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Crystallographic Evidence of Nitrate– π Interactions Involving the Electron-Deficient 1,3,5-Triazine RingPalanisamy Uma Maheswari,[†] Barbara Modec,[‡] Andrej Pevec,[‡] Bojan Kozlevčar,[‡] Chiara Massera,^{*,§} Patrick Gamez,^{*,†} and Jan Reedijk[†]

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The reaction of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ with the star-shaped ligand 2,4,6-tris(di-2-picolyamino)[1,3,5]-triazine (dipicatriz) in acetonitrile results in the formation of the mono- or trinuclear coordination compounds $[\text{Zn}(\text{dipicatriz})(\text{NO}_3)_2]$ (**1**), $[\text{Zn}_3(\text{dipicatriz})(\text{NO}_3)_6](\text{CH}_3\text{CN})_3$ (**2**), and $[\text{Cu}_3(\text{dipicatriz})(\text{NO}_3)_2(\text{H}_2\text{O})_6](\text{NO}_3)_4$ (**3**), depending on the metal-to-ligand ratios used during the crystallization process. Their crystal structures exhibit unique supramolecular interactions. Compounds **1** and **2** show anion– π interactions between coordinated nitrate ions and the s-triazine ring. Compound **3** exhibits remarkable interactions between two noncoordinated nitrate anions and the two faces of the electron-deficient heteroaromatic ring, corroborating earlier theoretical investigations in this area. New theoretical investigations have been carried out on nitrate– π interactions, taking into account the particular position of the anion toward the aromatic ring observed in the crystal structures.

Introduction

The interactions with π aromatic clouds play an important role in biological systems.¹ Thus, face-to-face π -stacking interactions between the aryl rings of nucleobase pairs help to stabilize the DNA double helix.² Cation– π interactions are commonly found in Nature, where they are significant contributors to the structure and function of biomolecules.^{3,4} On the contrary, the concept of anion– π interactions is much less intuitive, since this type of interaction between an electron donor and a π aromatic cloud is expected to be repulsive.^{5,6} However, the development of anion hosts

involving noncovalent interactions is a rising topic of supramolecular chemistry.⁷ Anion recognition is a very important process in biochemical systems since more than 70% of substrates and cofactors are negatively charged.⁸ Accordingly, the preparation of synthetic anionic receptors may lead to potential medicinal and biological applications.⁹ The common strategy to design anion host materials is principally based on two different approaches: (1) the anion receptor is positively charged and can thus bind a negatively charged entity;^{10,11} (2) the anion chelating ligand is a Lewis acid.^{12,13} Lately, an alternative to the aforementioned methods has arisen from theoretical investigations on anion– π interactions.¹⁴ Several research groups have clearly demon-

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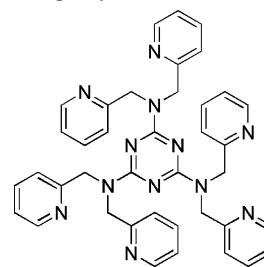
strated that an anion could interact with an electron-deficient aromatic ring. All computational calculations indicate energetically favorable noncovalent interactions between a negative ion and electron-poor aromatic systems such as fluorobenzene derivatives,^{15–17} *s*-triazine^{18,19} and *s*-tetrazine²⁰ derivatives, and tetrafluoroethene.²¹ Such binding properties were first established in the early 1990s by NMR studies,^{22–24} but the first crystallographic evidence of it was reported in 2004.²⁵

Recently, we have undertaken research investigations on coordination compounds involving *s*-triazine-based N-donor ligands. 1,3,5-Triazine derivatives have certainly found tremendous applications in the field of supramolecular chemistry, where the heteroaromatic ring is implicated in crucial supramolecular interactions, i.e., hydrogen bonds and/or π interactions.²⁶

To take advantage of these special properties of the triazine ring, a series of polydentate ligands have been prepared,²⁷ according to a straightforward synthetic pathway starting from cyanuric chloride, i.e., 2,4,6-trichloro-1,3,5-triazine,²⁸ and the physical or structural properties of their metal complexes have been studied.^{29–31}

In the present study, the first coordination compounds of the star-shaped 2,4,6-tris(di-2-picolylamino)[1,3,5]triazine ligand (dipicatriz; Chart 1)²⁸ are reported. Reaction of zinc(II) or copper(II) nitrate with the ligand dipicatriz in acetonitrile leads to the formation of mono- or trinuclear metal complexes depending on the metal:ligand ratio as well as the experimental conditions used during the crystallization process. As expected, these coordination compounds feature the anticipated noncovalent anion– π interactions.

Chart 1. 2,4,6-Tris(di-2-picolylamino)[1,3,5]triazine



Experimental Section

General Procedures. Dipicatriz²⁸ was prepared under argon by a literature method. All other reagents were purchased from commercial sources and used without further purification. Elemental analyses (C, H, and N) were performed with a Perkin-Elmer 2400 analyzer. FTIR spectra were recorded with a Perkin-Elmer Paragon 1000 FTIR spectrophotometer, equipped with a Golden Gate ATR device, using the reflectance technique (4000–300 cm^{-1}). Ligand-field spectra were obtained on a Perkin-Elmer Lambda 900 spectrophotometer using the diffuse reflectance technique, with MgO as a reference, over the range 2000–200 nm at room temperature.

Preparation of [Zn(dipicatriz)(NO₃)₂] (1). A solution of Zn(NO₃)₂·6H₂O (0.044 g, 0.15 mmol) in acetonitrile (10 mL) was added dropwise to a solution of dipicatriz (0.100 g, 0.149 mmol) in acetonitrile (10 mL). The resulting reaction mixture was warmed to 50 °C and stirred for 5 min. The solution was subsequently filtered, and the filtrate was left unperturbed for the slow evaporation of the solvent. After 4 days, colorless crystals suitable for X-ray diffraction were obtained. Yield: 75% (97 mg). Anal. Calcd for C₃₉H₃₆N₁₄O₆Zn: C, 54.33; H, 4.21; N, 22.74. Found: C, 53.85; H, 4.33; N, 21.54. Main IR absorption bands for **1** (cm^{-1}): 2974(m), 1612(w), 1542(m), 1472(s), 1278(s), 1168(m), 1021(m), 768(m), 652(w), 424(m).

Preparation of [Zn₃(dipicatriz)(NO₃)₆](CH₃CN)₃ (2). A solution of Zn(NO₃)₂·6H₂O (0.133 g, 0.447 mmol) in acetonitrile (10 mL) was added dropwise to a stirred solution of dipicatriz (0.100 g, 0.149 mmol) in acetonitrile (10 mL). After a few minutes at 50 °C, the resulting light yellow solution was filtered with paper, and the filtrate was left unperturbed for the slow evaporation of the solvent. After 3 days, colorless rectangular single crystals suitable for X-ray crystallography were obtained. Yield: 78% (158 mg). Anal. Calcd for C₄₅H₄₅N₂₁O₁₈Zn₃: C, 39.62; H, 3.32; N, 21.56. Found: C, 38.72; H, 2.89; N, 20.89. Main IR absorption bands for **2** (cm^{-1}): 2989(m), 1594(w), 1564(m), 1468(s), 1281(s), 1174(m), 1022(m), 752(s), 621(m), 420(m).

Preparation of [Cu₃(dipicatriz)(NO₃)₂(H₂O)₆](NO₃)₄ (3). A solution of Cu(NO₃)₂·3H₂O (0.108 g, 0.447 mmol) in acetonitrile (10 mL) was added dropwise to a solution of dipicatriz (0.100 g, 0.149 mmol) in acetonitrile (10 mL). After 5 min at 50 °C, the resulting solution was filtered and left unperturbed to allow the slow evaporation of the solvent. After 4 days, dark blue crystals suitable for X-ray crystallography were obtained. Yield: 82% (164 mg). Anal. Calcd for C₃₉H₄₈Cu₃N₁₈O₂₄: C, 34.86; H, 3.60; N, 18.77. Found: C, 36.25; H, 4.35; N, 18.25. Main IR absorption bands for **3** (cm^{-1}): 3480(br s), 3122(w), 2990(w), 1613(w), 1582(m), 1545(m), 1441(m), 1372(s), 1368(s), 1286(s), 1162(m), 1026(m), 768(s), 593(w), 423(m). UV–vis (reflectance, nm): 268 (shoulder), 351, 723 (br), 993 (br), 1124 (shoulder).

X-ray Crystallographic Analysis and Data Collection. Crystallographic data and refinement details are given in Table 1. Intensity

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Table 1. Crystallographic Data and Refinement Details for **1–3**

	1	2	3
empirical formula	C ₃₉ H ₃₆ N ₁₄ O ₆ Zn	C ₃₉ H ₃₆ N ₁₈ O ₁₈ Zn ₃ ·3(C ₂ H ₃ N)	C ₃₉ H ₄₈ N ₁₄ O ₁₂ Cu ₃ ·4(NO ₃)
fw	862.19	1364.13	1343.57
cryst syst	triclinic	triclinic	monoclinic
space group	P1 (No. 2)	P1 (No. 2)	P2 ₁ /n (No. 14)
a/Å	11.6307(1)	13.0972(2)	13.476(5)
b/Å	13.2620(2)	15.1275(3)	25.455(5)
c/Å	13.9744(2)	16.6703(3)	16.537(5)
β /deg	103.975(1)	108.237(1)	101.635(5)
V/Å ³	2007.93(5)	2958.71(9)	5556(3)
Z	2	2	4
D _c /(g cm ⁻³)	1.426	1.531	1.606
F(000)	892	1392	2748
μ /mm ⁻¹	0.677	1.293	1.235
cryst dims/mm ³	0.18 × 0.15 × 0.10	0.25 × 0.13 × 0.10	0.15 × 0.16 × 0.30
temp/K	293(2)	150(2)	293(2)
$\theta_{\min, \max}$ /deg	5.3, 27.5	2.6, 27.5	1.5, 27.0
no. of reflns collected	17059	22415	23959
no. of independent reflns	9063 ($R_{\text{int}} = 0.0173$)	13341 ($R_{\text{int}} = 0.042$)	10342 ($R_{\text{int}} = 0.0186$)
R1 ^a [$F_o > 4\sigma(F_o)$]	0.0605	0.0486	0.0548
wR2 ^a	0.1951	0.1260	0.1310
$\Delta\rho_{\min, \max}/\text{e Å}^{-3}$	-0.55, 1.92	-0.52, 1.23	-0.48, 0.77
S ^b	1.06	1.06	1.12

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$. ^b Goodness-of-fit $S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$, where n is the number of reflections and p the number of parameters.

data for single crystals of **1–3** were collected using Mo K α radiation ($\lambda = 0.71073$ Å) on a Nonius Kappa CCD diffractometer with an area detector at 293(2) K for **1** and 150(2) K for **2** and on a Bruker AXS Smart 1000 single-crystal diffractometer equipped with a CCD area detector at 293(2) K for **3**. The structures of **1** and **2** were solved by direct methods implemented in SHEIXS-97³² and refined by a full-matrix least-squares procedure based on F_o^2 using SHELXL-97.³³ The data reduction for **3** was performed using the SAINT³⁴ and SADABS³⁵ programs. The structure was solved by direct methods using the SIR97 program³⁶ and refined on F_o^2 by full-matrix least-squares procedures using the SHELXL-97 program.³³ All the non-hydrogen atoms were refined with anisotropic atomic displacements, with the exclusion of the four noncoordinated nitrate groups. 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 $w = 1/[\sigma^2 F_o^2 + (0.1202P)^2 + 1.1414P]$, $w = 1/[\sigma^2 F_o^2 + (0.0454P)^2 + 4.3176P]$, and $w = 1/[\sigma^2 F_o^2 + (0.0488P)^2 + 5.9255P]$ (where $P = (F_o^2 + 2F_c^2)/3$) for **1**, **2**, and **3**, respectively. All calculations for **3** were performed with a DIGITAL Alpha Station 255 computer. CCDC-615090 (**1**), -615091 (**2**), and -289390 (**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 Rd., Cambridge CB2 1EZ, U.K., fax +44-1223/336-033, e-mail deposit@ccdc.cam.ac.uk). Geometric calculations and molecular

graphics were performed with the PARST97 program³⁷ and the PLATON package.³⁸

Computational Methods. The calculations of the triazine–nitrate interactions, as well as the geometry optimizations on the 1:1 and 2:1 systems, have been carried out at the HF and MP2 levels,^{39,40} as implemented in Gaussian03,⁴¹ using both the 6-311++G and the 6-311++G(3df,p) basis sets. No frozen core approximation was used for the atoms’ core electrons. Default optimization procedures were used, and symmetry was disabled in all calculations. The geometries of the isolated nitrate and 1,3,5-triazine molecules were optimized at the MP2/6-311G** level and then used as such when the potential energy surface was scanned for selected NO₃⁻/triazine distances. The basis set superposition error (BSSE)⁴² was corrected in all calculations with the method of Simon⁴³ as implemented in Gaussian03. Calculations have been carried out on an IBM SP5/512 supercomputer at CINECA.⁴⁴

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Table 2. Selected Bond Distances (Å) for **1–3**

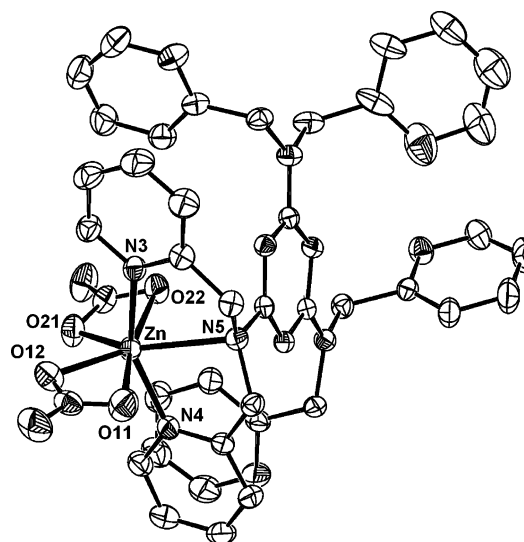
compd 1		compd 2		compd 3	
Zn–N(3)	2.042(3)	Zn(1)–N(5)	2.527(3)	Cu(1)–N(4)	2.007(5)
Zn–N(4)	2.041(3)	Zn(1)–N(7)	2.013(3)	Cu(1)–O(1)	2.082(3)
Zn–N(5)	2.480(2)	Zn(1)–N(8)	2.009(3)	Cu(1)–O(1w)	2.100(4)
Zn–O(11)	2.427(3)	Zn(1)–O(1)	2.082(2)	Cu(1)–N(5)	1.940(5)
Zn–O(12)	2.140(3)	Zn(1)–O(4)	2.075(3)	Cu(1)–N(6)	1.968(5)
Zn–O(21)	2.081(3)	Zn(1)–O(5)	2.453(3)	Cu(1)–O(2)	2.540(4)
Zn–O(22)	2.516(3)	Zn(2)–N(9)	1.987(3)	Cu(2)–N(8)	2.002(3)
		Zn(2)–N(10)	2.001(3)	Cu(2)–N(9)	2.007(4)
		Zn(2)–O(7)	2.062(2)	Cu(2)–O(2w)	1.997(5)
		Zn(2)–O(10)	2.075(2)	Cu(2)–O(3w)	1.984(3)
		Zn(2)–O(11)	2.457(3)	Cu(2)–N(7)	2.605(7)
		Zn(3)–N(11)	2.067(3)	Cu(2)–O(4w)	2.341(6)
		Zn(3)–N(12)	2.066(3)	Cu(3)–N(11)	2.035(4)
		Zn(3)–O(13)	1.996(2)	Cu(3)–N(12)	2.001(5)
		Zn(3)–O(16)	2.531(3)	Cu(3)–O(5w)	1.977(3)
		Zn(3)–O(17)	1.984(2)	Cu(3)–O(6w)	2.003(5)
				Cu(3)–N(10)	2.512(7)
				Cu(3)–O(4)	2.435(6)

Results and Discussion

Synthesis of 1–3. Compounds **1–3** were obtained by treatment of the metal nitrate with the ligand dipicatriz in acetonitrile at room temperature. The molecular structures and unusual supramolecular characteristics of **1–3** are shown in Figures 1–6. The selected bond distances and bond angles of **1–3** are listed in Tables 2 and 3. Details of the structures will be discussed below.

Structure of 1. **1** is obtained by reaction of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and the ligand dipicatriz in acetonitrile, in a 1:1 metal-to-ligand ratio. The molecular structure of **1**, along with the atom labeling scheme adopted, is illustrated in Figure 1. Selected bond lengths and angles are given in Tables 2 and 3, respectively.

The zinc atom is heptacoordinated by one dipicolylamine group from the ligand and two bidentate nitrate ions. This heptacoordination can be best described as a distorted pentagonal bipyramid⁴⁵ with the N(3) and N(4) pyridine nitrogen atoms occupying the axial positions at normal distances (Table 2). The plane is defined by four oxygen atoms from two nitrate anions and the amine nitrogen atom N(5) connected to the triazine ring. The oxygens O(12) and O(21) are located at normal distances from the metal center, while the Zn–O(11) and Zn–O(22) bond lengths are rather long, namely, about 2.5 Å (Table 2). This semicoordination is most likely due to the small bite angle of the bidentate

**Figure 1.** ORTEP drawing (30% probability level) of **1**. Hydrogen atoms have been omitted for clarity.

nitrate ligand, which also induces the distortion of the pentagonal bipyramid geometry. The pentagon is completed by the semicoordinated atom N(5) at a distance close to 2.5 Å. The in-plane angles vary from 55° to 86° (Table 3), away from the ideal angle of 72° for a perfect pentagon. The axial angle N(3)–Zn–N(4) is also far from best with a value of 151.27(11)°.

This coordination compound exhibits a very interesting feature, that is, the interaction between the oxygen atom O(22) of the nitrate anion coordinated to the Zn^{II} and the π cloud of the 1,3,5-triazine ring, with a short centroid \cdots O(22) distance of 3.006(1) Å and an angle of the centroid \cdots O(22) axis to the plane of 75.2(3)° (Figure 2). As mentioned above, noncovalent anion– π interactions are quite uncommon and have only recently been investigated.^{16,19} The present compound illustrates the possibility to have interaction between a nitrate oxygen atom and an electron-poor aromatic ring.

Structure of 2. Reaction of 3 equiv of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in acetonitrile with 1 equiv of dipicatriz yields an expected trinuclear complex. A molecular plot of the crystal structure of **2** without the lattice acetonitrile molecules is shown in Figure 3, and the interatomic distances and angles relevant to the zinc coordination spheres are given in Tables 2 and 3, respectively. The trinuclear complex consists of one

Table 3. Selected Angles (deg) for **1–3**

compd 1		compd 2		compd 3	
N(5)–Zn–O(22)	86.28(8)	N(5)–Zn(1)–O(5)	89.84(9)	N(4)–Cu(1)–N(6)	81.8(2)
O(22)–Zn–O(21)	54.66(9)	O(5)–Zn(1)–O(4)	56.10(10)	N(4)–Cu(1)–N(5)	84.3(2)
O(21)–Zn–O(12)	81.96(10)	O(4)–Zn(1)–O(1)	83.62(11)	N(5)–Cu(1)–O(1)	95.8(1)
O(12)–Zn–O(11)	54.87(12)	O(1)–Zn(1)–N(5)	130.45(10)	N(6)–Cu(1)–O(1)	94.2(1)
O(11)–Zn–N(5)	83.60(10)	N(7)–Zn(1)–N(8)	149.41(11)	O(2)–Cu(1)–O(1w)	153.2(1)
N(3)–Zn–N(4)	151.27(11)	N(9)–Zn(2)–N(10)	147.71(12)	N(8)–Cu(2)–N(9)	94.9(1)
		N(10)–Zn(2)–O(10)	102.49(11)	N(9)–Cu(2)–O(3w)	86.7(1)
		O(10)–Zn(2)–N(9)	104.62(11)	N(9)–Cu(2)–O(2w)	87.5(1)
		O(7)–Zn(2)–O(11)	141.93(10)	O(2w)–Cu(2)–N(8)	90.2(1)
		N(12)–Zn(3)–O(13)	90.81(11)	N(7)–Cu(2)–O(4w)	166.5(1)
		O(13)–Zn(3)–O(17)	131.15(10)	N(11)–Cu(3)–N(12)	94.0(1)
		O(17)–Zn(3)–N(12)	115.34(11)	N(12)–Cu(3)–O(5w)	91.6(1)
		N(11)–Zn(3)–O(16)	148.88(12)	O(5w)–Cu(3)–O(6w)	86.3(1)
				O(6w)–Cu(3)–N(11)	88.0(1)
				N(10)–Cu(3)–O(4)	167.0(1)

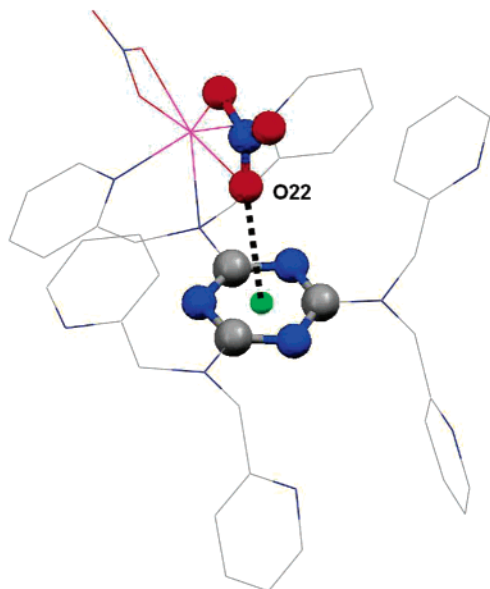


Figure 2. Oxygen- π interaction in **1** between the coordinated nitrate anion and the *s*-triazine ring. Centroid \cdots O(22) = 3.006(1) Å, and triazine plane-centroid-O(22) axis = 75.2(3)°.

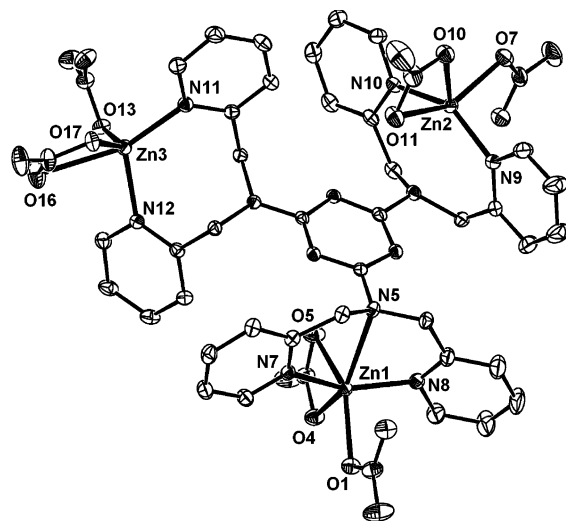


Figure 3. ORTEP drawing (30% probability level) of **2**. Hydrogen atoms and acetonitrile molecules have been omitted for clarity.

hexacoordinated zinc ion, Zn(1), and two pentacoordinated zinc ions with a closely related coordination environment, Zn(2) and Zn(3) (see Figure 3). Zn(1) is in a highly distorted octahedral environment with the oxygen atoms O(1), O(4), and O(5) from two coordinated nitrate anions in the basal plane which is completed by the semicoordinated nitrogen atom N(5) from the ligand. The axial positions are occupied by the nitrogen atoms N(7) and N(8) from a dipicolylamino unit of the ligand dipicatriz (at distances of about 2 Å). The angles in the basal plane range from 56° to 130°, reflecting the strong distortion generated by the bidentate binding mode of one of the nitrate anions and the semicoordination of the

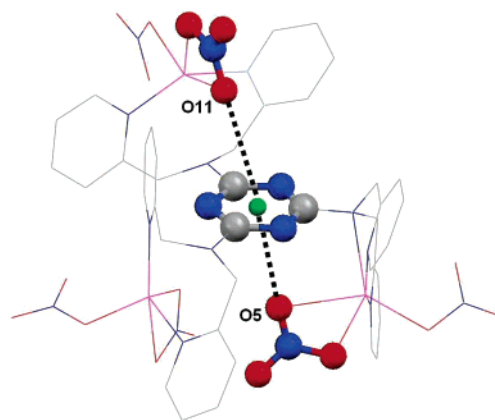


Figure 4. Oxygen- π interactions in **2** between two coordinated nitrate anions and the two faces of the *s*-triazine ring. Centroid \cdots O(5) = 3.097(2) Å, and triazine plane-centroid-O(5) axis = 76.14(3)°. Centroid \cdots O(11) = 3.515(1) Å, and triazine plane-centroid-O(11) axis = 68.15(3)°.

amine N(5) atom [Zn(1)-N(5) bond length of 2.527(3) Å]. The zinc center Zn(2) is in a distorted trigonal bipyramidal coordination environment ($\tau = 0.75$, where τ is 0 and 1 for the perfect square pyramidal and trigonal bipyramidal geometries, respectively).⁴⁶ The basal plane of the trigonal bipyramid around the Zn(2) ion is made up of the nitrogen atoms N(9) and N(10) of two pyridine rings and the oxygen atom O(10) of a bidentate anion. The axial positions are occupied by the oxygen atoms O(7) and O(11) of two nitrate counterions. The in-plane angles vary from 102° to 148° (Table 3), away from the ideal angle of 120° for a perfect trigonal bipyramid geometry.

The third zinc ion is pentacoordinated, with a N_2O_3 donor set. The geometry around the Zn(3) ion is a distorted tetrahedron, if the long Zn(3)-O(16) bond [2.531(3) Å] of the semicoordinated oxygen atom of the bidentate nitrate is not considered to describe its coordination sphere. The tetrahedral N_2O_2 set is thus formed by two pyridine nitrogen atoms, N(11) and N(12), from one dipicolylamine unit of the ligand and two oxygen atoms O(13) and O(17) from two nitrate anions. The angles within the tetrahedron vary from 91° to 115°, illustrating once more the distortion owing to the semicoordination of the oxygen O(16) of the bidentate nitrate which exhibits a small bite angle of 55.62(11)°.

Similarly to **1**, this trinuclear zinc(II) complex shows evidence of anion- π interactions. Thus, the oxygen atom O(5) of the bidentate nitrate anion coordinated to Zn(1) once again strongly interacts with the electron-deficient aromatic ring. The distance centroid \cdots O(5) is 3.097(2) Å, and the angle of the centroid \cdots O(5) axis to the plane amounts to 76.14(3)° (Figure 4). In addition, a second nitrate anion amazingly interacts with the same triazine unit. Indeed, the oxygen atom O(11) is located on top of the other face of the aromatic ring, with a longer centroid \cdots O(11) distance of 3.515(1) Å and a smaller angle of the centroid \cdots O(11) axis to the triazine plane of 68.15(3)° (Figure 4). This result represents one of the first examples⁴⁷ of two anions interacting with one aromatic ring. In fact, all theoretical investiga-

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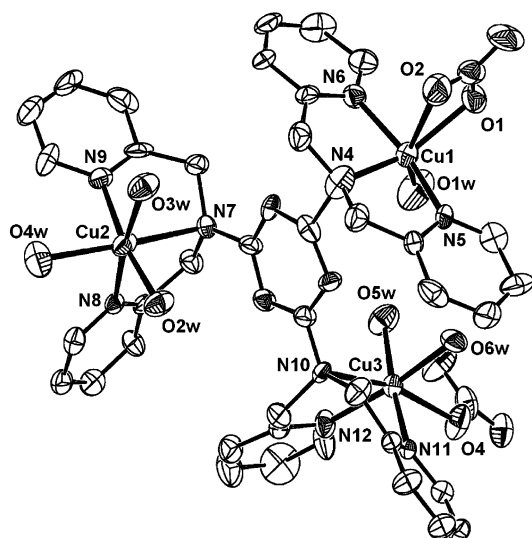


Figure 5. ORTEP drawing (30% probability level) of **3**. Hydrogen atoms and noncoordinated nitrate anions have been omitted for clarity.

tions performed so far have been devoted to the potential interaction of one anion with one electron-poor aromatic host.¹⁸ Recently, computational calculations on possible interactions of one anion with two or three π systems have been carried out,⁴⁸ but the interactions between two anions and one π cloud have not yet been investigated.

In the present example, one can logically consider that the nitrate–triazine interactions are facilitated by the fact that these two anions are bonded to the metal centers, forcing the anion– π contacts (this is also true for complex **1**). However, the preparation of the copper complex **3** corroborates the statements made above.

Structure of 3. Indeed, the reaction of 3 equiv of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in acetonitrile with 1 equiv of dipicatriz also yields a trinuclear complex which exhibits unusual supramolecular interactions. The molecular structure of **3** consists of three Cu^{II} ions coordinated by one nonadentate dipicatriz ligand (Figure 5). The three copper ions show different N_3O_3 octahedral environments, with one [Cu(1)], two [Cu(3)], or three [Cu(2)] water molecules coordinated to the metal centers.

The octahedral N_3O_3 coordination sphere around Cu(1) is very distorted, most likely as a result of the bidentate binding mode of the nitrate ion with one long Cu–O bond (Table 2). The equatorial plane is formed by the tertiary amine nitrogen atom N(4), the oxygen atom O(1) from a bidentate nitrate, and the nitrogen atoms N(5) and N(6) from two pyridine rings at normal distances (Table 2). The axial positions are occupied by the oxygen atom O(1w) from a water molecule and by the other oxygen atom O(2) of the bidentate nitrate ion. The in-plane *cis* angles around the Cu(1) ion vary from $81.8(2)^\circ$ to $95.8(1)^\circ$ (Table 3). The axial O(1w)–Cu(1)–O(2) angle of $153.2(1)^\circ$ is indicative of a significant distortion from a regular octahedral geometry.

Also the coordination sphere around the second copper ion Cu(2) is rather distorted. The equatorial plane around the Cu(2) ion is formed by two *cis* located nitrogen atoms, N(8) and N(9), from two pyridine groups belonging to one dipicolylamine unit of the ligand. The other two positions are occupied by the oxygen atoms O(2w) and O(3w) from two water molecules (Figure 5). The axial positions are occupied by the oxygen atom O(4w) of a third water molecule at a relatively long distance (Table 2) and by a weakly bound nitrogen N(7) atom; however, the long Cu–N distance still matches the range of bond lengths observed for copper–nitrogen bonds along the Jahn–Teller axis.⁴⁹ The in-plane *cis* angles vary in the range $86.7(1)^\circ$ – $94.9(1)^\circ$ (Table 3). The angle N(7)–Cu(2)–O(4w), which should be equal to 180° in the regular octahedron, is only $166.5(1)^\circ$, probably due to the coordination constraint of the tridentate dipicolylamine moiety.

The basal plane around Cu(3) is formed by two nitrogen atoms, N(11) and N(12), from a dipicolylamine group, and two oxygen atoms, O(5w) and O(6w), from two water molecules (Figure 5). The in-plane Cu–N distances are in the usual range, as well as the Cu–O distances (Table 2). The axial positions, along the Jahn–Teller axis, are occupied by the oxygen atom O(4) from a nitrate and the tertiary amine nitrogen donor N(10) at common distances.^{50,51} The angles around Cu(3) in the basal plane vary from $86.3(1)^\circ$ to $94.0(2)^\circ$ (Table 3). Similarly to Cu(2), the axial angle, i.e., O(4)–Cu(3)–N(10), is equal to $167.0(1)^\circ$, indicating once again the distortion generated by the bite angle of the tridentate dipicolylamine moiety [the angles N(10)–Cu(3)–N(11) and N(10)–Cu(3)–N(12) are $75.0(1)^\circ$ and $76.3(1)^\circ$, respectively, where they should be 90° for a perfect octahedron].

The molecular structure of **3** also exhibits the unusual and remarkable ability of the triazine ring to interact with two nitrate anions, which are, in the present case, not coordinated to any metal ions (Figure 6). The oxygen atoms O(9) and O(11) of the two negative ions are clearly on top of each face of the electron-deficient aromatic moiety. The distance centroid \cdots O(9) is $3.202(1)$ Å, and the angle of the centroid–O(9) axis to the plane is equal to $65.9(2)^\circ$ (Figure 6). The second oxygen atom O(11) is at a longer distance, $3.502(5)$ Å, from the centroid, and the triazine plane–centroid–O(11) axis is $68.0(2)^\circ$. In addition to this interaction, the spatial orientation of the two nitrate groups is also influenced by a network of hydrogen atoms involving the hydrogens of the coordinated water molecules and the oxygens of the nitrate ions. Although the hydrogens of these water molecules could not be calculated or located in the difference Fourier map, the presence of the hydrogen bonds is suggested by the following short contacts: O(1w) \cdots O(9) = $2.741(8)$ Å, O(5w) \cdots O(9) = $2.683(8)$ Å, O(2w) \cdots O(11) = $2.644(6)$ Å, O(3w) \cdots O(10) = $2.646(7)$ Å. The interaction between one

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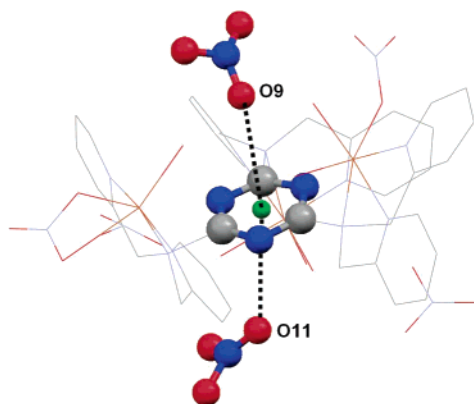


Figure 6. π interactions in **3** between the oxygen atoms of noncoordinated nitrate anions and the two faces of the electron-deficient 1,3,5-triazine ring. Centroid \cdots O(9) = 3.202(1) Å, and triazine plane-centroid-O(9) axis = 65.9(2)°. Centroid \cdots O(11) = 3.502(5) Å, and triazine plane-centroid-O(11) axis = 68.0(2)°.

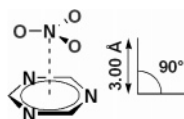


Figure 7. Optimized structure of the NO_3^- complex with the 1,3,5-triazine ring. Reprinted from ref 21. Copyright 2004 American Chemical Society.

nitrate ion and the *s*-triazine ring has been favorably predicted using computational methods,²¹ but the resulting optimized structure shows a different structural arrangement (Figure 7). The nitrate plane is located parallel to the triazine ring, and the nitrogen atom is axial on the centroid. The three oxygen atoms are thus facing the carbon atoms of the symmetric heterocycle at a N-centroid distance of 3.00 Å. The centroid \cdots O(9) distance of 3.202(1) Å, reported for the present crystallographic example, is close to the calculated values found for monatomic anions such as chloride or bromide.^{19,21,52} To consolidate the presence of an attractive interaction in our complex, we have carried out ab initio calculations on both the 1:1 and the 2:1 nitrate-triazine systems, analyzing the interaction energies between the fragments as a function of the distances *R* and *R'* (see Figure 8). The geometry of each fragment was previously optimized at the MP2/6-311G** level, while the orientation of the nitrate groups with respect to the triazine ring was derived from the crystal structure coordinates.

The interaction energies have been calculated with both the HF and MP2 methods using the 6-311++G and 6-311++G(3df,p) basis sets, varying *R* and *R'* from 2.2 to 5.0 Å (increment 0.2 Å). The results are summarized in Tables SI1 and SI2 (Supporting Information). The interaction energies (corrected for BSSE) as a function of *R* and *R'* for the 1:1 and the 2:1 nitrate-triazine systems are shown in Figures 9 and 10, respectively. At the MP2/6-311++G(3df,p) level, the highest binding occurs at *R* = 3.0 Å for the 1:1 complex (*E* = -22.38 kJ/mol) and at *R* = *R'* = 3.2 Å (*E* = -23.98 kJ/mol) for the 2:1 complex; this clearly shows the presence of an attractive interaction between the fragments at *R* and *R'* values close to those obtained from our crystal

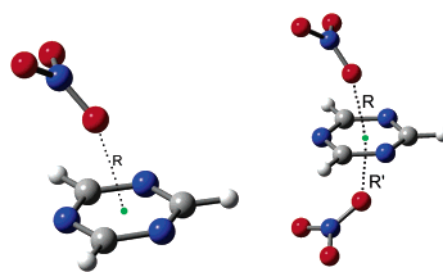


Figure 8. Geometries used for the calculations of the intermolecular interactions in the 1:1 (left) and 2:1 (right) nitrate-triazine complexes. The reciprocal spatial orientation of the fragments in the complex was derived from the crystal structure (see also Figure 6); in the different calculations the values of *R* and *R'* have been varied from 2.2 to 5.0 Å with an increment of 0.2 Å. In the case of the 2:1 system *R* and *R'* have been varied symmetrically. Color code: N, blue; C, gray; H, white; O, red; centroid, green.

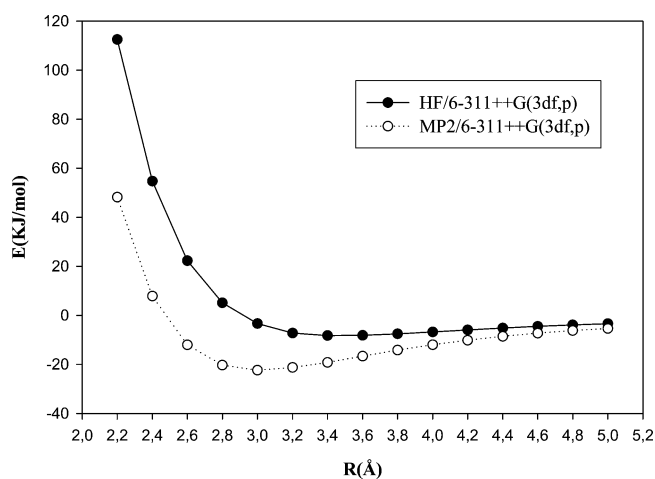


Figure 9. Calculated HF and MP2 interaction energies of the 1:1 nitrate-triazine system at different values of *R*.

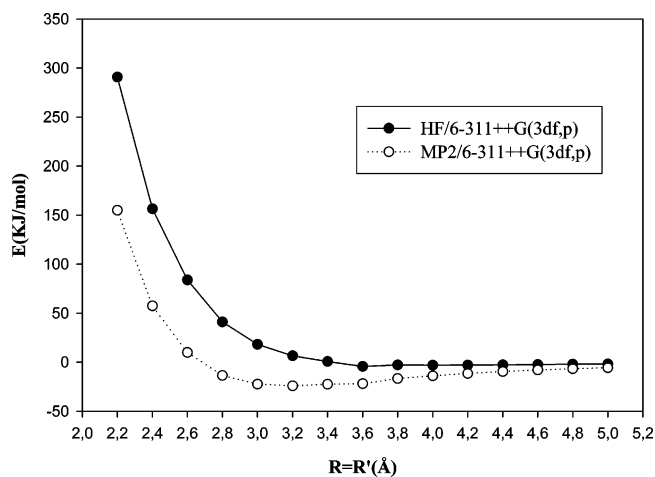


Figure 10. Calculated HF and MP2 interaction energies of the 2:1 nitrate-triazine system at different values of *R* = *R'*.

structure analysis. These attractive interactions contribute to the spatial orientation of the nitrate groups, together with the electrostatic forces between the charged species and with the above cited hydrogen bonds involving the coordinated water molecules. At this point, it has to be mentioned that the interaction energies calculated for this peculiar position of the nitrate pointing toward the aromatic ring through one of its oxygen atoms, which is a priori unfavored, are

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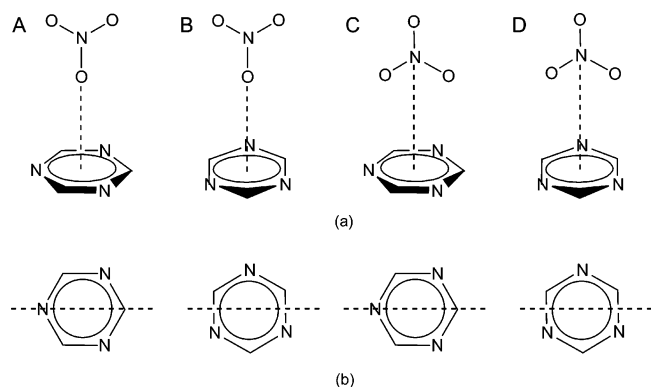


Figure 11. Initial geometries used for the geometry optimization of the T-shaped dimers: (a) side view, (b) top view (the nitrate is omitted for clarity, and only the plane passing through it and bisecting the triazine ring is shown).

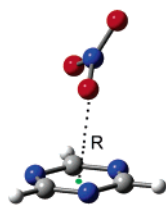


Figure 12. Optimized triazine–nitrate structure deriving from the T-shaped system. The equilibrium oxygen...centroid distance R is 2.75 Å, and the triazine plane–centroid–O axis is 86.21°. Color code: N, blue; C, gray; H, white; O, red; centroid, green.

comparable to those determined for the optimized, more rational nitrate position, parallel to the triazine, where the oxygen atoms are facing the carbon atoms (Figure 7).²¹ Nevertheless, following a reviewer's suggestion, we have also carried out geometry optimizations (first at the HF level and then at the MP2 level using the 6-311++G basis set) of the 1:1 system starting from a T-shaped geometry of the dimer to search for another local energy minimum. Four different initial geometries (**A**, **B**, **C**, and **D**; see Figure 11) were chosen, in which the plane of the nitrate ion was always kept perpendicular to the triazine ring. In **A** and **B** the nitrate ion faces the heterocycle with one oxygen atom, while in **C** and **D** it faces the triazine moiety with two oxygen atoms (Figure 11a, side view). In **A** and **C** the plane passing through the nitrate group bisects the triazine ring along the N–C–H direction, and in **B** and **D** it bisects two C–N bonds (Figure 11b, top view). In all four cases, the geometry optimizations lead to very similar final isoenergetic structures, which are thus all local minima on the potential energy surface (no imaginary frequencies). Since the difference in geometry among the resulting structures is negligible, only one of them is reported in Figure 12. The nitrate ion is no longer perpendicular with respect to the triazine ring, but faces the heterocycle with two oxygen atoms, thus resembling the original **C** structure. The oxygen...centroid equilibrium distance (R) is 2.75 Å, and the triazine plane–centroid–O axis is 86.21°. A single-point energy calculation at the MP2/6-311++G(3df,p) level was then carried out on these optimized structures, leading to an interaction energy (corrected for BSSE) of –35.21 kJ/mol. Even if this disposition is slightly different from the one found in the crystal

structure, the centroid...oxygen distance and the energies are again comparable.

In addition to the single-point calculations of the interaction energies of the 2:1 system at different values of R and R' , we have also carried out a full geometry optimization at the MP2/6-311++G level; the initial spatial orientation of the fragments in the complex was as usual derived from the crystal structure, starting from $R = R' = 2.6$ Å. In this case a local minimum is found when the two ions are roughly 10 Å from the triazine ring, and the reciprocal orientation of the fragments has changed dramatically. The discrepancy between this result and the result obtained when the only optimized geometrical parameters are R and R' (see above) is a frequent problem in theoretical calculations for systems in which the intermolecular interactions are weak. Indeed, when a geometry optimization is performed with a frozen geometry, allowing only the R and R' distances to be optimized, the forces decrease to a first situation of minimum already at an R/R' value of ca. 3.7 Å. However, the flat potential prevents a full convergence of the optimization, and the method of obtaining interaction energies via single-point calculations corrected by BSSE remains more accurate and significant for the scope of the present study.

In summary, this copper coordination compound is unique for two reasons: (1) it represents the first crystallographic evidence of nitrate– π interactions; (2) it exhibits anion– π –anion interactions which are among the first examples reported in the literature, both theoretically and crystallographically.

Conclusions

Anion coordination chemistry is an important and challenging topic of contemporary supramolecular chemistry, since the design of efficient anion-sensing receptors would be paramount for the preparation of new drugs. Several theoretical investigations have clearly indicated that receptors based on anion– π interactions are promising candidates for the formation of anion-sensing receptors. These calculations have also suggested that the electron-deficient 1,3,5-triazine ring is a potentially effective anion host. The present study clearly supports these first computational predictions, both crystallographically and theoretically. These significant experimental results thus strengthen the anion– π approach to synthesize neutral anion host–guest systems, and other triazine-based receptors are currently being investigated. In particular, the design and synthesis of compounds involving multiple anion– π interactions (π –anion– π , for example) as well as the selectivity of the host molecules toward different anions are now being explored.

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Supporting Information Available: X-ray crystallographic data for species **1–3** (CIF) and summary of the HF and MP2 interaction energies of the nitrate–triazine systems (Tables SI1 and SI2). This

material is available free of charge via the Internet at <http://pubs.acs.org>.

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