





Article

Coordination Polymers in Dicyanamido-Cadmium(II) with Diverse Network Dimensionalities

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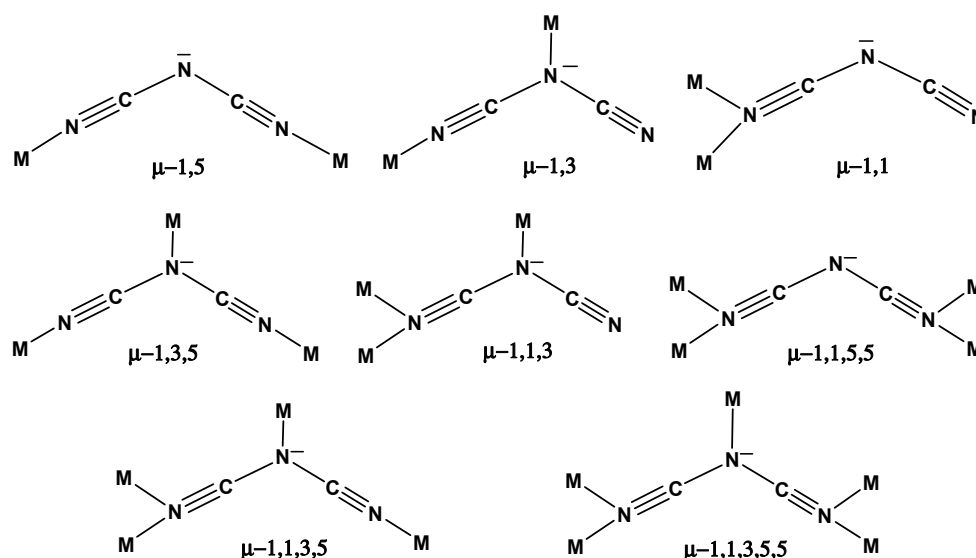
Abstract: The synthesis and structural characterization of six dicyanamido-cadmium(II) complexes are reported: *catena*-[Cd($\mu_{1,3}$ -dca)($\mu_{1,5}$ -dca)(3-ampy)] (**1**), *catena*-[Cd₃($\mu_{1,3,5}$ -dca)₂($\mu_{1,5}$ -dca)₄(pyNO)₂(H₂O)₂] (**2**), *catena*-[Cd(H₂O)₂($\mu_{1,5}$ -dca)₂](2,6-lut-NO) (**3**), *catena*-[Cd(Me₂en)($\mu_{1,5}$ -dca)₂] (**4**), *catena*-[Cd(Me₄en)($\mu_{1,5}$ -dca)₂] (**5**), and [Cd(1,8-damnp)₂(dca)₂] (**6**), where dca = dicyanamide anion, 3-ampy = 3-aminopyridine, pyNO = pyridine-N-oxide, 2,6-lut-NO = 2,6-lutidine-N-oxide, Me₂en = N,N-dimethyl-ethylenediamine, Me₄en = N,N,N',N'-tetramethyl-ethylenediamine, and 1,8-damnp = 1,8-diaminonaphthalene. The coordination polymers have different dimensionalities: **1** and **5** form 3D networks structures; **3** and **4** form polymeric 1D chains and 1DD double chains, respectively. Ribbons of three fused polymeric chains are observed in **2**. In **6**, the mononuclear complex units form a hydrogen-bonded supramolecular 3D network. In the coordination polymer compounds, the dca linkers display three bonding modes: the most common $\mu_{1,5}$ -dca and the least popular $\mu_{1,3}$ - and $\mu_{1,3,5}$ -dca bonding. The luminescence emission and thermal properties of the complexes were investigated.

Keywords: cadmium; dicyanamide; coordination polymer; X-ray; thermal properties

1. Introduction

Cadmium(II) ion forms complexes with phosphates, amino acids, peptides, nucleobases, nucleotides, and nucleic acids ([1] (a,b)). The most common coordination geometry in cadmium(II) complexes is octahedral, but tetrahedral and five-coordinate geometries were also formed, depending on the steric coordination environment [2–16]. The interaction of small pseudo halides (N₃[−], NCS[−], and NCO[−]) and the longer dicyanamide, dca (dca = N(CN)₂[−]) with the divalent metal(II) ions and co-ligands, are considered to be the most studied pseudohalide compounds. These anions have the capability of assembling metal ions, leading to the formation of bridged dinuclear and polynuclear, as well as coordination polymers (CPs) with various architecture topologies [2–16] and interesting potential applications [17–23]. One of the most obvious reasons for the formation of these compounds is their wide range of coordination bonding modes. With the focus on the relatively less-studied bent-shaped dca system, the anion can display two terminal bonding sites (end-to-end), or two sites of the same atom (end-on) [5,7,14,15,24–27], in addition to

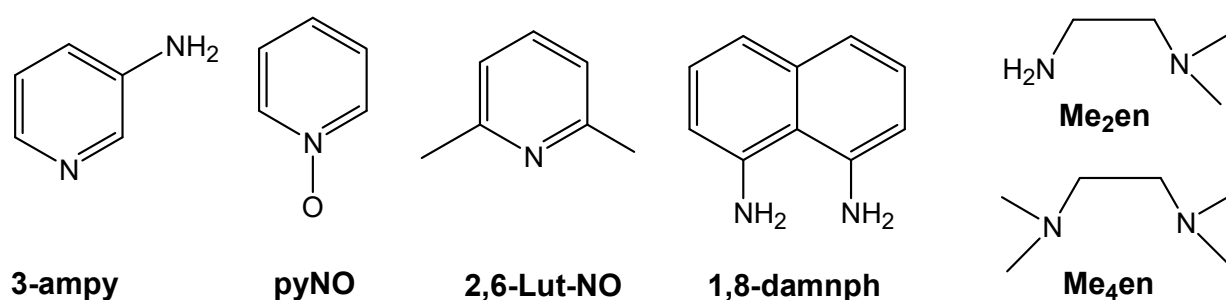
the central amide nitrogen [28,29]. The various coordination bonding modes of dca have been previously summarized [30,31], and they are illustrated in Scheme 1.



Scheme 1. Bridging modes of dicyanamide anion.

One of the very important property associated with $(n-1)d^{10}$ metal ions such as Cd(II) is their tendency to produce photoluminescence emission [5,15,24,25,32], a phenomenon which can possibly be used in photochemical devices [32–35] and in the catalytic activity of some organic reactions, such as Knoevenagel condensation [36]. In addition, cadmium(II) coordination chemistry and coordination polymers, as well as metal organic framework materials, were successfully employed in the crystal engineering architecture, for the design of many interesting compounds, which showed diverse structural properties and promising applications [33–40].

Herein, we examine the interaction of Cd(II) and dca in the presence of a wide range of auxiliary *N*-donors ligands with variable skeletons simple monodentates, such as *N*-pyridyloxide (ONpy) and 2,6-lutidine-*N*-oxide (ON-2,6-lut); bidentate ligands, *N,N*-dimethyl-(Me₂en) and *N,N,N',N'*-tetramethyl-ethylenediamine (Me₄en); and 1,8-diaminonaphthalene (1,8-damnp), in addition to the ambidentate 3-aminopyridine ligand (3-ampy), which possibly can act as a bridging ligand, too. The structural formulas of these ligands are shown in Scheme 2. The selected ligands should provide vacant coordination sites at the cadmium center and, hence, allow its interaction with the dca linker(s) to propagate the formation of bridging coordination polymers. The photoluminescence emission and thermal properties of the complexes were also investigated.



Scheme 2. The structural formulas and abbreviations of ligands used in this study.

2. Experimental

2.1. Materials and Physical Measurements

Sodium dicyanamide was purchased from TCI, and 3-aminopyridine was purchased from Aldrich. All other materials were reagent-grade quality. Infrared spectra of the solid complexes were performed on a Bruker Alpha P (platinum-ATR-cap) or Cary 630 (ATR-IR) spectrometer. Thermal analyses were measured on solid samples, using NETSCH STA (N₂ atmosphere; heating rate, 10 °C/min). PXRD measurements of the microcrystalline bulk material were performed with a Bruker D8 Advance powder diffractometer. Emission spectra were recorded with a Perkin-Elmer Lambda LS55 spectrofluorometer. Elemental CHN microanalyses were carried out with an Elementar Vario EN3 analyzer and by the Atlantic Microlab, Norcross, GA, USA.

2.2. Preparation of the Compounds

Catena-[Cd(3-ampy)(μ_{1,3}-dca)(μ_{1,5}-dca)] (1): Cadmium(II) nitrate tetrahydrate, Cd(NO₃)₂·4H₂O (0.345 g, 1 mmol), sodium dicyanamide (0.18 g, 2 mmol), and 3-aminopyridine (0.19 g, 1 mmol) were dissolved in 80 mL H₂O/MeOH (1:2 v:v). The solution was heated up to 85 °C and stirred for 30 min. This was then filtered, and the clear solution was allowed to stand at ambient temperature. After about one week, brown-tinted needle-shaped crystals were obtained (yield: 0.28 g, 83%). These were collected by filtration and dried in air. Analytical Calculated for C₉H₆CdN₈ (338.63 g/mol): 31.9% C, 1.8% H, and 33.1% N. Found: 31.7% C, 1.7% H, and 33.3% N. IR (ATR, cm⁻¹): 3224 (w) ν(N-H); 2926 (w), 2888 (w), and 2838 (m) ν(C-H); 2293 (m), 2229 (s), and 2162 (s) ν(C-N, dca); 1629 (s), 1581 (m), 1492 (w), 1449 (m), 1356 (m), 1305 (m), 1269 (m), 1194 (m), 1140 (m), 1054 (w), 922 (w), 889 (m), 853 (w), 796 (m), 694(m), 646 (m), 599 (m), 514 (s), and 413 (w).

Catena-[Cd₃(μ_{1,3,5}-dca)₂(μ_{1,5}-dca)₄(pyNO)₂(H₂O)₂] (2): This complex was prepared, using a similar procedure to that described for 1, except pyridine-*N*-oxide (0.032 g, 0.34 mmol) was used instead of 3-ampy. The isolated colorless needle-shaped crystals were collected by filtration (yield: 0.23 g, 72%). Analytical Calculated for C₂₂H₁₄Cd₃N₂₀O₄ (959.72 g/mol): 27.5% C, 1.5% H, and 29.2% N. Found: 27.3% C, 1.6% H, and 29.4% N. IR (ATR, cm⁻¹): 3571 (w), 3400 (m,br) ν(O-H); 3107 (w), 3065 (w) ν(C-H); 2312 (m) 2284 (m), 2286 (s), 2256 (m), 2226 (m), 2190 (m), 2166 (s), and 2128 (s) ν(C-N, dca); 1905 (w), 1667 (w), 1468 (m), 1360 (m), 1342 (m), 1320 (m), 1318 (m), 1240 (m), 1207 (m), 1168 (m), 1071 (m), 1016 (w), 947 (w), 818 (m), 771 (m), 675 (m), 660 (m), 547 (w), 514 (s), 487 (m), and 448 (m).

Catena-[[Cd(H₂O)₂(μ_{1,5}-dca)₂](2,6-lut-N-oxide)] (3): This complex was prepared, using a similar procedure to that described for 1, except 2,6-lutidine-*N*-oxide (0.123 g, 1 mmol) was used instead of 3-ampy. Colorless needle-shaped crystals were obtained (yield: 0.31 g, 77%). Analytical Calculated for C₁₁H₁₃CdN₇O₃ (403.69 g/mol): 32.7% C, 3.2% H, and 24.3% N. Found: 32.5% C, 3.1% H, and 24.4% N. IR (ATR, cm⁻¹): 3570 (w), 3343 (m,br) ν(O-H); 3075 (w), 2928 (m,br) ν(C-H); 2285 (s), 2229 (m), 2168 (s), and 2148 (m) ν(C-N, dca); 1686 (w), 1579 (m), 1496 (w), 1457 (m), 1419 (m), 1377 (m), 1338 (s), 1210 (s), 1162 (m), 1100 (w), 1034 (w), 930 (w), 863 (m), 830 (w), 785 (m), 668 (m), 602 (m), and 520 (s).

The three dicyanamido complexes 4–6 were synthesized by using a general procedure: An aqueous solution of Nadca (0.091 g, 1 mmol in 5 mL H₂O) was added to a mixture containing Cd(NO₃)₂·4H₂O (0.155 g, 0.5 mmol), and the corresponding ligand (0.5 mmol) dissolved in MeOH (15 mL). The resulting solution was heated for 5–10 min, on a steam-bath, filtered through celite, and then allowed to crystallize at room temperature.

Catena-[Cd(Me₂en)(μ_{1,5}-dca)₂] (4): The colorless single crystals, which were obtained after one week, were collected by filtration and dried in air (yield 41%). Characterization: Analytical Calculated for C₈H₁₂CdN₈ (332.47 g/mol): C, 28.89%; H, 3.64%; and N, 33.69%. Found: C, 28.89%, H, 3.51%; and N, 33.58%. IR bands (ATR, cm⁻¹): 3282 (w) ν(N-H); 3077 (vw), 2989 (vw), 2955 (vw), 2922 (vw), 2877 (vw) ν(C-H); 2287 (s), 2234 (m), 2157 (vs) ν(C-N, dca); 1443 (w), 1430 (s), 1281 (w), 1140 (w), 1095 (w), 1074 (m), 1003 (m), 925 (s), 841 (s), 821 (m), and 668 (m).

Catena-[Cd(Me₄en)(μ_{1,5}-dca)₂] (5): The long colorless needles, obtained on the following day, were collected by filtration and dried in air (yield 76%). Characterization: Analytical Calculated for C₁₀H₁₆N₈Cd (360.70 g/mol): C, 33.30%; H, 4.47%; and N, 31.07%. Found: C, 33.45%, H, 4.44%; and N, 30.77%. IR bands (ATR, cm⁻¹): 3058 (vw), 2880 (vw), 2840 (vw) ν(C-H); 2285 (m), 2227 (m), 2154 (vs) ν(C-N, dca); 929 (s), 833 (s), and 794 (m).

[Cd(1,8-damnph)(dca)₂] (6): This complex was isolated as off-white-colored crystals after two days of standing at room temperature. Crystals were collected and dried in air (yield 47%). Characterization: Analytical Calculated for C₂₄H₂₀CdN₁₀ (560.89 g/mol): C, 51.39%; H, 3.59%; and N, 24.97%. Found: C, 50.99%; H, 3.66%; and N, 25.00%. IR bands (ATR, cm⁻¹): 3255 (m) ν(N-H) stretching; 3153 (m), 3064 (vw) ν(C-H); 2257 (s), 2219 (s), 2156 (s) (vs) ν(C-N, dca); 1620 (m), 1573 (s), 1396 (s), 1330 (s), 1280 (s), 1049 (vs), 988 (vs), 908 (m), 812 (s), and 754 (vs).

2.3. Single-Crystal Structure Determination

Suitable single crystals of the six title compounds were mounted on a Bruker-AXS APEX II CCD diffractometer and measured at 100(2) K with Mo-Kα radiation (λ = 0.71073 Å). Table 1 summarizes refinement and data collection features and crystallographic data. The following program packages were used for data processing, LP and absorption corrections, structure solution and refinement (F² full-matrix least-squares), and visualization and analysis: APEX [41], SADABS [42], SHELX program library [43,44], Mercury [45], PLATON [46], and ToposPro [47]. Depository codes: CCDC 1982387 (for 1) and CCDC 2059063-2059067 (for 2–6).

Table 1. Crystallographic data and processing parameters of 1–6.

Compound	1	2	3
Empirical formula	C ₉ H ₆ CdN ₈	C ₂₂ H ₁₄ Cd ₃ N ₂₀ O ₄	C ₁₁ H ₁₃ CdN ₇ O ₃
Formula mass	338.62	959.76	403.69
System	Monoclinic	Triclinic	Triclinic
Space group	Cc	P-1	P-1
a (Å)	14.3557(7)	6.6636(12)	7.4407(4)
b (Å)	11.0239(6)	7.7098(17)	7.6936(4)
c (Å)	7.3916(4)	16.035(3)	15.6387(8)
α (°)	90	77.982(9)	88.291(2)
β (°)	104.588(2)	78.672(9)	86.251(2)
γ (°)	90	86.459(12)	61.252(2)
V (Å ³)	1132.05(10)	789.9(3)	783.22(7)
Z	4	1	2
D _{calc} (Mg/m ³)	1.987	2.018	1.712
θ max (°)	26.992	30.309	30.040
Data collected	25470	15429	22948
Unique refl./R _{int}	2441/0.0657	4675/0.0441	4564/0.0455
Parameters/Restraints	169/4	231/0	212/10
Goodness-of-Fit on F ²	1.036	1.162	1.333
R1/wR2 (all data)	0.0176/0.0414	0.0261/0.0606	0.0388/0.0921
Residual extrema (e/Å ³)	0.517/−0.603	0.936/−1.352	0.744/−1.168

Table 1. Cont.

Compound	4	5	6
Empirical formula	C ₈ H ₁₂ CdN ₈	C ₁₀ H ₁₆ CdN ₈	C ₂₄ H ₂₀ CdN ₁₀
Formula mass	332.67	360.72	560.90
System	Monoclinic	Orthorhombic	Monoclinic
Space group	P2 ₁ /c	Pnma	P2 ₁ /n
a (Å)	7.4137(3)	16.8193(7)	7.6234(3)
b (Å)	13.8858(5)	11.9291(6)	11.1927(4)
c (Å)	12.2685(5)	7.6217(3)	13.3631(5)
α (°)	90	90	90
β (°)	90.251(2)	90	99.803(2)
γ (°)	90	90	90
V (Å ³)	1262.97(9)	1529.21(12)	1125.90(7)
Z	4	4	2
D _{calc} (Mg/m ³)	1.750	1.567	1.656
θ max (°)	33.274	30.549	33.303
Data collected	107447	97158	106749
Unique refl./R _{int}	4849/0.0852	2444/0.0509	4323/0.0642
Parameters/Restraints	164/0	130/0	176/0
Goodness-of-Fit on F ²	1.042	1.108	1.050
R1/wR2 (all data)	0.0190/0.0491	0.0244/0.0618	0.0192/0.0517
Residual extrema (e/Å ³)	0.792/−0.934	1.084/−0.657	0.800/−0.694

3. Results and Discussion

3.1. Synthetic Aspects and IR Spectra of the Complexes

With the high tendency of Cd(II) ion to predominantly form six-coordinate complexes, one expects that its interaction with the long dicyanamide anion (NCNCN)[−] (dca), in the presence of small non-sterically hindered mono- or bi-dentate co-ligands, to generate coordination polymeric compounds. With this hypothesis in mind, the reaction of a methanolic mixture containing Cd(NO₃)₂·4H₂O and ligands such as 3-ampy, NO-py, Me₂en, and Me₄en and an aqueous solution of Nadca in the stoichiometric ratio 1:1:2 afforded the expected CPs: *catena*-[Cd(3-ampy)(μ_{1,3}-dca)(μ_{1,5}-dca)] (**1**), *catena*-[Cd₃(μ_{1,3,5}-dca)₂(μ_{1,5}-dca)₄(pyNO)₂(H₂O)₂] (**2**), *catena*-[Cd(Me₂en)(μ_{1,5}-dca)₂] (**4**), and *catena*-[Cd(Me₄en)(μ_{1,5}-dca)₂] (**5**), respectively. Interestingly, the corresponding reactions with the sterically planar molecules of 2,6-lut-NO and 1,8-damnph yielded the CP *catena*-{[Cd(H₂O)₂(μ_{1,5}-dca)₂](2,6-lut-NO)} (**3**) and the discrete mononuclear complex [Cd(1,8-damnph)(dca)₂] (**6**), respectively. The former complex constitutes a CP, in which the 2,6-lutidine-N-oxide is not encountered in the coordination sphere of the complex, whereas, in **6**, the dca is acting as a monodentate ligand. The purity of the isolated complexes was checked by X-Ray Powder Diffraction and the XRD method, and the graphs of these patterns are depicted in Supplementary Materials Figures S1–S6 for complexes **1–6**, respectively. The complexes were structurally characterized by single-crystal X-ray crystallography, as well as elemental microanalyses and IR spectroscopy.

The IR spectra of the complexes reveal the general characteristic features of the dicyanamide group. In general, the complexes display three medium–strong intense bands over the vibration ranges 2290–2260, 2230–2220, and 2160–2150 cm^{−1} regions. The later band is attributable to ν_s(C≡N), and the former two vibrational bands are attributable to

$\nu_{\text{as}}(\text{C}\equiv\text{N})$ and $\nu_{\text{s}} + \nu_{\text{as}}(\text{C}\equiv\text{N})$, respectively [3–7,14,26–29,48,49]. These bands are clearly pronounced in the complexes **1**, **4**, **5**, and **6**. The observed split of bands in complexes **2** and **3** is most likely attributed to the involvement of the aqua ligands in hydrogen bonds of the type $\text{O}-\text{H}\cdots\text{N}$ to N2 and/or N5 atoms of the adjacent dca groups (see Section 3.2). The further split of the bands in *catena*- $[\text{Cd}_3(\mu_{1,3,5}\text{-dca})_2(\mu_{1,5}\text{-dca})_4(\text{pyNO})_2(\text{H}_2\text{O})_2]$ (**2**) results from two dca coordination bonding modes. These two complexes also display medium broad bands over the range $3570\text{--}3340\text{ cm}^{-1}$ assigned for the $\nu(\text{O}-\text{H})$ stretching frequency of the coordinated aqua molecules [50]. The weak–medium intense band(s) located over the $3280\text{--}3220\text{ cm}^{-1}$ region is/are due to the $\nu(\text{N}-\text{H})$ stretching frequencies in complexes **1**, **4**, and **6**. The weak $\nu(\text{C}-\text{H})$ stretching frequencies were shown for all complexes over the $3100\text{--}2840\text{ cm}^{-1}$ region [50]. Representative IR spectra of compounds **1–3** are shown in Supplementary Materials Figures S7–S9.

3.2. Description of the Structures

3.2.1. *Catena*- $[\text{Cd}(\mu_{1,3}\text{-dca})(\mu_{1,5}\text{-dca})(3\text{-ampy})]$ (**1**)

A molecular plot of the title compound **1** is given in Figure 1 and bond parameters are listed in Supplementary Materials Table S1. The Cd(II) is octahedrally coordinated by 4 N donor atoms of the dicyanamide anions, and two N donor atoms of the μ_2 -bridging 3-aminopyridine ligand in *cis*-configuration. The Cd–N bond lengths are in the range from 2.297(3) to 2.392(4) Å. The dicyanamide anions reveal two different bonding modes $\mu_{1,3}$ - and $\mu_{1,5}$ -bridging, to form a 3D network structure, together with the μ_2 -bridging 3-ampy ligands with their metal–metal bridging distances of 6.1863(5), 7.1006(5), and 7.2195(7) Å, respectively. The μ_2 -bridging 3-ampy and $\mu_{1,3}$ -bridging dca anions form a 2D sublattice extended along the *b*- and *c*-axis directions, consisting of square layers with rings of type $[\text{Cd}-\mu_{1,3}\text{-dca}(\text{Cd}-\mu_2\text{-3-ampy})_2\text{-Cd}-\mu_{1,3}\text{-dca}]$, which are further linked by the $\mu_{1,5}$ -dca anions, to generate the 3D network (Figure 1).

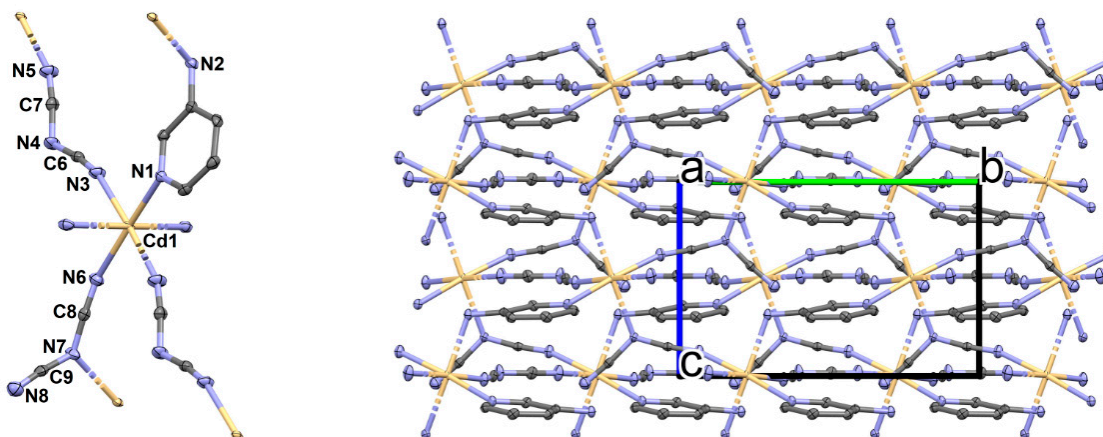


Figure 1. Coordination (left) and 3D network (right) of complex **1**. (Color code: yellow, Cd; blue, N; black, C.)

Topological investigations show that the uninodal six-connected network of **1** has **rob** topology (point symbol: $4^8.6^6.8$). The Cd–dca bridges have the following bond parameters: Cd–N–C, from $116.4(3)$ to $160.2(3)^\circ$; N–C–N, $172.1(4)$ to $174.4(5)^\circ$; C–N–C, $119.4(4)$ and $123.6(4)^\circ$; C–N (nitril), from $1.150(5)$ to $1.160(5)$ Å; and N–C (amin), $1.305(5)$ to $1.332(6)$ Å. The amino group forms hydrogen bonds (H-bonds) of the type $\text{N}-\text{H}\cdots\text{N}$ to the non-ligated N4 and N8 atoms of the dca anions (Supplementary materials Figure S10 and Table S2). Non-covalent $\pi\cdots\pi$ ring \cdots ring interactions are found between neighboring aromatic rings with a separation of their centers of gravity (Cg) of $3.760(2)$ Å, which further stabilizes the network structure.

Metal complexes containing both types of $\mu_{1,3}$ - and $\mu_{1,5}$ -bridging dca ligands have been published, e.g., for $\text{M}(\text{dca})_2$ [51] or mixed ligand compounds [52]. However, only one

Cd(II) complex containing $\mu_{1,3}$ - and $\mu_{1,5}$ -bridging dca and additional bridging co-ligand (μ_2 -2,2'-bis(4-pyridylmethoxy)-1,1'-biphenylene) has been described [53]. The *catena*-[M(3-ampy) $_2(\mu_{1,5}$ -dca) $_2$] (M = Cd(ii), Zn(ii), Mn(ii), Co(ii) and Cu(ii)) complexes form 1D chain systems, where the 3-ampy acts as a terminal ligand [54].

3.2.2. Catena-[Cd $_3(\mu_{1,3,5}$ -dca) $_2(\mu_{1,5}$ -dca) $_4(\text{pyNO})_2(\text{H}_2\text{O})_2$] (2)

Two crystallographic independent metal centers exist in **2**, and both have CN 6 (Figure 2). Each Cd1 center is octahedrally ligated by two oxygen atoms of terminal aqua and pyridine-N-oxide molecule in *trans* positions and by four N donor atoms of the dicyanamide bridging ligands, with two acting in the $-\mu_{1,5}$ -dca and the other two in $-\mu_{1,3,5}$ -dca bridging mode. The Cd1-N/O bond lengths vary from 2.2916(16) to 2.332(2) Å. The axially elongated octahedron around each Cd2 that has site symmetry -1 is formed by six N atoms of dca groups only. The equatorial positions are occupied by N7 and N9 donor atoms of four $-\mu_{1,5}$ -dca bridging ligands [Cd2-N7 = 2.274(2), Cd2-N9 = 2.3041(19) Å], and the axial sites by N5 atoms of two $-\mu_{1,3,5}$ -dca bridging groups [Cd2-N5 = 2.3858(19) Å]. Thus, each Cd2 center is linked to 4 Cd1 centers by two $-\mu_{1,3,5}$ -dca bridging groups.

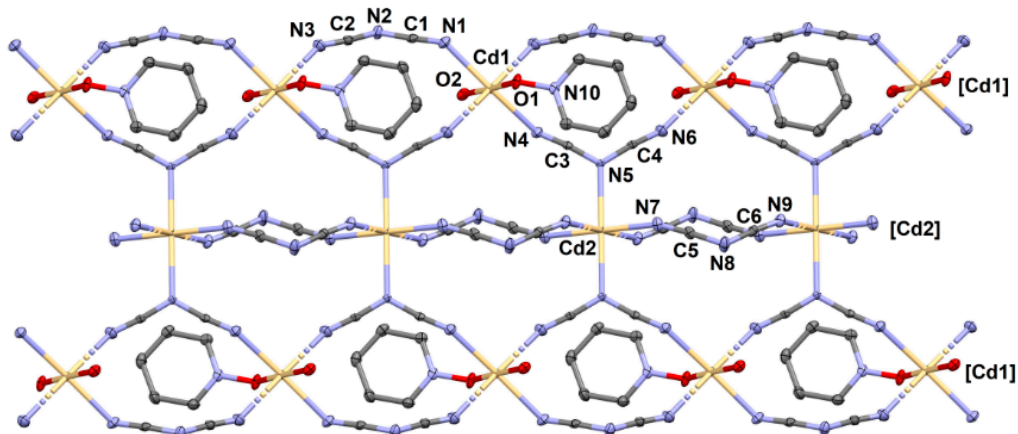


Figure 2. Ribbons consisting of three 1D chains in complex **2**. (Color code: yellow, Cd; red, O; blue, N; black, C.)

The resulting coordination polymer of compound **2** may be described as “ribbons” consisting of three polymeric *trans*-Cd-bis($-\mu_{1,5}$ -dca) 1D chains, where the central polymeric [Cd2] chains are crosslinked to the two external polymeric [Cd1] chains by the N5 atoms of the $-\mu_{1,3,5}$ -dca (Figure 2). The ribbons are running along the *b*-axis direction. The Cd⋯Cd separations within the ribbons are 6.2840(14), 6.4363(14), and 7.7098(17) Å. The bond parameters of Cd-dca bridges are as follows: Cd-N-C, from 119.32(14) to 159.13(19)°; N-C-N, 172.7(3) to 174.7(2)°; C-N-C, 119.17(19) to 121.0(2)°; C-N(nitrile), from 1.150(5) to 1.160(5) Å; and N-C(amine), 1.301(3) to 1.320(3) Å. H-bonds between O2 of aqua ligand to adjacent N2 of dca group and O1 of pyridine-N-oxides form a supramolecular 2D system (Supplementary Materials Figure S11 and Table S2).

3.2.3. Catena-[[Cd(H $_2$ O) $_2(\mu_{1,5}$ -dca) $_2$](2,6-lut-NO)] (3)

Compound **3** consists of two crystallographic independent polymeric [Cd(dca) $_2(\text{H}_2\text{O})_2$] 1D chains and non-coordinated two-fold disordered 2,6-lutidine-N-oxides (Figure 3). Each Cd(ii) with site symmetry -1 is ligated by two O atoms of terminal aqua ligands in *trans* positions and four N atoms of $\mu_{1,5}$ -bridging dca anions. The Cd-O bond lengths are 2.279(3) and 2.284(3) Å, and the Cd-N bond lengths vary from 2.314(3) to 2.331(3) Å. The bond parameters of Cd-dca are as follows: Cd-N-C, from 140.2(3) to 164.1(3)°; N-C-N, 173.0(4) to 174.6(4)°; C-N-C, 120.2(3) and 120.6(3)°; C-N(nitrile), from 1.150(5) to 1.154(5) Å; and N-C(amine), 1.311(4) to 1.319(4) Å. The Cd⋯Cd intra-chain separations are 7.6936(4) and 7.7130(4) Å. The aqua ligands form H-bonds of the type O-H⋯N to N2 and N5 of

neighboring dca groups and H-bonds of type O-H...O, to link the $[\text{Cd}(\text{dca})_2(\text{H}_2\text{O})_2]$ polymeric chains with O3 atom of non-coordinated 2,6-lutidine-N-oxide molecules, to create a supramolecular 3D network structure (Supplementary Materials Table S2).

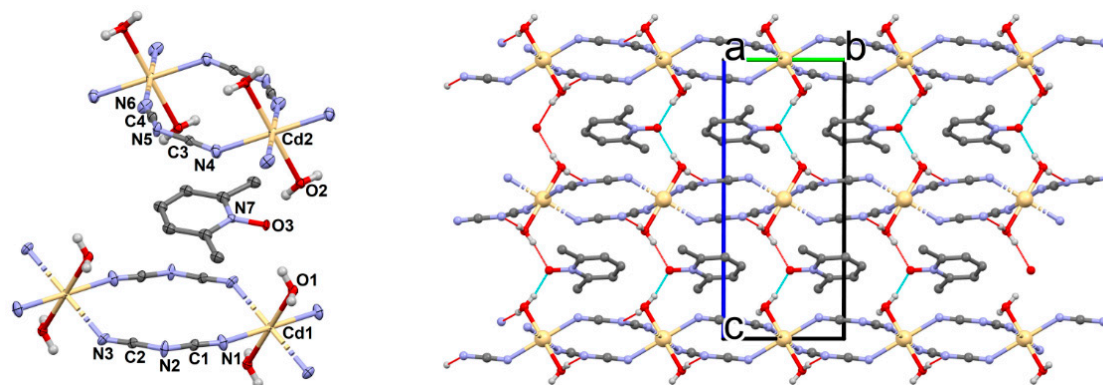


Figure 3. Coordination (left) and 1D system (right) of complex 3. Dotted lines indicate H-bonds. (Color code: yellow, Cd; red, O; blue, N; black, C; gray, H.)

3.2.4. Catena- $[\text{Cd}(\text{Me}_2\text{en})(\mu_{1,5}\text{-dca})_2]$ (4)

In this complex, each Cd(ii) center is ligated by two N of the chelating Me_2en in *cis* positions and four N of $\mu_{1,5}$ -bridging dca anions. Centrosymmetric pairs of CdN_6 polyhedra are linked by bis($\mu_{1,5}$ -bridging) dca groups, to form dimeric subunits. Furthermore, these subunits are connected by four single $\mu_{1,5}$ -bridging dca anions, to create 1D double chains running along the *a*-axis direction (Figure 4). The Cd-N(dca) bond distances vary from 2.2916(11) to 2.3545(11) Å, and the Cd-N(en) bond lengths are 2.2938(11) and 2.4523(10) Å. The bond parameter of Cd-dca bridges are as follows: Cd-N-C, from 126.04(9) to 161.76(10)°; N-C-N, 172.64(14) to 174.28(13)°; C-N-C, 119.49(11) and 121.36(11)°; C-N(nitrile), from 1.1550(17) to 1.1668(16)°; and N-C(amine), 1.3040(15) to 1.3397(16)°. The amino function forms H-bonds of the type N-H...N to the non-ligated N4 and N8 atoms of the dca anions (Supplementary Materials Table S2 and Figure S12).

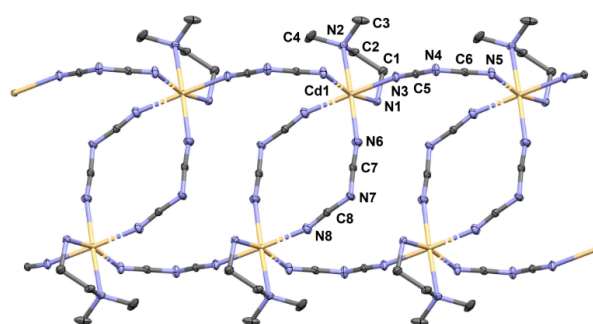


Figure 4. One-dimensional double chains in complex 4. (Color code: yellow, Cd; blue, N; black, C.)

3.2.5. Catena- $[\text{Cd}(\text{Me}_4\text{en})(\mu_{1,5}\text{-dca})_2]$ (5)

Crystals of compound 5 have orthorhombic space group Pnma (no 62). Cd1 and ordered dicyanamide group (dca1: N1/C1/N2/C2/N3) have site symmetry *m*. The second dicyanamide group (dca2: N4/C4/N5/C4/N6) and the Me_4en molecule are located on general positions and show two-fold disorder. The distorted CdN_6 octahedra are generated by the two donor atoms of chelating Me_4en molecule in *cis*-position and four terminal N of dca groups. The Cd-N bond distances vary from 2.267(9) to 2.3907(6) Å. The $\mu_{1,5}$ -dca bridging anions link each Cd1 center with four neighboring ones, to create a 3D network structure (Figure 5). Cd1 and dca1 groups on mirror planes at $y = 0.25$ and 0.75 form

“polymeric chains” running along the *a*-axis direction. These “polymeric chains” are further “cross-wise” linked by alternating zig-zag chains of dca2 groups, to create the 3D network. The bond parameters of the Cd-dca bridges are affected by the partial disorder (Supplementary Materials Table S1).

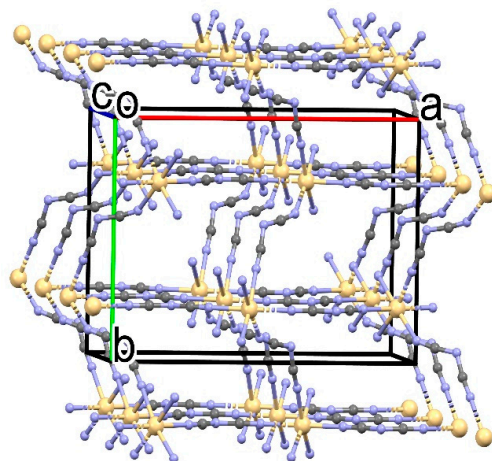


Figure 5. The 3D Cd-dca network in **5**. The C and H atoms of Me₄en and one orientation of disordered dca2 group were omitted for clarity. (Color code: yellow, Cd; blue, N; black, C.)

3.2.6. [Cd(1,8-damnph)₂(dca)₂] (**6**)

In the centrosymmetric mononuclear complex **6**, [Cd(1,8-damnph)₂(dca)₂] (Figure 6), the Cd(ii) center is forming a compressed octahedron by ligation of four amine-N donor atoms of two *trans*-coordinated 1,8-diaminonaphthalene molecules and of two terminal dicyanamide anions. The Cd1-N(dca) distance is 2.3655(9), and the Cd1-N(amine) distances are 2.3051(9) and 2.3565(10) Å, respectively. The N1-Cd1-N5 bite angle is 74.19(3), and the N1-Cd1-N5 bond angle is 105.81(3)°, whereas the other N-Cd-N cisoid bond angles deviate less than 3.1° from rectangular angle. The naphthalene-rings are inclined by 57.9° to the mean CdN₄ (amine) plane. The bond parameters of the terminal dca anions are as follows: Cd-N-C, 162.29(8)°; N-C-N, 172.23(11) and 172.70(11)°; C-N-C, 121.82(9)°; C-N(nitrile), 1.1588(14) and 1.1608(13) Å; and N-C (amine), 1.3075(13) and 1.3196(13) Å. H-bonds of type N-H⋯N form a supramolecular 3D network structure with **bcu** topology (Supplementary Materials Table S2, and Figure 6).

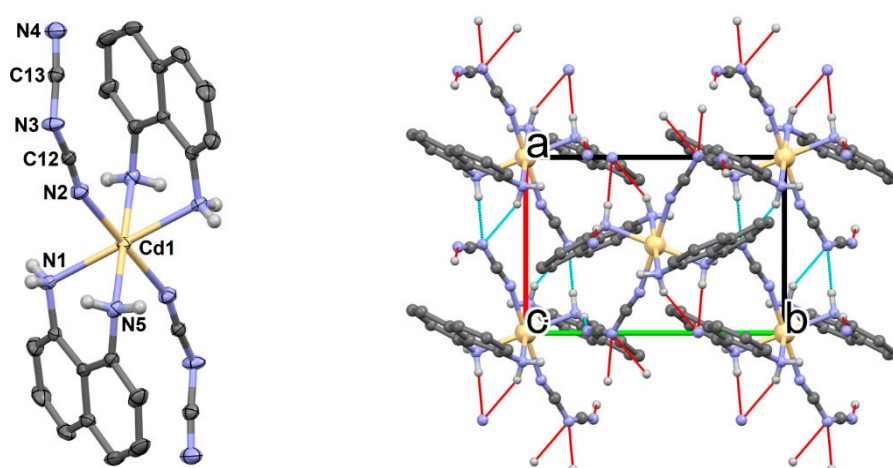


Figure 6. Coordination (left) and H-bonded network with **bcu** topology (right) of complex **6**. Dotted lines indicate H-bonds. (Color code: yellow, Cd; blue, N; black, C; gray, H).

3.3. Luminescence Emission

The photoluminescence emission of solid Cd-dca complexes were examined at room temperature. Unfortunately, the complexes 3–6 did not show any significant luminescence, whereas enhancement fluorescence emissions were observed in complexes 1 and 2, compared to their parent ligands and Nadca. Excitation of the two complexes at 366 nm revealed single emission maxima at 460 and 445 nm for 1 and 2, respectively. The corresponding ligands 3-ampy in 1 (Supplementary Materials Figure S13) and pyNO in 2 (Supplementary Materials Figure S14) showed a maximum intensity band at 429 and 454 nm, respectively. While a red shift was observed in the former complex, a small blue shift was detected in 2. The observed fluorescence enhancement in complexes 1 and 2 is most likely attributed to the increase of the conformational rigidity of the ligand upon coordination. The strong the overlap in the Cd-N (3-ampy) or Cd-O (pyNO) bond reduces the non-radiative decay within the intra-ligand ($n-\pi^*$) excited state, hence enhancing the fluorescence intensity [6,7,55]. Thus, the non-radiative processes in complexes 3–6 are superior.

3.4. Thermal Analyses

The heating curves (TG and DSC) of the title compounds are presented in the Supplementary Materials section (Figures S15–S20), for 1–6, respectively. The heating curve of 2 shows a first step of weight loss of 3.51% (DSC signal at 121.0 °C), which corresponds to release of aqua ligand (Calculated 3.75%). The anhydrous product of 2 shows an explosive decomposition at 332.6 °C. The heating curve of 3 exhibits three narrow steps of weight loss, namely –2.52, –2.45, and –3.07% (sum 8.34%), with two resolved DSC peaks at 103.6 and 136.4 °C. These three steps of weight losses can be attributed to the release of the aqua ligands (Calculated 8.93%). The anhydrous title compounds show first steps of weight loss of 11.77, 0.83, 17.48, and 6.47%, with sharp DSC signals at 204.1, 194.7, 197.9, and 185.3 °C, for compounds 1 and 4–6, respectively. The subsequent steps of weight loss at higher temperatures are accompanied by deflagration.

4. Conclusions

In the studied Cd-dca complexes 1–6, we demonstrated that four types of dca coordination bonding modes were observed: terminal, $\mu_{1,5}$ -dca, $\mu_{1,3}$ -dca, and $\mu_{1,3,5}$ -dca (Scheme 1). In complex 1, three different linkers build the 3D network $\mu_{1,5}$ -dca, $\mu_{1,3}$ -dca, and μ_2 -3-ampy, whereas, in 5, only $\mu_{1,5}$ -dca-bridges exist. Unique ribbons of three 1D polymeric chains were observed in 2 that had never been reported in transition metal-dca complexes. In addition, 1DD double chains were found in 4 with mono-($\mu_{1,5}$ -dca) and bis-($\mu_{1,5}$ -dca) polymeric chains, which are quite common in these class of compounds. Moreover, the *catena*- $\{[\text{Cd}(\text{H}_2\text{O})_2(\mu_{1,5}\text{-dca})_2](2,6\text{-lut-NO})\}$ (3) complex revealed the presence of 1D chains via bis($\mu_{1,5}$ -dca) and non-coordinated two-fold disordered 2,6-lutidine-N-oxide molecules. However, it is interesting to note that an aqua ligand containing $[\text{M}(\text{H}_2\text{O})_2(\mu_{1,5}\text{-dca})_2]$ chain was only reported once in the corresponding Mn(II) complex with non-coordinating tetramethylpyrazine-N,N'-dioxide by A. L. Rheingold and J. S. Miller, CSD Communication (Private Communication: 2019, CCDC Refcode: NOZZIO). On the other hand, the mononuclear complex $[\text{Cd}(1,8\text{-damnph})_2(\text{dca})_2]$ (6) with terminal dca-bonding forms a supramolecular 3D network structure through N-H...N hydrogen bonds. One of the crucial key steps in designing coordination polymers is the use of mono-dentate or less sterically hindered bidentate ancillary ligands in conjunction with suitable linkers, such as pseudohalides and polycarboxylates.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2073-4352/11/2/181/s1>, Supplementary data: bond parameters (Table S1), hydrogen bond systems (Table S2), and XRD powder pattern (Figures S1–S6) for compounds 1–6, respectively; IR spectra (Figures S7–S9) for 1–3; packing plots (Figures S10–S12) for 1, 2, and 4; luminescence spectra (Figures S13 and S14) for compounds 1 and 2, and thermal analysis plots (Figures S15–S20) for compounds 1–6, respectively.

Author Contributions: F.A.M., R.C.F. and A.T. performed the X-ray structural analysis. S.S.M., P.V.J., K.J.G., F.R.L., and N.M.H.S. contributed to the synthesis and spectral characterization of the designed compounds. F.A.M. and K.R. contributed to studying the thermal and luminescence properties of the complexes. F.A.M., S.S.M., F.R.L., K.J.G., and N.M.H.S. contributed to the writing of the manuscript. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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