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The new multi-directional polydentate ligand 2,4,6-(di-pyridin-2-yl-amino)-[1,3,5]triazine (dpyatriz) can discriminate between Zn(II) and Co(II) nitrate

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Abstract

The rigid multidentate tri-directional and potentially nonadentate ligand 2,4,6-(di-pyridin-2-yl-amino)-[1,3,5]triazine (dpyatriz) is able to differentiate between Co(II) and Zn(II) nitrate. With Co(II) nitrate, a dinuclear $[Co_2(dpyatriz)_2(NO_3)_2(MeOH)_2](NO_3)_2(MeOH)_2$ complex is formed. Dpyatriz acts as a tetradentate (bisdidentate) ligand, with the octahedral coordination completed by a MeOH molecule and a monodentate nitrate anion. With Zn(II) nitrate, dpyatriz acts as an hexadentate ligand (trisdidentate), where each ligand binds to three Zn ions. Two of the Zn ions are five coordinated in a ZnO_3N_2 chromophore (the trigonal bipyramidal geometry is completed by two monodentate nitrato ligands). The other two Zn ions are hexacoordinated in a ZnN_4O_2 chromophore, formed by four pyridine-type ligands and a chelating, didentate nitrato ligand. The molecular structure of the free ligand has also been determined using XRD. For the Zn and Co complexes, the IR and IR+UV spectra, are reported as well.

Keywords: Zn(II) complexes; Co(II) complexes; Crystal structures; Multi-directional ligand; Polydentate pyridine ligand; N-donor ligand

1. Introduction

Since the late 1980s, the design and synthesis of supramolecular polynuclear metal complexes has been a topic of growing interest [1–3]. During the last decade, a remarkable development in the preparation of self-assembled architecture through metal ion coordination has been observed [4]. Fujita [5,6] and Champness [7] have described the use of multi-directional ligands in the self-assembly of outstanding discrete nanostructures. 1,3,5-Triazine derivatives are widely used as herbicides [8], drugs [9] or polymers [10], like melamine–formaldehyde that has excellent thermal and electrical properties. Furthermore, a very large number of supramolecular non-covalently bond assemblies between melamine and barbituric or cyanuric acid derivatives have been reported [11], but only a few examples of 1,3,5-triazine-containing ligands have been published so far [12,13].

In the present study, it was investigated whether the large, potentially nonadentate polypyridyl ligand 2,4,6-(di-pyridin-2-yl-amino)-[1,3,5]triazine (dpyatriz) [14], could discriminate between two rather similar metal ions such as Zn(II) and Co(II). Therefore, representative nitrate complexes were prepared and structurally characterized; for comparison also the structure of the free ligand is reported.

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2. Experimental

2.1. Materials and syntheses

Solvents and chemicals were commercially available as A.R. grade and used as received. CHN analyses were done using an automatic Perkin–Elmer 2400 Series II CHNS/O microanalyzer. Infrared spectra were recorded on a Perkin–Elmer Paragon 1000 spectrophotometer equipped with a Golden Gate Diamond ATR as a sample support, and peaks are reported in cm^{-1}. Ligand field spectra of the solid compounds were recorded on a Perkin–Elmer Lambda 900 UV–Vis–NIR spectrometer in the diffuse reflectance mode with MgO as reference. 2,4,6-(Di-pyridin-2-yl-amino)-[1,3,5]triazine (dpyatriz) was prepared as previously described [15].

2.2. $[Zn_4(dpyatriz)_2(NO_3)_8]$ (**2**)

A solution of dpyatriz (200 mg, 0.34 mmol) in acetonitrile (40 ml) was added dropwise to a solution of $Zn(NO_3)_2\cdot 6H_2O$ (303 mg, 1.02 mmol) in acetonitrile (40 ml). An air-sensitive colorless crystalline compound (188 mg) formed after 2 days which was isolated and dried (0.10 mmol, 61%). Found: C, 44.15; H, 2.84; N, 24.45. Calc. for $C_{66}H_{48}N_{32}O_{24}Zn_4$: C, 43.94; H, 2.68; N, 24.84%.

2.3. $[Co_2(dpyatriz)_2(NO_3)_2(MeOH)_2](NO_3)_2$-$(MeOH)_2$ (**3**)

A solution of dpyatriz (160 mg, 0.27 mmol) and $Co(NO_3)_2\cdot 6H_2O$ (79 mg, 0.27 mmol) in methanol (80 ml) was layered with 80 ml of *n*-hexane. After 3 days, 92 mg of an air-sensitive light pink–orange crystalline compound formed. It was isolated and dried (0.06 mmol, 44%). Found: C, 46.49; H, 4.55; N, 23.22. Calc. for $C_{66}Co_2H_{66}N_{28}O_{21}$: C, 46.49; H, 3.90; N, 23.00%.

2.4. X-ray crystallographic study

Data collection and cell refinement were carried out on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97 [16a], structures **1** and **3**; SIR-97 [16b], structure **2**) and refined with SHELXL-97 [17] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters, hydrogen atoms were refined as rigid groups. In structure **1**, one pyridine moiety was refined with a disorder model. In structure **3**, the coordinated nitrate anion was disordered over two positions. Structures **2** and **3** contain large voids with volumes of 1266.2 and 1174.0 $Å^3$ per unit cell, respectively. These voids are filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the program PLATON [18], amounting to 196 and 238 electrons per unit cell, respectively. Details of the structure determinations are given in Table 3.

3. Results and discussion

3.1. Ligand synthesis, structure and general observations

2,4,6-(Di-pyridin-2-yl-amino)-[1,3,5]triazine (dpyatriz, (**1**), Fig. 1) was synthesized from 2,4,6-trichloro-1,3,5-triazine and 2,2′-pyridylamine according to a published procedure [15].

Single-crystals of **1** were obtained by slow crystallization from acetonitrile and analyzed by X-diffraction. A molecular plot [18] of its structure in the crystal is shown in Fig. 2.

Synthetic details of complexes **2** and **3** are given in Section 2.

3.2. Structure of $[Zn_4(dpyatriz)_2(NO_3)_8]$ (**2**)

Fig. 3 shows the molecular structure of $[Zn_4(dpyatriz)_2(NO_3)_8]$ together with the atom labeling scheme adopted. Selected bond lengths and angles are given in Table 1. Compound **2** crystallizes in the monoclinic space group $P2_1/c$ (Table 3).

The molecule is located on a crystallographic inversion center. As can be seen in Fig. 1, the tetranuclear complex is formed by two pentacoordinated zinc ions and two hexacoordinated zinc ions. The weakly coordinating nitrate anions bind to the pentacoordinated zinc in a monodentate and to the hexacoordinated zinc in a didentate fashion. The pentacoordinated zinc ions occupy the center of a distorted trigonal-bipyramid. The distortion of the polyhedron can be quantified using the τ factor [19]. This calculation affords 1 for a perfect trigonal-bipyramidal environment and 0 for a square-pyramidal geometry. The calculated value for **2** is 0.66,

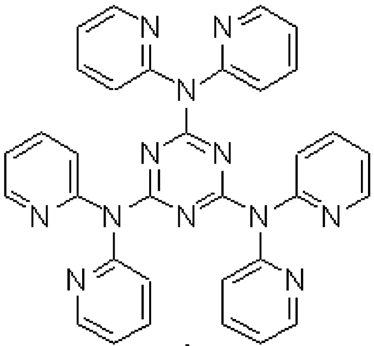
1

Fig. 1. 2,4,6-(Di-pyridin-2-yl-amino)-[1,3,5]triazine (dpyatriz).

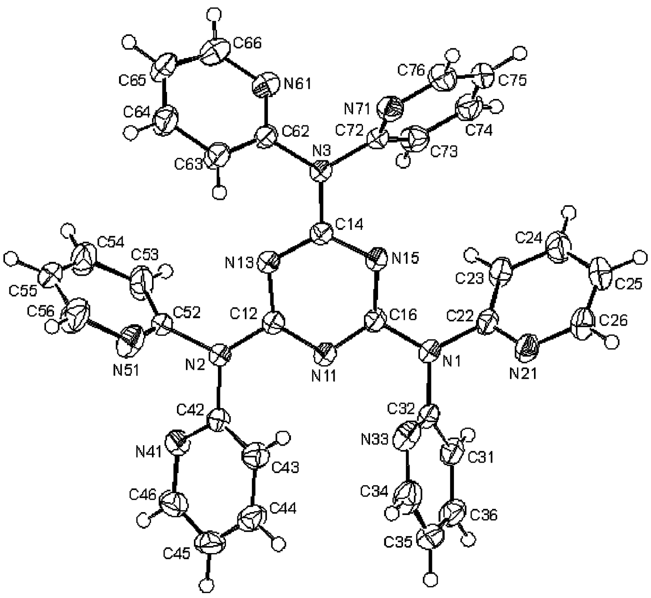

Fig. 2. Displacement ellipsoid plot (50% probability) for **1**. The pyridine ring N31–C36 is rotationally disordered with an occupancy of 54.2:45.8%. Shown is the major conformation.

thus illustrating the trigonal-bipyramidal character of coordination. The coordination environment involves two nitrogen atoms belonging to two pyridine moieties and three oxygen atoms from three monodentate nitrate ions. The coordination geometry is characterized by an $N(21)_{axial}–Zn(1)–O(86)_{axial}$ angle of 170.84(7)° and $N_{equatorial}–Zn(1)–O_{axial}$, $N_{equatorial}–Zn(1)–N_{axial}$, $O_{equatorial}–Zn(1)–O_{axial}$ and $O_{equatorial}–Zn(1)–N_{axial}$ an-

Table 1
Selected bond lengths (Å) and angles (°) for complex **2**

Bond lengths	
Zn(1)–O(81)	2.0148(15)
Zn(1)–O(86)	2.1197(16)
Zn(1)–O(91)	2.0717(15)
Zn(1)–N(21)	2.1621(17)
Zn(1)–N(31)	2.0963(18)
Zn(2)–O(96)	2.3887(17)
Zn(2)–O(97)	2.1247(16)
Zn(2)–N(41)	2.1460(17)
Zn(2)–N(51)	2.0855(17)
Zn(2)–N(61)^{i}	2.0850(16)
Zn(2)–N(71)^{i}	2.1398(17)
Bond angles	
O(81)–Zn(1)–O(86)	95.64(6)
O(81)–Zn(1)–O(91)	126.54(6)
O(81)–Zn(1)–N(21)	93.16(6)
O(81)–Zn(1)–N(31)	131.47(6)
O(86)–Zn(1)–O(91)	80.39(6)
O(86)–Zn(1)–N(21)	170.84(6)
O(86)–Zn(1)–N(31)	89.03(7)
O(91)–Zn(1)–N(21)	92.30(6)
O(91)–Zn(1)–N(31)	101.91(7)
N(21)–Zn(1)–N(31)	87.07(7)
N(51)–Zn(2)–N(61)^{i}	112.64(6)
O(96)–Zn(2)–O(97)	56.54(6)
O(96)–Zn(2)–N(41)	88.24(6)
O(96)–Zn(2)–N(51)	90.13(6)
O(96)–Zn(2)–N(61)^{i}	157.17(6)
O(96)–Zn(2)–N(71)^{i}	89.06(6)
O(97)–Zn(2)–N(51)	146.58(7)
N(51)–Zn(2)–N(61)^{i}	112.64(6)
N(41)–Zn(2)–N(71)^{i}	177.25(6)

Symmetry operation i: $1-x$, $1-y$, $1-z$.

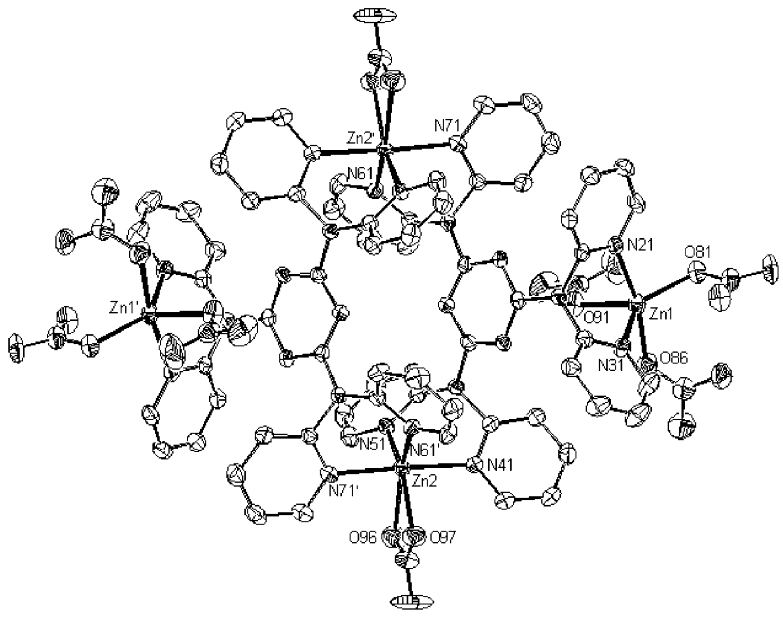

Fig. 3. Perspective view of $[Zn_4(dpyatriz)_2(NO_3)_8]$ (**2**). Hydrogen atoms and disordered solvent molecules are omitted for clarity. Ellipsoids represented at 50% probability level. Symmetry operation i: $1-x$, $1-y$, $1-z$.

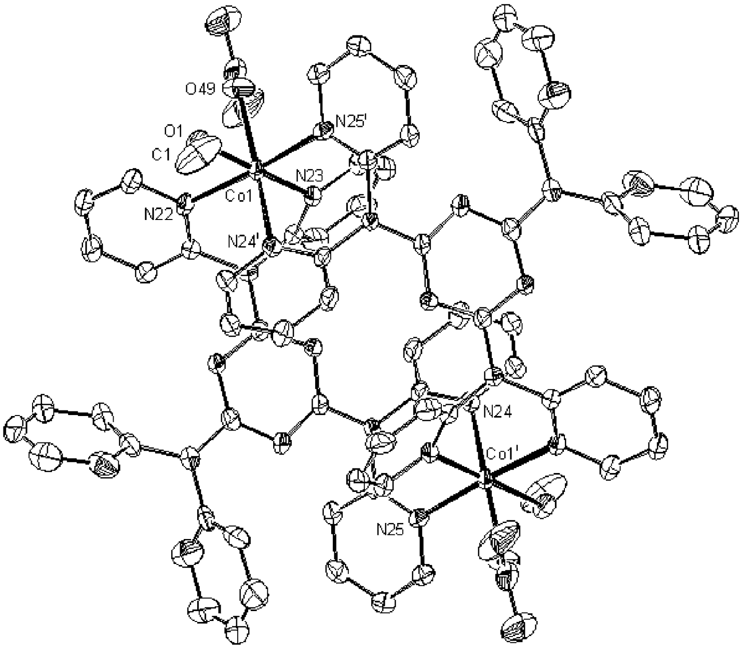

Fig. 4. Perspective view of $[Co_2(dpyatriz)_2(NO_3)_2(MeOH)_2](NO_3)_2(MeOH)_2$ (**3**). Hydrogen atoms, non-coordinated solvent molecules, and the non-coordinated nitrate anions are omitted for clarity. Ellipsoids represented at 50% probability level. The coordinated nitrate is disordered over two positions with an occupancy of 52:48%. Only the major component is shown. Symmetry operation i: $1-x, 1-y, 1-z$.

gles ranging from 80.39(6)° to 95.64(6)°. N(31), O(81) and O(91) are located in the same plane. The angles found inside the bipyramid base vary from 101.91(7)° to 131.47(6)°. The axial distances are 2.1197(16) and 2.1621(17) Å for Zn(1)–O(86) and Zn(1)–N(21), respectively, and can be considered as normal. The equatorial bond lengths of 2.0148(15) (Zn(1)–O(81)), 2.0717(15) (Zn(1)–N(21)) and 2.0963(18) Å (Zn(1)–N(31)) are normal for trigonal-bipyramid geometry [20].

The hexacoordinated zinc ions are in a distorted octahedral environment formed by two pairs of N-coordinating 2-pyridyl moieties belonging to two different dpyatriz ligands and two oxygen atoms from a didentate nitrate anion. The small bite angle (O(96)–Zn(2)–O(97) 56.54(6)°) of the didentate nitrate ligand is the main reason for the distortion. The axial bond lengths of 2.1460(17) and 2.1398(17) Å (Zn(2)–N(41) and Zn(2)–N(71)^{i}, respectively) can be considered as normal as well as the axial N(41)–Zn(2)–N(71)^{i} angle of 177.25(6)°. The equatorial plane is formed by two nitrogen atoms from two different dpyatriz ligands and two oxygen atoms of an asymmetrically bound didentate group. The Zn–N distances (Zn(2)–N(51) 2.0855(17) and Zn(2)–N(61)^{i} 2.0850(16) Å) are usual for this type of geometry as well as the Zn–O distances (Zn(2)–O(96) 2.3887(17) and Zn(2)–O(97) 2.1247(16) Å) [21]. The angles around Zn(2) in the equatorial plane range from 56.54(6)° to 157.17(6)° reflecting the strong distortion.

3.3. Structure of $[Co_2(dpyatriz)_2(NO_3)_2(MeOH)_2](NO_3)_2\cdot(MeOH)_2$ (3)

The molecular structure of $[Co_2(dpyatriz)_2(NO_3)_2(MeOH)_2](NO_3)_2\cdot(MeOH)_2$, along with the atom labeling scheme, is illustrated in Fig. 4. Selected bond lengths and angles are given in Table 2. Compound **3** crystallizes in the monoclinic space group $P2_1/c$ (Table 3), with the cobalt complex located on an inversion center.

The cobalt atom is located in a slightly distorted octahedral environment formed by two pairs of N-coordinating 2-pyridyl groups belonging to two different dpyatriz ligands, one methanol molecule and one disordered nitrate anion. The distortion is mainly due to the disordered nitrate molecule. The coordination geometry is characterized by an $N(22)_{axial}$–Co(1)–$N(25a)_{axial}$ angle of 175.59(12)° and $N_{equatorial}$–Co(1)–N_{axial} and $O_{equatorial}$–Co(1)–N_{axial} angles varying from 81.5(3)° to 95.12(12)°. The angles found within the equatorial plane range from 82.6(4)° to 95.6(3)°, considering the major disorder component of the nitrate. The axial bond lengths are 2.143(3) and 2.118(3) Å for Co(1)–N(22) and Co(1)–N(25a), respectively, and can be regarded as normal. The equatorial bond lengths of 2.116(3) (Co(1)–O(1)), 2.134(3) (Co(1)–N(23)), 2.130(3) (Co(1)–N(24a)), and 2.077(12) Å (Co(1)–O(49)) are normal for this geometry [22]. In addition, two non-coordinate nitrate ions and two methanol molecules are located in the unit cell.

Table 2
Selected bond lengths (Å) and angles (°) for complex **3** [a]

Bond lengths	
Co(1)–O(1)	2.116(3)
Co(1)–N(22)	2.143(3)
Co(1)–N(23)	2.134(3)
Co(1)–N(24)^{i}	2.130(3)
Co(1)–N(25)^{i}	2.118(3)
Co(1)–O(49)	2.077(14)
Bond angles	
O(1)–Co(1)–N(22)	88.84(10)
O(1)–Co(1)–N(25)^{i}	87.10(12)
O(1)–Co(1)–N(24)^{i}	88.92(10)
N(22)–Co(1)–N(23)	88.89(12)
N(22)–Co(1)–N(24)^{i}	94.59(12)
N(23)–Co(1)–N(25)^{i}	95.12(12)
N(23)–Co(1)–N(24)^{i}	92.96(13)
N(25)^{i}–Co(1)–N(24)^{i}	87.07(13)
N(25)^{i}–Co(1)–N(22)	175.59(12)
O(49)–Co(1)–O(1)	82.6(4)
O(49)–Co(1)–N(25)^{i}	88.0(4)
O(49)–Co(1)–N(22)	89.7(4)
O(49)–Co(1)–N(23)	95.6(3)

Symmetry operation i: $1-x$, $1-y$, $1-z$.

[a] Only the major disorder component (O49) of the coordinated nitrate is given.

3.4. Spectroscopic properties

3.4.1. Electronic spectra

The electronic reflectance spectrum of **2** exhibits a strong band at 31 190 cm^{-1} due to ligand-to-metal charge transfer transitions (LMCT). The electronic spectrum of **3** is typical for octahedral high-spin cobalt(II) complexes [23]. Characteristic bands appear over the visible and near-IR regions. The first of these bands emerges over the near-IR range at $\nu_1 = 9493$ cm^{-1} and can be assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ electron transition. In the visible range of the spectrum, only one asymmetric band is present at 20 188 cm^{-1} corresponding to the $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ transition. On the low-energy side of this band, a shoulder is observed at approximately 18 500 cm^{-1} and can be ascribed to the $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ transition. In addition, a strong LMCT is observed at 31 141 cm^{-1}.

3.4.2. IR spectra

The most relevant feature of the infrared spectrum in **2** is the evidence for the chelating and monodentate coordination of the nitrate anions. As the nitrate ion has characteristic absorption frequencies at approximately 1390 (ν_3), 1050 (ν_1), 831 (ν_2) and 720 (ν_4) cm^{-1} for D_{3h}

Table 3
Crystal data and details of data collection and structure refinement for **1**, **2** and **3** [a]

	Compound **1**	Compound **2**	Compound **3**
Empirical formula	$C_{33}H_{24}N_{12}$	$C_{66}H_{48}N_{32}O_{24}Zn_4$ + disordered solvent	$C_{70}H_{64}Co_2N_{28}O_{16}$ + disordered solvent
Formula weight	588.64	1934.92 [b]	1671.35 [b]
Temperature (K)	150	150	110
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
Unit cell dimensions			
a (Å)	12.8873(1)	15.4641(1)	12.6373(3)
b (Å)	19.0091(2)	17.2167(1)	12.0093(3)
c (Å)	12.7088(1)	18.7923(1)	30.2813(6)
β (°)	116.1305(3)	108.3668(3)	92.6627(19)
V (Å^3)	2795.14(4)	4748.40(5)	4590.68(18)
Z	4	2	2
D_{calc} (g cm^{-3})	1.399	1.353 [b]	1.209 [b]
Absorption coefficient, μ (mm^{-1})	0.090	1.080 [b]	0.433 [b]
F (000)	1224	1960 [b]	1724 [b]
Crystal size (mm)	0.12 × 0.24 × 0.46	0.15 × 0.15 × 0.50	0.30 × 0.50 × 0.50
Θ Range for data collection (°)	1.8–27.5	1.8–27.5	1.6–23.9
Index ranges	−16/15, 0/24, 0/16	−19/19, 0/22, 0/24	−14/14, 0/13, 0/34
Reflections collected	51 024	70 312	40 765
Independent reflections	6416	10 808	7107
Absorption correction	multi-scan	multi-scan	none
Transmission range	0.88–1.05	0.74–0.81	
Goodness-of-fit on F^2	1.083	0.812	1.053
Residual electron density (e Å^{-3})	−0.23/0.31	−0.40/0.39	−0.43/0.76
R [$F_0 > 4\sigma(F_0)$]	0.0386	0.0303	0.0621
R (all data)	0.0505	0.0527	0.0776
wR_2 (all data)	0.1096	0.0763	0.1465

[a] Details in common: Mo Kα, $\lambda = 0.71073$ Å.

[b] Derived values do not contain the contribution of the disordered solvent.

symmetry [24–26] and there is no nitrate ion in this complex; the strong bands at 1278 and 1243 cm^{-1}, and a medium band at 646 cm^{-1} are involved in monodentate and didentate chelating modes of coordination. It is impossible to distinguish between mono- and didentate ligands as the nitrate ion (D_{3h}) coordination to one or two oxygen atoms lowers the symmetry to that of C_{2v}. A strong absorption band at 1319 and a medium band at 650 cm^{-1} are observed for **3** which are due to the coordinated monodentate nitrate ions. In addition, small bands are present at 1050 and 820 cm^{-1} and can be attributed to the presence of non-coordinated nitrate anions.

4. Conclusion

The new polynuclear complexes $[Zn_4(dpyatriz)_2(NO_3)_8]$ and $[Co_2(dpyatriz)_2(NO_3)_2(MeOH)_2](NO_3)_2(MeOH)_2$ were prepared by reaction of, respectively, $Zn(NO_3)_2 \cdot 6H_2O$ and $Co(NO_3) \cdot 6H_2O$ with the novel multi-directional hexadentate dpyatriz ligand. X-ray and spectroscopic analyses have shown unique crystallographic structures, in particular for the mixed penta- and hexacoordinated zinc ions of the tetranuclear complex **2**.

5. Supplementary material

Crystallographic data for the compounds have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 192109 (**1**), 192110 (**2**) and 192111 (**3**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-3360333 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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