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Review

Recent Insights into Magneto-Structural Properties of Co(II) Dicyanamide Coordination Compounds †

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† This article was originally going to be dedicated to the distinguished scientists and my friends Miguel Julve and Francesco Lloret on their retirement. When this article was almost ready for submission to Magnetochemistry, I learned of the tragic news of the death of my dear friend Miguel, an outstanding scientist, internationally recognized for his invaluable contributions to coordination chemistry and molecular magnetism, with a great enthusiasm for science and a bright personality. I dedicate this article to his blessed memory. You will live on in our memory, dear Miguel.

Abstract: In recent decades, the chemistry of transition metal coordination compounds has undergone continuous development at both scientific and application levels. The diversity of metal(II) complexes, along with their structural features and physicochemical properties, makes them attractive for a wide range of applications. The dicyanamide ion ($N(CN)_2$) has the ability to form various transition metal compounds characterized by different architectures and topologies. The interaction of π-electrons from the nitrile groups with the π-system of the central nitrogen may enable electron delocalization, potentially facilitating electron transfer between the metal centers through the bridging dicyanamide (dca) ligand. This review focuses on dca–Co(II) compounds and, after a brief introduction, the structural aspects and magnetic properties are analyzed in detail.

Keywords: cobalt(II) complexes; dicyanamide ion; coordination polymers; structural studies; magnetic properties

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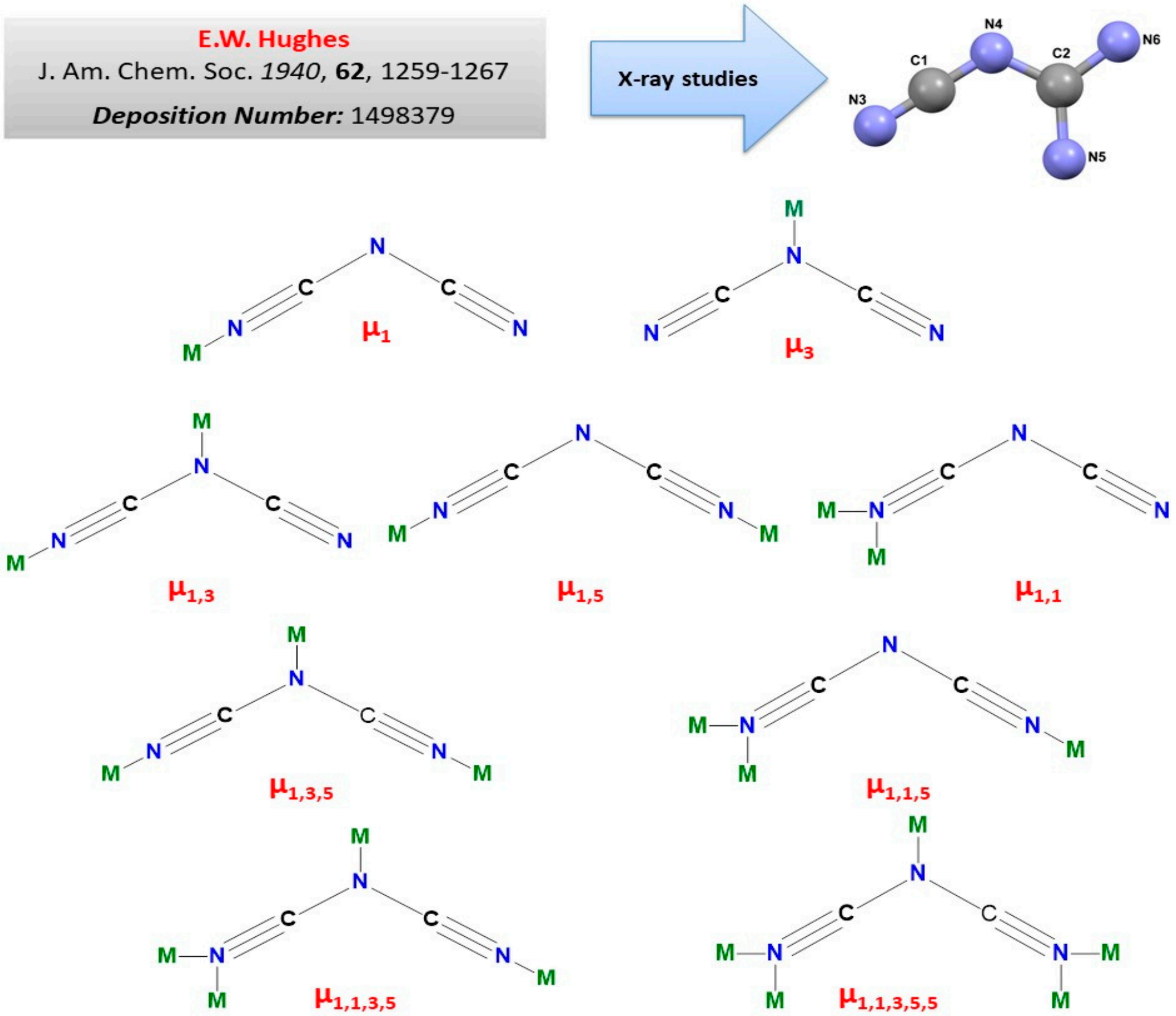
1. Introduction

Before dicyanamide (cyanoguanidine, $N(CN)_2^-$, dca) gained popularity in supramolecular architecture and crystal engineering, it was primarily employed in a completely different branch of chemistry. This popular, versatile ligand was used as an effective nitrification inhibitor, helping to reduce leaching losses by retaining applied nitrogen in the ammoniacal form [1]. It has been proven that the addition of *dca* to ammonium or urea salt increased the yields of crops including rice, wheat and citrus trees [1]. Dicyanamide was also successfully tested in hydrophobic ionic liquids (ILs) for efficient extraction of Cu(II), Ni(II), Pb(II) and Cd(II) from water [2]. Regardless of its initial applications, the boomerang-shaped dicyanamide anion is widely known as an effective linker between 3d and 4d metal ions, making it perfect for the design and construction of coordination polymers (CPs) with different frameworks and topologies. Importantly, dicyanamide–metal coordination compounds have demonstrated significant diversity in the application horizon in the fields of molecular sensors, electrical conductivity, non-linear optical activity (NLO), catalysis, molecular magnetism, microporous materials for gas adsorption and storage [3–12].

Preliminary studies of the first compounds of the formula $[M(dca)_2]$ (M = Cu(II), Hg(II), Pb(II) were performed by Madelung and Kern in 1922, and later were continued by Köhler and Hvastijová [13–15]. Shortly thereafter, in 1940, E. W. Hughes made a successful attempt to determine the crystal structure of dicyanamide by confronting other proposed structures of this compound (Deposition Number: 1498379) [16]. Many of these early complexes have been re-investigated using modern X-ray analysis methods. The dca^- geometry favors the action of the anion as a terminal or bridging ligand, and prevents the formation of chelated coordination species. In homo- or heteronuclear complexes, the dicyanamide anion has been shown to be a versatile ligand and can bind two to five metal ions in a variety of ways, either through its terminal nitrile nitrogen group(s), the central amide nitrogen, or both. These possible coordination modes have been illustrated in Scheme 1. In the literature, various naming conventions have been used for dca coordination modes. Following the most common notification, the form $\mu_{x,y,z}$ will be used, where x, y and z are represent the nitrogen atoms which are coordinating with Co(II) ion(s). The dca ligand can have the values of 1, 3 or 5, where 1 or 5 are assigned to a nitrile nitrogen atom, while 3 is attributed to an amide nitrogen atom. However, for the sake of thoroughness, an alternative notation will also be discussed below.



Scheme 1. Coordination modes of dicyanamide ligand [16].

The coordination bonding modes of dca^- with divalent metal(II) ions in most compounds are primarily established through its two terminal N-nitrile groups (μ_1) or through less common central amide nitrogen (μ_3), or through both. The most common coordination modes of the dicyanamide ion in coordination polymers are $\mu_{1,5}$ (*end-to-end*, *EE*) and $\mu_{1,1}$ (*end-to-on*, *EO*). Other bonding modes such as μ-$_{1,1,5}$, μ-$_{1,3,5}$, μ-$_{1,1,3,5}$ or μ-$_{1,1,3,5,5}$ have also been isolated and structurally studied [17,18]. Other possibilities of impossible notations for the bridging dca ion include bidentate μ_2-bonding ($\mu_{1,5}$, $\mu_{1,3}$ and $\mu_{1,1}$), μ_3-bonding for μ-$_{1,1,5}$ and μ-$_{1,3,5}$, μ_4-bonding for μ-$_{1,1,3,5}$ and finally μ_5-bonding for μ-$_{1,1,3,5,5}$. In the literature, the letter "*η*" is sometimes used instead of "μ". Typically, the "*η*" denotes coordination involving more than one bridging atom; therefore, notations such as μ-$_{1,3,5}$, μ-$_{1,1,3,5}$ or μ-$_{1,1,3,5,5}$ can be alternatively written as η^3-1,3,5, η^4-1,1,3,5, or η^5-1,1,3,5,5, respectively.

A search of the Cambridge Structural Database (CSD, version 2024.2.0) reveals 1466 structures of transition metal complexes containing dicyanamide as a ligand (either terminal or bridging) [19]. Further refinement of this initial hitlist shows that the cobalt(II) complexes constitute 14% of all structures, ranking third after copper(II) and manganese(II) compounds. Although new structures of metal(II) complexes based on dicyanamide bring great excitement to scientists, these compounds are studied not only because of their structural attractiveness, but also because of their intriguing and fascinating magnetic properties. Since the discovery of long-range magnetic ordering in the isomorphous series of α-[M(dca)$_2$] compounds [M = Cr, Mn, Fe, Co, Ni, Cu], these kinds of compounds have received a lot of attention. This review provides an overview of the chemistry of dicyanamide-Co(II) complexes, in which magneto-structural relationships have been extensively explored. Emphasis is placed on recent results for monomers, dimers and coordination polymers.

2. Synthetic Methods of Dicyanamide Co(II) Complexes

The major challenge in synthesizing dicyanamide compounds is obtaining single crystals suitable for X-ray measurements, particularly due to their tendency to form poorly soluble crystalline precipitates. Improving synthesis methods is necessary, because the reactions with the same starting materials, assuming the synthesis method changes, can sometimes lead to different coordination compounds. Another common factor is the dependence of the resulting complex compound on the cobalt(II) salt used and/or the stoichiometry of the reaction. Representative examples of such Co(II) compounds will be presented and discussed below.

Based on the analyzed dca–Co(II) compounds, two main synthetic strategies were found to be used.

- *Saturation Method*
  The synthesis is carried out by mixing cobalt(II) salts with the appropriate amount of the ligand, and then a dicyanamide solution is added. The resulting solution is kept for evaporation at room temperature and X-ray-quality crystals grow in saturated solutions, usually few days.
- *Diffusion Method*
  This method is especially dedicated to those compounds that precipitate during the reaction in the form of poorly soluble or non-soluble precipitates. Generally, two approaches can be used. The first technique involves dissolving the reactants in two different solvents. Then, the layers of these two solutions should be dropped on top of each other and separated by a layer of pure solvent. The second one assumes that the compound was obtained using the traditional method. Then, the impurities from the reaction solution have to be filtered off and the obtained filtrate should be placed under a layer of precipitating solvent. This type of crystallization is most often carried out in a narrow vial, i.e., a test tube or an H-tube, and requires some skill because the boundary between the two solutions must be clear and distinct. Crystals most often form at the phase boundary after a few weeks. The following examples of compounds can serve as representatives of these two approaches: [Co(L1)(dca)$_2$] [20], [Co(phen)(dca)$_2$] [21], [Co(bpp)(dca)$_2$]$_n$ [22], [Co(4-bpmp)$_2$(dca)$_2$(H$_2$O)$_2$]$_n$ [23], {[Co(dca)$_2$(H$_2$O)$_2$]·(hmt)}$_n$ [24], or [Co(HFlu)$_2$(dca)$_2$]$_n$ [25].

Interestingly, L. Váhovská et al. obtained two complexes with the same formula [Co(phen)(dca)$_2$] using the saturation method [21]. The first compound appeared as an orange precipitate during synthesis, while the second crystallized after two weeks of slow evaporation in the dark. Both structures are compared in the section "*Description of Mononuclear and Dinuclear Complexes*". The list of abbreviations is presented at the end of the article.

3. Description of Mononuclear and Dinuclear Complexes

Summarized structural data can be found in Table S1 in Supplementary Materials

Based on the results from the CSD, it can be concluded that mononuclear dca-Co(II) complexes are relatively uncommon, with there being only 12 structures of cobalt(II) complexes with a terminal dca ligand. On the other hand, examples of dimeric compounds are even rarer, with only two structurally characterized examples. There may be various reasons for this, but it seems that the divergent nature of the coordinating nitrile groups in dca is a key factor [26]. Of course, it does not imply that these complexes are difficult to synthesize, but their lower prevalence could be due to their reduced attractiveness compared to coordination polymers. Among the mononuclear compounds, only one Co(II) complex is known in which terminal dicyanamide coordinates with a metal atom via amide nitrogen. In complex $[Co(H_2biim)_2(dca)_2]$, two bidendate N-donor ligands are coordinated to the octahedral Co(II) ion forming an equatorial plane, while the axial positions are occupied by amide nitrogen from two *dca* anions [23]. Typically, coordination through the nitrile nitrogen is preferred due to its higher electronegativity and more delocalized electrons. The formation of this unique complex is thought to be influenced by the electron-donating properties of H_2biim, which increase the Co(II) cation's affinity for the softer amide nitrogen over the nitrile group of the dca anion. (Figure 1). Analysis of the structural data shows that the $Co–N_{H2biim}$ lengths fall in the typical range of 2.168(12)–2.1435(12) Å, consistent with bond lengths observed in other mononuclear cobalt(II) compounds (see Tables 1 and S1). This is the only similarity of this compound in comparison to the remaining eleven $[Co(L)_{1–4}(dca)_2]$ complexes, where L is a mono–, bi–, tri– or tetradentate organic ligand and dicyanamide coordinates with the Co(II) ion through nitrile nitrogen (see Tables 1 and S1). In $[Co(H_2biim)_2(dca)_2]$, the $Co–N_{dca}$ bond lengths [2.1912(13) Å] are longer compared to the bond lengths in other cobalt(II) complexes, which these range from 2.003(3) Å to 2.1546(15) Å. This difference results from the diversity of the coordination modes of the dicyanamide anion.

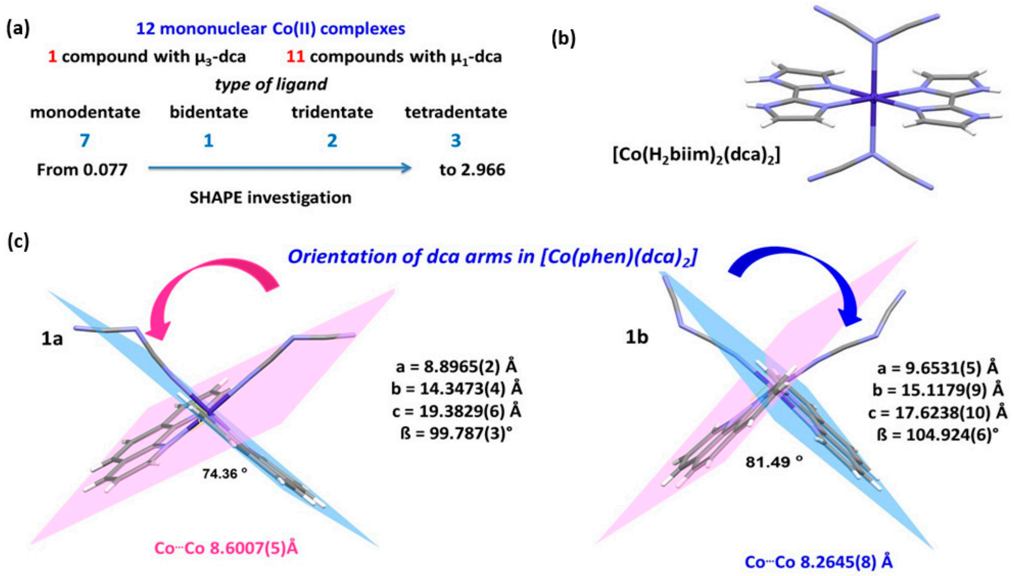


Figure 1. Summary of data for mononuclear Co(II) compounds (**a**); molecular structure of $[Co(H_2biim)_2(dca)_2]$ [27] (**b**); structural differences between two structures with the same formula $[Co(phen)(dca)_2]$ [21] (**c**).

In $[Co(H_2biim)_2(dca)_2]$, the Co–N–C angles are 118.72° and 120.47(10)°, while the C–N–C angle has one of the lowest values of 119.27(13)°, probably due to the fact that the nitrogen in the C–N–C group participates in bonding to the metal atom. Interestingly, the metal···metal separation of 7.162(1) Å is one of the lowest values. In other mononuclear Co(II) compounds, metal atoms are generally better separated, with distances ranging from 7.187(1) to 9.686(2) Å.

Table 1. Structural parameters for the selected cobalt(II) mononuclear complexes (for the full version, see Table S1).

Compound	Co–N_{ligand} [Å]	Co–N_{DCA} [Å]	Angles [°]		Co···Co [Å]	Ref.
			Co–$NC_{(dca)}$	C–N–$C_{(dca)}$		
			Monodentate ligands			
[Co(bim)$_4$(dca)$_2$]	2.1546(15) 2.1489(15)	2.1575(18)	155.32(18)	122.8(3)	9.686(2)	[28]
			Bidentate ligands			
[Co(H$_2$biim)$_2$(dca)$_2$]	2.1435(12) 2.1268(12) 2.1435(12) 2.1258(12)	2.1912(13) 2.1912(13)	118.82(10) 120.47(10)	119.27(13)	7.162(1)	[27]
[Co(phen)$_2$(dca)$_2$] Crystal 1a	**193 K** 2.149(1) 2.147(1) 2.145(1) 2.173(2) **293 K** 2.142(2) 2.142(2) 2.141(2) 2.166(2)	**193 K** 2.093(2) 2.070(2) **293 K** 2.092(2) 2.066(2)	173.8(1) 169.4(2)	121.4(2) 122.4(2)	8.6007(5)	[21]
[Co(phen)$_2$(dca)$_2$] Crystal 1b	**293 K** 2.139(3) 2.175(3) 2.132(3) 2.157(3)	**293 K** 2.071(3) 2.069(3)	171.3(3) 168.3(3)	124.6(4) 125.8(4)	8.2645(8)	[21]
			Tridentate organic ligand			
[Co(tppz)$_2$](dca)$_2$]	**125 K** 1.855(5) 1.917(5) 1.977(4) 2.155(4) **330 K** 1.870(3) 1.912(3) 2.003(2) 2.128(2)	– uncoordinated dca	–	**125 K** 120.5(6) **330 K** 123.2(7)	**125 K** 8.9361(7) **330 K** 9.0081(4) Å	[29]
			Tetradentate organic ligand			
[Co(L^1)(dca)$_2$]	**100 K** 2.340(2) 1.920(2) 2.315(2) 1.909(2) **280 K** 2.002(2) 2.351(2) 1.999(3) 2.324(2)	**100 K** 1.927(2) 1.942(2) **280 K** 2.003(3) 2.024(3)	**100 K** 173.7(2) 166.5(2) **280 K** 170.4(3) 164.3(3)	**100 K** 117.8(2) 116.2(1) **280 K** 121.9(4) 118.0(3)	**100 K** 8.9101(6) **280 K** 9.0233(8)	[20]

H_2BiIm = 2,2A-biimidazole; **L^1** = N,N′-di-tertbutyl-2,11-diaza[3,3](2,6)pyridinophane; **bim** = 1 benzylimidazole; **tppz** = 2,3,5,6-tetrakis(2-pyridyl)pyrazine; **phen** = 1,10-phenanthroline.

Generally, the *cis* configuration of dicyanamide in Co(II) complexes is favored over the *trans* conformation. *Trans*-coordinated dca has been observed only in compounds based on monodentate derivatives, with four N–donor ligands of the same type in [Co(bim)$_4$(dca)$_2$] [28] or with two different types of ligands in [Co(4-bpo)$_2$(H$_2$O)$_2$(dca)$_2$](H$_2$O)$_2$ [30] and [Co(nitppy)$_2$(H$_2$O)$_2$(dca)$_2$] [31]. In the cases of complexes based on tetradentate and bidentate ligands (with the exception of the previously discussed [Co(H$_2$biim)$_2$(dca)$_2$]), the dca anions are coordinated in a *cis* arrangement. Introducing tridentate N-donor derivatives into the coordination environment of the Co(II) ion results in the lack of coordination of the dca ion. Such a situation occurred only in one complex [Co(tppz)$_2$](dca)$_2$, where two N–donor molecules coordinate to the cobalt(II) ion in a *mer* fashion, equatorially through pyridyl and axially via pyrazine nitrogen atoms, while dicyanamide plays a role of a counteranion [29].

Among the mononuclear Co(II) complexes, an intriguing example concerns two compounds of the same formula, [Co(phen)(dca)$_2$], which were obtained by two different synthetic methods [21] (see Figure 1c). The first noticeable difference between the structures is the orientation of the *dca* arms, which also results in differences in structural parameters [N_{phen}–Co–N_{phen} = 92.15°/96.02°; Co–N–C = 173.83° and 169.36°/171.31° and 168.33°]. This small change involves another change in the arrangement of *phen* ligands, which are best described by dihedral angles 72.71(2)° and 81.56(7)°. As a result, differences in Co···Co separations and the supramolecular arrangement have been observed. Moreover, these two compounds exhibit different packing structures. In the first one (1a), the weak C–H···N interactions link molecules in layers, which are further bound into a 3D supramolecular network via face-to-face π···π interactions. In the second complex, due to weaker π···π stacking, chains instead of layers are created. Due to the different orientation of the *dca* and phen ligands, C–H···N interactions link the [Co(phen)(dca)$_2$] molecules into a 3D net, not layers. These structural differences will prove to be important in describing the axial *zfs* parameters (see *Magnetic properties in Terms of Structural Relationship*).

The coordination geometry of the cobalt(II) atom in mononuclear dicyanamide complexes has also been analyzed using the Continuous Shape Measures methodology [32]. The lowest Shape value with respect to the octahedral geometry is observed in Co(II) systems based on monodentate ligands (0.077–0.122), while the most distorted octahedron has been confirmed in the case of Co(II) with tridentate and tetradentate derivatives (1.316–2.966) (see Figure 1a and Table S2). These findings highlight the impact of ligand denticity on the distortion of the coordination environment in Co(II) complexes.

As mentioned above, dimeric structures of dicyananamide cobalt(II) complexes are extremely rare, with only two examples reported: $[Co(bpm)_2(dca)]_2(ClO_4)_2$ [33] and $[Co(tptz)(H_2O)(dca)]_2(ClO_4)_2$ [34]. In both complexes, metal atoms are bridged by two dca anions in a $\mu_{1,5}$ (*end–to–end)* fashion. Each cobalt(II) atom is octahedrally coordinated by two nitrogen atoms of dca ligands and four donor atoms from one molecule of tridentate *tptz* and one molecule of water in $[Co(tptz)(H_2O)(dca)]_2(ClO_4)_2$ or two molecules of bidentate *bpm* derivatives in $[Co(bpm)_2(dca)]_2(ClO_4)_2$. Bond lengths of $Co–N_{Ligand}/O_{H_2O}$ are longer than those of $Co–N_{dca}$ by ~0.06 Å (see Table S3). The Co···Co distance spanned by the bridging ligands varies in the range of 7.377(3)–7.592(2) Å, while the shortest intermolecular metal–metal distance is within 9.266(3)–10.577(2) Å.

4. Structural Diversity in the Family of Coordination Polymers

Summarized structural data can be found in Tables S3–S5 in Supplementary Materials

The dca-Co(II) coordination polymers are much more diverse than the previous one. Only in the group of one-dimensional cobalt(II) coordination polymers can we distinguish four subgroups among which the dicyanamide ion plays different roles.

The first two groups include 13 and 22 Co(II) structures with single and double $\mu_{1,5}$-dca bridges, respectively. These chains generally adopt either a linear or *zig-zag* geometry. Searching structural relationships between both groups, it can be concluded that the tri– or tetradentate ligands are favored during the formation of Co(II) chains with a single $\mu_{1,5}$-dca$^-$. On the other hand, in the case of double-bridged 1D dca-Co(II) systems, definitely monodentate ligands predominate, leading to the formation of linear chains. Among the first group, the most common motif is the linear chain in complexes $[Co(etpybzam)(dca)_2]_n$ [35], $\{[Co(imph)_4(dca)](ClO_4)\cdot 4(EtOH)(H_2O)\}_n]$ [36], $[Co(L1)(dca)(ClO_4)_2(MeOH)]_n$ [37], $\{[Co(enbzpy)(dca)](PF_6)\}_n$ [38], $[Co(3\text{-}pyo)(3\text{-}pyOH)(dca)(MeOH)]_n$ [39], $\{[Co(enbzpy(dca)](ClO_4)\}_n$ [40], and $\{[Co(pypz)(dca)(H_2O)]\cdot dca\}_n$ [41] followed by the five examples of *zig-zag* chains in $[Co(azpyph)(dca)]BF_4\cdot MeOH\}_n$ [42], $\{[Co(bpm)_2(dca)](ClO_4)\}_n$ [30], $\{[Co(bdpb)(dca)](ClO_4)\}_n$ [43], $[Co(pybiu)(dca)]_n$ [44] and two exceptions: the helical arrangements in $\{[Co(H_2BiIm)_2(dca)_2]Cl\}_n$ [27] and $\{[Co(H_3daps)(dca)](MeOH)_2(MeCN)\}_n$ [45]. The type of ligand affects the binding mode of the dca linker, which in turn influences the intra- and interchain Co···Co distances—structural parameters that are important for further studies of magnetic properties (Tables 2 and S3). Multidentate ligands used for a single $\mu_{1,5}$-Co(II) CP provide longer distances by about ~0.6Å between metal atoms in comparison to compounds, where cobalt(II) atoms are connected through a double *dca* linker.

Table 2. Structural parameters for the selected cobalt(II) 1D coordination polymers (for the full version, see Table S3).

Compound	$Co–N_{ligand}$ [Å]	$Co–N_{DCA}$ [Å]	Angles [°]		Co···Co in Chain or (Between Chains)	Ref.
			$Co–NC_{(dca)}$	$C–N–C_{(dca)}$		
Single $\mu_{1,5}$-dca bridge						
$\{[Co(H_2BiIm)_2(dca)_2]Cl\}_n$	2.1386(18) 2.1593(18) 2.1372(18) 2.1325(18)	2.1900(19) 2.1133(19)	124.4(2) 172.3(2)	120.4(2)	7.2860(5) 7.9690(6)	[27]

Table 2. *Cont.*

Compound	Co–N$_{ligand}$ [Å]	Co–N$_{DCA}$ [Å]	Angles [°]		Co···Co in Chain or (Between Chains)	Ref.
			Co–NC$_{(dca)}$	C–N–C$_{(dca)}$		
$\{[Co(pypz)(dca)(H_2O)]\cdot dca\}_n$	2.1082(18) 2.1891(19) 2.1685(18)	2.057(2) 2.096(2)	155.6(2) 165.03(19)	121.7(2)	7.447(6) 8.4287(7)	[41]
$[Co(pybiu)(dca)]_n$	1.986(3) 1.952(4) 1.966(3)	2.330(4) 1.956(5)	121.3(4) 158.1(4)	120.6(5)		[44]
Double $\mu_{1,5}$-dca bridge						
$\{[Co(azpyph)(dca)](BF_4)\cdot MeOH\}_n$	2.309(2) 2.041(2) 2.346(3) 2.045(2)	2.070(3) 2.100(3)	156.3(2) 177.2(2)	125.3(3)	8.3790(9) 9.276(1)	[42]
$\{[Co(dca)_2(H_2O)_2]\cdot(hmt)\}_n$	2.082 2.082	2.123 2.118 2.123 2.118	162.0 162.6	118.2(2) 118.2(2)	7.3617 7.1243	[24]
Double bridges (ligand + dca)						
$[Co_2(tppz)(dca)_4]_n$	2.156(2) 2.156(2) 2.114(2) 2.114(2) 2.140(2) 2.140(2)	2.044(2) 2.044(2) 2.141(2) 2.141(2)	168.9(2) 152.3(2)	119.1(2)	7.377 A 5.9262(5)	[46]
dca as a co-ligand						
$[Co(bimb)_2(dca)_2]_n$	2.168 2.154 2.168 2.154	2.139 2.139	169.9 169.9	124.1(2) 124.1(2)	10.146 7.583	[23]
$[Co(bte)_2(dca)_2]_n$	2.165 2.165 2.124 2.124	2.132 2.132	157.0	119.4(3)	8.345 9.597	[47]

H_2BiIm = 2,2′-biimidazole; **azpyph** = N,N′-di-tert-butyl-2,11 diaza[3,3](2,6)pyridinophane; **bimb** = 1,4-bis(im idazol-1-yl)-butane; **hmt** = hexamethylenetetramine; **pybiu** = N-(picolinoyl)-biurate; **tppz**= tetra-2-pyridylpyrazine (2,3,5,6-tetrakis(2-pyridyl)pyrazine); **bte** = 1,2-bis(1,2,4-triazol-1-yl)ethane; **pypz** = 2,6-bis(pyrazol-1-yl)pyridine.

The second-to-last group of 1D structures includes five Co(II) compounds, in which two types of linkers have been identified: the dicyanamide anion and an organic ligand with appropriately arranged donor atoms. Finally, the last group consists of three compounds where the dca ligand does not serve a linking function. Both groups are relatively small, containing only four examples each. Nevertheless, an intriguing question arises: what factor determines whether the dca$^-$ is eliminated from, or retained in, its role as a bridge? This, of course, can be partially addressed during the design and synthesis stage through the use of the following:

(1) *Ligands with appropriately arranged donor atoms*, which usually increase the chance of a double bridge. This has been observed for multidentate tetra-2-pyridylpyrazine (*tppz*) in $[Co_2(tppz)(dca)_4]_n$ [46] or anionic heterodonor nicotinate anion (*nic*) in $\{[Co_3(nic)_4(dca)_2(H_2O)_8]\cdot(H_2O)_2\}_n$ [48].

(2) *Flexible, easily bent organic ligands*—if the ligand contains an additional spacer between the aromatic rings containing donor atoms, then there is a high probability that the *dca* anion will not participate in the formation of bridges. Such a situation was observed in $[Co(bimb)_2(dca)_2]_n$ [23] and $[Co(4\text{-}bpmp)_2(dca)_2(H_2O)_2]_n$ [49], where butane in *bimb* and piperazine in *4-bpmp* had separation functions, respectively. Also noteworthy is the compound $[Co(bte)_2(dca)_2]_n$ [47], where the $CH_2{=}CH_2$ group acts as an effective spacer, reducing *dca* to the role of a co-ligand. Interestingly, replacing this group with a disulfide in $[Co(bpds)(dca)_2]_n$ [49] causes the *dca* ion to return to its role as a linker. The reason seems to lie in the bond lengths: the distance between carbon atoms in $CH_2{=}CH_2$ in $[Co(bte)_2(dca)_2]_n$ is 1.520(1) Å, which makes it more rigid in comparison to the disulfide group [1.782(5) Å] in $[Co(bpds)(dca)_2]_n$.

(3) Of course, utilizing the geometrical properties of organic ligands is an important and powerful tool in the design of coordination compounds. Therefore, the donor-acceptor strength of organic derivatives is a crucial factor in coordination chemistry and should be taken into consideration.

A very interesting case is that of the pair of complexes $[Co(pydz)_2(dca)_2]_n$ and $[Co(pydz)(dca)_2]_n$ [50]. The first one is a typical 1D coordination polymer, where each of the cobalt(II) atoms are bound via double *end–to–end* ($\mu_{1,5}$) dicyanamide. What is interesting is that the second compound has been prepared through the thermal decomposition of ligand-rich precursor $[Co(pydz)_2(dca)_2]_n$. The $[Co(pydz)(dca)_2]_n$ is derived from a 1D compound; however, dicyanamide's coordination of $\mu\text{-}_{1,3,5}$ and $\mu\text{-}_{1,5}$ manners provides it with a layer structure, which definitively ends the topic of 1D polymers and begins the discussion of 2D polymers. In this unique structure, the slightly distorted octahedral cobalt(II) cations are coordinated by five *dca* ions and one pyridazine (*pydz*) ligand. In structure two, a type of dicyanamide bridges exists to form linear Co–$(dca)_2$–Co chains. The central nitrogen atom of $\mu\text{-}_{1,3,5}$–dca binds chains into layers, in which each cation is coordinated by two $\mu\text{-}_{1,5}$ and three $\mu\text{-}_{1,3,5}$ dca anions (Figure 2a).

The same unique type of dicyanamide coordination mode has been confirmed in $[Co(H_2O)(dca)_2{\cdot}phz]_n$ [51]. There are two crystallographically independent octahedral metal(II) atoms and two types of dca^- ligands (one bidentate $\mu_{1,5}$ and one tridentate $\mu_{1,3,5}$). The resulting sheets can be described as being composed of two alternating chains, which are perpendicular to each other, but propagate in the same direction. *Phz* molecules are stacked between these layers, but do not coordinate directly to the metal atoms. Apart from the above-described Co(II) compounds, the family of two-dimensional coordination polymers is rich in structural gems. As before, here, five subgroups can be distinguished. The first one concerns unique coordination modes of the *dca*$^-$ anion and three compounds of the formulas $\{[Co(dca)_2]_2{\cdot}(pzdo)\}_n$ [52], $\{[Co(dca)_2]_2{\cdot}(mpdo)\}_n$ [52], and $[Co_2(dmdpy)(dca)_2]_n$ [53] should be mentioned. In the first two structures, each of the crystallographically independent metal(II) ions (Co1 and Co2) are connected by double $\mu_{1,5}$ and μ_3–dca bridges, leading to a triangular 2D lattice (Figure 2b). On the other hand, in the $[Co_2(dmdpy)(dca)_2]_n$ [53], two types of bridges, $\mu_{1,3}$ and $\mu_{1,5}$ coordination modes, bind metal atoms, forming 2D sheets (Table 3, Figure 2c).

As can be expected, the most numerous are two subgroups of 2D Co(II) compounds, where the central atoms are connected by a single $\mu_{1,5}$-dca bridge (16 structures) and by a pair of bridges: double + single $\mu_{1,5}$-dca (9 structures). Comparing both groups, two interesting differences can be noticed:

- *Role of the accompanying ligand*

In general, the use of a bidentate ligand leads to the formation of compounds with two types of single + double $\mu_{1,5}$-dca bridges. On the other hand, 2D Co(II) compounds based on a single $\mu_{1,5}$ linker are formed in the presence of a monodentate ligand.

- *Motifs*

The most diverse in terms of motifs are cobalt(II) compounds based on two types of bridges. The topology of the herringbone-waved grid has been confirmed for $[Co(dca)_2(phen)]_n$ and $[Co(4,7\text{-}dmphen)(dca)_2]_n$ [54], a brick wall was observed in $[Co(dmpzm)(dca)_2]_n$ [55]. Structures of $[Co(ptzda)_2(dca)]_n$ [56] and $\{(Ph_4As)[Co(dca)_3]\}_n$ [57] consist of layers of ladder-like chains joined into a 2D net by an *end-to-end* dca anion. However, in most complexes of the second group, single $\mu_{1,5}$ dicyanamide connects Co(II) atoms into a rhombus grid. The only structurally different exceptions are the compounds $[Co(bzim)_2(dca)_2]_n$ [58] and $[Co(DAT)_2(dca)_2]_n$ [59]. In both dca–Co(II) systems, metal cations are link into a 2D network, forming an hourglass-shaped 24-membered $Co_4(dca)_4$ metallacycle (Figure 3a–e).

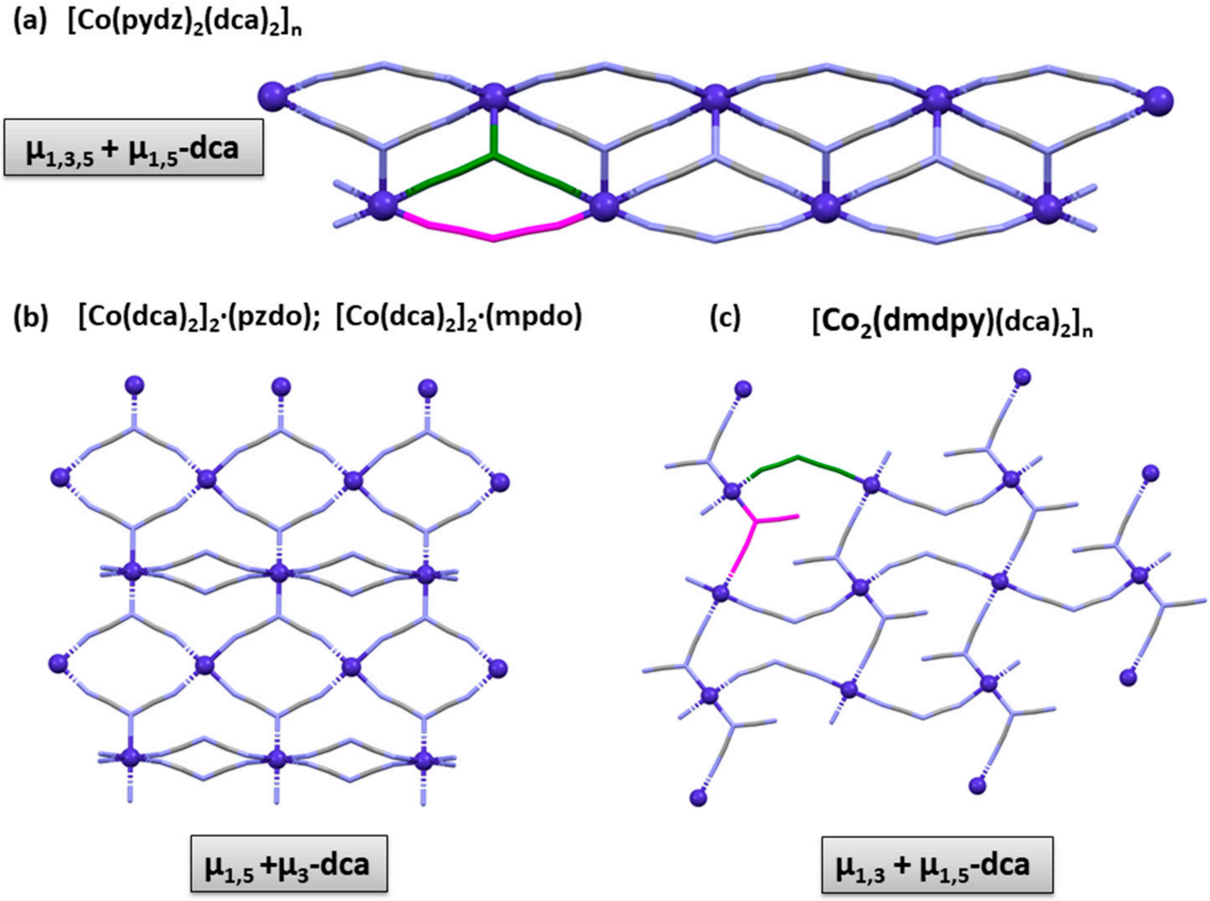
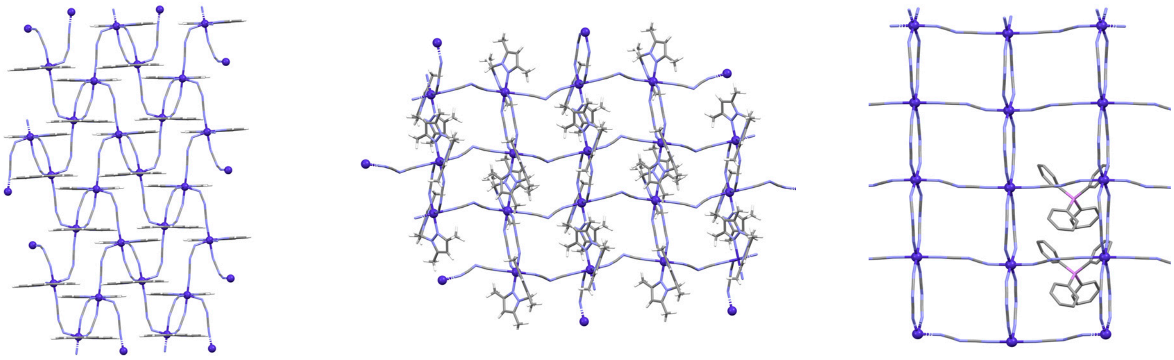


Figure 2. Summary of data for 2D Co(II) CP with two types of *dca* bridges [10,52,60]. The molecules of co-ligands have been omitted for clarity.

Despite these differences, the geometry of the dicyanoamide ions does not differ in any significant way. This, in turn, does not affect the metal···metal distances, which for both groups oscillate in the ranges of 7.274(4)–8.968(2) and 7.201(1)–8.748(1), respectively.

The second to last family gather five Co(II) complexes with mixed linkers—a dca$^-$ anion together with a molecule of an organic ligand both play roles as bridges. The common feature for all these compounds with formulas $\{[Co(btrm)_2(dca)]ClO_4\}_n$ [61], $\{[Co(pypypz)_2(dca)]{\cdot}(OH)(gly)_2\}_n$ [62], $[Co(DPNDI)(dca)]_n{\cdot}2nDMF{\cdot}nH_2O$ [63], $[Co(bnzd)(dca)_2]_n$ [30], $[Co(3\text{-}bpo)(dca)_2]_n$ [30] and $\{[Co(bipy)(dca)_2{\cdot}0.5H_2O{\cdot}0.5MeOH\}_n$ [64] is the presence of an organic ligand with appropriately arranged donor centers, whose structure suggests it was designed as an organic linker. This is best evidenced by the Co···Co distances measured through an organic bridge, which range from 8.910(1) in $\{[Co(btrm)_2(dca)]ClO_4\}_n$ to 14.527(1) Å in $\{[Co(pypypz)_2(dca)]{\cdot}(OH)(gly)_2\}_n$. Interestingly, changing the synthesis of complex $\{[Co(pypypz)_2(dca)]{\cdot}(OH)(gly)_2\}_n$ [61] through changes in the selection of the solvent led to surprising changes. In two obtained complexes, $[Co(pypypz)_2(dca)]_n$ and $\{[Co(pypypz)_2(dca)_2]{\cdot}(H_2O)\}_n$ [61], the N–donor ligand acts as a linker eliminating the dca$^-$ of the bridging role. In those structures, the distance between the nearest cobalt(II) atoms is even greater ([16.465(1) Å in $[Co(pypypz)_2(dca)]_n$; 17.535(1) Å in $\{[Co(pypypz)_2(dca)_2](H_2O)\}_n$). In comparing these three compounds, the reason seems to be quite simple: in $\{[Co(pypypz)_2(dca)]{\cdot}(OH)(gly)_2\}_n$, rectangular interlayer channels are occupied by the intercalated glycol guest molecules and each glycol forms a pair of strong O–H···N bonds with two pyrazole nitrogen atoms from one adjacent layer. (Tables 3 and S5)

(a) Herringbone **(b) Brick wall** **(c) Ladder-like**



(d) Hourglass **(e) Rhombus grid** **(f) Square grid**

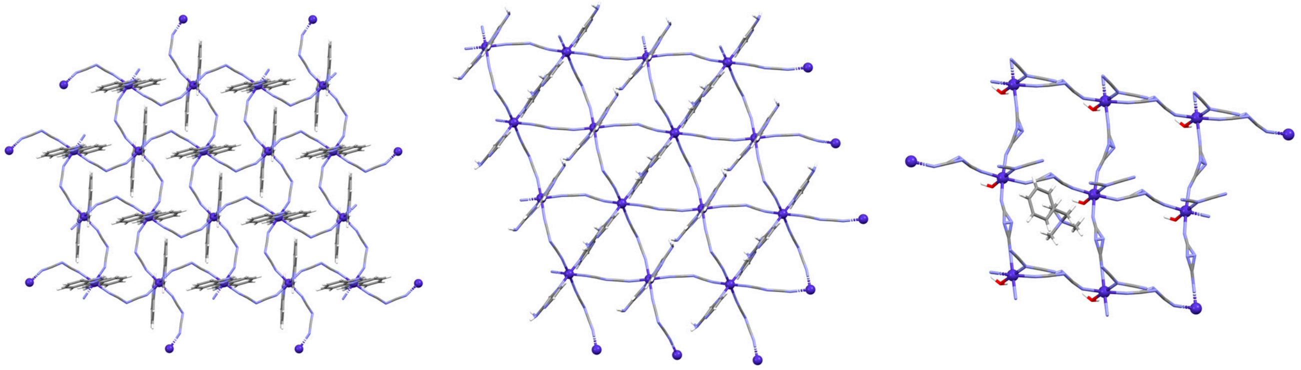


Figure 3. Representative motifs in 2D Co(II) CP based on dca⁻ linker: (**a**) $[Co(phen)(dca)_2]_n$ [54]; (**b**) $[Co(dmpzm)(dca)_2]_n$ [56]; (**c**) $\{Ph_4As)[Co(dca)_3]\}_n$ [57]; (**d**) $[Co(bzim)_2(dca)_2]_n$ [58]; (**e**) $\{[Co(dca)_2(NH_2pyz)_2]\cdot H_2O]\}_n$ [65]; (**f**) $BeTriMe[Co(dca)_3(H_2O)]_n$ [66].

The final compound, $\{BeTriMe[Co(dca)_3(H_2O)]\}_n$, is difficult to assign to a distinct group [66]. In this square-grid network, the octahedral metal cations are bound by single $\mu_{1,5}$-dca units, while the roles of the accompanying ligands are fulfilled by water molecules and non-bridging dca anions, coordinating in a μ_3 manner. The Co–N$_{\mu1,5dca}$ bond lengths fall in the range of 2.082(3)–2.118(3) Å, while the bond distance Co–N$_{\mu3dca}$ is slightly longer [2.225(4) Å]. The non-bridging *dca* ligands together with the hydrogen-bonded coordinated water form a stable honeycomb-like assembly, and the presence of O–H···N interactions causes this elongation of this bond (Figure 3f).

Table 3. Structural parameters for the selected cobalt(II) 2D coordination polymers (for the full version, see Table S4).

Compound	Co–N$_{ligand}$ [Å]	Co–N$_{DCA}$ [Å]		Angles [°]		Co···Co	Ref.
				Co–NC$_{(dca)}$	C–N–C$_{(dca)}$		
		$\mu_3 + \mu_{1,5}$					
$[Co(pzdo)(dca)_2]_n$	Co1 2.138 2.138	Co1 $\mu_{1,5}$ 2.099 2.099 2.099 2.099	Co(2) $\mu_{1,5}$ 2.089 2.089 2.089 2.089 μ_3 2.179 2.179	$\mu_{1,5}$ 149.5 149.5 μ_3 160.5 160.5	119.9 120.8	Co1···Co1 7.4313 Co2···Co2 7.4313 Co1···Co2 6.0188	[52]

Table 3. *Cont.*

Compound	$Co–N_{ligand}$ [Å]	$Co–N_{DCA}$ [Å]	Angles [°]		Co···Co	Ref.
			$Co–NC_{(dca)}$	$C–N–C_{(dca)}$		
μ_3 + $\mu_{1,3,5}$						
$[Co(H_2O)(dca)_2{\cdot}phz]_n$	2.049	$\mu_{1,5}$ 2.080 2.086 $\mu_{1,3,5}$ 2.213 2.121 2.163	$\mu_{1,5}$ 159.4 160.4 $\mu_{1,3,5}$ 164.4 163.0 120.9 122.5	119.5(2) 116.4(2)	7.4110	[51]
Single $\mu_{1,5}$ + double $\mu_{1,5}$						
$\{[Ph_4P]\{Co[dca]_3\}$	–	Single 2.155 2.155 Double 2.118 2.118 2.114 2.114	Double 161.8 159.6 Single 161.8 149.5	118.8(2) 126.5(6)	Double 7.4426 Single 8.7948	[57]
Single $\mu_{1,5}$						
$[Co(atz)_2(dca)_2]_n$	2.168 2.168	2.097 2.097 2.089 2.089			8.0415	[67]
$[Co(bim)_2(dca)_2]_n$	2.128(3) 2.134(3)	2.190(3) 2.220(3) 2.209(3) 2.219(3)	169.5(3) 158.3(3)	125.1(4) 123.8(4)	8.927(2) 8.968(2)	[28]
Single $\mu_{1,5}$ + ligand						
$\{[Co(btrm)_2(dca)]ClO_4\}_n$	Co1 2.140(6) 2.146(6) 2.142(6) 2.150(6) Co2 2.136 2.157	Co1 single 2.072(5) 2.082(5) Co2 single 2.085 2.085	160.3(6) 164.4	122.6(9)	Co1···Co1 8.894(4) Co2···Co2 8.526	[68]
Three types of bridges						
$[Co(3\text{-}bpo)(dca)_2]_n$	2.175(5) 2.160(5)	2.091(5) 2.136(5) 2.103(4) 2.114(4)	154.3(4) 164.1(4) 161.6(4) 156.4(4)	121.8(5) 119.1(4)	7.383(3) 7.587(2)	[30]
dca as a co-ligand						
$\{[Co(pypypz)_2(dca)](OH)(gly)_2\}_n$	2.182 2.163	2.163 2.182 2.175 2.175	166.3 171.1 173.6 171.1	129.0(5) 129.0(5)	14.537	[61]

atz = 2-amino-1,3,5-triazine; **bim** = 1-benzylimidazole; **btrm** = 1,2-bis(1,2,4-triazole-1-yl)methane; **3-bpo** = 2,5-bis(3-pyridyl)-1,3,4-oxadiazole; **pzdo** = pyrazinedioxide; **phz** = phenazine; **pypypz** = bis[3,5- dimethyl-4-(4′-pyridyl)pyrazol-1-yl]methane.

Paradoxically, the last, but historically the most important, is the class of 3D dca-Co(II) coordination polymers. The observation of long-range magnetic order in dicyaniamide transition metal complexes of the formula $[M(dca)_2]_n$ (M = Co, Cu, Ni, Fe, Mn etc.) caused great interest and excitement and overall it resulted in a large number of articles that appeared in short time intervals. This research ranges from studies focused on structural aspects related to the employment of the dicyanamide ion in the design and synthesis of d-block coordination compounds, up to issues related to the expansion of horizons related to new examples of molecular network materials. Thanks to these first works, it is possible to distinguish four main groups in the 3D polymer family. The first one includes the well-known rutile (TiO_2) networks $[M(dca)_2]_n$ with six connecting Co(II) centers and three connecting centers (*dca* ligands) in the ratio of 1:2 [69]. The cobalt(II) atoms are six-coordinated with four nitrile nitrogens from dca^- in the equatorial plane and two amide nitrogens from two axial dicyanamide ligands. In this group, two types of bridges have been observed: $\mu_{1,3,5}$ [70–73] and $\mu_{1,5}$ [74–76] (see Table S6). In Co(II) structures based on $\mu_{1,3,5}$-dca, the bond lengths between the metal cations and nitrile nitrogens [2.085(1)–2.097(2) Å] are shorter than those of the Co–N_{amide} [2.150(1)–2.153(1) Å]. This is a typical feature for these compounds because in all isostructural metal(II) structures, the M(II) cation–amide nitrogen bonds are longer than the M(II)–nitrile bonds [70]. The dicyanamide bridges show their tendency to bend in angles of Co–$N_{nitrile}$C and C–N–C which vary from 159.9–164.0(2)° to 117.1–118.6°, respectively. In those structures, where Co(II) centers are bound via $\mu_{1,5}$–dca, the Co–N–C angles tend to be linear [160.5(4)–179.6°] with the exceptions of {$(MePh_3P)[Co(dca)_3]$}$_n$ and {$(EtPh_3P)[Co(dca)_3]$}$_n$ [76]. In these two structures, the network consists of sheets, which are cross linked into a 3D net with hexagonal channels, and what is rare in this structure is that the Schläfi symbol of this net is $4^6.6^4$. The second subgroup is represented by $[Co(Phpyk)(dca)_2]_n$ [77], $[Co(tmeda)(dca)_2]_n$ [78] and $[Co(deen)(dca)_2]_n$ [79], which are compounds, where organic ligands coordinate with the cobalt(II) ion and each metal atom displays a distorted octahedral coordination environment, and is linked by single $\mu_{1,5}$-dca bridges (in an *end–to–end* fashion). In $[Co(Phpyk)(dca)_2]_n$, *dca* linkers gives rise to a 3D net of a 6^6 topology, which in most cases refers to diamondoid network. No less interesting is $[Co(tmeda)(dca)_2]_n$, where 3D helical CP is built from helical chains, which are further linked by a single dicyanamide anion. In $[Co(deen)(dca)_2]_n$, the *dca* ligand behaves as an interconnecting grid to give rise to a scaffolding-like 3D structure with distorted rectangular cavities [size: 8.1 × 6.9 Å]. Following the trend of the previous two groups of coordination polymers, the co-ligands can also act as linkers and such a situation can be observed in {$[Co(bpe)_2(dca)](dca)_2{\cdot}4H_2O$}$_n$ [80], {$[Co(bte)(dca)_2]{\cdot}H_2O$}$_n$ [47], $[Co(bpeado)(dca)_2]_n$ [81], $[Co(bpy)(dca)_2]_n$ [82], $[Co(dbtp)(dca)_2]_n$ [83], $[Co(bipy)(dca)_2]_n$ [64], {$[Co(bipim(dca)](dca)$}$_n$ [84] and {$[Co(bipim)(dca)]_2{\cdot}(ClO_4)_2{\cdot}(CH_3OH)_2{\cdot}H_2O$}$_n$ [84]. In the first of the six Co(II) examples, the authors employed organic derivatives with well-arranged nitrogen as a donor atom that is already known from the discussion concerning 2D dca-Co(II) CP. This type of derivatives like, i.e., bpe (1,2-bis(4-pyridyl)ethane) or *bte* (1,2-bis(1,2,4-triazol-1-yl)ethane) were widely used in the 2000s, guarantees the separation of metal(II) atoms over large distances (>9 Å), which in turn ensures synthetic success in the synthesis of 2D or even 3D polymers. In analyzed compounds, the longest Co⋯Co distances [14.0137(1) Å] was observed in $[Co(bpeado)(dca)_2]_n$ [81]. What is interesting, the shortest metal⋯metal separation [6.809(1) Å] is in {$[Co(bte)(dca)_2]{\cdot}H_2O$}$_n$ [47], and hydrogen bonding interaction between the solvent water molecule and the uncoordinated nitrogen atom of the triazole ring of *bte* is responsible for this state of affairs. In two last complexes {$[Co(bipym(dca)](dca)$}$_n$ and {$[Co(bipym)(dca)]_2{\cdot}(ClO_4)_2{\cdot}(CH_3OH)_2{\cdot}H_2O$}$_n$ [84] the bis-bidentate 2,2′-bipyrimidine (*bipym*) with multidentate coordination sites plays a role of organic, bridging ligand (see Table S6). The last group to be discussed contain only one example of formula {$[Co_4(CH_3O)_4(CH_3OH)_4(dca)_4]$}$_n$ [85]. These compound is built up from cubane Co_4O_4 core, where Co(II) cations display octahedral coordination sphere. Finally, the cubane building blocks are connected to other four cores by eight $\mu_{1,5}$-dca bridging mode. An interesting fact is the synthesis of this complex, because it was obtain during solvatothermal synthesis between Nadca and Co(II) salt in methanol at 75 °C and this is only one examples of such synthesis in the group of 3D network. Usually described Co(II) compounds were prepared by direct reaction of metal(II) salt, *dca* and organic ligands in different solvent at room temperature.

5. Magnetic Properties in Terms of Structural Relationships

Summarized magnetic data can be found in Tables S1, S3–S5 in Supplementary Materials

As previously mentioned, the phenomenon of long-range magnetic ordering in the isomorphous series of α-$[M(dca)_2]_n$ has driven extensive research into this group of compounds. It has been demonstrated that the nature of the ordering is closely dependent on the specific d-block metal involved. The rutile-like 3D networks formed by six coordinated metal ions and three connecting connectors ($\mu_{1,3,5}$-dca) in the 1:2 metal to dca molar ratio exhibit a broad diversity of long-range magnetic ordering at very low temperatures. This magnetic behavior depends on the nature of the metal ion, such as the weakly ferromagnetic Co(II) (9 K) Cu(II) (<1.7 K) and Ni(II) (21 K)], whereas Cr (47 K), Mn (16 K) and Fe (19 K) complexes are canted antiferromagnets [26]. The modification of the M-dca architecture by employing an N-donor organic ligand into the structures resulted in the formation of numerous architectures of the general formula $[M(dca)_2(L)_n]_n$ (n = 1 or 2), including chains, 2D (4,4) nets, triangular lattices with $\mu_{1,3,5}$- and $\mu_{1,5}$- dca linkers, and even 3D networks. In contrast to the rutile-like α-$[M(dca)_2]_n$ compounds, many magneto-structurally studied heteroleptic compounds display very weak antiferromagnetic couplings ($J < 1$ cm^{-1}) due to the poor ability of the extended $\mu_{1,5}$-dca bridges to mediate electronic interaction. The family of high-spin cobalt(II) complexes with $\mu_{1,5}$-dca bridges, although they are somewhat hard due to the presence of first-order spin–orbit coupling in the ground state, can be very interesting because they can exhibit a slow relaxation of magnetization, behaving as single-ion magnets (SIMs). The origin of this magnetic behavior arises from the large magnetic anisotropy of the Co(II) ion, combined with a flexible zero-field that depends on its coordination geometry and the degree of distortion in its environment, as well as the sufficient magnetic isolation of the metal centers (as mentioned above, due to their poor ability for transmitting magnetic interactions).

This chapter will present the results of magnetic studies in the context of the previously discussed structural relationships. All the studied dicyanamide Co(II) coordination compounds have been extensively investigated using a wide variety of techniques ranging from DC magnetic susceptibilities and magnetization, AC magnetic susceptibilities, Mössbauer spectroscopy and EPR spectroscopy. However, upon reviewing all of these materials, it is noteworthy that the greatest interest appears to be focused on Co(II) systems, often referred to as "single-ion magnet" (SIM) or spin crossover (SCO) Co(II) materials.

In the relatively small group of mononuclear dca-Co(II)complexes, two examples showing spin crossover behavior can be distinguished. In 2017, J. Palion-Gazda, M. Julve and their co-workers studied the thermally induced spin crossover (SCO) behavior of the $[Co(tppz)_2](dca)_2$ from a high-spin state (HS; S = 3/2) at a high temperature region to a low-spin state (LS; S =1/2) at lower temperatures, with the low-spin phase being reached at $T \leq 200$ K. Additionally, X-band EPR measurements were performed to characterize the low-spin state, revealing a quasi-isotropic spin-doublet rather than hyperfine splitting, which appeared as eight lines [29]. The SCO phenomenon was also observed in the *cis*-dicyanamido complex of formula $[Co(L1)(dca)_2]$, which displays a reversible thermoinduced HS to LS with a $T_{1/2}$ value around 238 K [20]. The measured χT was 2.55 cm^3 mol^{-1} K at 400 K and it was a consistent value for one Co(II) ion in the HS state (S = 3/2, g = 2.0 and $\chi T = 1.875$ cm^3 mol^{-1} K). Upon decreasing the temperature, the value of χT decreased gradually to reach a plateau with the values of 0.52–0.49 cm^3 mol^{-1} K in the temperature range of 80–20 K, which in turn is expected for the LS Co(II) ion (S = 1/2, g = 2.0, $\chi T = 0.375$ cm^3 mol^{-1} K) [86]. As an alternative to the EPR technique, an electrochemical method including cyclic voltammetry, square wave voltammetry and differential pulse voltammetry was used to study the nature of HS/LS. Voltammograms of $[Co(L1)(dca)_2]$ displayed a reversible oxidation for HS Co(II) to LS Co(III) at 0.05 V vs, Fc^+/Fc ($E_{pc} = 0.13$ V and $E_{pa} = -0.03$ V) as well as a reduction process at -1.67 V vs. Fcc^+/Fc. These two compounds represent a rare example of the successful use of a pseudohalide in the design and synthesis of SCO cobalt(II) systems.

Considerations regarding the dynamic mechanisms for magnetic relaxation were carried out for two complexes, $[Co(bim)_4(dca)_2]$ [28] and $[Co(12\text{-}TMC)(dca)_2]$ [87]. In the first complex, frequency-dependent alternating current magnetic susceptibility measurements were carried out below 8 K down to 2 K and this showed no out-of-phase (χ'') signal under the 0 G static field, suggesting a fast tunneling of the magnetization. However, the frequency depended on the in-phase (χ') and out-of-phase (χ'') under the external dc fields (of 500, 1000 and 2500 G). The value of the relaxation time followed the Arrhenius law characteristic of a thermally activated mechanism ($\tau = \tau_o \exp(U_{eff}/kT)$). At 1000 G, the relaxation time τ_0 and activation energy U_{eff} (E_a) are equal to $0.87 \cdot 10^{-6}$ s and 7.74 cm^{-1}, respectively. What is interesting, for this complex, is that an almost perfect semicircle in the Cole–Cole plot was observed in temperature ranges of 2.5–3.5 K, which could be fitted using the Debye model. On the other hand, Y-Q. Zhang, Z. Wang et al. showed that in [Co(12-TMC)(dca)$_2$], QTM and direct processes do not dominate in the whole studied temperature range [87]. The Raman process dominates in the low-temperature region, while the Orbach mechanism dominates in the high-temperature range. The fitting of the data gave the following parameters of $\tau_0 = 1.14 \times 10^{-8}$ s and $U_{eff} = 27.31$ cm^{-1}. Furthermore, the axial (D) and/or rhombic (E) zero-field splitting parameter were calculated and analyzed [Table S1]. An interesting situation has been found in two isomers of formula [Co(phen)$_2$(dca)$_2$] [21]. The temperature dependences of magnetic susceptibility for both compounds are quite similar, but the magnetization data show saturation at a higher value in the second isomer. Furthermore, the fitting procedure applied gave D = 99.1 cm^{-1} for the first isomer, and D = 84.8 cm^{-1} for the second one. The differences in the packing of these two compounds, discussed in detail in the structural part of this paper, are the reason for such results. The μ_3 coordination mode found in [Co(H$_2$biim)$_2$(dca)$_2$] does not seem to significantly affect the result of parameter D which is 23.3 cm^{-1} [27]. Similar values have been found in other octahedral pseudohalide Co(II) complexes. In the family of binuclear Co(II) compounds, the magnetic properties of [Co(tptz)(H$_2$O)(dca)]$_2$(ClO$_4$)$_2$ have been studied in detail. Variable temperature (300–2 K) magnetic measurements of this complex reveal that dicyanamide ligands transmit a weak antiferromagnetic interaction between the Co(II) centers. Typically for octahedral Co(II), the χT value continuously decreased from room temperature to 20 K [χ_MT = 6.019 cm^3 mol^{-1} K at 300 K and χ_MT = 4.41 cm^3 mol^{-1} K at 20 K]. Below 20 K, the presence of a small number of ferromagnetic or canted antiferromagnetic ordered impurities, i.e., α-or β-[Co(dca)$_2$], has been detected [34].

In the family of 1D Co(II) coordination polymers, two examples of Co(II) SCO systems have been carefully studied. In {[Co(enbzpy)(dca)](PF$_6$)}$_n$ [38] and {[Co(enbzpy)(dca)](ClO$_4$)}$_n$ [40], the χT value [2.67 and 2.43 cm^3 mol^{-1} K] decreases gradually until it reaches a temperature at which it becomes almost constant, which has been attributed to a low-spin Co(II) atom. Surprisingly, for {[Co(enbzpy)(dca)](ClO$_4$)}$_n$, the HS↔LS transition occurs with a small hysteresis loop of 3 K in width. The presence of a hysteresis loop was confirmed by calorimetric measurements and repeated over four times in the 227–160 K temperature range to demonstrate the robust SCO behavior in this Co(II) coordination polymer. Moreover, in both cases, the significant role of innocent counteranions in the SCO behavior of the polycationic coordination polymers has been carefully examined. Interestingly, a typical feature in almost all octahedral cobalt(II) complexes is that the value of χ_MT or μ_{eff} at room temperature is usually greater than that expected for one isolated spin-only ion [χ_MT = 1.87 cm^3 mol^{-1} K for a S = 3/2 ion], which can be attributed to the significant orbital contribution. Another common observation is the differences in the χ_MT value at lower temperatures (T < 15 K) when small magnetic fields are applied. This feature indicates the presence of a small amount of ferromagnetic or canted antiferromagnetic ordered impurities, likely α- or β-[Co(dca)$_2$]$_n$, which have T$_c$ at 9–10 K [69,86,88]. Unfortunately, dca-Co(II) derivatives tend to decompose after some time and the presence of these magnetic ordered impurities is very frequent. At room temperature, typical values of χ_MT vary in the range of 2.25–3.36 cm^3 mol^{-1} K. With decreasing temperature, the χ_MT usually remains almost constant until ~50 K, after which it rapidly decreases until reaching 2 K [see Table S4]. The magnetic behavior of these Co(II) complexes corresponds to a weak antiferromagnetically coupled system. The obtained data were analyzed and fitted in a variety of ways in order to calculate Curie (C) and Weiss (θ) constants and coupling constant J values. To evaluate these magnetic parameters, different approaches have been used. Generally, some parts of the compounds were fitted using a classical spin Heisenberg model for a chain or by the fitting of the low-temperature region to an Ising chain model [89]. Also, an analytical expression for the infinite chain of classical spins was derived by Fisher through the Hamiltonian method [90]. However, reasonable results were obtained using the phenomenological approach for some low-dimensional Co(II) systems that allows us to estimate the strength of the antiferromagnetic exchange interactions [91]. Rueff and coworkers postulated the equation $\chi_M T = A \exp(E_1/kT) + B \exp(E_2/kT)$, where A + B represents the Curie constant, while E$_1$ and E$_2$

equal the activation energies corresponding to the spin–orbit coupling, and the antiferromagnetic exchange interaction, respectively. The C, θ and J values vary in the ranges of 1.394–3.64 cm^3 mol^{-1} K, −42 to +0.1 K and −24.8 to −1.1 cm^{-1}, respectively (Table S4), in five complexes, namely $\{[Co(H_2BiIm)_2(dca)_2]Cl\}_n$ [27], $\{[Co(azpyph)(dca)](BF_4)\cdot MeOH\}_n$ [42], $[Co(5,6\text{-}(Me)_2\text{-}bzim)_2(dca)_2]_n$ [92], $[Co(5\text{-}Mebzim)_2(dca)_2]_n$ [92] and $\{[Co(H_3daps)(dca)](MeOH)_2(MeCN)\}_n$ [45]. Also, an analysis of the axial zero-field splitting parameter (D) has been made. It is well known that the D parameter is sensitive to many factors, which makes it difficult to find specific relationships. However, for octahedral cobalt(II) complexes, a positive D parameter is rather expected, but a negative D value has also recently been observed [93,94]. In $\{[Co(azpyph)(dca)](BF_4)\cdot MeOH\}_n$ [42], magnetic data were treated using the spin Hamiltonian $\hat{H} = D(\hat{S}x^2 - \hat{S}^2/3) + E(\hat{S}x^2 - \hat{S}y^2) + \mu_B B_g \hat{S}a - zj< \hat{S}a > \hat{S}a$. An analysis of the experimental data provided the D, E/D and molecular field correction parameter zj equal to −72.3 cm^{-1}, 0.0 and −0.273 cm^{-1}, respectively. On the other hand, in $\{[Co(H_2BiIm)_2(dca)_2]Cl\}_n$, the axial *zfs* parameter was +40.3 cm^{-1}. The fitting DC magnetic data for $[Co(5,6\text{-}(Me)_2\text{-}bzim)_2(dca)_2]_n$ and $[Co(5\text{-}Mebzim)_2(dca)_2]_n$ [92] also gave a positive value of D, which was 63(19) and 60(8) cm^{-1}. Interestingly, FIRMS measurements were performed for these two samples. For the first compound, there was a zero-field transition at 134.0 cm^{-1}, which represents the splitting between the $m_s = \pm 1/2$ and $m_s = \pm 3/2$ Kramers doublets. The D parameter (62.5 cm^{-1}) calculated from equation $\Delta = 2\sqrt{D^2 + 3E^2}$ has good agreement with magnetic data fitting. The same procedures were performed for $[Co(5\text{-}Mebzim)_2(dca)_2]_n$, and the splitting between the Kramers doublets seen in the FIRMS spectra was 124 cm^{-1}. Further analysis demonstrates that the FIRMS spectra show good agreement with the experimental data using the same parameters, giving D = 60 cm^{-1} and E = 9 cm^{-1}. The same Hamiltonian equation was used to determine the *zfs* parameters in $\{Co(H_3daps)(dca)](MeOH)_2(MeCN)\}_n$ [45]. The best fit presented a positive value of D = 41.3(5) cm^{-1}, E = 0.81(3) cm^{-1} and a very weak antiferromagnetic exchange interaction, J = 0.004 cm^{-1}. Furthermore, to analyze the electronic structure and magnetic anisotropy of the Co(II) complex, quantum chemical calculations with ORCA4.0 and MOLCAS8.2 were performed. However, the last program showed anisotropic parameters that were a little bit higher in comparison with ORCA 4.0. Finally, the *ac* measurements were performed for $\{[Co(H_3daps)(dca)](MeOH)_2(MeCN)\}_n$ [45], $\{[Co(pypz)(dca)(H_2O)]\cdot dca\}_n$ [41], $[Co(5,6\text{-}(Me)_2\text{-}bzim)_2(dca)_2]_n$ [92] and $[Co(5\text{-}Mebzim)_2(dca)_2]_n$ [92]. Unfortunately, no out-of-phase signal on AC susceptibility was observed in the absence of an external magnetic field; therefore, those complexes are not natural single-ion magnets. The reason for this lies in the strong QTM (quantum tunneling of magnetization), which leads to fast relaxation as commonly observed in transition metal-based compounds [95]. With the increasing external field, the χ_M'' component rises and passes through a maximum, which confirms that dca–Co(II) 1D complexes exhibit a field-supported slow magnetic relaxation. The nature of the semicircle of the Cole–Cole plot showed the single relaxation process in $\{[Co(H_3daps)(dca)](MeOH)_2(MeCN)\}_n$ [45]. The generalized Debye model was used to extract the magnetization relaxation time (τ) and, later, the fitting of the Arrhenius using well-known equation $\ln(\tau) = \ln(\tau_0) + U_{eff}/kT$, where the energy barrier is 9.9 K (6.88 cm^{-1}), while $\tau_0 = 5.3 \times 10^{-6}$ s. In this compound, S. Konar and co-workers demonstrate that the relaxation process does not follow the Orbach process. The magnetization relaxation process is mainly controlled by QTM together with some shortcut path through virtual states (the Raman process). A similar situation was observed in $\{[Co(pypz)(dca)(H_2O)]\cdot dca\}_n$ [41], where both QTM and Orbach processes are involved in relaxation processes. The energy barrier and relation time are equal to 103 K and $\tau_0 = 1.2 \times 10^{-11}$ s. However, the authors note that the spin reversal U_{eff} might be underestimated because the last three data do not fit perfectly on the straight line. For this reason, further analysis is carried out and the involvement of the Raman process or even the phonon bottleneck process is considered. Interestingly, for $[Co(5,6\text{-}(Me)_2\text{-}bzim)_2(dca)_2]_n$ [92] and $[Co(5\text{-}Mebzim)_2(dca)_2]_n$ [92], no indication of the quantum tunneling of magnetization was found based on the Arrhenius-like plot. It has been proven that a single Raman-like term is insufficient to reproduce the whole data set. However, when two of them were considered, combined with phonon bottleneck relaxation mechanisms, the relaxation parameters could be accurately determined.

Interesting structural-magnetic relationships can be observed in three 2D coordination polymers with the formulas $[Co(pzdo)(dca)_2]_n$ [52], $[Co(mpdo)(dca)_2]_n$ [52] and $[Co(2,5\text{-}dmpdo)(dca)_2]_n$ [96]. The ferromagnetic ordering confirmed in the first two complexes results from the existence of μ_3- and $\mu_{1,5}$-dca coordination modes. On the other hand, bridging ligand 2,5-dmpdo in the third compound was found to mediate antiferromagnetic coupling [60,97,98]. In the first two complexes, the magnetic susceptibility above 40–50 K obeys the Curie–Weiss law, with the Weiss constant C equal to −9.4 K and −13.7 K and the Curie constant C equal to 3.17 and 3.34 $cm^3\ mol^{-1}$ K, respectively. The divergence of $\lambda_M T$ below 20 K is attributed to the ferromagnetic couplings between the effective spins of Co(II). For both complexes, FCM and ZFCM measurements in a low field show the occurrence of two long-range ferromagnetic transitions. The temperature dependence of ac magnetic susceptibility confirms phase transitions below 9 and 3 K in $[Co(pzdo)(dca)_2]_n$ and 1.9 K and 8.6 K in $[Co(mpdo)(dca)_2]_n$. Additionally, the field dependence of the magnetization measurements shows the rapid saturation of magnetization, which is a typical feature of long-range ferromagnetic ordering. Furthermore, hysteresis measured at 1.74 K in $[Co(pzdo)(dca)_2]_n$ and 1.78 K in $[Co(mpdo)(dca)_2]_n$ reveals that both complexes are soft magnets. The magnetic behavior of $[Co(2,5\text{-}dmpdo)(dca)_2]_n$ [60] is quite different from the two previous one compounds. The Curie and Weiss constants are 6.61 $cm^3\ mol^{-1}$ K and −33.5 K, respectively. The antiferromagnetic ordering was confirmed using the field dependence of the magnetization, which was measured below the Neel temperature (T_N = 10.8 K). $[Co(H_2O)(dca)_2{\cdot}phz]_n$ has attracted considerable attention due to the presence of μ_3– and $\mu_{1,3,5}$-dca coordination modes in its structure, along with the topological relationship between 2D sheets and 3D rutile-like structures [51]. Unfortunately, no bifurcation in the FCM and ZFCM plots was observed due to the presence of weak intra-network ferromagnetic coupling. In other Co(II) complexes based on single, double or mixed (single and double) dicyanamide bridges, temperature-dependent susceptibilities obey the Curie–Weiss law. At room temperature, the values of $\lambda_M T$ are in the range of 2.30–4.21 $cm^3\ mol^{-1}$ K and when the temperature is lowered, $\lambda_M T$ slowly decreased and reaches 1.21–2.85 $cm^3\ mol^{-1}$ K at ~2 K. The observed decrease typically can be the result of antiferromagnetic coupling between Co(II) ions or the depopulation of the higher-energy Kramers doublets of the cobalt(II) centers [99,100] (see Table S5, ESI). The magnetic data were fitted to the Curie–Weiss law, leading to C and θ constants in the ranges of 2.29–4.47 $cm^3\ mol^{-1}$ and −4.62–20.09 K, respectively. Only in one example, $[Co(bzim)_2(dca)_2]_n$ [58], does the θ constant have a positive sign (17.14 K), and together with $zJ = 0.648\ cm^{-1}$ indicates weak ferromagnetic coupling between the Co(II) ions. Moreover, for eight complexes: $[Co(biq)(dca)_2]_n$ [101], $\{[Co(NH_2pyz)_2(dca)_2]{\cdot}H_2O\}_n$ [65], $[Co_3(HOpyz)_5(dca)_6(H_2O)_2]_n$ [65], $[Co(atz)_2(dca)_2]_n$ [67], $[Co(bim)_2(dca)_2]_n$ [28], $[Co(bmim)_2(dca)_2]_n$ [28], $[Co(dmdpy)(dca)_2]_n$ [53] and $[Co(2\text{-}Mebzim)(dca)_2]_n$ [92], estimations of the magnitude of anisotropy and exchange interactions were conducted. In all of them, the axial *zfs* parameter was positive and ranged from +66.4 to +95.4 cm^{-1}. Bearing in mind that the increase in EPR signal intensity with decreasing temperature supports and confirms a positive value of D, EPR spectra were recorded in low temperatures in the X-band spectrometers. In the case of $[Co(biq)(dca)_2]_n$ [101], only a very broad featureless line was observed, caused by intermolecular interactions. However, the typical EPR spectrum for Co(II) compounds with a positive D was observed in $\{[Co(NH_2pyz)_2(dca)_2]{\cdot}H_2O\}_n$ [65] and $[Co_3(HOpyz)_5(dca)_6(H_2O)_2]_n$ [65]. Interestingly, the FIRMS spectrum of $[Co(2\text{-}Mebzim)(dca)_2]_n$ [92] showed multiple zero-field transitions at around 138 cm^{-1}. To estimate the value of D, a simulation using a spin Hamiltonian was conducted, resulting in $D = 67\ cm^{-1}$ and $E = 10\ cm^{-1}$, which were in agreement with the experimental data.

In 2015, B. Machura, M. Julve and co-workers confirmed the single-ion magnet (SIM) behavior for a 2D coordination polymer of formula $[Co(atz)_2(dca)_2]_n$ with the cobalt(II) ions bridged by single $\mu_{1,5}$-dicyanamide bridges. One year later, the same research team published magneto-structural studies on $[Co(bim)_2(dca)_2]_n$ [28] and $[Co(bmim)_2(dca)_2]_n$ [28] in comparison to $[Co(atz)_2(dca)_2]_n$. In the following years, numerous papers were published describing the phenomenon of slow magnetic relaxation in cobalt(II) coordination polymers. These studies highlighted the potential of cobalt(II) complexes as single-ion magnets (SIMs) due to their ability to exhibit a slow relaxation of magnetization under certain conditions. The coordination environment, the nature of the bridging ligands, and the geometry of the cobalt(II) centers were identified as key factors influencing this magnetic behavior, expanding the understanding of SIM phenomena in 3d metal-based systems.

Of course, it is impossible to ignore the characteristics of the magnetic properties of α-$[Co(dca)_2]_n$ and β-$[Co(dca)_2]_n$ described in detail by two research teams in 1998 [70,102,103]. The long-range ferromagnetic ordering with a Curie temperature T_C of 9 K was confirmed for $[Co(dca)_2]$. The authors anticipated ferromagnetic properties after calculating a positive Weiss constant, $\theta = +6.1$ K. In a small field, the χT value increase sharply, reaching a much higher value than expected for a short-range order. The ferromagnetic behavior of $[Co(dca)_2]_n$ was supported by the low-field field-cooled (FC) and zero-field-cooled (ZFC) temperature dependence of the magnetization and by the 5.5 T saturation magnetization. To confirm the magnetic ordering, the temperature dependencies of the in-phase (real, $\lambda'(T)$) and out-of-phase (imaginary, $\lambda''(T)$) components' ac susceptibilities were measured. The studies demonstrated clear ferromagnetic coupling due to the presence of a $\lambda''(T) \neq 0$ component [104,105]. Since then, many articles have been published exploring transition metal complexes exhibiting long-range ferromagnetic order, similar to the rutile-like compound $[Co(dca)_2]_n$, though with varying degrees of success. The 3D complexes $\{(MePh_3P)[Co(dca)_3]\}_n$ and $\{(EtPh_3P)[Co(dca)_3]\}_n$ exhibit a decreasing magnetic moment from 4.9 μB at room temperature to 3.5 μB at 4 K, which is typical for antiferromagnetic coupling. A sharp increase at 9 K in low fields was observed during measurements for $\{(EtPh_3P)[Co(dca)_3]\}_n$, but this was only indicated in the presence of traces of α-$[Co(dca)_2]_n$ [76]. A similar situation was observed for $[Co(dbtp)(dca)_2]_n$ and $\{[Co(bte)(dca)_2]\cdot H_2O\}_n$, where the μ_{eff} values remained independent from the applied field, varying between 0.01 and 1 T in the 4–100 K region, ruling out any long-range magnetic ordering [47,83]. In the remaining three-dimensional Co(II) compounds, the negative value of the Weiss constant clearly indicates the transmission of antiferromagnetic interactions through the dca bridges (see Table S6).

6. Conclusions

The chemistry of coordination compounds of d-block metals, particularly those involving cobalt(II) ions, has consistently amazed researchers with the subtle beauty of their crystal structures and their diverse physicochemical properties. Given the remarkable simplicity of the dicyanamide ligand, this anionic pseudohalide ligand has proven to be one of the most excellent inorganic spacers to use to construct magnetic coordination compounds, displaying multiple bridging coordination modes. The versatility of $dcac^-$ has enabled the design and synthesis of mononuclear and dinuclear species, as well as numerous one-, two- and three-dimensional coordination polymers with diverse magnetic couplings, ranging from antiferromagnetism to ferromagnetism, including slow magnetic relaxation phenomena in single-ion magnet (SIM) systems.

Reflecting on past research, it is evident that transition metal compounds based on the dca anion have contributed significantly to the fundamental knowledge across various fields. This article focuses on the magnetic–structural relationships in cobalt(II) compounds, representing only a small part of the deeper amount of research on dicyanamide complex compounds of copper(II), manganese(II, III), nickel(II), iron(II), zinc(II) and other d-block metal cations, which have been thoroughly investigated from diverse physicochemical properties.

What about future perspectives? It might seem that the chemistry of the dicyanamide anion has been fully explored, but recent articles in top scientific journals prove otherwise. Over the past five years, researchers have shown that there is still much to discover—not only in the field of coordination chemistry, but also in the development of dicyanamide-based ionic liquids [106,107] or in electrochemistry, where β-[Zn(dca)$_2$]$_2$ was efficiently used as a negative electrode material for lithium-ion batteries [108].

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/magnetochemistry10110090/s1, Table S1: Magneto-structural data for mononuclear dca-Co(II) compounds; Table S2: Shape values for mononuclear Co(II) complexes; Table S3: Magneto-structural data for binuclear dca-Co(II) compounds; Table S4: Magneto-structural data for one-dimensional dca-Co(II) coordination polymers; Table S5: Magneto-structural data for two-dimensional dca-Co(II) coordination polymer; Table S6. Magneto-structural data for three-dimensional dca-Co(II) coordination polymer.

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Abbreviations

atz	2-amino-1,3,5-triazine	**H$_3$daps**	2,6-bis(1-salicyloylhydrazonoethyl) pyridine
azpyph	N,N′-di-tert-butyl-2,11 diaza[3,3](2,6)pyridinophane	**L^1**	N,N′-di-tertbutyl-2,11-diaza[3,3](2,6)pyridinophane
bim	1-benzylimidazole	**nitppy**	2-(4′-pyridyl)-4,4,5,5–tetramethylimidazoline-1-oxyl-3-oxide
biq	2,2′-biquinoline	**nic**	isonicotinamide
bimb	1,4-bis(im idazol-1-yl)-butane	**NH$_2$pyz**	2-aminopyrazine
bipy	4,4′-bipyridine	**MeCN**	acetonitrile
bipim	2,2-bipyrimidine	**mpdo**	2-methyl pyrazine dioxide
bmim	1-benzyl-2-methylimidazole	**phz**	phenazine
bpp	1,3-bis(4′-pyridyl)propane	**phen**	1,10-phenanthroline
bpm	bis[(3,5-di methyl)pyrazolyl]methane	**pybiu**	N-(picolinoyl)-biurate
bte	1,2-bis(1,2,4-triazol-1-yl)ethane	**pydz**	pyridazine
bpds	4,4′-bipyridyl disulfide	**pzdo**	pyrazinedioxide
bpeado	1,2-bis(4-pyridyl)ethane-N,N′-dioxide		
BeTriMe	benzyltrimethylammonium	**ptzda**	2,4-diamino-6-pyridyl-1,3,5-triazine
bdpb	N,N-bis(3,5-dimethyl-1H-pyrazol-1-yl) methyl-N2-phenylethane-1,2-diamine	**pypypz**	bis[3,5- dimethyl-4-(49-pyridyl)pyrazol-1-yl]methane
bpe	1,2-bis(4-pyridyl)ethane	**Phpyk**	2-benzoylpyridine
bte	1,2-bis(1,2,4-triazol-1-yl)ethane	**pypz**	2,6- bis(pyrazol-1-yl)pyridine
btrm	1,2-bis(1,2,4-triazole-1-yl)methane	**pzda**	2,4-diamino-6-pyridyl-1,3,5-triazine
bzim	benzimidazole	**tmeda**	tetra methylethylenediamine
DAT	1,5-diaminotetrazole	**tptz**	2,4,6-tris(2-pyridyl)-1,3,5-triazine
dmdpy	5,5′-dimethyl-2,2′-dipyridine	**tppz**	2,3,5,6-tetrakis(2-pyridyl)pyrazine
dmpzm	bis(3,5-dimethylpyrazolyl)methane	**3-bpo**	2,5-bis(3-pyridyl)-1,3,4-oxadiazole
deen	N,N-diethyl-ethylenediamine	**3-pyo**	3-hydroxypyridine
dbtp	1,3-di(benzotriazol-1 yl)propane	**4-bpo**	2,5-bis(4-pyridyl)-1,3,4-oxadiazole
etpybzam	(N,N-diethyl,N′-(pyridin-2-yl)benzylidene)ethane-1,2-diamine	**4-bpmp**	bis(4-pyridylmethyl)piperazine
imph	4-(imidazol 1-yl)phenol	**4,7-dmphen**	4,7-dimethylphenanthroline
HOpyz	2-hydroxypyrazine	**4-bpmp**	bis(4-pyridylmethyl)piperazine
hmt	hexamethylenetetramine	**5,6-(Me)$_2$-bzim**	5,6-dimethylbenzimidazole
HFlu	fluconazole	**5-Mebzim**	5-methyl benzimidazole
H$_2$biim	2,2′-biimidazole		

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