6\text{-}MP)_2 \cdot 2H_2O]_n$ (a), and $[Ni(6\text{-}ThioG)_2 \cdot 2H_2O]_n$ (b). Black (red) lines show majority (minority) spin bands.

Our previous calculations indicated that compound **1** is a semiconductor, presenting a HOMO–LUMO gap of 0.66 eV, in the theoretical structure. In the present work, using the same convergence parameters as in this previous calculation, we obtain very similar results, which are explained by the fact that the differences between the theoretical and experimental structures are relatively small. The main difference is that the lattice constant obtained by GGA-DFT calculations is 2.2% smaller than that obtained by X-ray analysis. This leads to an increase of ~14% in the HOMO–LUMO gap (0.77 eV for the X-ray structure, as shown in Figure 3a) with respect to the value obtained for the theoretical geometry. We have also calculated the electronic structure of **2** with the coordinates of the X-ray structure. This coordination polymer presents similar electronic properties to those observed for **1**, with a calculated HOMO–LUMO gap of 0.69 eV (Figure 3b).

By comparing the band structures of **1** and **2**, we observe that the amino group, present in the $[Ni(6\text{-}ThioG)_2 \cdot 2H_2O]_n$, mainly introduces modifications in the deep level states lying at about −1.25 eV from the Fermi level, and below.

The gap decrease observed for **2**, when compared with **1**, is due to the fact that the former presents a smaller lattice constant (3.65 Å) than the latter (3.68 Å). By using the value we obtained for the difference in band gaps between the two coordination polymers, we have estimated that polymer **2** should have about 20 times more thermally activated intrinsic carriers, at room temperature, than **1**, which is consistent with the experimental conductivity measurements.

Once the electrical conductivity was verified in the crystal phase, to go a further step we tried to form nanostructures of the polymers on the surfaces. As is well-known, most 1D coordination polymers are fairly insoluble in organic and inorganic solvents, otherwise their solubilization frequently leads to decomposition,[3] as is the case with these two compounds. However, we have recently developed a variety of methods to isolate different types of 1D coordination polymers on surfaces.[29]

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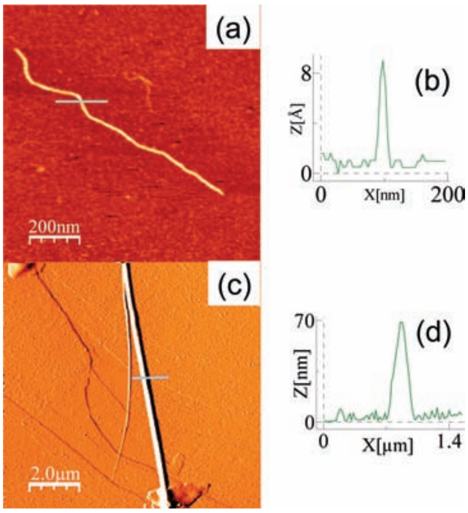

Figure 4. AFM topographic images of the fibers of **1** adsorbed on mica treated with poly-L-lysine (a) and HOPG (c). (b,d) Topographic height profiles across the line in (a) and (c).

Thus, following similar procedures to those that we reported for the isolation of single chains of $[Cd(6\text{-}MP)_2]_n$,[4] we have successfully isolated single chains and bundles of compound **1** on mica and HOPG. Adsorption of a drop of a sonicated and centrifuged suspension of crystals of compound **1** in ethanol allows isolation of single chains of **1**. Figure 4a shows an example of a chain isolated on a modified mica surface with a typical linear morphology and a length of ~1 μm and a height of 0.9 nm (Figure 4b, value in good agreement with the X-ray height of a single chain). However, adsorption on HOPG generated micrometer length linear bundles with heights close to 70 nm (Figures 4c and 4d). A closer view of these images shows some smaller bundles and individual chains connected to the central root of the bundle.

In summary, following the rational design of conductive coordination polymers[7] we have been able to obtain $[Ni(6\text{-}MP)_2 \cdot 2H_2O]_n$ [**1**] and extended the analogous $[Ni(6\text{-}ThioG)_2 \cdot 2H_2O]_n$ [**2**], both showing fairly similar X-ray structures to those previously calculated by DFT. These two new coordination polymers show electrical conduction at room temperature with some remarkable differences between them and those of the Cd(II) analogue, which have been rationalized by new DFT calculations. Preliminary surface studies show that it is possible to isolate single chains of **1** on surfaces. These results suggest the potential use of coordination polymers on nanomaterials for molecular electronics and confirm the potential of DFT calculations for the design of the electronic properties of coordination polymers.

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Supporting Information Available: X-ray crystallographic files in CIF format for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.