N-Donor Ligand Coordination Polymers of Cu^{II}, Zn^{II}, and Cd^{II} Obtained at Elevated Temperature and Pressure

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Reactions of Copper(II), Zinc(II), and Cadmium(II) nitrate with 2,4,6-tris(dipyridin-2-ylamino)-1,3,5-triazine (dpyatriz) at elevated temperature and pressure lead to new 1D coordination polymers which exhibit solid-state structures significantly different from those obtained at room temperature and atmospheric pressure. In addition, these coordination compounds exhibit unusual anion–π interactions.

Introduction

Supramolecular interactions are important in several fields of contemporary chemistry. Supramolecules are often self-assembled systems by means of a variety of interactions which may interplay. In crystal engineering, synergistic effects between intermolecular non-covalent interactions are of great importance and must be regarded as a single interrelated entity. The targeted molecular self-assembly of coordination architectures from tailored molecular components is a potential route to novel one-, two-, and three-dimensional networks.[1,2] The preparation of polymeric complexes can be accomplished by using rationally designed polydentate ligands. Many advanced 2D and 3D metallosupramolecular structures[3] have been generated in this way with encouraging applications in catalysis,[4] drug design,[5] separation studies,[6] gas storage,[7] and molecular recognition.[8] Furthermore, their preparation has highlighted another consideration: it is not only the building blocks that are important, but also the experimental parameters such as solvent, temperature, pressure, etc. used during the synthesis may lead to different species.[9] For example, the reaction of $Cu^{I}Br$ with 2,2′-dipyridyl under ambient conditions leads to a 1:1 adduct, while a polymeric structure is formed at 170 °C and autogenous pressure.[10]

In the course of research investigations to prepare triazine-based coordination polymers and study their physical and catalytic properties,[11–13] the ligand 2,4,6-tris(dipyridin-2-ylamino)-1,3,5-triazine (dpyatriz) has been synthesized (Figure 1).[14,15] Coordination compounds of Cu^{II} and Zn^{II} nitrate with dpyatriz obtained at room temperature and normal pressure in acetonitrile have been recently reported.[11,16] In this paper, new coordination polymers obtained from dpyatriz and various metal nitrates in acetonitrile at 105 °C in a closed pressure tube are described, showing significantly different coordination networks, as well as uncommon supramolecular interactions.

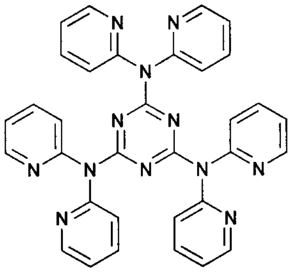

Figure 1. 2,4,6-Tris(dipyridin-2-ylamino)-1,3,5-triazine (dpyatriz).

Results and Discussion

Reaction of $Cu(NO_3)_2{\cdot}3H_2O$ in acetonitrile with dpyatriz yields light-blue parallelepipeds of $[Cu_2(dpyatriz)(NO_3)_4](H_2O)$ (**1**), whose crystal structure was determined by X-ray diffraction (Figure 2). The dinuclear building blocks consist of one pentacoordinate copper ion Cu(1) involved in the self-assembly of the coordination polymer and one isolated pentacoordinate copper ion Cu(2). Cu(1) is in a square-pyramidal geometry (τ = 0.167)[17] with N(6) in an axial position (Table 1). The basal plane is formed by three N-coordinating 2-pyridyl moieties [N(5), N(11), and N(12)] from two didentate dipyridylamine units belonging to a symmetry-related dpyatriz ligand. The in-plane Cu–N dis-

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tances can be regarded as normal (Table 1). The fourth position is occupied by the oxygen atom O(1) of a nitrate counter-anion. The angles around Cu(1) in the basal plane are close to 90°, varying from 83.7(3) to 93.5(3)° (Table 2). Cu(2) is also in a square-pyramidal geometry ($\tau = 0.137$).[17]

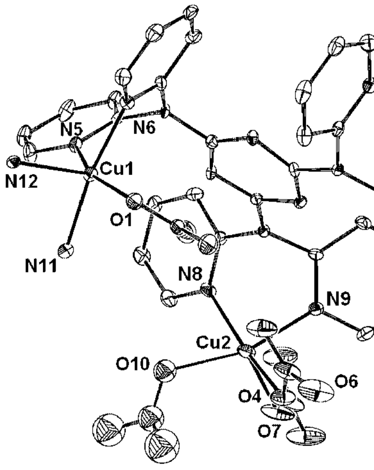

Figure 2. ORTEP plot of the repeating unit of **1**, where the N11 and N12 atoms belong to a symmetry-related unit. The water molecule and the hydrogen atoms are omitted for clarity; thermal ellipsoids are at the 20% probability level.

The basal plane around Cu(2) is constituted of two nitrogen atoms N(8) and N(9), from a dipyridylamine group, and two oxygen atoms O(7) and O(10), from two nitrate anions (one of these oxygen atoms is statistically distributed over two different positions indicated with O10 and O10′). The in-plane Cu–N distances are in the usual range, as well as the Cu–O distances (Table 1).[18] The axial position is occupied by the oxygen atom O(4) from a third coordinated nitrate ion, at a somewhat longer distance. The angles around Cu(2) in the basal plane vary from 86.1(5) to 95.9(4)° (Table 2). In addition, a water molecule O(18) is present in the crystal lattice (not depicted in Figure 2). This water molecule is hydrogen-bonded to the oxygen atom O(6a) of a nitrate group coordinated to Cu(2a) of an adjacent polymer chain [O(1S)–H···O(6a) 2.931(8) Å] (Figure 3).

This dinuclear copper complex makes up a 1D zigzag polymer through the coordination of Cu(1) by a dipyridylamine moiety from an adjacent repeating unit (Figure 3). Most interestingly, a quite different 1D ladder coordination polymer has been obtained from $Cu(NO_3)_2{\cdot}3H_2O$ and dpyatriz in acetonitrile, at room temperature and atmospheric pressure.[11] The different crystal packing observed in the present study is obviously due to the higher temperature and pressure used during the crystallisation process. This result illustrates the difficulty to predict a crystal structure. Indeed, crystal growth involves several intermolecular synergistic noncovalent interactions between all synthons,[19] i.e. ligands, metal ions, anions and solvents, which have certainly to be considered for a better crystal structure prediction. In addition, the temperature and the pressure applied during the crystallisation are clearly important and should also be taken into account.

Table 1. Selected bond lengths [Å] for $[Cu_2(dpyatriz)(NO_3)_4](H_2O)$ (**1**), $[Zn_2(dpyatriz)(NO_3)_4](H_2O)$ (**2**), and $[Cd_3(dpyatriz)_2(NO_3)_6]$ (**3**).

1	2	3
Cu(1)–N(6) 2.136(7)	Zn(1)–N(6) 2.083(14)	Cd(1)–N(6) 2.402(5)
Cu(1)–N(5) 2.011(8)	Zn(1)–N(11) 2.085(14)	Cd(1)–N(11′) 2.474(4)
Cu(1)–N(11) 1.995(7)	Zn(1)–O(1) 2.257(13)	Cd(1)–N(12′) 2.379(5)
Cu(1)–N(12) 2.025(7)	Zn(1)–O(2) 2.409(17)	Cd(1)–N(5) 2.450(5)
Cu(1)–O(1) 2.022(6)	Zn(1)–N(5) 2.155(17)	Cd(1)–O(5) 2.568(5)
	Zn(1)–N(12) 2.145(17)	Cd(1)–O(4) 2.646(7)
Cu(2)–N(8) 1.978(7)		
Cu(2)–N(9) 1.981(7)	Zn(2)–N(8) 2.128(18)	Cd(2)–N(9) 2.348(5)
Cu(2)–O(7) 1.975(7)	Zn(2)–N(9) 2.134(13)	Cd(2)–N(8) 2.435(7)
Cu(2)–O(10′) 1.942(12)	Zn(2)–O(4) 2.026(15)	Cd(2)–O(7) 2.400(9)
Cu(2)–O(4) 2.270(9)	Zn(2)–O(10) 2.296(19)	
	Zn(2)–O(11) 2.133(18)	
	Zn(2)–O(7) 2.131(22)	

Table 2. Selected angles [°] for $[Cu_2(dpyatriz)(NO_3)_4](H_2O)$ (**1**), $[Zn_2(dpyatriz)(NO_3)_4](H_2O)$ (**2**), and $[Cd_3(dpyatriz)_2(NO_3)_6]$ (**3**).

1	2	3
N(5)–Cu(1)–O(1) 91.7(3)	N(6)–Zn(1)–N(11) 107.7(6)	N(6)–Cd(1)–(N11′) 82.65(15)
N(11)–Cu(1)–O(1) 83.7(3)	N(11)–Zn(1)–O(2) 102.3(6)	N(12′)–Cd(1)–N(11′) 80.91(14)
N(11)–Cu(1)–N(12) 88.0(3)	O(1)–Zn(1)–O(2) 56.6(6)	N(12′)–Cd(1)–O(5) 74.17(15)
N(5)–Cu(1)–N(12) 93.5(3)	N(6)–Zn(1)–O(1) 96.3(6)	O(5)–Cd(1)–O(4) 49.77(15)
	N(12)–Zn(1)–N(5) 171.1(6)	N(6)–Cd(1)–O(4) 73.24(15)
N(8)–Cu(2)–N(9) 88.0(3)		O(1)–Cd(1)–N(5) 165.92(15)
O(7)–Cu(2)–N(9) 87.9(3)	O(4)–Zn(2)–N(8) 118.0(7)	
O(7)–Cu(2)–O(10) 90.4(5)	O(4)–Zn(2)–O(10) 86.0(7)	N(9)–Cd(2)–N(8) 83.57(19)
O(10′)–Cu(2)–O(7) 95.9(4)	O(11)–Zn(2)–O(10) 61.2(7)	N(9)–Cd(2)–N(8′) 96.43(19)
N(8)–Cu(2)–O(10) 86.1(5)	N(8)–Zn(2)–O(11) 96.3(7)	O(7′)–Cd(2)–O(7) 180.000(1)
O(10′)–Cu(2)–N(8) 92.7(4)	O(7)–Zn(2)–N(9) 168.9(7)	

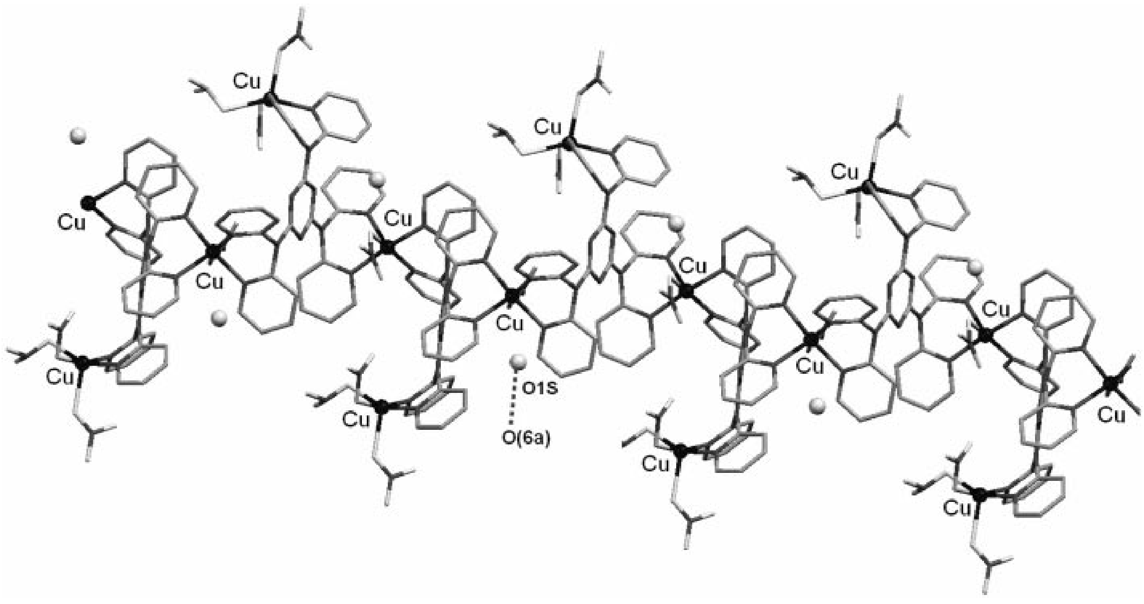

Figure 3. Representation of the copper(II) 1D zigzag coordination polymer.

Another very interesting feature of this high-temperature-prepared supramolecular species is the interaction between the oxygen atom O(2) of the nitrate anion coordinated to Cu(1) and the π-cloud of a 1,3,5-triazine ring, with a centroid···O(2) distance of 3.67(1) Å and an angle of the centroid···O(2) axis to the plane of 67.7(3)° (Figure 4). Noncovalent anion–π interactions are quite uncommon and have only recently been discovered, owing to the electron-donating character of an anion which is expected to lead to repulsive interactions with aromatic π-clouds.[20,21] This type of interactions has been first demonstrated by NMR studies.[22–24] Several recent articles have reported theoretical calculations on the binding of uncoordinated anions with electron-deficient triazine derivatives, indicating energetically favorable noncovalent interactions.[21,25,26] Very recently, first crystallographic evidences of such interactions has been described between 1,3,5-triazine groups and free anions.[27,28] The present compound reveals the possible interaction between a nitrate and an electron-poor aromatic ring.

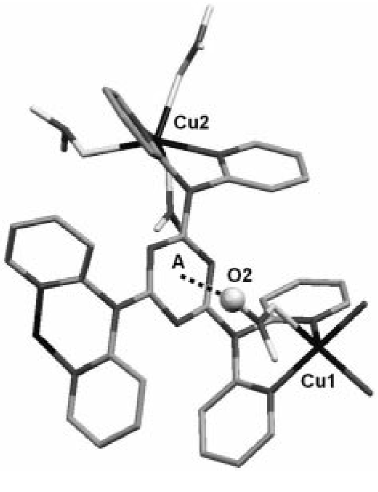

Figure 4. Oxygen–π interaction in **1** between a nitrate anion and an *s*-triazine ring. A···O(2) = 3.67(1) Å; triazine plane–A–O(2) axis = 67.7(3)°.

A different, but related coordination polymer has been obtained by reaction of $Zn(NO_3)_2{\cdot}6H_2O$ and dpyatriz in

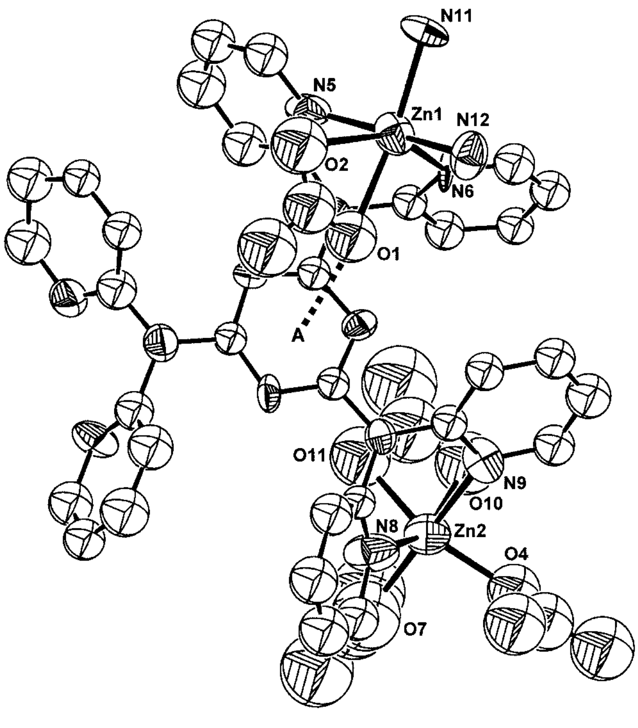

Figure 5. ORTEP plot of the repeating unit of **2** where the N11 and N12 atoms belong to a symmetry-related unit. The water molecule and the hydrogen atoms are omitted for clarity; thermal ellipsoids are at the 50% probability level. A···O(1) = 3.11(3) Å; triazine plane–A–O(2) axis = 67.2(5)°.

acetonitrile at the same temperature. The dinuclear repeating unit of the zig-zag polymer present in the compound $[Zn_2(dpyatriz)(NO_3)_4](H_2O)$ (**2**) is depicted in Figure 5.

Zn(1), which is involved in the self-assembly of the coordination polymer, is in a highly distorted octahedral environment, due to the coordination of the nitrate anion in a didentate fashion. The basal plane of the octahedron is formed by two N-coordinating pyridine rings [N(6) and N(11)] of two symmetry-related dpyatriz ligands, and by two oxygen atoms, O(1) and O(2), of a nitrate ion. The in-plane Zn–N distances can be regarded as normal (Table 1).[29] The large in-plane Zn–O distances stem from the didentate coordination mode of the anion which induces a great distortion. The axial positions are taken up by two N-donors, N(5) and N(12), of two symmetry-related dipyatriz ligands. The angles around Zn(1) in the basal plane vary from 56.6(6) to 107.7(6)°, showing once again the important distortion resulting from the particular coordination of the nitrate ion (Table 2). Zn(2) is in a distorted octahedral geometry as well. The basal plane is constituted of one N-atom N(8) from a pyridine group at a normal distance (Table 1). The remaining positions are occupied by three O-atoms, O(4), O(10), and O(11), of two nitrate ions. The axial positions are occupied by one N-atom, N(9), of a pyridine group and by the O-atom O(7) of a third nitrate ion. The angles around Zn(2) in the basal plane are far from 90°, varying from 61.2(7) to 118.0(6)°, due to the didentate binding mode of one nitrate ion (Table 2). In addition, a water molecule is present in the crystal lattice.

This dinuclear zinc complex represents the repeating unit of a 1D zigzag polymer closely related to the one obtained with copper(II) nitrate (Figure 3). A completely different coordination compound, i.e a tetranuclear zinc(II) complex, has been reported as obtained at room temperature and ambient pressure from the same reactants,[16] just like in the case of the copper polymer.

Like the copper coordination polymer, the zinc polymer exhibits anion–π interactions. Indeed, anion–π interactions are realised between the oxygen atom O(1) of the didentate nitrate anion coordinated to Zn(1) and the 1,3,5-triazine ring with a centroid···O(1) distance of 3.11(3) Å and an angle of the centroid···O(1) axis to the plane of 67.2(5)° (Figure 5).

Finally, the reaction of $Cd(NO_3)_2{\cdot}4H_2O$ in acetonitrile at 105 °C with dpyatriz yields colorless diamond-shaped crys-

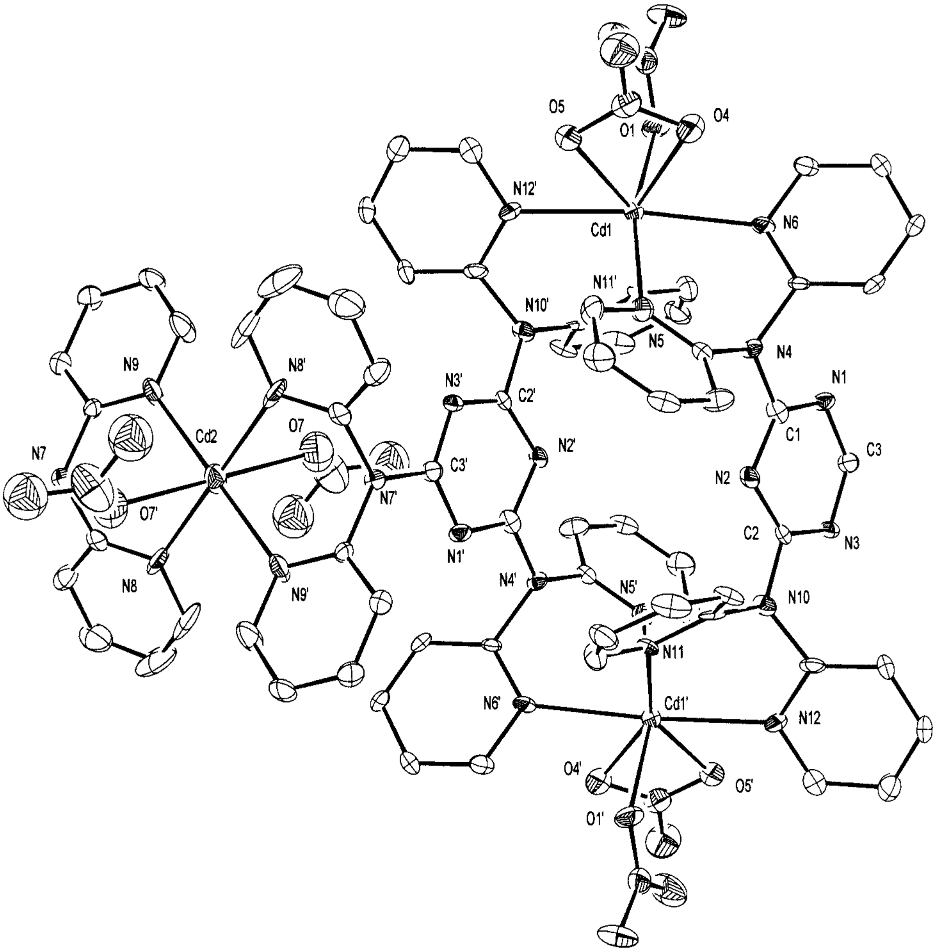

Figure 6. ORTEP view of the building block (containing two asymmetric units) forming the polymeric chain. Hydrogen atoms are omitted for clarity; thermal ellipsoids are at the 20% probability level.

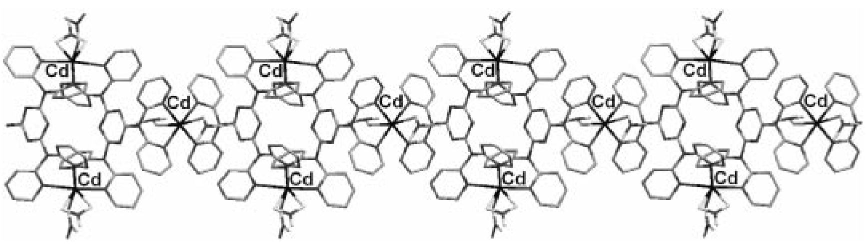

Figure 7. Representation of the cadmium(II) 1D linear coordination polymer.

tals of [$Cd_3(dpyatriz)_2(NO_3)_6$] (**3**) whose crystal structure was determined by X-ray diffraction (Figure 6).

Cd(1) shows a pentagonal bypiramid configuration due to the coordination of a nitrate ion acting as a chelating ligand. The basal plane of the bipyramid is constituted by three *N*-pyridyl donor atoms, N(6), N(11′), and N(12′), of two didentate dipyridylamine groups belonging to different dpyatriz ligands and by two oxygen atoms, O(4) and O(5), of the chelating anion (Table 1). The in-plane Cd–N distances are normal; the large in-plane Cd–O distances are due to the chelating nitrate ion. The axial positions are occupied by one N-donor atom, N(5), of a dipyridylamino group and by an oxygen atom, O(1), of a monodentate nitrate ion. The angles around the cadmium(II) ion in the basal plane vary from 73.2(2) to 82.7(2)° with the exception of the O(4)–Cd(1)–O(5) angle of 49.8(2)°, distorted because of the chelating behaviour of the nitrate ion (Table 2). Cd(2), which lies on an inversion center, is in an octahedral environment constituted of four N-coordinating 2-pyridyl groups located in the basal plane [N(8) and N(9)], and two axially coordinated O-atoms of two monodentate nitrate ions [O(7)]. The in-plane Cd–N distances are typical as well as the axial Cd–O bond length (Table 1).[30] The angles around Cd(2) in the basal plane vary from 83.6(2) to 96.9(3)° (Table 2).

This trinuclear cadmium unit represents the building block of a 1D linear polymer through the coordination of Cd(2) by a dipyridylamino moiety of an neighbouring repeating unit (Figure 7).

Electron–π interactions further stabilize the polymer chains. Indeed, the symmetrically related oxygen atoms O(8) and O(8′) of the monodentate nitrate ions coordinated to Cd(2) are strongly interacting with electron-poor triazine rings with a short centroid···O distance[21] of 3.26(1) Å (Figure 8, A and A′). The angle of the centroid···O axis to the plane is 79.9(2)°. In addition, the remaining oxygen atoms of the anions, O(9) and O(9′), are interacting with pyridine groups of dipyridylamino units, probably due to the fact that the pyridine rings involved are coordinated to a cadmium ion, thus enhancing their electron-poor character (Figure 8, B and B′). The centroid···O distance is 3.58(2) Å and the centroid···O axis to the plane angle is 49.0(3)°. To the best of our knowledge, this is the first crystallographic example of such nitrate–pyridine π-cloud interactions. The distances and angles observed are far from the theoretical calculated values for the extensively studied model system *s*-triazine anion.[21,26] Unfortunately, no theoretical investigations have been yet performed on the *less electron-deficient, dissymmetric* pyridine ring, but one would rationally anticipate *longer ring–anion bonds* as well as an *optimal plane–axis angle inferior to 90°*.

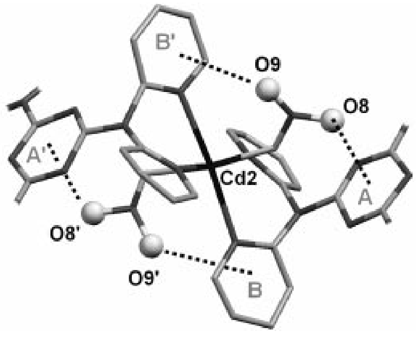

Figure 8. π interactions in **3** between the oxygen atoms of nitrate anions and electron-deficient 1,3,5-triazine and pyridine rings. A···O(8) = 3.26(1) Å; triazine plane–A–O(8) axis = 79.9(2)°. B′···O(9) = 3.58(2) Å; pyridine plane–B′–O(9) axis = 49.0(3)°.

Conclusions

In conclusion, the supramolecular molecules **1**, **2**, and **3** have been obtained at elevated temperature and pressure. The polymeric complexes show anion–π interactions, and experimental evidence of coordinated nitrate anions interacting with triazine or pyridine rings is described, demonstrating the possible existence of anion–π interactions. In addition, the high temperature and pressure applied during their synthesis resulted in notably different crystal structures when compared to those of the coordination compounds prepared from the same reactants, at room temperature and atmospheric pressure.

Experimental Section

General Remarks: Infrared spectra were collected with a Perkin–Elmer Paragon 1000 spectrophotometer equipped with a Golden Gate Diamond ATR as a sample support. Vis/NIR spectra were measured with a Perkin–Elmer Lambda 900 spectrophotometer using the diffuse reflectance technique, with MgO as a reference. Elemental analyses were performed at the Microanalytical Laboratory of the Leiden Institute of Chemistry, The Netherlands. X-band EPR spectra were recorded with a JEOL electron spin resonance spectrometer, equipped with an Esprit 330 data system, at room temperature and at 77 K, with dpph as an internal reference (g = 2.0036).

Table 3. Summary of crystal data and refinement parameters for complexes **1**, **2**, and **3**.

	1	**2**	**3**
Empirical formula	$C_{33}H_{26}Cu_2N_{16}O_{13}$	$C_{33}H_{26}Zn_2N_{16}O_{13}$	$C_{66}H_{48}Cd_3N_{30}O_{18}$
Formula mass	981.78	985.44	1886.54
Crystal system	orthorhombic	orthorhombic	triclinic
Space group	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)	$P\bar{1}$ (No. 1)
a [Å]	13.749(5)	13.912(5)	11.063(5)
b [Å]	14.762(5)	14.458(5)	12.468(5)
c [Å]	19.432(5)	19.890(5)	15.891(5)
α [°]	90	90	110.315(5)
β [°]	90	90	105.067(5)
γ [°]	90	90	92.877(5)
V [Å^3]	3944(2)	4001(2)	1961(2)
Z	4	4	1
ρ(calcd.) [g·cm^{-3}]	1.653	1.636	1.598
μ [mm^{-1}]	1.165	1.285	0.893
Measured reflections	17662	17748	16660
Unique reflections	5684	2529	7564
Observed reflections	2650	1429	5940
R_{int}	0.0895	0.1694	0.0251
R [$I > 2\sigma(I)$]	0.0479	0.0551	0.0596
wR [$I > 2\sigma(I)$]a	0.0831	0.1000	0.1223

Preparation of [Cu_2(dpyatriz)(NO_3)$_4$](H_2O) (1): $Cu(NO_3)_2$·$3H_2O$ (7.1 mg, 0.0293 mmol) was added to a suspension of dpyatriz (11.5 mg, 0.0195 mmol) in acetonitrile (6 mL). After dissolving the copper salt, the closed pressure tube was placed in an oven at 105 °C. Single crystals of **1** suitable for X-ray analysis were obtained as light-blue needles at 105 °C after 2 d. Yield: 16 mg (83%). $C_{33}H_{26}Cu_2N_{16}O_{13}$ (981.78): calcd. C 40.37, H 2.67, N 22.83; found C 39.85, H 2.21, N 22.17. IR (neat): $\tilde{\nu}$ = 1607, 1558, 1471, 1374, 1278, 1005, 772, 668 cm^{-1}. UV/Vis (reflectance): λ = 262 (LMCT), 643 and 975 (d–d transitions) nm. Solid-state EPR: g = 2.12 (room temp.), 2.11 (77 K).

Preparation of [Zn_2(dpyatriz)(NO_3)$_4$](H_2O) (2): $Zn(NO_3)_2$·$6H_2O$ (8.1 mg, 0.0273 mmol) was added to a suspension of dpyatriz (10.7 mg, 0.0182 mmol) in acetonitrile (6 mL). After dissolving the zinc salt, the closed pressure tube was placed in an oven at 105 °C. Single crystals of **2** suitable for X-ray analysis were obtained as colorless parallelepipeds at this temperature after 2 d. Yield: 14 mg (77%). $C_{33}H_{26}Zn_2N_{16}O_{13}$ (985.44): calcd. C 40.22, H 2.66, N 22.74; found C 39.98, H 2.28, N 22.62. IR (neat): $\tilde{\nu}$ = 3080, 1608, 1558, 1378, 1286, 1022, 771, 667 cm^{-1}. UV/Vis (reflectance): λ = 269 (LMCT) nm.

Preparation of [Cd_3(dpyatriz)$_2$(NO_3)$_6$] (3): $Cd(NO_3)_2$·$4H_2O$ (9.3 mg, 0.0301 mmol) was added to a suspension of dpyatriz (11.8 mg, 0.0200 mmol) in acetonitrile (12 mL). After dissolving the cadmium salt, the closed pressure tube was placed in an oven at 105 °C. Colorless diamond-shaped single crystals of **3** suitable for X-ray analysis were obtained at 105 °C in a pressure tube after 3 d. Yield: 17 mg (91%). $C_{66}H_{48}Cd_3N_{30}O_{18}$ (1886.54): calcd. C 42.01, H 2.54, N 22.26; found C 41.89, H 2.28, N 21.64. IR (neat): $\tilde{\nu}$ = 3082, 1603, 1550, 1378, 1292, 1014, 768, 664 cm^{-1}. UV/Vis (reflectance): λ = 288 (LMCT) nm.

X-ray Crystallographic Study: The molecular structures were determined by single-crystal X-ray diffraction methods. Crystallographic and experimental details for the different structures are summarized in Table 3. Intensity data and cell parameters were recorded at room temperature (293 K) with a Bruker AXS Smart 1000 single-crystal diffractometer (Mo-K_α radiation), equipped with a CCD area detector. The data reductions were performed using the SAINT[31] and SADABS[32] programs. The structures were solved by direct methods using the SIR97 program[33] and refined on F_o^2 by full-matrix least-squares procedures, using the SHELXL-97 program.[34] Most of the non-hydrogen atoms were refined with anisotropic atomic displacements. The hydrogen atoms were included in the refinement at idealized geometries (C–H 0.95 Å) and refined "riding" on the corresponding parent atoms. The weighting scheme used in the last cycle of refinement was $w = 1/[\sigma^2(F_o^2) + (0.0347P)^2]$ (**1**), $w = 1/[\sigma^2(F_o^2) + (0.0411P)^2]$ (**2**) and $w = 1/[\sigma^2(F_o^2) + (0.0400P)^2 + 6.1257P]$ (**3**), where $P = (F_o^2 + 2F_c^2)/3$. Molecular geometry calculations were carried out using the PARST97 program.[35] All calculations were carried out with a DIGITAL Alpha Station 255 computer. CCDC-255636 (**1**), -255637 (**2**), and -255638 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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