

Research Article

Synthesis of a One-Dimensional Coordination Polymer of Nickel(II) Complex with a β -Oxodithioester Ligand

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Bis-[methyl-1-hydroxy-1-cyclopentene-2-dithiocarboxylate-O,S]nickel(II) **1** was prepared starting from methyl 2-hydroxycyclopent-1-encarbodithioate ligand (CPDT) and Ni(II), and catena-[(μ_2 -4,4'-Bipyridyl)-bis-(methyl-2-hydroxy-1-cyclopentene-2-dithiocarboxylate-O,S)]nickel(II) **2** was prepared in good yields from **1** plus 4,4'-bipyridyl (bpy) by shish-kebab methodology. The structure of **1** was confirmed by FTIR, elemental analysis, ¹H NMR, UV-vis in chloroform solution and in solid, XPS, and PXRD. Compound **2** was characterized by FTIR, elemental analysis, UV-vis in chloroform solution, and in solid, XPS, PXRD, ESR, and solid state magnetization measurements. The structure of the polymer was established mostly by PXRD, ESR, and magnetization.

1. Introduction

Discrete metallosupramolecular assemblies have been prepared towards potential applications in catalysis, gas-storage, separation, sensing, magnetism, optics, and electrochemistry, among others [1–6]. The design of well-defined structures is based on the directional-bonding approach, using rigid ligands with highly directional coordinating groups and geometrically constrained metals entities. In this sense, the wheel-and-axle approach is being applied to obtain 1D polymers [7], which are also described as shish-kebab coordination polymers [8, 9]. This type of linear supramolecules is formed when an ambidentate ligand bridges metalloporphyrins with hexacoordinated metals [10]. Shish-Kebab approach has three variables (macrocycle, bridging group, and transition metal) wherein metalloporphyrins were commonly used as macrocycle-metal moiety, and *N,N'*-bidentate ligands perform as bridging group, towards the control of optical, magnetic, and electrical properties [11].

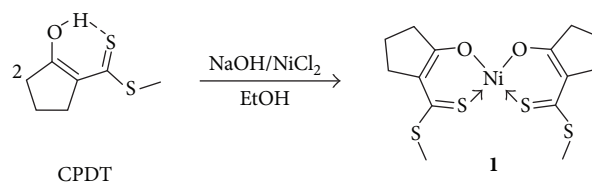
Not only are metalloporphyrins used in shish-kebab coordination polymers, but square planar complexes with two vacancies have also been used to obtain 1D coordination polymers [12–14]. We are interested in nickel(II) complexes with O,S-donor ligands and in the study of the structure and chemical properties given by the S-donor atoms in the nickel coordination sphere. Dorange et al. reported the synthesis of the NiL₂ diamagnetic complex (L = methyl 3-hydroxy-3-phenyl-2-propenedithioate) [15] and a paramagnetic [NiL₂(Py)₂] bis-pyridine derivative. This work shows the possible use of bis-chelated complexes in square planar structure for the preparation of shish-kebab coordination polymer with a 4,4'-bipyridyl bridge. Herein we report the syntheses and structural characterization of two nickel(II) complexes *bis*-[Methyl 1-hydroxy-1-cyclopentene-2-dithiocarboxylate-O,S] nickel(II) **1** and catena-[(μ_2 -4,4'-bipyridyl)-*bis*-(methyl 2-hydroxy-1-cyclopentene-2-dithiocarboxylate-O,S)]nickel(II) **2**, starting from methyl 2-hydroxycyclopent-1-encarbodithioate ligand [16] and its 1D coordination

polymer bridged by bpy. The structure of the latter was evidenced by spectroscopy in solid state, being unstable in solution.

2. Experimental Section

2.1. Materials and Methods. Cyclopentanone, methyl iodide, potassium *tert*-butoxide, 4,4'-bipyridyl (Aldrich), carbon disulfide, and nickel(ii) chloride (J. T. Baker) were used without further purification. Solvents were distilled before use. Melting points were determined in a Melt-temp II. ^1H and ^{13}C NMR spectra were recorded using a Bruker-Advance 300 MHz spectrometer, using TMS as internal standard. IR spectra were recorded on a Nicolet Avatar 360 in KBr and ATR FT-IR Shimadzu, IR Prestige-21 model with 4 cm^{-1} of resolution. Electronic absorption spectra were obtained on a Perkin Elmer lambda 25 spectrophotometer. The XPS spectra were acquired using a JEOL JPS-9200, equipped with a Mg X-ray source (1253.6 eV) at 200 W; the area of analysis was 1 mm, and the vacuum was in the order of 10^{-8} Torr for all samples. The spectra were analyzed using the SpecSurf software included with the instrument; all spectra were charge-corrected using the carbon signal (C 1s) at 284.5 eV as a reference. The Shirley method was used for the background subtraction, while in the curve fitting process the Gauss-Lorentz method was used. Electron Paramagnetic Resonance spectra were recorded on JOEL JES-TE300 of 1.4 T spectrometer, operated on X-band at FM 100 KHz in cylindrical cavity on TE011 method. The samples were handled as solid into Wilmad quartz tubes. Magnetization measurements were performed with a Quantum Design MPMS SQUID magnetometer, MPMS-5. Field-cooling (FC) cycle was performed at magnetic field intensity of 1000 Oe in the range 2 up to 300 K. Powder X-ray diffraction data were acquired in a Bruker D8 advance diffractometer equipped with a Linxeye detector, using Ni-filtered Cu $K\alpha$ radiation. Tube conditions were 30 kV, 30 mA; 2θ range $5-50^\circ$; step size 0.02° ; step time 32 s.

2.2. Synthesis of the Methyl 2-Hydroxycyclopent-1-encarbo-dithioate Ligand (CPDT). To potassium *tert*-butoxide (8.3 g, 74 mmol) in 200 mL of dry ethyl ether was added cyclopentanone (3 mL, 34 mmol) under stirring at -10°C . After 30 minutes, a solution of CS_2 (2.2 mL, 36 mmol) in the same solvent (20 mL) was added, continuing the stirring for 1.5 h more. Methyl iodide (2.2 mL, 36 mmol) was then added and a reddish suspension was obtained. The solvent was removed under vacuum, the solid was dissolved in water and acidified with HCl 2M, extracted with CH_2Cl_2 , dried by Na_2SO_4 , and concentrated. A yellow crystalline solid was obtained by silica-gel chromatography using hexane as eluent. Yield: 3.15 g (53%), mp: 37.6°C . IR (KBr, cm^{-1}): 3427 br, 2924 m, 2853 m, 1644 w, 1553 s, 1523 m, 1447 m, 1423 w, 1330 w, 1242 m, 1072 w, 1020 w, 984 w, 949 w, 789 w. IR (ATR, cm^{-1}): 2953 w, 2915 w, 2851 w, 1547 s, 1443 m, 1418 m, 1237 m, 793 m. ^1H RMN (300 MHz, CDCl_3): δ 1.89 (q, 2H, $J = 7.4, 7.9$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.63 (s, 3H, SCH_3), 2.67 (t, 2H, $J = 7.9$ Hz, $\text{CH}_2\text{CH}_2\text{C}=\text{O}$), 2.80 (t, 2H, $J = 7.4$ Hz, $\text{C}(\text{O})\text{CH}_2\text{CH}_2$), 14.27 (s, 1H, OH). ^{13}C NMR (75 MHz, CDCl_3): δ 16.79 (SCH_3), 18.39



SCHEME 1: Synthesis of **1** from CPDT ligand.

($\text{CH}_2\text{CH}_2\text{C}=\text{O}$), 30.79 ($\text{CH}_2\text{CH}_2\text{CH}_2$), 35.07 ($\text{C}(\text{O})\text{CH}_2\text{CH}_2$), 119.30 (C_{vin}), 179.47 (CO), 213.63 (CS_2). UV-Vis (CHCl_3), [λ_{max} nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 319 (17650), 354 (13450), 374 (17160).

2.3. Synthesis of bis-[Methyl 1-Hydroxy-1-cyclopentene-2-dithiocarboxylate-O,S]nickel(II) **1.** An aqueous NaOH solution (5 mL, 0.4 M) was added to a warm ethanolic solution of CPDT (0.34 g, 1.95 mmol) under stirring. $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (0.24 g, 0.99 mmol) in 25 mL of ethanol was then added to the mixture, producing an orange solid. The precipitate was filtered and washed with ethanol and hexane, yielding 0.34 g, (87%), mp: $d250^\circ\text{C}$. Calc. for $\text{C}_{14}\text{H}_{18}\text{NiO}_2\text{S}_4\cdot\text{H}_2\text{O}$: C, 39.73; H, 4.76; S, 30.30. Found: C, 39.89; H, 4.31; S, 30.16. IR (KBr, cm^{-1}): 2904 w, 1546 s, 1406 s, 1287 m, 972 w, 934 w, 910 m, 846 w, 669 w. IR (ATR, cm^{-1}): 2951 w, 2908 w, 2863 w, 1545 s, 1441 s, 1409 s, 1288 w, 847 m. ^1H RMN (300 MHz, CDCl_3): δ 1.86 (m, 2H, $J = 7.6, 7.8$ Hz $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.46 (t, 2H, $J = 7.8$ Hz, $\text{CH}_2\text{CH}_2\text{C}=\text{O}$), 2.59 (s, 3H, SCH_3), 2.65 (t, 2H, $J = 7.6$ Hz, $\text{C}(\text{O})\text{CH}_2\text{CH}_2$). UV-Vis (CHCl_3), [λ_{max} nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 238 (28330), 245 (26260), 277 (25350), 313 (31160), 334 (25950), 378 (5600), 439 (4190). UV-Vis-NIR (solid), [λ_{max} nm]: 405, 513, 705.

2.4. Synthesis of catena-[(μ_2 -4,4'-Bipyridyl)-bis-(methyl 2-Hydroxy-1-cyclopentene-2-dithiocarboxylate-O,S)nickel(II)] **2.** A solution of bpy (0.08 g, 0.53 mmol) in 10 mL of CHCl_3 was added to a 50 mL of chloroform solution of **1** (0.104 g, 0.25 mmol) under stirring at room temperature for 1 h. The yellow solid was filtered, washed with CHCl_3 and dried under vacuum. Yield 0.106 g (73%), mp: $d270^\circ\text{C}$. Calc. for $\text{C}_{24}\text{H}_{26}\text{N}_2\text{NiO}_2\text{S}_4\cdot 0.25\text{CHCl}_3$: C, 49.99, H, 4.58, S, 22.01, N, 4.81. Found: C, 49.85, H, 4.46, S, 21.53, N, 4.71. IR (ATR, cm^{-1}): 2874 w, 2954 w, 2911 w, 2834 w, 1575 m, 1483 s, 1419 s, 1375 s, 1274 m, 801 m, 727 m, 625 m. UV-Vis-NIR (solid), [λ_{max} nm]: 441, 614, 876, 928, 1008.

3. Results and Discussion

3.1. Synthesis and Characterization of **1.** **1** was obtained according to similar methodology (Scheme 1) previously reported for the nickel complexes of the methyl 3-hydroxy-3(4'-R-phenyl)-2-propenedithiocarboxylate ligands [15]. The proposed structure of **1** was built by its spectroscopic characteristics and single crystal analysis.

In the IR spectrum of **1**, the loss of the centered band is observed at 3427 cm^{-1} , which was assigned to H-O enol group in the ligand. The signals at 1405 and 909 cm^{-1} were assigned to $\delta(\text{C-O})$. These signals were low energy-shifted

TABLE 1: Deconvoluted UV-vis signals (nm) of compounds **1** and **2**.

Assignment	1	2
	<i>CHCl₃ solution</i>	
$\pi^* \leftarrow n$ O	280	279
α, β -unsat	315	314
$\pi^* \leftarrow n$ CS	337	336
S-Ni LMCT	384	378
O-Ni LMCT	445	442
	<i>Solid</i>	
$\pi^* \leftarrow n$ CS	350	351
S-Ni LMCT	399	406
O-Ni LMCT	449	459
	501	499
	714	
${}^3T_{1g}(P) \leftarrow {}^3A_{2g}(\nu_1)$		571
${}^3T_{1g}(F) \leftarrow {}^3A_{2g}(\nu_2)$		886
${}^3T_{2g}(F) \leftarrow {}^3A_{2g}(\nu_3)$	934	922

respecting to the ligand (1422 and 949 cm^{-1} , $\Delta\nu = -17$ and -39 cm^{-1} , resp.) probably due to the O-Ni σ -donation. The stretching mode of thiocarbonyl group (C=S) is observed at 1286 cm^{-1} in the spectrum of **1**, and this signal is high energy-shifted from ligand (1242 cm^{-1} , $\Delta\nu = 44$ cm^{-1}) [17]. This fact could be provoked to the back donation of electron density from nickel to ligand. The $\nu(\text{C}=\text{C})$ at 1545 cm^{-1} is shifted towards lower wavenumbers from those of the ligand (1552 cm^{-1} , $\Delta\nu = -7$ cm^{-1}). The changes on C-O, C=S, and C=C energy vibrations suggest the electron delocalization on the 6-membered chelated ring of the complex [17].

The ${}^1\text{H}$ NMR spectroscopy complements the structural information of **1**. The enol proton observed at 14.27 ppm for CPDT ligand disappears in the spectrum of **1**. In general, the rest of the signals are upfield-shifted compared to the ligand, except SMe protons, which are not significantly affected by coordination (2.63 ppm in CPDT). The multiplets at 1.87, 2.46, and 2.66 ppm assigned to cyclopentene moiety are less shifted from the ligand (at 1.89, 2.68, and 2.81 ppm in ligand, $\Delta\delta = -0.02$, -0.22 , and -0.15 ppm, resp.) due to the increase of electron delocalization by the coordination.

The chloroform UV-vis spectrum of **1** (Figure 1) shows electronic transitions in both UV and visible part of the spectrum (Table 1). In the UV range, two main absorption bands are observed corresponding to a ligand transition. Overall, the absorption bands are blue shifted respecting ligand by the nickel coordination. The band at 280 nm was assigned to the $\pi^* \leftarrow n$ transition of the oxygen atom. The band assigned to α, β -unsaturated system centered at 315 nm has an important hyperchromic effect, evidencing the increase of π -conjugation in **1**. The band at 337 nm was assigned to a $\pi^* \leftarrow n$ transition of dithiocarbonyl group. Two bands on the visible region at 383 and 445 nm may belong to S-Ni and O-Ni LMCT transitions [18, 19]. In the solid electronic spectrum, the deconvoluted signal centered at 350 nm was assigned to a $\pi^* \leftarrow n$ transition of dithiocarbonyl group

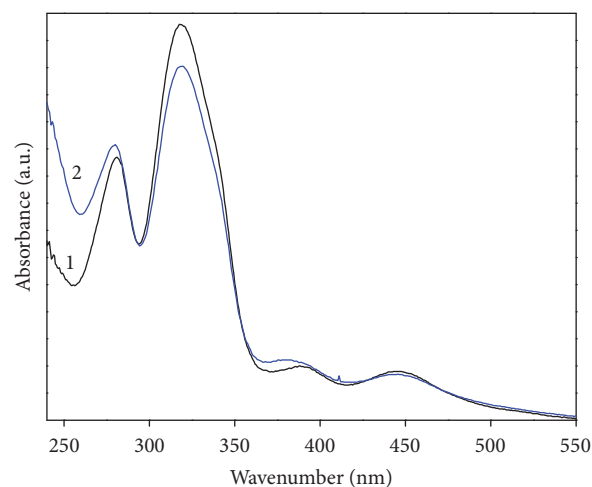


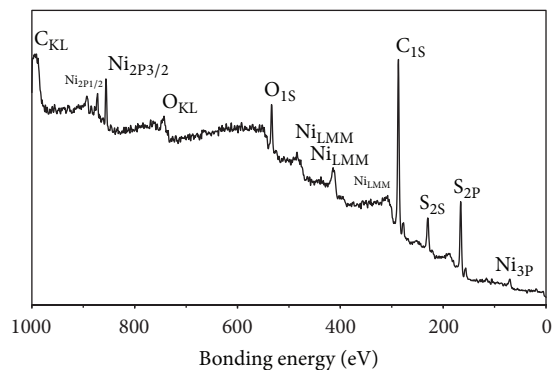
FIGURE 1: Absorption spectra of chloroform solution of **1** and **2**, in chloroform.

(Figures S1–S6 in Supplementary Material available online at <https://doi.org/10.1155/2017/7623210>) and S-Ni and O-Ni LMCT transitions were observed at 399 and 449 nm, and an additional band appears around 405 nm among two weaker bands at 501 and 714 nm, which were assigned to ${}^1A_{2g} \leftarrow {}^1A_{1g}$ and ${}^1B_{1g} \leftarrow {}^1A_{1g}$, corresponding to a square planar geometry on nickel(II) center [20, 21].

The XPS spectrum of **1** shows the presence of carbon, oxygen, sulfur, and nickel signals (Figure 2 and Table 2). The Ni $2p_{3/2}$ signal at 854.87 eV (Table 1) could be assigned to a nickel(II) atom surrounded by O,S-donors similar to the reported $[\text{Ni}(\text{SC}(\text{SCH}_3)\text{CHC}(\text{C}_6\text{H}_5)\text{O})_2]$ complex, (855.00 eV) [22]. The absence of satellite peaks confirms the diamagnetic behavior of nickel center and the square planar geometry of the complex.

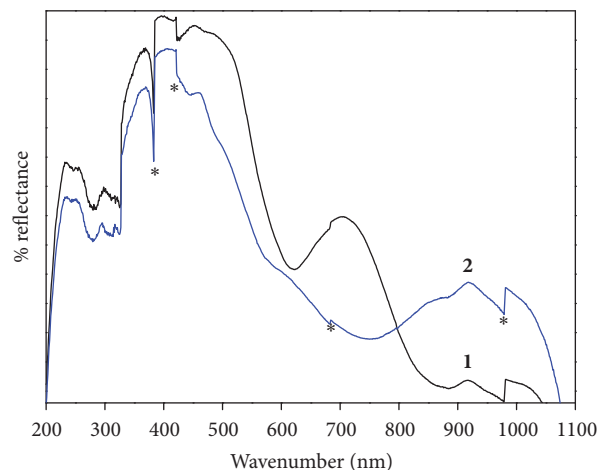
TABLE 2: Binding energies (eV) of the different components observed in XPS spectra for **1** and **2**.

BE (eV)	1	2	Corresponding peak
O 1s	530.38	530.29	O=C
	531.99	531.92	O-C
S 2p	161.12	160.90	S=C 2p _{3/2}
	162.04	161.81	S=C 2p _{1/2}
	163.06	162.75	S-C 2p _{3/2}
	164.11	163.82	S-C 2p _{1/2}
Ni 2p	854.87	855.01	Ni 2p 3/2

FIGURE 2: Wide-scan XPS spectrum of $[\text{Ni}(\text{cpdt})_2]$ complex.

The S 2p band region shows a single broad peak in 162 eV, with a FWHM = 2.6 eV by the presence of the 2p_{1/2} and 2p_{3/2} core levels as well as two different sulfur atoms, expected by the ligand structure (Table 2). The peak separation of each S 2p peak is about 0.92 and 1.06 eV. The peaks at 161.12 and 163.06 correspond to the 2p_{3/2} core level and correspond to S-C and S=C, respectively. The O 1s spectrum shows a broad peak centered at 530 eV with a FWHM = 2.9 eV, being in accord with the presence of more than one species. Gaussian deconvolution of O 1s spectrum shows two peaks at 530.1 and 531.3 eV (Table 2) which were assigned to a O-C and O=C moieties, respectively. Ketoenolate resonance is proved by the presence of these peaks and the same intensity of both gives further evidence of π -delocalization on the chelated ring.

3.2. Preparation of 2. One-dimensional coordination polymer was obtained in a straightforward process, from the synthesis of **1** and bpy in chloroform media. The color change from orange to light yellow was the initial evidence of its presence. The FTIR spectrum of **2** shows the signals associated with bpy bridge at 2954, 1575, 1483, 1375, and 625 cm⁻¹ towards low wavenumbers respecting the free ligand, due to the nickel coordination. The vibrational energy decreases, probably due to the slight electron density from the σ -donation of the bpy. When the UV-vis spectra of **1** and **2** in CHCl₃ were compared (Figure 1), both of them contain the same bands with a general hypochromic effect on the former, associated with the coordination of the bpy molecule. The main changes were in the visible region with a blue shift of LMCT band at 379 nm, respecting those of **1** (383 nm). The slight decrement of the LMCT energy comes

FIGURE 3: Absorption spectra of **1** and **2** by Diffuse Reflectance spectroscopy; *systematic signals associated with the nature of the spectrophotometer.

from the minor molecular orbital energy associated with the metal center, from the pyridine coordination. The solid spectrum shows a notable difference respecting precursor (Figure 3). The band LMCT at 459 nm is notably red shifted from **1** (449 nm), similar to similar systems [23]. Three more bands were observed at 571, 886, 922 and 955 nm, which were assigned to the transitions ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}(\nu_1)$, ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}(\nu_2)$, and ${}^3T_{2g}(F) \leftarrow {}^3A_{2g}(\nu_3)$, respectively, in an octahedral environment around the nickel ion [24–28], due to the coordination of two bipyridyl molecules.

The XPS spectrum of **2** (Table 2) shows the decrease on S 2p binding energies respecting **1** complex (Table 2) due to the small nuclear effective charge of the sulfur atom with bpy coordination. The 2p_{3/2} nickel signal shows a slight increase on BE with bpy coordination; this might be due to a decrease of its electron density. These facts could be related to the π -back donation of nickel to S-donor ligand, for the N-donor ligand, attached to metal center.

No crystals of **1** and **2** suitable for single crystal were obtained, but PXRD analyses were performed. The powder pattern of **2** has a different phase than those observed for bpy and **1** (Figure 4) confirming a new phase, different to those. The diffractogram of **1** shows broader peaks, probably due to a less ordered solid, than those narrow peaks of **2**, which could be associated with a higher ordered solid structure.

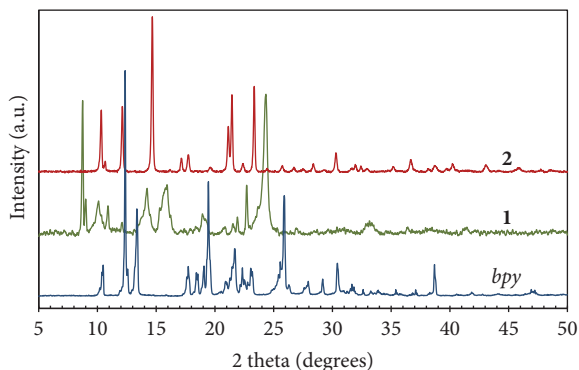


FIGURE 4: X-ray powder diffractograms of **1** and **2**. The mixture of **1** and **bpy** phases is not observed in the polymer diffraction pattern.

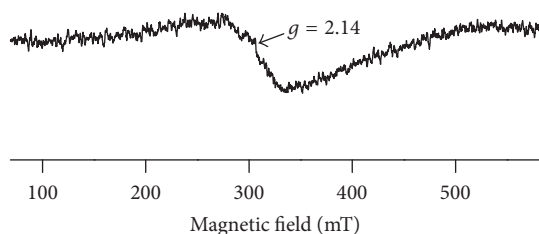


FIGURE 5: ESR spectra at 300 K of powdered sample of **1**.

The ESR analysis of **2** displays a broad singlet centered at $g = 2.14$ (Figure 5), corresponding to a paramagnetic center of nickel(II) [29, 30]. The line shape of the wide spectrum is associated with Ni (II) centers with $s = 1$ [31] and magnetic interactions among them are present [32]. Wide endings of the spectrum show that the interactions are present even before applying the magnetic field and at higher frequencies than the allowed for the ESR spectrometer.

The polymeric structure of **2** was confirmed by its magnetic behavior. Figure 6 shows the temperature dependence of magnetic susceptibility of **2** at 1000 Oe applied field. The values of magnetic susceptibility slightly increase with the decrease of the temperature, from 300 to 34 K. The magnetization is drastically enhanced below 30 K, showing a tendency towards a lower antiferromagnetism at lower temperatures. The magnetization at high temperatures strongly agrees with Curie-Weiss law, as could be seen in $1/\chi$ versus T curve (Figure 6) [33]. The fitting result has $\theta = -99$ K and $C = 0.375$ K mol⁻¹ values. The negative value of θ suggests an antiferromagnetic behavior of **2**. A J value was calculated through the Weiss constant using the molecular-field theory (MFT) [33], affording an average coupling constant $J = -8.63$ cm⁻¹, when $s = 1$ and $z = 6$ (coordination magnetic number) were used.

The temperature dependence of the effective magnetic moment (Figure 7) shows at 300 K a value of $\mu_{\text{eff}} = 1.52 \mu_B$, which is lower than those spin only values calculated for $s = 1/2$ ($1.73 \mu_B$) and $s = 1$ ($2.83 \mu_B$), confirming the antiferromagnetic behavior of the polymer. The value of μ_{eff} decreases linearly as the temperature decrease up to ~ 35 K. At this point, μ_{eff} increases with temperature, up to a maximum

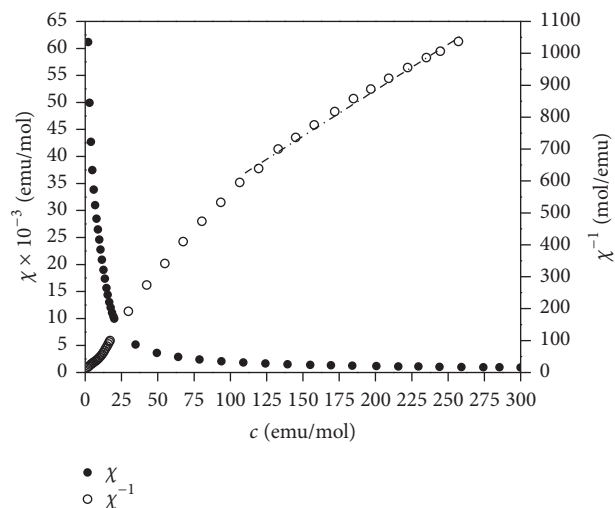


FIGURE 6: Temperature dependence of χ for **2** (filled circles) and Curie plot (open circles) with the best fit to Curie-Weiss law (dotted line) at 1000 Oe applied field.

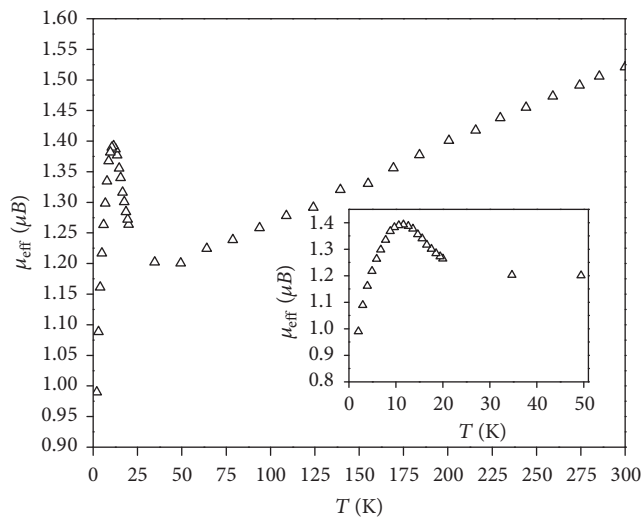


FIGURE 7: Effective magnetic moment (μ_{eff}) versus T for **2** at a magnetic field of 1000 Oe.

at ~ 12 K decreasing at the lowest temperatures. This is a typical antiferromagnetic exchange behavior with a Neel temperature at 12 K.

4. Conclusions

The coordination compound **1** was obtained following the reported methodology. The spectroscopy characterization allows us to propose in a square planar conformation, feasible to prepare a 1D coordination polymer bridging by **bpy**. The complex shows electron delocalization over the chelated ring and a diamagnetic behavior, as seen in XPS analyses. The straightforward synthesis of the polymer yields a compound with different physicochemical and structural properties than initial complex. In solution compared to in solid state, the CP was stable, and the solid has a different phase than the

precursor complex. The paramagnetism of **2** is established at $T > 100$ K. These results aim to propose the bridge of bipyridyl molecules within **1**, confirming the presence of a 1D coordination compound. Importantly, further crystallization techniques are in progress to confirm the molecular structure of the polymers **1** and **2**.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this article.

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