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Article

Low-Dimensional Copper(II) Complexes with the Trinucleating Ligand 2,4,6-Tris(di-2-pyridylamine)-1,3,5-triazine: Synthesis, Crystal Structures, and Magnetic Properties[†]

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The preparation and structural characterization of three new copper(II) complexes of formula $[Cu_3(dipyatriz)_2(H_2O)_3](ClO_4)_6 \cdot 2H_2O$ (**1**), $\{[Cu_4(dipyatriz)_2(H_2O)_2(NO_3)_2(ox)_2](NO_3)_2 \cdot 2H_2O\}_n$ (**2**), and $[Cu_6(dipyatriz)_2(H_2O)_9(NO_3)_3(ox)_3](NO_3)_3 \cdot 4H_2O$ (**3**) [dipyatriz = 2,4,6-tris(di-2-pyridylamine)-1,3,5-triazine and ox = oxalate] are reported. The structure of **1** consists of trinuclear units $[Cu_3(dipyatriz)_2(H_2O)_3]^{6+}$ and uncoordinated perchlorate anions. The two dipyatriz molecules in **1** act as tris-bidentate ligands with the triazine cores being in a quasi eclipsed conformation. Each copper atom in **1** exhibits a distorted square pyramidal geometry CuN_4O with four pyridyl-nitrogen atoms from two dipyatriz ligands building the basal plane and a water molecule occupying the axial position. The values of the intratrimer copper−copper separation are 8.0755(6) and 8.3598(8) Å. Compound **2** exhibits a layered structure of copper(II) ions which are connected through bis-bidentate dipyatriz ligands and bidentate/outer monodentate oxalato groups. The copper atoms in **2** exhibit six- $[Cu(1)N_4O_2]$ and five-coordination $[Cu(2)N_2O_3]$. A water molecule and three pyridyl-nitrogen atoms [Cu(1)] and two pyridyl-nitrogen plus two oxalate-oxygen atoms [Cu(2)] define the equatorial plane whereas either an oxalate-oxygen and a pyridyl-nitrogen [Cu(1)] or a nitrate-oxygen [Cu(2)] fill the axial positions. The copper−copper separation through the bridging oxalato is 5.6091(6) Å whereas those across dipyatriz vary in the range 7.801(1)−9.079(1) Å. The structure of compound **3** contains discrete cage-like hexacopper(II) units $[Cu_6(dipyatriz)_2(H_2O)_9(NO_3)_3(ox)_3]^{3+}$ where two trinuclear $[Cu_3(dipyatriz)]^{6+}$ fragments are connected by three bis-bidentate oxalate ligands, the charge being balanced by three non-coordinated nitrate anions. The values of the intracage copper−copper distance are 5.112(3)−5.149(2) Å (across oxalato) and 7.476(2)−8.098(2) Å (through dipyatriz). Magnetic susceptibility measurements of polycrystalline samples of **1**−**3** in the temperature range 1.9−295 K show the occurrence of a weak antiferromagnetic interaction across dipyatriz in **1** [$J = -0.08(1)$ cm^{-1}, the Hamiltonian being defined as $\hat{H} = -J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1 \cdot \hat{S}_3 + \hat{S}_2 \cdot \hat{S}_3)$] and weak ferro- (**2**) and strong antiferromagnetic (**3**) interactions through the oxalato bridge in **2** [$J = +0.45(2)$ cm^{-1}] and **3** [$J = -390(1)$ cm^{-1}]. The use of the dipyatriz-containing copper(II) species as a building block to design homo- and heterometallic magnetic compounds is analyzed and discussed.

Introduction

1,3,5-Triazine-containing ligands such as 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tpyt) and 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (tpymt) (see Scheme 1), whose synthesis was reported half a century ago,[1,2] are stable molecules which only undergo hydrolysis in the presence of concentrated mineral acids and temperatures above 150 °C.[3] The first studies with these organic molecules focused on their use as analytical reagents for different metal ions,[4] and further investigations illustrated their capability as ligands for metal assembling because of the

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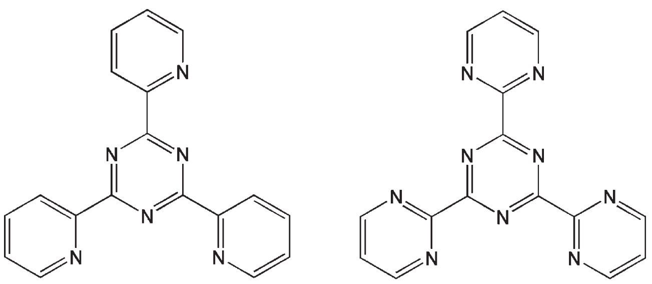
tridentate terpyridine- and bidentate bipyridine-like binding sites that they possess.[2b,5−9]

Surprisingly, these 2,4,6-triaryl-substituted triazines undergo a copper(II)-promoted hydrolysis in mild conditions resulting in the highly stable $[Cu(bpca)]^+$ (tpyt) and $[Cu(bpcam)]^+$ (tpymt) species [bpca = bis(2-pyridylcarbonyl)amidate and bpcam = bis(2-pyrimidylcarbonyl)amidate],[2a,10,11] This hydrolytic reaction that has been proved to be also assisted by other cations such as ruthenium(II) and rhodium(III)[5b,5c,12] is the source of the building blocks $[M(bpca)_x]^{(m-x)+}$ and $[M(bpcam)_x]^{(m-x)+}$ (M = di- or trivalent transition metal ion and x = 1 or 2).[2a,5b,10,11c,12,13] Their use as Lewis acid and base respectively has provided a plethora of homo-[11a,11d,14] and heterometallic[13f,15−17] polynuclear species with interesting magnetic properties, two of the most exciting results being the design of honeycomb layered heterobimetallic materials[16c,16d] and an unprecedented homometallic single chain magnet with regular alternating low-spin iron(III)/high-spin iron(II) ions.[14k,14l]

Scheme 1



Tptz Tpymt

At first sight, although tptz and tpymt offer the possibility to bind three metal ions in a trigonal array, there is no structural report to support this coordination mode in the case of tptz, and it was only observed in two structures with lead(II) for tpymt.[9] This apparent difficulty of tpyt and tpymt ligands to coordinate three metal ions together with the metal-promoted hydrolysis that they undergo limit their extensive use to develop supramolecular systems. In the search for more stable 1,3,5-triazine based ligands which were able to form tridirectional tricopper(II) complexes to be used as precursors of multifunctional metallo-supramolecular structures, we focused on the 2,4,6-tris(di-2-pyridylamine)-1,3,5-triazine molecule (hereafter noted dipyatriz; see Scheme 2). This polypyridyl ligand is prepared in a one-pot synthesis by reacting 2,4,6-trichloro-1,3,5-triazine with di-2-pyridylamine in toluene in basic medium, and it has been shown that it is able to function as a blue emitter in electroluminescent devices.[18] Its X-ray structure shows the expected star-shape where the six 2-pyridyl rings are not coplanar with the central triazine ring because of intramolecular steric interactions.[18a] The availability of these three potentially bidentate dipyridylamino moieties together with the supramolecular effects caused by *s*-triazine ring (for instance, π-stacking,

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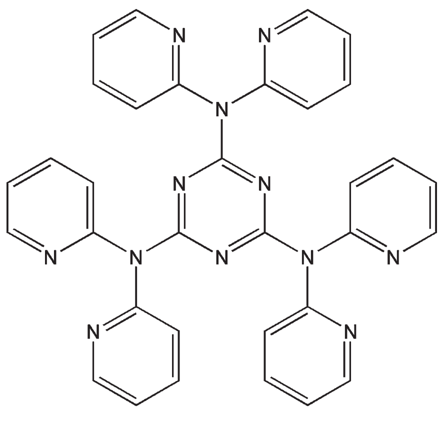
Scheme 2



Dipyatriz

hydrogen bonding and anion-π interactions)[19] have attracted the attention to this ligand by different research groups.[20,21] In fact, a survey of the structural reports of dipyatriz-containing metal complexes shows that this polypyridyl ligand usually exhibits the expected tris- or bis-bidentate coordination modes by using its three or two dipyridylamino fragments as donors.[19−22] Surprisingly, it can also adopt the rather unexpected bi- (through a dipyridylamino moiety) and tridentate (across one triazine-nitrogen and two nonadjacent pyridyl rings) binding modes simultaneously.[20d] These features support the versatility and richness of the dipyatriz molecule as a ligand.

In the present work we report the preparation and X-ray characterization of the trinuclear $[Cu_3(dipyatriz)_2(H_2O)_3](ClO_4)_6 \cdot 2H_2O$ (**1**), 2D $\{[Cu_4(dipyatriz)_2(H_2O)_2(NO_3)_2(ox)_2](NO_3)_2 \cdot 2H_2O\}_n$ (**2**), and cage-like $[Cu_6(dipyatriz)_2(H_2O)_9(NO_3)_3(ox)_3](NO_3)_3 \cdot 4H_2O$ (**3**) copper(II) complexes (ox = oxalate) together with the investigation of their magnetic properties as a function of the temperature.

Experimental Section

Materials and Methods. Reagents (except dipyatriz) and solvents used in the synthesis of **1**−**3** were purchased from commercial sources and used without further purification. Dipyatriz was prepared as previously reported.[18] Slow evaporation of solvent under ambient conditions, slow diffusion in an H-shape tube, and hydrothermal methods[23] were used to grow X-ray quality crystals of **1**, **2**, and **3**, respectively. Elemental analysis (C, H, N) was conducted by the Microanalytical Service of the Universitat de València.

Caution! *Perchlorate salts are potentially explosive, especially in the presence of organic ligands. We worked at the mmol scale and heating was avoided.*

Synthesis of the Complexes. $[Cu_3(dipyatriz)_2(H_2O)_3](ClO_4)_6 \cdot 2H_2O$ (1). This compound was obtained by reacting copper(II) perchlorate hexahydrate (0.370 g, 1 mmol) and dipyatriz (0.196 g, 1/3 mmol) in a H_2O-CH_3CN 1:1 (v/v) mixture. Crystals of **1** as dark blue prisms were grown from the resulting dark blue solution by slow evaporation at room temperature in a hood. The yield is practically quantitative. Anal. Calcd for $C_{66}H_{58}Cl_6Cu_3N_{24}O_{29}$ (**1**): C, 38.59; H, 2.82; N, 16.36. Found: C, 39.45; H, 2.75; N, 16.25%. Main IR peaks (KBr, cm^{-1}): 3440s,br (O−H); 3105w, 3035w, and 3010w (C−H aromatic); 1605s (C=N); 1550s (C=C); 1482s, 1467s, 1385s (C−C + C−N); 1145s, 113s, 1085s, and 945w (Cl−O, uncoordinated perchlorate).[24]

$\{[Cu_4(dipyatriz)_2(H_2O)_2(NO_3)_2(ox)_2](NO_3)_2 \cdot 2H_2O\}_n$ (2). Single crystals of **2** were grown by slow diffusion in an H-shaped tube containing concentrated aqueous solutions of sodium oxalate in one arm (0.034 g, 0.25 mmol) and a mixture of copper(II) nitrate trihydrate (0.121 g, 1/2 mmol) and dipyatriz (0.098 g, 1/6 mmol) in the other one. The two arms were carefully filled by dropwise addition of water until the H-tube was full (total volume ca. 40 cm^3). It was covered with parafilm to avoid any evaporation of the solvent and allowed to diffuse at room temperature. The diffusion was finished after 2 months. Blue plate-like crystals of **2** together with a small amount of $Cu(ox) \cdot 1/3H_2O$ as a pale green solid were obtained separately. The yield based on dipyatriz is about 90%. Anal. Calcd for $C_{70}H_{58}Cu_4N_{28}O_{25}$ (**2**): C, 43.23; H, 2.98; N, 20.16. Found: C, 43.05; H, 2.92; N, 20.05%. Main IR peaks (KBr, cm^{-1}): 3420s,br (O−H), 3110w, 3085w and 3015w (C−H aromatic); 1710w and 1675s (ν_{as}CO); 1605s (C=N) and 1550s (C=C); 1485s, 1470s and 1380s, (C−C + C−N); 2430w, 1390s, and 830w (N−O uncoordinated nitrate).[24b]

$[Cu_6(dipyatriz)_2(H_2O)_9(NO_3)_3(ox)_3](NO_3)_3 \cdot 4H_2O$ (3). A mixture of copper(II) nitrate trihydrate (0.241 g, 1 mmol), dpyatriz (0.196 g, 1/3 mmol), sodium oxalate (0.111 g, 0.83 mmol), and 30 cm^3 of water were sealed in a 45 mL stainless-steel reactor with a Teflon linear, and heated at 150 °C during 48 h. After cooling, a few X-ray quality dark blue prisms of **3** were collected from the Teflon liner and air-dried. The formula of **3** was determined by X-ray diffraction. IR (KBr, cm^{-1}): 3422s,br (O−H), 3115w, 3080w, 3050w, and 3010w (C−H aromatic); 1677s (ν_{as}CO), 1360m and 1320m (ν_sCO) and 805m (δOCO); 1608s (C=N) and 1550s (C=C); 1483s and 1470s (C−C + C−N); 2430w, 1390s, and 830w (N−O uncoordinated nitrate).

Physical Measurements. IR spectra of **1**−**3** as KBr pellets were registered on a Bruker IF S55 spectrometer. Magnetic susceptibility measurements on polycrystalline samples of **1**−**3** were carried out in the temperature range 1.9−295 K with a SQUID magnetometer under applied magnetic fields of 1 T ($T \geq 100$ K) and 1000 G ($T < 100$ K). Diamagnetic corrections of the constituent atoms were estimated from Pascal constants[25] and found to be as -998×10^{-6} (**1**), -471×10^{-6} (**2**), and -1090×10^{-6} cm^3 mol^{-1} (**3**) per three (**1**), two (**2**), and six (**3**) copper(II) ions. Magnetic data were also corrected for the temperature-independent paramagnetism [60 cm^3 mol^{-1} K per copper(II) ion] and the sample holder.

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Table 1. Crystal Data and Details of the Structure Determination for the Complexes $[Cu_3(dipyatriz)_2(H_2O)_3](ClO_4)_6\cdot 2H_2O$ (**1**), $\{[Cu_4(dipyatriz)_2(H_2O)_2(NO_3)_2(ox)_2](NO_3)_2\cdot 2H_2O\}_n$ (**2**), and $[Cu_6(dipyatriz)_2(H_2O)_9(NO_3)_3(ox)_3](NO_3)_3\cdot 4H_2O$ (**3**)

compound	1	2	3
formula	$C_{66}H_{58}Cl_6Cu_3N_{24}O_{29}$	$C_{70}H_{58}Cu_4N_{28}O_{25}$	$C_{144}H_{148}Cu_{12}N_{60}O_{86}$
M	2054.68	1945.60	4857.70
crystal system	orthorhombic	orthorhombic	tetragonal
space group	*C2cb*	*Pcab*	*P42bc*
a, Å	15.793(3)	15.1193(11)	30.383(4)
b, Å	19.766(3)	21.965(2)	30.383(4)
c, Å	27.921(4)	24.3216(8)	22.292(5)
V, Å^3	8716(2)	8077.1(10)	20578(6)
Z	4	4	4
T, K	293(2)	293(2)	100(2)
ρ_{calc} (Mg m^{-3})	1.566	1.600	1.568
λ(Mo Kα, Å)	0.71073	0.71073	0.75130
μ(Mo Kα, mm^{-1})	1.001	1.135	1.319
$R1$, $I > 2\sigma(I)$ (all)	0.0695 (0.1494)	0.0708 (0.0909)	0.0896 (0.0899)
w$R2$, $I > 2\sigma(I)$ (all)	0.1056 (0.1305)	0.2038 (0.2323)	0.2698 (0.2714)
measured reflections (R_{int})	25020 (0.1130)	30711 (0.0725)	574924 (0.1750)
independent reflections [$I > 2\sigma(I)$]	6074 (3506)	9854 (7812)	20831 (20642)
goodness-of-fit on F^2	1.052	1.108	1.369

Crystal Structure Determination and Refinement. X-ray diffraction data on single crystals of **1**−**3** of dimensions 0.10 × 0.10 × 0.30 (**1**), 0.04 × 0.30 × 0.30 (**2**), and 0.30 × 0.30 × 0.60 mm (**3**) were collected on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K (**1** and **2**) and at the ESRF synchrotron BM16 beamline (Grenoble, France) using λ = 0.75130 Å at 100 K (**3**). Data were indexed, integrated, and scaled using the EVALCCD (**1** and **2**) and HKL2000 programs.[26] The values of the minimum and maximum transmission factors were 0.7533/0.9065 (**1**), 0.7260/0.9560 (**2**), and 0.5049/0.6930 (**3**).

The structures of **1**−**3** were solved by direct methods through the SHELX97 computational program.[27] All non-hydrogen atoms of **1**−**3** (except the nitrate groups from **3**) were refined anisotropically by full-matrix least-squares techniques based on F^2 using SHELX97. The hydrogen atoms of the dipyatriz molecule in **1**−**3** were positioned geometrically and refined with a riding model. The hydrogen atoms of all water molecules from **1**−**3** were neither found nor considered in the refinement. In **2**, the O4NA, O5NA, and O6NA oxygen atoms present an occupancy factor of 0.74 while O4NB, O5NB, and O6NB show an occupancy factor of 0.26, indicating an alternation of the absolute position of the nitrate group between the cells of the nitrate coordinated to one copper(II) atom. Also two crystallization water molecules in **2** share their occupancy factor, O2W (0.51) and O3W (0.49), while O4W present an occupation of 0.50. The crystallization water molecules [O11W to O17W] in **3** present an occupancy factor of 0.5.

A summary of the cell parameters and refinement conditions for **1**−**3** are listed in Table 1, whereas main bond lengths and bond angles together with the hydrogen bonds are given in Tables 2 (**1**), 3 (**2**), and 4 (**3**). The final geometrical calculations and the graphical manipulations were carried out with the PARST,[28] PLATON,[29] and DIAMOND[30] programs.

Crystallographic data for the structures **1**−**3** have been deposited at the Cambridge Crystallographic Data Centre with CCDC reference nos. 722374 (**1**), 722375 (**2**), and 722376 (**3**).

Table 2. Selected Bond Lengths (Å), Angles (deg) and Hydrogen Bonds in **1**[a]

Copper Environment			
Cu(1)−N(7)	1.978(11)	Cu(2)−N(11)	2.039(8)
Cu(1)−N(8)	2.010(10)	Cu(2)−N(12)	2.000(8)
Cu(1)−N(9a)	2.032(9)	Cu(2)−O(2W)	2.181(8)
Cu(1)−N(10a)	2.041(9)		
Cu(1)−O(1W)	2.154(6)		
N(7)−Cu(1)−N(8)	85.5(4)	N(11)−Cu(2)−N(12)	86.0(3)
N(7)−Cu(1)−N(10a)	160.5(4)	N(11)−Cu(2)−N(11a)	165.0(5)
N(7)−Cu(1)−N(9a)	94.6(4)	N(11)−Cu(2)−N(12a)	92.0(3)
N(7)−Cu(1)−O(1w)	102.6(4)	N(11)−Cu(2)−O(2W)	97.5(3)
N(8)−Cu(1)−N(10a)	89.4(3)	N(12)−Cu(2)−N(12a)	164.6(5)
N(8)−Cu(1)−N(9a)	167.9(4)	N(12)−Cu(2)−O(2W)	97.7(2)
N(8)−Cu(1)−O(1W)	94.7(4)	N(12a)−Cu(2)−O(2W)	97.7(2)
N(10a)−Cu(1)−N(9a)	86.6(4)		
N(10a)−Cu(1)−O(1W)	96.5(4)		
N(9a)−Cu(1)−O(1W)	97.1(4)		
Intermolecular O···O Distances (Å)			
O(1W)···O(3 Wb)	2.612(18)	O(2W)···O(5a)	2.845(8)
O(1W)···O(10c)	2.930(15)	O(3W)···O(11)	3.08(2)
O(2W)···O(5)	2.845(8)	O(3W)···O(3d)	3.10(2)

[a] Symmetry code: (a) = x, $-y$, $1-z$; (b) = $1+x$, $-y+1/2$, $1/2+z$; (c) $1+x$, $-y$, $1-z$; (d) $-1/2+x$, $-y+1/2$, $1-z$.

Results and Discussion

Description of the Structures. $[Cu_3(dipyatriz)_2(H_2O)_3](ClO_4)_6\cdot 2H_2O$ (1). The structure of **1** consists of alternating $[Cu_3(dipyatriz)_2(H_2O)_3]^{6+}$ cations and perchlorate anions leading to an ionic three-dimensional (3D)-network (Figure 1). The tricopper(II) units of formula $[Cu_3(dipyatriz)_2(H_2O)_3]^{6+}$ can be described as the *face-to-face* assembly of two dipatriz molecules acting as tris-bidentate ligands though their dipyridylamino moieties toward three copper(II) ions (Figure 2, panels a and b). The distance between the mean planes of the two triazine rings is 3.9809(6) Å and although this value is somewhat greater than the distance usually found for aromatic stacking (3.5 Å), such lengthening is often observed for aromatic nitrogen-containing ligands.[31] It deserves to be noted that this triazine centroid-to-centroid distance in **1** remains within the range of previously reported

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Table 3. Selected Bond Lengths (Å), Angles (deg), and Hydrogen Bonds in **2**[a,b]

	Copper Environment		
Cu(1)−N(7)	1.983(3)	Cu(2)−N(9b)	2.066(3)
Cu(1)−N(8)	1.996(3)	Cu(2)−N(10b)	2.008(3)
Cu(1)−O(1)	1.939(3)	Cu(2)−N(12)	2.009(3)
Cu(1)−O(2)	1.934(3)	Cu(2)−O(1W)	2.110(3)
Cu(1)−O(5NA)	2.420(5)	Cu(2)−N(11)	2.271(3)
		Cu(2)−O(4c)	2.336(3)
N(7)−Cu(1)−N(8)	90.85(13)	N(9b)−Cu(2)−N(10b)	88.14(12)
N(7)−Cu(1)−O(1)	172.96(14)	N(9b)−Cu(2)−O(1W)	172.70(12)
N(7)−Cu(1)−O(2)	90.55(13)	N(9b)−Cu(2)−N(12)	91.49(12)
(7)−Cu(1)−O(5NA)	103.07(18)	N(9b)−Cu(2)−N(11)	102.34(11)
N(8)−Cu(1)−O(1)	92.91(13)	N(9b)−Cu(2)−O(4c)	89.02(11)
N(8)−Cu(1)−O(2)	171.69(15)	N(10b)−Cu(2)−O(1W)	91.24(13)
N(8)−Cu(1)−O(5NA)	83.49(18)	N(10b)−Cu(2)−N(12)	178.14(11)
O(1)−Cu(1)−O(2)	84.89(13)	N(10b)−Cu(2)−N(11)	92.29(11)
O(1)−Cu(1)−O(5NA)	83.28(18)	N(10b)−Cu(2)−O(4c)	88.48(11)
O(2)−Cu(1)−O(5NA)	104.16(19)	O(1W)−Cu(2)−N(12)	88.90(13)
		O(1W)−Cu(2)−N(11)	84.95(12)
		O(1W)−Cu(2)−O(4c)	83.69(12)
		N(12)−Cu(2)−N(11)	89.58(11)
		N(12)−Cu(2)−O(4c)	89.69(11)
		N(11)−Cu(2)−O(4c)	168.63(11)
	Oxalate Ligand		
O(1)−C(34)	1.270(5)	O(2)−C(35)	1.255(5)
O(3)−C(34)	1.214(6)	O(4)−C(35)	1.231(5)
C(34)−C(35)	1.552(6)		
O(1)−C(34)−O(3)	125.0(4)	O(2)−C(35)−O(4)	125.0(4)
O(1)−C(34)−C(35)	114.8(4)	Cu(1)−O(1)−C(34)	112.3(3)
O(3)−C(34)−C(35)	120.2(4)	Cu(1)−O(2)−C(35)	113.0(3)
C(34)−C(35)−O(2)	115.0(4)	Cu(2d)−O(4)−C(35)	131.1(3)
C(34)−C(35)−O(4)	120.0(4)		
	Intermolecular O···O Distances (Å)		
O(1W)···O(6NAe)	2.831(8)	O(3W)···O(1N)	2.70(2)
O(1W)···O(2Ne)	2.847(7)	O(3W)···O(4W)	3.18(4)
O(2W)··· O(3)	2.917(15)	O(4W)···O(6NAg)	3.05(2)
O(2W)−O(1Nf)	3.179(16)		

[a] Symmetry code: (b) = $-x+2, -y, -z$; (c) = $x-1/2, -y, -z+1/2$; (d) = $x+1/2, -y, -z+1/2$; (e) $x-1/2, -y+1/2, z$; (f) = $-x+5/2, -1/2+y, -z$; (g) = $-x+5/2, y, -1/2+z$. [b] Only components with greater occupancy factors [O(5NAa), O(4NA) and O(3NA)] of the coordinated nitrate anion are given.

values in analogous dipyatriz-containing copper(II) complexes (from 3.67 to 4.125 Å).[20f,21,22] The positive charge of the trinuclear entity in **1** is compensated by six noncoordinated perchlorate anions. Two of them are located very close to each triazine ring evidencing the occurrence of anion-π interactions with a centroid···O(6) distance of 3.097(12) Å and an angle of the centroid···O(6) axis to the plane of 78.5° (Figure 2c). This type of noncovalent triazine centroid-anion interaction have been studied by means of high level ab initio calculations,[20f] and it has been proposed as a new anion recognition module in cyclophane chemistry.[32] Hydrogen bonds involving some of the perchlorate-oxygen atoms and the coordinated and free water molecules further stabilize the structure of **1** (see end of Table 2).

The copper(II) ions in **1** are in square-pyramidal coordination geometry [τ = 0.012 and 0.003 for Cu(1) and Cu(2), respectively],[33] with the basal positions

Table 4. Selected Bond Lengths (Å), Angles (deg), and Hydrogen Bonds in **3** [a]

Cu(1)−N(7)	2.006(5)	Cu(4)−N(21)	1.987(6)
Cu(1)−N(8)	2.013(5)	Cu(4)−N(22)	1.998(6)
Cu(1)−O(1)	1.976(5)	Cu(4)−O(6)	1.983(6)
Cu(1)−O(3)	2.016(4)	Cu(4)−O(8)	1.989(5)
Cu(1)−O(1W)	2.430(7)	Cu(4)−O(6W)	2.255(6)
Cu(1)−O(2W)	2.385(6)	Cu(4)−O(18N)	2.7443(11)
Cu(2)−N(19)	1.978(6)	Cu(5)−N(11)	2.007(6)
Cu(2)−N(20)	2.011(5)	Cu(5)−N(12)	1.976(6)
Cu(2)−O(2)	2.000(5)	Cu(5)−O(9)	2.005(6)
Cu(2)−O(4)	1.990(4)	Cu(5)−O(11)	2.012(7)
Cu(2)−O(3W)	2.395(7)	Cu(5)−O(7W)	2.442(10)
Cu(2)−O(4W)	2.366(9)	Cu(5)−O(8W)	2.309(5)
Cu(3)−N(9)	2.015(5)	Cu(6)−N(23)	2.019(6)
Cu(3)−N(10)	1.983(5)	Cu(6)−N(24)	1.951(7)
Cu(3)−O(5)	1.971(6)	Cu(6)−O(10)	1.981(7)
Cu(3)−O(7)	1.999(5)	Cu(6)−O(12)	1.973(7)
Cu(3)−O(5W)	2.353(7)	Cu(6)−O(9W)	2.421(14)
Cu(3)−O(13N)	2.477(7)	Cu(6)−O(1N)	2.347(2)
N(7)−Cu(1)−N(8)	89.8(2)	N(21)−Cu(4)−N(22)	90.3(2)
N(7)−Cu(1)−O(3)	174.5(2)	N(21)−Cu(4)−O(8)	169.3(2)
N(7)−Cu(1)−O(1)	90.6(2)	N(21)−Cu(4)−O(6)	88.3(3)
N(7)−Cu(1)−O(1W)	94.9(2)	N(21)−Cu(4)−O(6W)	91.8(3)
N(7)−Cu(1)−O(2W)	91.0(2)	N(21)−Cu(4)−O(18N)	103.0(2)
N(8)−Cu(1)−O(3)	95.61(19)	N(22)−Cu(4)−O(8)	94.5(2)
N(8)−Cu(1)−O(1)	177.4(3)	N(22)−Cu(4)−O(6)	170.6(3)
N(8)−Cu(1)−O(1W)	91.7(2)	N(22)−Cu(4)−O(6W)	93.6(3)
N(8)−Cu(1)−O(2W)	87.6(2)	N(22)−Cu(4)−O(18N)	103.02(16)
O(1)−Cu(1)−O(3)	83.91(19)	O(6)−Cu(4)−O(8)	85.3(2)
O(1)−Cu(1)−O(1W)	90.8(3)	O(6)−Cu(4)−O(6W)	95.7(4)
O(1)−Cu(1)−O(2W)	89.9(3)	O(6)−Cu(4)−O(18N)	68.0(2)
O(3)−Cu(1)−O(1W)	86.2(3)	O(8)−Cu(4)−O(6W)	97.4(3)
O(3)−Cu(1)−O(2W)	88.0(2)	O(8)−Cu(4)−O(18N)	70.05(17)
O(1W)−Cu(1)−O(2W)	174.0(3)	O(6W)−Cu(4)−O(18N)	159.67(16)
N(19)−Cu(2)−N(20)	88.8(2)	N(11)−Cu(5)−N(12)	92.1(3)
N(19)−Cu(2)−O(4)	176.4(2)	N(11)−Cu(5)−O(9)	175.1(2)
N(19)−Cu(2)−O(2)	93.5(2)	N(11)−Cu(5)−O(11)	93.9(3)
N(19)−Cu(2)−O(3W)	93.2(29	N(11)−Cu(5)−O(7W)	90.9(3)
N(19)−Cu(2)−O(4W)	87.5(3)	N(11)−Cu(5)−O(8W)	92.3(2)
N(20)−Cu(2)−O(4)	93.4(29	N(12)−Cu(5)−O(9)	89.7(3)
N(20)−Cu(2)−O(2)	177.0(2)	N(12)−Cu(5)−O(11)	173.6(2)
N(20)−Cu(2)−O(3W)	94.1(2)	N(12)−Cu(5)−O(7W)	93.9(3)
N(20)−Cu(1)−O(4W)	88.9(2)	N(12)−Cu(5)−O(8W)	93.0(2)
O(2)−Cu(2)−O(4)	84.2(29	O(9)−Cu(5)−O(11)	84.1(3)
O(2)−Cu(2)−O(3W)	83.9(3)	O(9)−Cu(5)−O(7W)	84.4(3)
O(2)−Cu(2)−O(4W)	93.1(3)	O(9)−Cu(5)−O(8W)	92.1(2)
O(4)−Cu(2)−O(3W)	83.8(2)	O(11)−Cu(5)−O(7W)	83.8(3)
O(4)−Cu(2)−O(4W)	95.4(3)	O(11)−Cu(5)−O(8W)	88.9(2)
O(3W)−Cu(2)−O(4W)	177.0(3)	O(7W)−Cu(5)−O(8W)	172.2(3)
N(9)−Cu(3)−N(10)	91.2(2)	N(23)−Cu(6)−N(24)	91.2(3)
N(9)−Cu(3)−O(7)	175.1(2)	N(23)−Cu(6)−O(10)	176.4(4)
N(9)−Cu(3)−O(5)	91.2(2)	N(23)−Cu(6)−O(12)	92.1(3)
N(9)−Cu(3)−O(5W)	94.5(2)	N(23)−Cu(6)−O(9W)	94.2(3)
N(9)−Cu(3)−O(13N)	91.8(1)	N(23)−Cu(6)−O(1N)	105.2(2)
N(10)−Cu(3)−O(7)	92.7(2)	N(24)−Cu(6)−O(10)	92.4(3)
N(10)−Cu(3)−O(5)	177.5(3)	N(24)−Cu(6)−O(12)	176.7(3)
N(10)−Cu(3)−O(5W)	91.7(3)	N(24)−Cu(6)−O(9W)	94.2(6)
N(10)−Cu(3)−O(13N)	92.8(2)	N(24)−Cu(6)−O(1N)	99.9(2)
O(5)−Cu(3)−O(7)	84.8(2)	O(10)−Cu(6)−O(12)	84.4(3)
O(5)−Cu(3)−O(5W)	88.5(3)	O(10)−Cu(6)−O(9W)	84.9(4)
O(5)−Cu(3)−O(13N)	86.7(3)	O(10)−Cu(6)−O(1N)	74.9(3)
O(7)−Cu(3)−O(5W)	88.3(2)	O(12)−Cu(6)−O(9W)	85.2(7)
O(7)−Cu(3)−O(13N)	85.1(2)	O(12)−Cu(6)−O(1N)	79.6(4)
O(5W)−Cu(3)−O(13N)	172.2(2)	O(9W)−Cu(6)−O(1N)	155.7(5)
	Intermolecular O...O Distances[a] (Å)		
O(1W)...O(17N)	2.810(8)	O(9W)...O(15W)*	2.490(23)
O(2W)...O(7Na)	2.836(6)	O(11W)...O(5N)	3.122(13)
O(3W)...O(16N)	2.911(6)	O(13W)...O(11d)	2.943(11)
O(3W)...O(15W)*	2.676(17)	O(13W)...O(12We)*	2.802(20)
O(4W)...O(12N)	2.713(10)	O(14W)*...O(12We)*	2.9305(3)
O(4W)...O(12W)*	2.903(18)	O(14W)*...O(18Nd)	2.851(24)
O(6W)...O(16W)*	2.743(18)	O(16W)*...O(15Nc)	3.100(3)
O(6W)...O(7Nb)	2.747(7)	O(16W)*...O(2f)	2.880(2)
O(8W)...O(4Nc)	2.823(5)	O(17W)*...O(13W)*	2.716(33)
O(8W)...O(9Nc)	2.966(6)	O(17W)*...O(8 g)	2.971(3)
O(9W)...O(14Wc)*	2.708(4)		

[a] Symmetry codes: (a) = $1/2-x, 1/2-y, 1/2+z$; (b) = $x, 1-y, 1/2+z$; (c) = $x, y, 1+z$; (d) = $x, y, -1+z$; (e) = $x, 1-y, -1/2+z$; (f) = $1/2+x, 1/2-y, z$; (g) = $-1/2+x, 1/2+y, -1/2+z$. * These atoms have an occupancy factor of 50%.

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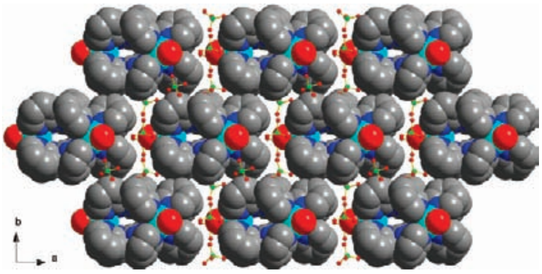

Figure 1. View along the *c*-axis of the crystal packing of **1**. The hydrogen atoms were omitted for clarity.

occupied by the pyridyl-nitrogen donors of the dipyatriz molecule and the axial sites pointing outward in a radial manner, being filled by water molecules. A crystallographic 2-fold axis going through the Cu(2)−O(2W) bond relates half of the molecule to the other. The basal Cu−N distances range from 1.978(11) to 2.041(9) Å, values which are somewhat shorter than the apical Cu−O(w) coordination bonds [2.154(6) and 2.181(8) Å for Cu(1)−O(1W) and Cu(2)−O(W2), respectively]. The Cu−N distances compare well with those observed in other structurally characterized dipyatriz-containing copper(II) complexes.[20a,20c,20f,21,22] The values of the dihedral angles between the mean basal planes of adjacent copper(II) ions are 51.48° [Cu(1)/Cu(2)] and 64.26° [Cu(1)/Cu(1a); (a) = x, $-y$, $-z+1$].

The triazine ring of the dipyatriz ligand is planar within the experimental error [largest deviation from the mean plane 0.026(10) Å for C(1)]. The values of the dihedral angle between the triazine ring and each of its pyridyl vary in the range 43.71−64.49°. Average values for the C−C [1.368 Å] and C−N [1.348 Å] bond lengths and C−N inter-ring bonds [1.426 Å] of the dipyatriz ligand in **1** compare well with those observed in the free molecule.[18a] The dipyatriz ligand adopts the tris-bidentate coordination mode through its six pyridyl nitrogen atoms toward three copper(II) ions, the values of the copper−copper separation within the resulting tricopper(II) core being 8.057(2) [Cu(1)···Cu(2)] and 8.351(2) Å [Cu(1)···Cu(1a)]. These values are somewhat shorter than the shortest intermolecular copper−copper distance [9.686(2) Å for Cu(1)···Cu(1e); (e) = $x+1/2$, y, $-z+3/2$].

$\{[Cu_4(dipyatriz)_2(H_2O)_2(NO_3)_2(ox)_2](NO_3)_2 \cdot 2H_2O\}_n$ (2). The structure of **2** consists of an unprecedented two-dimensional (2D) arrangement of copper(II) ions where centrosymmetric tetranuclear $[Cu_4(dipyatriz)_2(H_2O)_2(NO_3)_2]$ units [Figure 3 (left)] are connected by oxalate ligands exhibiting the bidentate/monodentate bridging mode [Figure 3 (right)] leading to cationic bilayers which grow in the *ac* plane (Figure 4). Non-coordinated nitrate groups and crystallization water molecules are also present in the crystal structure. One of these water molecules [O(4W)] has an occupancy factor of 0.5 whereas the other one occupies two regular alternating crystallographic sites with occupancy factors 0.51532 [O(2W)] and 0.48468 [O(3W)]. They are involved in an extensive network of hydrogen bonds together with the non-coordinated oxalate-oxygen [O(3)] and the coordinated water molecule [O(1W)] (see end of Table 3), the whole resulting in a 3D supramolecular structure (see Supporting Information, Figure S1).

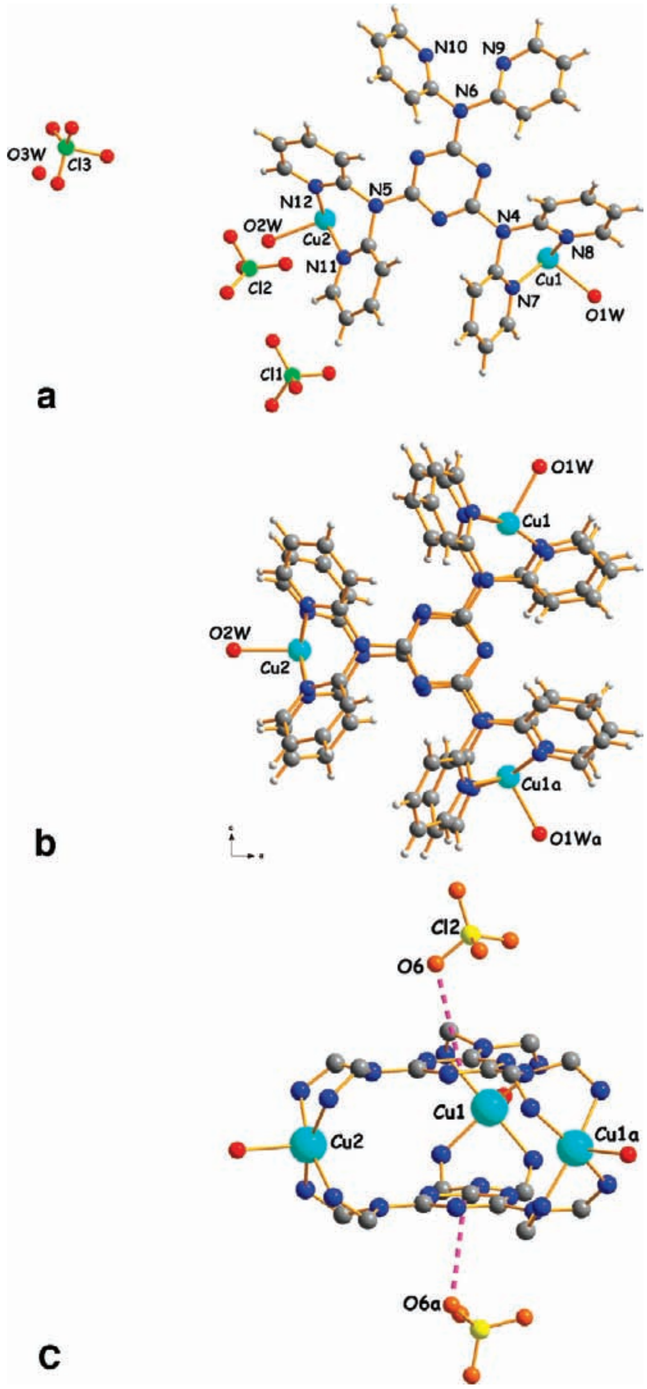

Figure 2. (a) Asymmetric unit of compound **1**. (b) Perspective view along the *b*-axis of of the trinuclear $[Cu_3(dipyatriz)_2(H_2O)_3]^{6+}$ cation in **1** showing the quasi *face-to-face* conformation of the *s*-triazine rings. (c) Side view of the tricopper(II) unit of **1** showing the anion-π interaction between one perchlorate-oxygen atom and the electron-deficient *s*-triazine ring. The hydrogen atoms and the pyridyl rings of the two dipyatriz ligands were omitted for the sake of clarity. Symmetry code: (a) = x, $-y$, $-z+1$.

Two crystallographically independent copper(II) ions [Cu(1) and Cu(2)] occur in **2**. Cu(1) is five-coordinate in a distorted square pyramidal surrounding with one bidentate dipyridylamine unit from a dipyatriz ligand [N(7) and N(8)] and two oxalate-oxygens [O(1) and O(2)] in the basal positions and an oxygen atom from a disordered unidentate nitrate [O(5NA)] in the apical site. Because of this disorder, the inclusion of the O(4NB) atom [occupancy factors for

O(5NA) and O(4NB) are 0.742(13) and 0.258(13), respectively] in the coordination sphere of Cu(1) could be considered, but we have kept the oxygen atom with the greater occupancy factor for a better clarity of the drawings. In such a case, the parameter τ for Cu(1) is 0.017. The equatorial Cu(1)−N [1.983(3) and 1.996(3) Å] and Cu(1)−O bonds [1.934(3) and 1.939(3) Å] can be considered as normal. The axially coordinated nitrate is at a somewhat larger distance [Cu(1)−O(N5A) = 2.420(5) Å and Cu(1)−O(N4B) = 2.39(2) Å]. Cu(2) is located in an elongated octahedral environment formed by two pairs of N-coordinating 2-pyridyl groups belonging to two different dipyatriz ligands [N(9b), N(10b), N(11) and N(12); (b) = $-x+2$, $-y$, $-z$], a water molecule [O(1W)] and an oxalate-oxygen atom [O(4c); (c) = $x-1/2$, $-y$, $-z+1/2$]. The bonds at Cu(2) in the equatorial plane vary in the range 2.009(3)−2.110(3) Å whereas the axial bond distances are 2.271(3) [Cu(2)−N(11)] and 2.336(3) Å [Cu(2)−O(4c)].

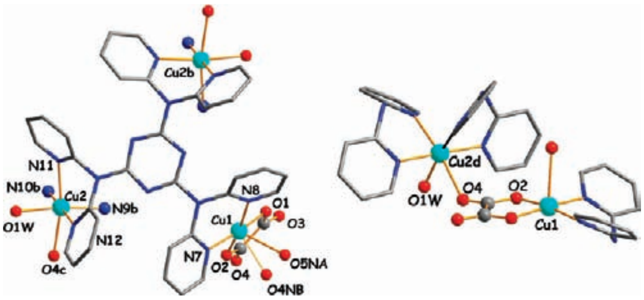

Figure 3. (Left) Perspective view of the tetranuclear fragment of **2** showing the copper assembling through the bridging dipyatriz ligands (the coordinated nitrate is disordered over two positions O5NA:O4NB with occupancy 74:26% and the hydrogen atoms were omitted for clarity. (Right) Bridging mode of the oxalate ligand in **2**. Symmetry code: (b) = $-x+2$, $-y$, $-z$; (c) = $x-1/2$, $-y$, $-z+1/2$; (d) = $-x+1/2$, $-y$, $-z+1/2$.

The two centrosymmetrically related dipyatriz ligands in **2** adopt the tris-bidentate coordination mode through the dipyridylamino fragments, as observed in **1.** However, here they are mutually shifted in contrast to the superimposed situation of the triazine rings occurring in **1**. This feature precludes any $\pi-\pi$ stacking between the *s*-triazine rings of the dipyatriz molecules in **2**. In addition, no anion···aromatic ring interactions occur in **2**. The copper−copper separation through the dipyatriz bridge are 8.011(1), 7.801(1), and 9.079(1) Å for Cu(1)···Cu(2), Cu(1)···Cu(2b), and Cu(2)···Cu(2b), respectively, the two former values being very close to those observed in **1**.

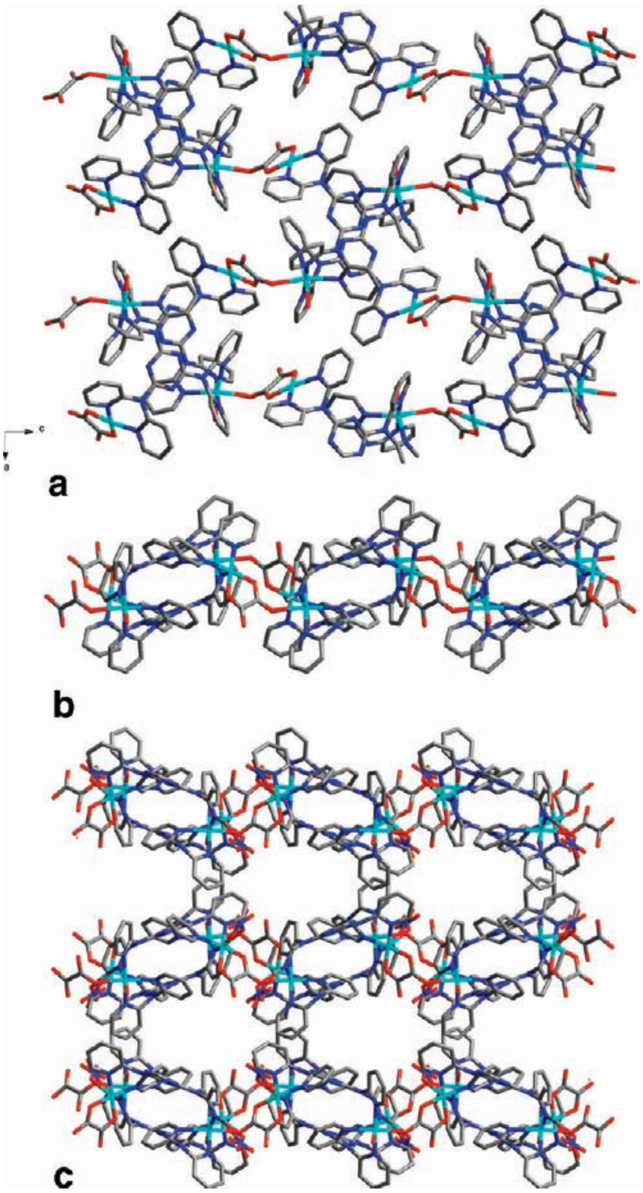

Figure 4. Views along the *b*- (a) and *c*-axes (b) of the cationic bilayer built by the $[Cu_4(dipyatriz)_2(H_2O)_2(NO_3)_2(ox)_2]^{2+}$ units. Counterions, crystallization water molecules, and hydrogen atoms have been omitted for clarity.

The oxalate ligand in **2** is practically planar [largest deviation from the mean plane is 0.038(6) Å at O(3)] and it adopts the asymmetric bidentate/monodentate (outer) bridging mode, the resulting copper−copper separation being 5.609(1) Å [Cu(1)···Cu(2d); (d) = $x+1/2$, $-y$, $-z+1/2$]. This asymmetric bridging mode of the oxalate ligand has been observed in a reduced number of homo-[34−37] and heterometallic[38,39]

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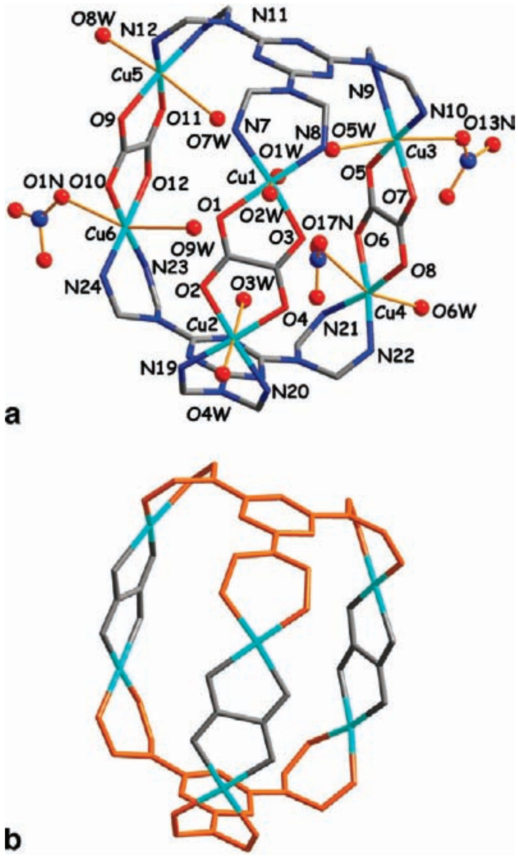

Figure 5. (a) Perspective view of the hexanuclear cage-like unit of **3** showing the atom numbering of the copper chomophores. (b) Schematic representation of the cage. Part of the pyridyl rings of the dipyatriz ligands and the hydrogen atoms were omitted for simplicity.

complexes, and it is not as common as the more frequently found bis-bidentate one. The value of the dihedral angle between the oxalate plane and the equatorial mean planes around Cu(1) and Cu(2) are 4.1(1) and 50.1(1)°, respectively. The carbon−carbon bond length of the oxalate ligand [C(34)−C(35) = 1.558(1) Å] is as expected for a single C−C bond, and it is very close to the carbon−carbon bond distance of 1.574(2) Å in uncoordinated oxalate.[40]

$[Cu_6(dipyatriz)_2(H_2O)_9(NO_3)_3(ox)_3](NO_3)_3\cdot 4H_2O$ (3). The structure of **3** is made up of hexanuclear $[Cu_6(dipyatriz)_2(H_2O)_9(NO_3)_2(ox)_3]^{4+}$ cations (Figure 5a) and nitrate counterions which are interlinked by electrostatic interactions and hydrogen bonds (see end of Table 4). The cationic unit can be viewed as two $[Cu_3(dipyatriz)]^{6+}$ trinuclear fragments which are pillared by three bis-bidentate oxalate ligands, the whole resulting in a cylinder-like cage motif which is unprecedented in the extensive coordination chemistry of the oxalate ligand (Figure 5b). Extensive hydrogen bonds involving crystallization and coordinated water molecules, and counterions link together the cationic moieties given a 3D supramolecular network. A view of the packing of the hexanuclear cage-like units is shown in Figure 6.

The six copper(II) ions from the cage [Cu(1), Cu(2), Cu(3), Cu(4), Cu(5), and Cu(6] are crystallographically independent, and all of them are six-coordinated in elongated octahedral surroundings. Two oxalate-oxygen and two pyridyl-nitrogen atoms occupy the equatorial positions at all copper atoms whereas two water molecules [at Cu(1), Cu(2), and Cu(5)] or a nitrate-oxygen atom and a water molecule [at Cu(3), Cu(4), and Cu(6)] fill the axial sites. The equatorial Cu−N and Cu−O bond lengths vary in the ranges 1.951(7)−2.019(6) and 1.972(6)−2.017(6) Å, respectively. These values are shorter than the axial $Cu-O_w$ [2.255(6)−2.442(10) Å] and $Cu-O_{nitrate}$ [2.347(2)−2.744(1) Å]. The short bite of the bis-chelating oxalato [values spanning in the range 83.9(2)−85.3(2)°] is one of the main factors accounting for the distortion of the ideal octahedron around each copper atom. The set of donor atoms in the equatorial positions at each copper atom are practically planar, the largest deviation from the mean plane being 0.046(9) Å for O(5) around Cu(3). The copper atoms do not exhibit significant deviations from the respective mean equatorial planes except Cu(4) which is shifted by 0.160(9) Å toward the axial O(6W) water molecule.

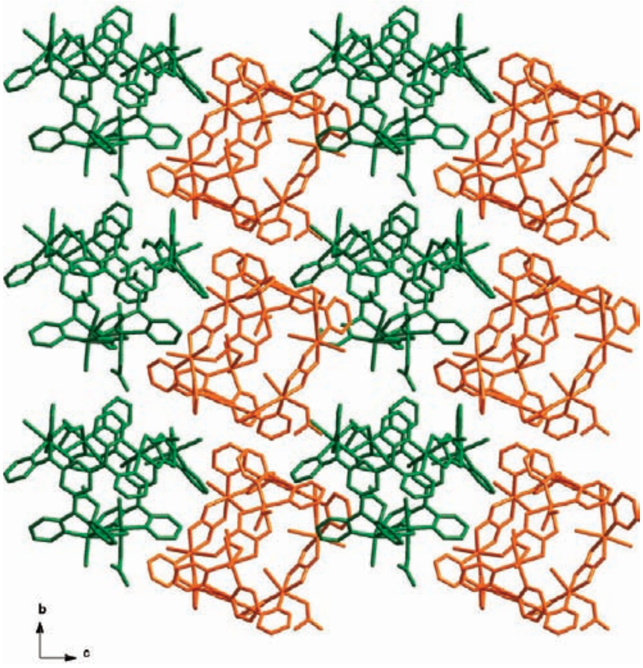

Figure 6. Projection along the *a*-axis of the packing of the hexanuclear units in **3**. The non-coordinated nitrate anions and the crystallization water molecules were omitted for clarity.

The two dipyatriz ligands in **3** adopt the tris-bidentate coordination mode observed in **1** and **2**. The values of copper−copper separation within the $[Cu_3(dipyatriz]$ trinuclear fragment are 7.728(4) [Cu(1)···Cu(5)], 7.476(2) [Cu(1)···Cu(3)], 7.673(2) [Cu(3)···Cu(5)], 8.098(2) [Cu(2)···Cu(4)], 7.835(4) [Cu(2)···Cu(6)], and 7.886(2) Å [Cu(4)···Cu(6)]. The two triazine rings from the cationic cage are somewhat shifted with respect to each other [the value of the angle between the normal to the triazine rings and the vector passing through the centroids of these rings being about 7.0° with a centroid···centroid distance of 9.963(1) Å]. The oxalate groups in **3** adopt the bis-bidentate coordination mode, and they are all planar. The bond lengths and angles within each oxalate in **3** agree with those

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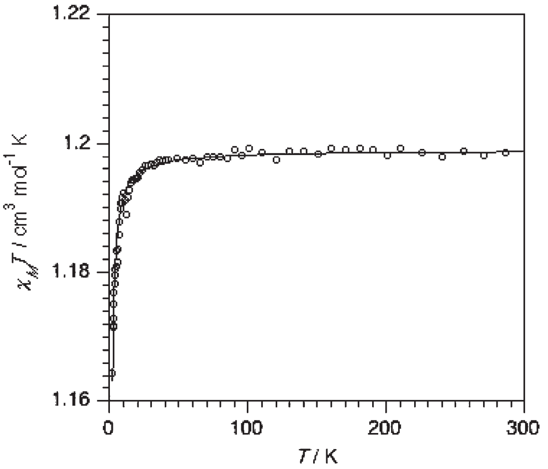

Figure 7. $\chi_M T$ versus T plot for complex **1**: (○) experimental data; ($^{\text{solid line}}$) best-fit curve through eq 1 (see text).

observed for other oxalato-bridged dicopper(II) complexes where the oxalate adopts the same coordination mode.[41] The values of the copper−copper separation across the oxalate bridge are 5.149(2) [Cu(1)···Cu(2)], 5.136(2) [Cu(3)···Cu(4)], and 5.112(3) Å [Cu(5)···Cu(6)].

Magnetic Properties of 1−3. The thermal dependence of the $\chi_M T$ product for **1** [χ_M is the magnetic susceptibility per three copper(II) ions] is shown in Figure 7. $\chi_M T$ at 290 K is equal to about 1.20 cm^3 mol^{-1} K, a value which in agreement with the presence of three magnetically isolated copper(II) ions (1.21 cm^3 mol^{-1} K with g = 2.08) Upon cooling, this value remains constant until T = 40 K, and it decreases slightly at lower temperatures to reach 1.16 cm^3 mol^{-1} K at 1.9 K. This plot is as expected for a very weak antiferromagnetic coupling within the trinuclear units.

Considering the trinuclear structure of **1**, its magnetic data were analyzed by means of eq (1)

$$\chi_M = N\beta^2 g^2/4kT[(1 + 5e^{3J/2kT})/(1 + e^{3J/2kT})] \quad (1)$$

which was derived through the isotropic Heisenberg−Dirac Hamiltonian for an equilateral triangle of spin doublets [eq 2]

$$\hat{H} = -J_{12}\hat{S}_1 \cdot \hat{S}_2 - J_{13}\hat{S}_1 \cdot \hat{S}_3 - J_{23}\hat{S}_2 \cdot \hat{S}_3 \quad (2)$$

with $J_{12} = J_{13} = J_{23} = J$ and all the other parameters having their usual meaning. Best-fit parameters through eq (1) are $J = -0.08(1)$ cm^{-1} and $g = 2.07(1)$. The weak antiferromagnetic interaction between copper(II) ions through the extended tris-bidentate dipyatriz ligand in **1** is of the same order than those obtained for the analogous tricopper(II) compounds [Cu$_3$(dipyatriz)$_2$Cl$_3$][CuCl$_4$]Cl (J = −0.42 cm^{-1})[21a] and [Cu$_3$(dipyatriz)$_2$Cl$_6$(dmso)$_3$] (dmso = dimethylsulfoxide; J = −1.42 cm^{-1})[21a] where the same exchange pathway occurs.

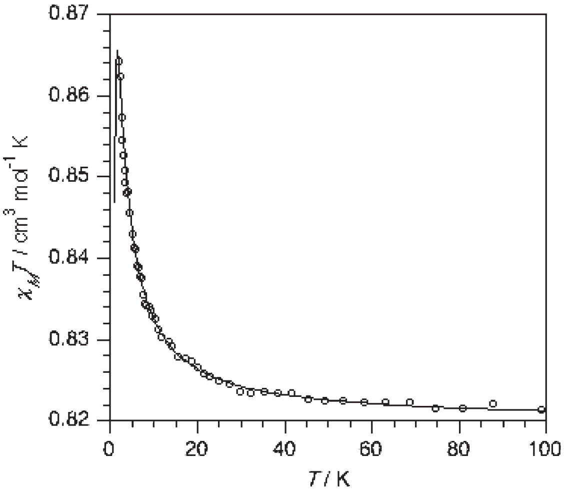

Figure 8. $\chi_M T$ versus T plot at $T \leq 100$ K for complex **2**: (○) experimental data; (solid line) best-fit curve through eqs (3)−(5) (see text).

The very weak intramolecular magnetic interaction in this family of complexes can be easily understood by considering the poor overlap between the magnetic orbitals through the triazine ring. The unpaired electron on each copper(II) ion is mainly delocalized in the basal plane (defined by the four pyridyl-nitrogen atom) which is practically perpendicular to the triazine ring. This feature together with the fact that the pyridyl rings are significantly tilted with respect to each other and also with respect to the triazine ring, preclude any significant spin density on the amino- and triazine nitrogen atoms, rendering practically inefficient the through-bond contribution to the magnetic coupling. However, a better ability of the dipyatriz molecule to mediate significant magnetic interactions and even of different nature can be envisaged if the triazine ring is directly bound to the spin carrier. Such a situation has been illustrated by a recent magneto-structural report on the dipyatriz-bridged diiron(II) complex [Fe$_2$(dipyatriz)$_2$Cl$_2$](CF$_3$SO$_3$)$_2$ where a ferromagnetic coupling (J=+0.46 cm^{-1}) occurs between two high-spin iron(II) ions.[20d]

The temperature dependence of the $\chi_M T$ product for **2** [χ_M is the magnetic susceptibility per two copper(II) ions] is shown in Figure 8. $\chi_M T$ at room temperature is equal to 0.82 cm^3 mol^{-1} K, a value which is as expected for two uncoupled copper(II) ions (0.81 cm^3 mol^{-1} K with g = 2.08). Upon cooling, $\chi_M T$ smoothly increases to reach a value of 0.864 cm^3 mol^{-1} K at 1.9 K. This plot is as expected for a weak overall ferromagnetic interaction.

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Although there are two possible exchange pathways in **2**, the tris-bidentate dipyatriz and the bidentate/monodentate (outer) oxalate, the former one can be discarded having in mind the very weak antiferromagnetic coupling which is observed in **1**. Then, assuming that the oxalate bridge is responsible for the ferromagnetic interaction occurring in **2**, we have analyzed the magnetic data of this compound by means of the expression for two magnetically interacting spin doublets [eqs (3)−(5)][42]

$$\chi_M = (\chi_{\parallel} + 2\chi_{\perp})/3 \quad (3)$$

$$\chi_{\parallel} = 2Ng_{\parallel}{}^2\beta^2/kT\{[\exp(-D/3kT)]/[\exp(2D/3kT + 2\exp(-D/3kT) + \exp(-J/kT)]\} \quad (4)$$

$$\chi_{\perp} = 2Ng_{\perp}{}^2\beta^2/D\{[\exp(2D/3kT - \exp(-D/3kT)]/[\exp(2D/3kT + 2\exp(-D/3kT) + \exp(-J/kT)]\} \quad (5)$$

which was derived through the Hamitonian [eq 6]

$$\hat{H} = -J\hat{S}_A\cdot\hat{S}_B + \hat{S}_A D\hat{S}_B + \beta \mathrm{H}(g_A\hat{S}_A + g_B\hat{S}_B) \quad (6)$$

where J is the magnetic coupling, D is the axial zero-field splitting within the triplet state, and $g_{\parallel} = g_{\perp} = g$ is the Landé factor (which is assumed to be isotropic for simplicity). Least-squares fitting leads to the following values: $J = +0.45(2)$ cm^{-1}, $g = 2.09(1)$, and $|D| = 1.0(2)$ cm^{-1}. As shown in Figure 8, the calculated curve reproduces well the magnetic data in the whole temperature range investigated. The lack local anisotropy of the copper(II) ion and the large copper−copper separation through the oxalato bridge (ca. 5.6 Å) cannot account for the relatively large value of D which has to be considered as the upper limit given that the antiferromagnetic interdimer interactions were not considered.

The weak magnitude of the magnetic coupling between the copper(II) ions across the oxalate bridge (Figure 3b) can be understood by considering the symmetry and relative orientation of the magnetic orbitals involved. The unpaired electron on each copper(II) ion in **2** is of the $d_{x^2-y^2}$ type with the x and y axis being roughly defined by the equatorial bonds to the copper atom. As the oxalate bridge occupy two equatorial positions at Cu(1) [O(1) and O(2) atoms] and an axial one at Cu(2d) [O(4)], it is clear that the spin density at the axial O(4) atom has to be very weak. Consequently, the overlap between the adjacent magnetic orbitals through this out-of-plane pathway has to be very small and a very weak antiferro- or even ferromagnetic coupling is predicted.[43] The weak ferromagnetic coupling observed in **2** is most likely due to the accidental orthogonality between the magnetic orbitals, a situation which depends on subtle structural parameters such as the axial copper to oxalate-oxygen bond length, angle at the apical oxygen, and dihedral angle between the mean basal planes. In that respect, either weak ferro- or antiferromagnetic interactions were reported for the copper(II) compounds of formula [Cu(2-MeIm)(ox)] (2-MeIm = 2-methylimidazole, $J = +0.63$ cm^{-1})[37b] and [Cu(en)$_2$][Cu(ox)$_2$] (en = ethylenediamine, $J = -3.0$ cm^{-1}),[37c] where the oxalate exhibits the same coordination mode observed in **2**.

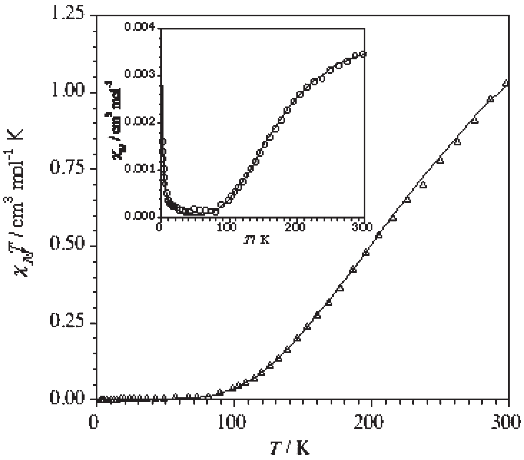

Figure 9. $\chi_M T$ (△) and χ_M (○) versus T plots for complex **3**. The solid line is the best-fit curve for three dicopper(II) units (see text).

The temperature dependence of the $\chi_M T$ product for **3** [χ_M is the magnetic susceptibility per six copper(II) ions] is shown in Figure 9. $\chi_M T$ at room temperature is equal to 1.05 cm^3 mol^{-1} K, a value which is much smaller than that expected for six uncoupled copper(II) ions (ca. 2.43 cm^3 mol^{-1} K with $g = 2.08$). Upon cooling, this value decreases very quickly, and it practically vanishes at 50 K. This plot is indicative of a strong antiferromagnetic coupling leading to a low-lying singlet spin state. The χ_M curve (see inset of Figure 9) is also typical for a strong antiferromagnetic coupling because of the occurrence of a rounded maximum about 300 K, the increase of the magnetic susceptibility χ_M in the low temperature range being due to a small amount of mononuclear copper(II) impurities.

Given the poor ability of the tris-bidentate dipatryz ligand to mediate magnetic interactions as shown by compound **1** (see above) and the well documented ability of the oxalate group to transmit strong antiferromagnetic interactions between copper(II) ions when adopting the symmetrical bis-bidentate bridging mode,[41b−41d,41f,41h−41p] the magnetic behavior of compound **3** would correspond to that of three oxalato-bridged dicopper(II) units with a strong antiferromagnetic coupling within each unit. Assuming the magnetic coupling for the three units is identical, the magnetic data of **3** [per diccoper(II) unit] have been analyzed through a Bleaney−Bowers expression for two spin doublets (the Hamiltonian being $\hat{H} = -J\hat{S}_1\cdot\hat{S}_2$). The best fit led to the following values: $J = -390(2)$ cm^{-1}, $g = 2.09(1)$, and $\rho = 0.3\%$ (ρ is the mass proportion of paramagnetic impurity).[41c] As shown in Figure 9, the calculated curve reproduces well the magnetic data in the whole temperature range. The strong antiferromagnetic coupling observed in **3** is in the upper range of those reported in other oxalato-bridged dicopper(II) complexes where the bis-bidentate oxalate links equatorial positions of the two copper(II) ions (see Table 5). The σ in-plane exchange pathway of the oxalate bridge which is responsible for this strong

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Table 5. Selected Magneto-Structural Data for Oxalate-Bridged Dicopper(II) Complexes of the Type [(NN)Cu(μ-ox)Cu(NN)]X_n Exhibiting the σ In-Plane Exchange Pathway

NN[a]	X	donor set	dihedral angle[b]	h_{Cu}[c]	$d_{Cu\cdots Cu}$[d]	J[e]	ref.
phen	NO_3	N_2O_2/O'	16.9	0.27	5.158(1)	−330	41e
phen	NO_3	N_2O_2/O_w	22.7	0.24	5.144(1)	−288	41p
bipy	NO_3	N_2O_2/O_wO'	3.2	0.16	5.154(1)	−386	41d,41i
bipy	ClO_4	N_2O_2/O_wO'	12.0	0.18	5.150(1)	−376	41i
bipy	BF_4	N2O2/OwF	10.4	0.16	5.144(1)	−378	41i
bipy	NO_3	N_2O_2/O_wO'	4.6	0.11	5.143	−382	41l
dpyam	ClO_4	N_2O_2/N'	14.5	0.19	5.194	−382	41m
dpyam	NO_3	$N_2O_2/O'O''$	7.0	0.08	5.220(2)	−305	41n
tmen	ClO_4	N_2O_2/O_w	8.4	0.18	5.147/5.167	−385	41b,41c
deen	ClO_4	N_2O_2/O_wO'	3.9	[f]	[f]	−300	41k
mpym	PF_6	N_2O_2/O_w	13.9	0.24	5.175	−402	41f
mpym	NO_3	N_2O_2/O_wO'	[f]	0.12/0.07	5.217	−284	41h
dpp	NO_3	N_2O_2/OwO′	7.3	0.16	5.171(1)	−312	41o
bpz	Cl	N_2O_2/OwCl	4.9	0.10/0.09	5.1345(16)	−345	41o
dipyatriz	NO_3	N_2O_2/OwO′	1.6/17.5[g]	0.16[h]	5.132[i]	−390	this work

[a] Abbreviations: phen = 1,10-phenanthroline; bipy = 2,2′-bipyridine; dpyam = 2,2′-diyridylamine; tmen = *N,N,N′,N′*-tetramethylethylenediamine; deen = *N,N*-diethylethane-1,2-diamine; mpym = meripirizole; dpp = 2,3-bis(2-pyridyl)pyrazine, bpz = 2,2′bipyrazine; dipyatriz = 2,4,6-tris (dipyridylamine)-1,3,5-triazine. [b] Dihedral angle (deg) between the mean oxalate and equatorial planes. [c] Out-of-equatorial plane displacement (Å) of the copper atom. [d] Copper−copper distance through the oxalate bridge (Å). [e] Magnetic coupling (cm^{-1}). [f] Value not reported. [g] Minimum and maximum values. [h] Value for Cu(4) (the other five copper atoms remaining practically in their respective equatorial planes). [i] Average value.

magnetic coupling in this family of complexes and the influence that the structural factors exert on J has been subject of several theoretical studies some years ago,[44−47] and further details are available therein for the interested readers.

Conclusions

In the present work, we have focused on three polynuclear dipyatriz-containing copper(II) complexes (compounds **1**−**3**) from a magneto-structural point of view. Complex **1** is a trinuclear species (**1**) having the $[Cu_3(dipyatriz)_2]^{6+}$ core with a weak intramolecular antiferromagnetic interaction. Remarkably, the triazine rings of this unit exhibit a practically eclipsed conformation, and they act as anion (perchlorate) hosts. In the presence of oxalate as coligand, a layered compound (**2**) and a unprecedented cage-like complex (**3**) resulted depending on the preparative conditions [slow diffusion of the aqueous solutions of the reactants at room temperature (**2**) and hydrothermal conditions (**3**)]. Both structures have in common the presence of the tris-bidentate dipytriz ligand leading to tetra- $[Cu_4(dipyatriz)_2]^{8+}$ (**2**) and trinuclear $[Cu_3(dipyatriz)]^{6+}$ (**3**) units which are interlinked through bidentate/monodentate (**2**) and bis-bidentate (**3**) oxalate groups. Weak ferro- (**2**) and strong antiferromagnetic (**3**) interactions occur between the copper(II) ions across the oxalate bridges. The triangular array of the metal ions resulting when dipyatriz acts as a tris-bidentate ligand is particularly aesthetic and appealing. In such a case, previous reports have shown the occurrence discrete tri-[20f,21,22] and tetranuclear[20b,20e,20f] species, as well as one-dimensional compounds.[20a,20c,21a] Interestingly, the electron deficient triazine ring of the dipyatriz ligand in its coordination compounds can be involved in anion−π and π−π interactions that regulate the self-assembly of the anion-triazine-triazine complexes. These supramolecular interactions, the variety of coordination modes, and the luminescent character of dipyatriz, as well as the possibility it offers as a bridge to mediate elecyronic effects, enhance the interest in the dipyatriz-containing metal complexes as potential multifunctional materials. Finally, the great number and different topologies and charge of the potential polyatomic bridges to be used as coligands toward the highly versatile $[M_x(dipyatriz)_y]^{xm+}$ unit opens new perspectives concerning the design of multifunctional metallo-supramolecular assemblies.

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Supporting Information Available: Further details are given in Figure S1, and crystallographic information as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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