Two coordination polymers containing the dicyanamide ligand: synthesis, crystal structures, and HFEPR studies

Lívia B. L. Escobar^{a,b}, Charlane C. Corrêa^a, Guilherme P. Guedes^c, Maria G.F. Vaz^b
Samuel M. Greer^{d,e}, Stephen Hill^{d,f}, Renata Diniz^a, Flávia C. Machado^{a,*}

^aDepartamento de Química, Universidade Federal de Juiz de Fora, Campus Universitário s/n, Martelos, Juiz de Fora, MG 36036-900, Brazil

^bInstituto de Química, Universidade Federal Fluminense, Niterói – RJ, 24020-150, Brazil

^cInstituto de Ciências Exatas, Departamento de Química, Universidade Federal Rural do Rio de Janeiro, Seropédica – RJ, 23.890-000, Brazil.

^dNational High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32310, United States.

^eDepartment of Chemistry, Florida State University, Tallahassee, FL 32306, United States.

^fDepartment of Physics, Florida State University, Tallahassee, FL 32306, United States.

* Corresponding author. Tel.: +55 32 21023310; fax: +55 32 21023314.

E-mail address: flavia.machado@ufjf.edu.br (F.C. Machado).

Abstract

Two new compounds [Ni(dca)₂(dmdpy)] (**1**) and [Zn(dca)₂(dmdpy)] (**2**), (dca = dicyanamide and dmdpy = 5,5'-dimethyl-2,2'-dipyridine) were synthesized and characterized by single crystal X-ray diffraction, FTIR and thermal analysis. In both compounds, the dmdpy ligand adopts a bidentate chelating coordination mode while dca anions act in a $\mu_{1,5}$ bridging fashion. In **1**, the Ni^{II} centers lie on a distorted octahedral geometry, whereas in **2** the Zn^{II} geometry is distorted square pyramidal. In compounds **1** and **2**, dca ligands connect the metal sites giving rise to 2D and 1D coordination polymers, respectively. The magnetic properties of **1** were studied by magnetic susceptibility and high field/frequency electron paramagnetic resonance (HFEPR) measurements.

Keywords: Coordination polymers, crystal structure, magnetic properties.

1. Introduction

Recently, the construction of supramolecular systems of metal–organic frameworks and coordination polymers has been a subject of significant interest.[1] The realm of crystal engineering has consequently achieved great success in the assembly of such systems. In addition to the resultant crystalline materials having diverse structures these materials display useful properties in gas storage, catalysis, ion exchange, optical, electric and molecular magnetism.[2-4]

The design, synthesis, and structural characterization of coordination polymers have been intensely investigated over the past two decades.[4, 5] Common spacers used for the connection of transition metals to polymeric structures include cyanides, azides, cyanates, thiocyanates, selenocyanates, dicyanamides, tricyanomethanides, N-heterocyclic auxiliary

ligands together with related anionic ligands such as tetracyanoethanide or tetracyanoquinodimethanide and many others.[6, 7]

It was proved that pseudohalides could behave as bridging ligands connecting transition metals to give complexes with various topological structures, including isolated molecular clusters, 1D chains, and 2D or 3D networks.[8, 9] Another advantage of using this ligand's family as spacers is their ability to effectively transmit magnetic coupling between the spin carriers through the delocalized *p*-bond skeleton of the bridging unit.[6]

In particular, the cyano group has been used extensively as a versatile mediator for magnetic coupling in molecule-based magnets.[10] The larger pseudohalide ligand dicyanamide (dca) has three potential nitrogen-donor sites and coordinates to metal ions in various modes (see Scheme 1). These different coordination modes allow for the preparation of compounds with various molecular architectures including mono- and polynuclear systems, as well as one-, two- and three-dimensional networks.[5, 11, 12]

Herein, we report the syntheses and crystal structures of two coordination polymers, $[\text{Ni}(\text{dca})_2(\text{dmdpy})]_n$ (**1**), and $[\text{Zn}(\text{dca})_2(\text{dmdpy})]_n$ (**2**). Compound **1** is isostructural to the $[\text{Co}(\text{dca})_2(\text{dmdpy})]_n$ described by us previously.[13] In the present work, we used HFEPR spectroscopy to characterize the magnetic anisotropy of **1**.

Scheme 1- Coordination modes of the dca ligand.

2. Experimental

2.1. Materials and methods

Analytical grade solvents and reagents were purchased from commercial sources and used without further purification. The elemental analyses (CHN) were carried out on a Perkin-Elmer 2400 Series II analyzer. Infrared spectra were recorded on a FT-IR Bomen MB102 spectrometer in the frequency range $4000\text{--}400\text{ cm}^{-1}$ with an average of 128 scans and 4 cm^{-1} of spectral resolution using KBr pellets. Thermal analysis (TG/DTA) for **1** and **2** were performed

using a TA instruments SDT Q600 using nitrogen gas purge atmosphere at 50 mL min⁻¹ and a heating rate of 10 °C min⁻¹ in a range from 25 to 1000 °C.

Single crystal X-ray data were collected using an Oxford GEMINI A Ultra diffractometer with Mo K α (λ = 0.71073 Å) radiation at room temperature (298 K). Data collection, reduction, and cell refinement were performed using the CrysAlis RED program, Oxford diffraction Ltda – Version 1.171.32.38.[14] The structures were solved and refined using SHELXS-97 and SHELXL-97 packages.[15] An empirical isotropic extinction parameter x was refined according to the method described by Larson;[16] a multiscan absorption correction was applied.[17] The structures were drawn by VESTA[18] and Mercury[19] programs. Details of data collection and structure refinement for compounds **1** and **2** are summarized in Table 1.

Magnetic measurements were performed on a Cryogenic SX-600 SQUID magnetometer in the range from 2–290 K with an applied field of 0.1 T. The samples were placed in a gelatin capsule and data were corrected for the diamagnetism and sample holder.

High-field, high-frequency EPR measurements were carried out at the National High Magnetic Field Laboratory(NHMFL), in Tallahassee, Florida. Spectra were collected on a constrained powder of **1** over a temperature range of ca. 5K to 30 K. The spectrometer is a transmission-type device in which microwaves are propagated through cylindrical light pipes.[20] The microwaves were generated by a phase-locked Virginia Diodes source along with a series of frequency multipliers. A superconducting magnet (Oxford Instruments) capable of reaching a field of 17 T was employed.

2.2. Synthesis

[Ni(dca)₂(dmdpy)]_n (1). A methanolic solution (5 mL) of NaN(CN)₂ (0.79 mmol) was added dropwise to an aqueous solution of Ni(NO₃)₂·6H₂O (0.39 mmol). Dmdpy (0.27 mmol) dissolved in MeOH (5 mL) was slowly added to the reaction mixture. Two days later blue single crystals were obtained and collected by filtration. Yield: 38 %. Anal. Calc. for C₁₆H₁₂N₈Ni: C, 51.2; H, 3.2; N, 29.8 %. Found: C, 50.3; H, 3.2; N, 28.6 %. IR (KBr, cm⁻¹): $\nu_{as} + \nu_s(\text{C}\equiv\text{N})$ 2310; $\nu_{as}(\text{C}\equiv\text{N})$ 2255; $\nu_s(\text{C}\equiv\text{N})$ 2219, 2187; $\nu_{CC/CN}$ 1608, 1574, 1504, 1479; $\nu_{as}(\text{C-N})$ 1365 and $\nu_s(\text{C-N})$ 927.

[Zn(dca)₂(dmdpy)]_n (2). This compound was synthesized as described for compound **1** except for the use of ZnCl₂ (0.39 mmol). Two days later colorless crystals were obtained and collected by filtration Yield 35%. Anal. Calc. for C₁₆H₁₂N₈Zn: C, 50.3; H, 3.2; N, 29.4%. Found: C, 50.2; H, 3.1; N, 29.2%. IR (KBr, cm⁻¹): $\nu_{as} + \nu_s(\text{C}\equiv\text{N})$ 2338; $\nu_{as}(\text{C}\equiv\text{N})$ 2258; $\nu_s(\text{C}\equiv\text{N})$ 2227, 2182; $\nu_{CC/CN}$ 1609, 1581, 1484; $\nu_{as}(\text{C-N})$ 1347; and $\nu_s(\text{C-N})$ 929.

3. Results and discussion

3.1. General Characterization

IR spectra (Fig. S1 in the supplementary material) exhibit dca stretching vibrations for **1** and **2** as strong absorptions in the region 2182–2227 cm^{-1} and two medium to strong absorptions in the range of 2255–2260 cm^{-1} and 2283–2310 cm^{-1} , which are attributed to $\nu_s(\text{C}\equiv\text{N})$, $\nu_{as}(\text{C}\equiv\text{N})$ and $\nu_{as} + \nu_s(\text{C}\equiv\text{N})$ modes, respectively. The shifts towards higher frequency values, when compared to the free dca ligand (2170, 2232 and 2286 cm^{-1}) are presumably due to the bidentate bridging ($\mu_{1,5}$) coordination mode of the pseudohalide.[21–23] Bands corresponding to $\nu_{as}(\text{C}-\text{N})$ and $\nu_s(\text{C}-\text{N})$ stretching frequencies are found in the ranges 1365–1392 and 927–929 cm^{-1} , respectively. The presence of bands in the region 1608–1479 cm^{-1} is assigned to $\nu(\text{CC/CN})$ of dmdpy ligand pyridyl rings. These bands were shifted to larger frequencies when compared to the free ligand (1590–1490 cm^{-1}) indicating the pyridyl coordination toward the metal centers.

In order to examine thermal stabilities of **1** and **2**, thermogravimetric and differential thermal analyses (TG/DTA) were carried out in dynamic nitrogen atmosphere. TG/DTA curves (Fig. S2 in the supplementary material) indicate that compounds **1** and **2** are stable up to 329 and 216 $^{\circ}\text{C}$, respectively. Above these temperatures thermal decomposition of the complexes occurs gradually in several steps through endothermic and exothermic events. In the case of compound **1**, the percentage residue (Exp., 23.1 %, Calc., 20,4 %) agrees with metallic nickel and carbonized material. The percentage residue (28.2 %) at 900 $^{\circ}\text{C}$ for compound **2** indicates an incomplete decomposition at this temperature.

Table 1- Crystallographic data for [Ni(dca)₂(dmdpy)]_n (**1**) and [Zn(dca)₂(dmdpy)]_n (**2**).

Compound	[Ni(dca) ₂ (dmdpy)] _n	[Zn(dca) ₂ (dmdpy)] _n
Formula	C ₁₆ H ₁₂ NiN ₈	C ₁₆ H ₁₂ Zn N ₈
Formula weight (g mol ⁻¹)	375.05	381.71
Crystal system	Orthorhombic	Triclinic
Space group	Pccn	P-1
Unit cell dimensions		
a (Å)	8.1716(2)	7.5469(3)
b (Å)	12.3047(2)	9.3700(3)
c (Å)	17.6924(4)	12.8380(4)
α (°)	90.00	101.219(3)
β (°)	90.00	102.340(3)
γ (°)	90.00	104.515(3)
V (Å ³)	1778.95(7)	828.47(5)
Z	4	2
Crystal size (mm)	0.605 x 0.260 x 0.154	0.315 x 0.259 x 0.066
dcalc (g cm ⁻³)	1.400	1.530
μ(Mo Kα) (cm ⁻¹)	1.106	1.499
T _{min} /T _{max}	0.872 / 1.000	0.954 / 1.000
Measured reflections	76216	18030
Unique reflections	1825	3384
Observed reflections ^a	1416	2617
No. parameters	115	226
R ^b	0.0367	0.0452
wR ^a	0.0949	0.0985
S	1.107	1.067
RMS peak (e Å ⁻³)	0.061	0.072

^a [$F_o^2 > 2\sigma F_o^2$]^b [$F_o > 2\sigma F_o$]

3.2. Structure descriptions

It was possible to observe that the use of the Ni^{II} ion favors the formation of a 2D coordination polymer, whilst the use of Zn^{II} contributes to obtaining a 1D coordination polymer (scheme 2).

Scheme 2- Formation of the coordination polymers according to the use of the metal ion.

A fragment of the crystal structure of **1** is shown in Figure 1a. Each Ni^{II} center is coordinated to six nitrogen atoms from one dmdpy ligand (N1 and N1ⁱ) and four dca ligands N2, N2ⁱ, N3ⁱⁱ and N3ⁱⁱⁱ in a distorted octahedral geometry. The dmdpy ligand is coordinated to the metal site in a bidentate chelate mode while the dca ligand acts in a bidentate $\mu_{1,5}$ bridge fashion. A tetragonal distortion is evidenced by bond distances values Ni1-N1 (2.092(2) Å), Ni1-N2 (2.075(2) Å) and Ni1-N3 (2.062(3) Å) [symmetry codes: *i*(1-x,y,1.5-z); *ii*(1-x,1-y,1-z) and *iii*(x,1-y,0.5+z)]. The bond distances are typical for coordination compounds containing dca and dmdpy ligands.[24] No clear distinction can be made between distance distortions (Table 2). The N–Ni–N angles range from 78.14(9) to 94.51(10)^o when the nitrogen atoms are neighbors in the octahedron and are all less than 180^o (when the nitrogen atoms are on opposite summits of the octahedron). Nevertheless, two groups of angles can be distinguished: when two nitrogen atoms are connected by a two-carbon-atom bridge from the dmdpy ligand, the corresponding N1ⁱ–Ni–N1 angle is small (78.14 (9)^o) and, for independent nitrogen atoms (no direct carbon link), the angles are larger (94.51(10)^o). These values demonstrate that the chelating power of the equatorial N–C–C–N of the dmdpy ligand group leads to smaller angles and to a contraction of the octahedron along the C₂ axis of the molecule.

Table 2- Selected bond lengths and angles for (**1**).

Bond lengths (Å)		Angle(°)	
Ni1-N1	2.092(2)	N1-Ni1-N1 ⁱ	78.14(9)
Ni1-N2	2.075(2)	N1-Ni1-N3 ⁱⁱ	94.51(10)
Ni1-N3 ⁱⁱ	2.062(3)	N3 ⁱⁱ -Ni1-N3 ⁱⁱⁱ	92.86(11)
Ni1-N1 ⁱ	2.092(2)	N1 ⁱ -Ni1-N3 ⁱⁱⁱ	94.51(10)
Ni1-N2 ⁱ	2.075(2)	N2-Ni1-N2 ⁱ	179.33(10)
Ni1-N3 ⁱⁱⁱ	2.062(3)		
Ni1...Ni ⁱⁱⁱ	8.035(2)		

The dca ligands connect the Ni^{II} sites through single bridges along two directions giving rise to a 2D undulated polymeric sheets (Figure 1b). The Ni...Ni distance across the $\mu_{1,5}$ -dca bridges is 8.0353(2) Å. By the comparison of this coordination polymer with similar compounds described in the literature, for example, the polymers containing the dca and 2,9-dimethyl-1,10-phenantroline ligands published by D. Armentano and coworkers[25] as well as T. Liu and coworkers[26], it is possible to highlight that the ancillary ligand leads to the formation of different networks depending on the position of the methyl substituent position. They observed that the introduction of the methyl substituents ortho to the nitrogen atoms results in the formation of a (6,3) grid. In the present work, if we consider the metal sites as nodes and dca ligands as connectors, the undulated rhombic sheet is topologically described as (4,4) grid. In addition, the values of the M...M distances through the single dca bridge is close to the reported values in the cited references. Finally, short CH... π contacts between dmdpy ligand methyl

group hydrogen atoms and adjacent pyridine rings, with a distance of 2.852 (4) Å, contributed to the stabilization of the crystal packing.

Fig. 1- (a) Fragment of the crystal structure of **1**. Symmetry codes: $i(1-x, y, 1.5-z)$; $ii(1-x, 1-y, 1-z)$ and $iii(x, 1-y, 0.5+z)$. (b) 2D polymer network. Hydrogen atoms are omitted for clarity.

Figure 2a shows a fragment of the crystal structure of **2**. The zinc ion is coordinated by two nitrogen atoms from one dmdpy ligand and by three nitrogen atoms from three dca ligands. Selected bond lengths and angles are listed in Table 3.

Table 3- Selected bond lengths and angles for **2**.

Bond lengths (Å)		Angle(°)	
Zn1-N1	2.117(3)	N1-Zn1-N2	76.55(10)
Zn1-N2	2.140(3)	N1-Zn1-N5 ⁱ	89.25(12)
Zn1-N3	2.014(3)	N2-Zn1-N4	91.13(13)
Zn1-N4	2.041(4)	N4-Zn1-N5	91.13(15)
Zn1-N5 ⁱ	2.086(4)	N3-Zn1-N1	103.36(13)
		N3-Zn1-N2	105.62(12)
		N3-Zn1-N4	101.33(15)
		N3-Zn1-N5 ⁱ	102.74(13)

[symmetry codes: $i(-1+x, y, z)$]

The coordination geometry adopted by the Zn^{II} ion is distorted square pyramidal as indicated by the angular structural parameter,[27] $\tau = 0.03$. As it was observed for **1**, the dmdpy ligand is coordinated to the metal site in a bidentate chelate mode. This coordination environment, as well as the values of the bond lengths, can also be found in other structures, including a very similar compound described by D. Mal and coworkers.[28-31]

The two independent dca ligands exhibit different coordination modes: monodentate and through a bidentate $\mu_{1,5}$ bridge fashion. This ligand connects the Zn^{II} sites along the crystallographic axis b giving rise to a 1D coordination polymer (Figure 2b). π stacking interactions between the dmdpy pyridine rings from interdigitated polymers with a centroid-to-centroid distance of 3.845(14) Å are observed in the crystal packing.

Fig. 2- (a) Fragment of the crystal structure of **2**, symmetry code $i(-1+x, y, z)$. (b) 1D polymer network. Hydrogen atoms are omitted for clarity.

One of the reasons to obtain two coordination polymers with different dimensionalities is the fact that the Zn^{II} ion has a completely filled $3d$ orbital. A metal ion with a d^{10} electronic configuration has no ligand field stabilization energy. As a consequence, Zn^{II} can easily attain variable coordination numbers.[31]

4. Magnetic properties

The thermal dependence of the $\chi_{\text{M}}T$ product for **1** is shown in Figure 3. The $\chi_{\text{M}}T$ value at 230 K is $1.05 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, close to that calculated for a magnetically isolated Ni^{II} ion with $g=2.00$ ($1.00 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$). This value remains constant from 230 to 30 K indicating paramagnetic behavior in this temperature range. Upon cooling, the $\chi_{\text{M}}T$ value decreases to a minimum of $0.854 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2.5 K which can be attributed to antiferromagnetic interactions and/or zero-field splitting (ZFS). The χ_{M}^{-1} versus temperature plot can be fitted to the Curie-Weiss law, leading to $C = 1.05 \text{ emu.mol}^{-1}$ and $\theta = -0.10 \text{ K}$ (Figure 3a and blue solid curve Figure 3b).

Fig. 3– a) χ_M^{-1} data as a function of temperature fitted to the Curie-Weiss law (solid line). b) Thermal dependence of the $\chi_M T$ product for compound **1**. The blue solid curve corresponds to the fit considering only the Curie-Weiss law and the red solid curve is the best fit of experimental data considering the ZFS anisotropy described by eq 1 with the mean field approximation described by eq 2.

The small Weiss constant value is due to the large distance between Ni^{II} ions in the 2D polymer, and the magnetic properties are best rationalized as arising from an isolated Ni^{II} ion. Despite the fact that the magnetic data can be fitted to the Curie-Weiss law, the quality of the fit improves significantly by the inclusion of ZFS, D , as shown in Figure 3b (red solid curve). Therefore, in order to reproduce the experimental data, we employ a model where we treat the on-site anisotropy by the spin Hamiltonian shown in equation (1), then we additionally include the mean field approximation in order to account for the magnetic coupling from nearby Ni^{II} ions,[32] as shown in equation (2).

$$\hat{H} = g\mu_B \vec{B} \cdot \hat{S} + D \hat{S}_z^2 \quad (1)$$

Here the first term represents the electronic Zeeman interaction and the last term defines the ZFS.

$$\chi_m = \frac{N\beta^2 g^2}{3kT} S(S+1) \quad \chi_m^{\text{MF}} = \frac{\chi_m}{1 - zJ'\chi_m} \quad (2)$$

Here z is the number of nearest neighbors around a given magnetic molecule in the crystal lattice, and J' is the interaction parameter between two nearest neighbors.

The fit of the magnetic data was performed with the MagProp routine, available under DAVE software.[33] The red solid line in Figure 3b shows the best fit curve for compound **1** found with $g = 2.05$, $D = +2.22 \text{ cm}^{-1}$ and the mean field parameter $\lambda = -0.26 \text{ emu/mol}$. The intermolecular magnetic interaction zJ' is related to λ and can be estimated by equation (3).

$$\lambda = \frac{zJ'}{g^2 \mu_B^2} \quad (3)$$

The calculated zJ' value is -0.23 cm^{-1} , this value is indicative of very weak antiferromagnetic interactions between adjacent Ni^{II} ions. In the present structure, the large Ni...Ni separation across the $\mu_{1,5}$ -dca bridges ($8.035(2) \text{ \AA}$) leads to the observed magnetic behavior. This shows the poor ability of the dca bridge to mediate magnetic interactions between the spin carriers when adopting the $\mu_{1,5}$ bridging mode.

As was mentioned in the crystal structure description, there is a compression of the octahedron in **1** that can be the origin of the positive D value observed in the magnetic properties. The data are similar to those observed in other Ni^{II} -dca coordination polymers.[7, 12]

It is well known that the susceptibility measurements provide only an average value of the g -factors, and the accuracy of this bulk technique in determining spin Hamiltonian parameters in general, and ZFS in particular, is inferior to that of EPR, a spectroscopic technique.[34] Therefore, high-field, high-frequency Electron Paramagnetic Resonance (HF-EPR) measurements were performed in order to accurately characterize the g -factors and confirm the ZFS parameters of the Ni^{II} ion in **1**.

5. EPR measurements

In the O_h point group Ni^{II} displays an orbitally non-degenerate $^3A_{2g}$ ground state with excited orbital-triplet terms, $^3T_{2g}(F)$, $^3T_{1g}(F)$, $^3T_{1g}(P)$. Spin-orbit coupling permits mixing of the $^3T_{2g}$ state into the ground term, but does not lift the spin degeneracy. However, lowering the point-group symmetry from O_h causes this admixture to be different for each component of the spin-triplet, resulting in ZFS. The magnitude and sign of the axial 2nd order ZFS parameter, D , depends on the splitting of the $^3T_{2g}$ term, but is inversely proportional to its separation from the ground state. A consequence of these two factors is that the ZFS is highly sensitive to the coordination geometry. The form of the observed spin-triplet ($S = 1$) EPR spectrum depends on the magnitude of the ZFS compared with the applied microwave frequency. [35]

Frequency and temperature dependent studies (50.8–204.8 GHz, 5–30 K) were performed. A representative spectrum recorded at 204.8 GHz and 5 K is displayed in Figure 4a.

Fig.4-a) High-field powder EPR spectrum (in black) recorded at 204.8 GHz and $T = 5$ K, for **1**. The simulated spectrum (in red) is displayed below the experimental one. The peaks marked by (♦ and *) correspond to the double quantum transitions (see main text for explanation). **b)** Temperature-dependent powder EPR spectra collected from 5 to 30 K at 204.8 GHz for **1**.

Most of the resonances observed in the EPR spectrum at 204.8 GHz in Figure 4 can be interpreted as allowed EPR transitions ($\Delta m_s = \pm 1$) within the triplet state, with the exception of the peaks around 3.16 T (marked by ♦) and 6.04 T (marked by *); these are explained further below.

The spectral simulation was performed using EasySpin[36] and is included below the experimental spectrum in figure 4a). The Hamiltonian described by Eq. (4) was considered:

$$\hat{H} = g\mu_B \vec{B} \cdot \hat{S} + D \hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2) \quad (4)$$

The best simulation was achieved using the following parameters: $D = +2.23 \text{ cm}^{-1}$, $E = 0.55 \text{ cm}^{-1}$, $g_x = 2.02$, $g_y = 2.02$, and $g_z = 2.36$. The parameters considered in the simulation are in the range observed for other octahedral Ni^{II} complexes reported in the literature.[9, 35,37-39] The D parameter agrees well with the magnetic measurements.

Based on the temperature dependence (Figure 4b) and Zeeman diagram (Figure S3) it is possible to observe strong resonances at 5.11, 6.76 and 8.19 T, corresponding to excitations from the ground state ($m_s = -1$ to 0) for $B//y$, x and z , respectively; here m_s represents the projection of the spin, S , onto the axis defined by the applied (high) field. Meanwhile, the weaker resonances at 4.15, 7.41 and 9.25 T are assigned to transitions from the excited state ($m_s = 0$ to +1), for $B//z$, x and y , respectively. This unambiguously indicates that the D parameter is positive.

Finally, we explain the two sharp features marked by ($\blacklozenge$ and $*$). The resonances (multiple overlapping peaks) clustered around 3.16 T (marked by $\blacklozenge$) correspond to normally forbidden double quantum transitions ($m_s = -1$ to $+1$) that are allowed in the present case due to the rhombic anisotropy, E , that mixes the $m_s = \pm 1$ spin sub-levels, giving rise to parallel-mode excitations (we note that the microwaves are not precisely polarized in the employed spectrometer). Meanwhile, the sharp peak observed at 6.04 T corresponds to a two-photon transition involving all-three triplet levels. Such two-photon transitions are often observed in octahedral Ni^{II} compounds [9, 35, 37] and are not accounted for in the EasySpin simulations. They occur for certain orientations of the applied field at which the triplet states are equidistant in energy (harmonic). Based on the best simulation parameters, the position of this peak is well reproduced.

4. Conclusion

We reported the synthesis, characterization and crystal structure of two new coordination polymers containing the 5,5'-dimethyl-2,2'-dipyridine ligand, dicyanamide anion and transition metals Ni^{II} and Zn^{II} . Compounds **1** and **2** are 2D and 1D coordination polymers, respectively. The magnetic properties of **1** were investigated by susceptibility measurements and very weak antiferromagnetic interactions were observed between the Ni^{II} ions. The ZFS parameters of the Ni^{II} ion in **1**, as well as its g-tensor, were characterized by HFEPR measurements.

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Graphical Abstract- Synopsis

Two new compounds [Ni(dca)₂(dmdpy)] (**1**) and [Zn(dca)₂(dmdpy)] (**2**), (dca = dicyanamide and dmdpy = 5,5'-dimethyl-2,2'-dipyridine) were synthesized and characterized by single crystal X-ray diffraction, FTIR and thermal analysis. In both compounds, the dmdpy ligand adopts a bidentate chelating coordination mode while dca anions act in a $\mu_{1,5}$ bridging fashion. The magnetic properties of **1** were studied by magnetic susceptibility and high field/frequency electron paramagnetic resonance (HFEPR) measurements.