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Supramolecular networks of transition metal sulfates templated by piperazine

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Abstract

Syntheses, structural studies from single-crystal X-ray diffraction and thermal behaviour of $(C_4H_{12}N_2)[M^{II}(H_2O)_6](SO_4)_2$ with $M^{II} = Mn$, Ni, Fe and Cu are reported. All compounds crystallise in monoclinic system, space group $P2_1/n$. The two isotypical compounds $(C_4H_{12}N_2)[Mn(H_2O)_6](SO_4)_2$ (I) and $(C_4H_{12}N_2)[Ni(H_2O)_6](SO_4)_2$ (II), are isostructural with the related cobalt and zinc phases, while the isotypical sulfates $(C_4H_{12}N_2)[Fe(H_2O)_6](SO_4)_2$ (III) and $(C_4H_{12}N_2)[Cu(H_2O)_6](SO_4)_2$ (IV) belong to another structure type. The three-dimensional structure networks for the four compounds consist of isolated $[M^{II}(H_2O)_6]^{2+}$ and $(C_4H_{12}N_2)^{2+}$ cations and $(SO_4)^{2-}$ anions linked by hydrogen-bonds only. The thermal behaviour of the precursors has been studied by powder thermodiffractometry and thermogravimetric analyses. The first stages of dehydration are discussed with respect to the hydrogen bonds within the compounds. © 2006 Elsevier B.V. All rights reserved.

Keywords: Crystal structure; Thermal behaviour; Temperature-dependent X-ray powder diffraction; Transition metal sulfate; Piperazine; Supramolecular

1. Introduction

The sulfate chemistry has regained interest for a few years, mainly with the idea of using amines as templates in hydrothermal syntheses [1], and also because of the tetrahedral shape of SO_4^{2-} that promises to extend the zeotype materials to sulfate compounds [2]. A wide range of structures have been obtained until now, with 1D [3,4], 2D [2,5–7] and 3D [2,8–10] characters, all of them consisting of inorganic frameworks built from strong metal–oxygen bonds. On the contrary, supramolecular networks of hexaaquametal sulfates including amine groups have been much less investigated. While the crystal engineering of supramolecular compounds is known to favour electric, magnetic and optical properties (see, for example, [11] and refs therein), only a few sulfate compounds have been described and studied in the literature [12–24]. In the course of our investigations on new sulfate materials having such properties [25], a series of 3d transition metal sulfates templated by piperazine, $(C_4H_{12}N_2)[M^{II}(H_2O)_6]$ - $(SO_4)_2$, have been prepared. They belong to two different structure types, which are described here. In addition, their thermal behaviour is discussed with respect to the hydrogen bonds as well as the nature of the metal.

2. Experimental

2.1. Chemical preparation

Single crystals of the compounds $(C_4H_{12}N_2)[M^{II}-(H_2O)_6](SO_4)_2$ $[M^{II} = Mn$ (I), Ni (II), Fe (III) and Cu (IV)] were grown as follows: 1 mmol of the metal sulfate hydrate $M^{II}SO_4 \cdot nH_2O$ [MnSO₄ · H₂O (99%, Merck); NiSO₄ · 6H₂O (99%, Merck); FeSO₄ · 7H₂O (99.5%, Merck) and CuSO₄ · 5H₂O (99%, Merck)], 1 mmol of piperazine hexahydrate (C₄H₁₀N₂) · 6H₂O (99%, Sigma) and 1 mmol of sulfuric acid H₂SO₄ (96%, Carlo Erba) were

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mixed together in a minimum amount of distilled water. The clear solutions were stirred for 15 mins and allowed to stand at room temperature. After a few days, single crystals having the specific M^{II} colour were formed. The products were filtered off and washed with a small amount of distilled water.

2.2. Single-crystal diffraction data collection and structure determination

Small crystals of the four compounds were glued to a glass fibre mounted on a four-circle Nonius Kappa CCD area-detector diffractometer (Centre de Diffractométrie X, UMR CNRS 6226). Intensity data sets were collected using Mo Ka radiation through the program collect [26]. Corrections for Lorentz-polarisation effect, peak integration and background determination were carried out with the program DENZO [27]. Frame scaling and unit cell parameters refinement were performed with the program SCALE-PACK [27]. Analytical absorption corrections were performed by modelling the crystal faces [28]. The main crystallographic data are listed in Table 1.

The structure analyses were carried out with the monoclinic symmetry, space group $P2_1/n$, according to the automated search for space group available in Wingx [29].

Table 1

Crystallographic o	lata for	$(C_4H_{12}N_2)[M]$	$(H_2O)_6](SO_4)_2$
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Transition metal atoms (M^{II}) and sulfur atoms were located using the direct methods with program SHELXS-97 [30]. The oxygen atoms and the organic moieties were found from successive Fourier calculations using SHELXL-97 [31]. The agua H atoms were located in a difference map and refined with O-H distance restraints of 0.85(2) Å and H...H restraints of 1.39(2) Å so that the H-O-H angle fitted to the ideal value of a tetrahedral angle. H atoms bonded to C and N atoms were positioned geometrically and allowed to ride on their parent atoms, with C-H = 0.97 Å and N-H = 0.90 Å. Bond distances and angles calculated from the final atomic coordinates, as well as probable hydrogen bonds, are given in Tables 2 and 3.

2.3. Thermal analyses

Temperature-dependent X-ray diffraction (TDXD) was performed with a D5005 powder diffractometer (Bruker AXS) using Cu K α radiation [$\lambda(K\alpha_1) = 1.5406$ Å, $\lambda(K\alpha_2) = 1.5444$ Å] selected with a diffracted-beam graphite monochromator, and equipped with an Anton Paar HTK1200 high-temperature oven camera. The thermal decomposition of the compounds was carried out in air, with a heating rate of 14.4 $^{\circ}$ C h⁻¹ from ambient to 870 $^{\circ}$ C.

Crystallographic data for (C_4)	$H_{12}N_2)[M^{-1}(H_2O)_6](SO_4)_2$			
Empirical formula	$C_{4}H_{24}MnN_{2}O_{14}S_{2}(I)$	$C_4H_{24}NiN_2O_{14}S_2$ (II)	$C_4H_{24}FeN_2O_{14}S_2$ (III)	$C_4H_{24}CuN_2O_{14}S_2$ (IV)
Formula weight	443.31	447.08	444.22	451.91
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
<i>a</i> (Å)	13.0215(2)	12.9271(2)	7.8389(1)	6.8506(1)
b (Å)	10.7710(2)	10.6210(2)	9.3839(2)	10.1536(2)
<i>c</i> (Å)	13.3648(2)	13.3150(2)	11.0944(2)	11.8890(2)
β (°)	113.868(1)	114.094(1)	91.257(1)	92.926(1)
$V(\text{\AA}^3)$	1714.17(5)	1668.86(5)	815.90(3)	825.90(3)
Z	4	4	2	2
$\rho_{\rm cal} ({\rm g}{\rm cm}^{-1})$	1.718	1.779	1.808	1.817
Crystal size (mm ³)	$0.282 \times 0.278 \times 0.233$	$0.221 \times 0.130 \times 0.121$	$0.470 \times 0.441 \times 0.422$	$0.722 \times 0.266 \times 0.240$
Habit-colour	prism-pale pink	prism-pale green	prism-green	needle-blue
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073
$\mu (\mathrm{mm}^{-1})$	1.083	1.483	1.252	1.646
θ Range (°)	3.33-27.49	2.91-34.97	2.84-42.16	2.64-27.09
Index ranges	$-16 \leqslant h \leqslant 16$	$-17 \leqslant h \leqslant 20$	$-14 \leqslant h \leqslant 11$	$-8 \leqslant h \leqslant 8$
-	$-13 \leq k \leq 13$	$-13 \leqslant k \leqslant 17$	$-13 \leq k \leq 17$	$-13 \leqslant k \leqslant 12$
	$-17 \leq l \leq 17$	$-21 \leqslant l \leqslant 21$	$-20 \leqslant l \leqslant 19$	$-15 \leq l \leq 13$
Unique data	3906	7314	5713	1796
Observed data $[I > 2\sigma(I)]$	3485	5264	4331	1714
<i>F</i> (000)	924	936	464	470
Extinction coefficient	0.031(2)	0.018(2)	0.167(9)	0.101(7)
Refinement method	full matrix	full matrix	full matrix	full matrix
	least-squares on $ f^2 $	least-squares on $ f^2 $	least-squares on $ f^2 $	least-squares on $ f^2 $
R_1	0.0347	0.0468	0.0437	0.0399
ωR_2	0.0979	0.1229	0.1294	0.1113
Goodness-of-fit	1.082	1.056	1.020	1.075
Number of parameter	257	257	131	131
Transmission factors	0.776 and 0.874	0.777 and 0.876	0.611 and 0.715	0.516 and 0.737
Largest difference map hole and peak ($e Å^{-3}$)	-0.437 and 0.570	-0.937 and 1.012	-0.880 and 0.840	-0.930 and 0.805

Table 2 Bond distances (Å) and angles (°) within metal complexes $[M(H_2O)_6]^{2+}$

$(C_4H_{12}N_2)[Mn(H_{12}N_2)]$	$(H_2O)_6](SO_4)_2(I)$				
Mn–Ow1	2.147(2)	Ow1-Mn-Ow2	89.14(6)	Ow2–Mn–Ow5	89.22(7)
Mn–Ow2	2.151(2)	Ow1-Mn-Ow3	92.00(6)	Ow2–Mn–Ow6	93.12(6)
Mn–Ow3	2.182(1)	Ow1-Mn-Ow4	84.71(7)	Ow3–Mn–Ow4	85.89(6)
Mn–Ow4	2.185(2)	Ow1-Mn-Ow5	91.75(6)	Ow3-Mn-Ow5	91.86(6)
Mn–Ow5	2.200(2)	Ow1-Mn-Ow6	176.31(6)	Ow3-Mn-Ow6	85.69(6)
Mn–Ow6	2.206(1)	Ow2–Mn–Ow3	178.41(6)	Ow4–Mn–Ow5	175.73(7)
		Ow2–Mn–Ow4	93.10(7)	Ow4–Mn–Ow6	92.25(7)
				Ow5–Mn–Ow6	91.20(6)
$(C_4H_{12}N_2)/Ni(H$	$(O_{1}) = l(SO_{4}) = (\mathbf{I})$				
Ni–Owl	2.031(1)	Ow1–Ni–Ow2	87.33(6)	Ow2–Ni–Ow5	87.31(7)
Ni–Ow2	2.042(2)	Ow1–Ni–Ow3	85.02(6)	Ow2–Ni–Ow6	94.35(6)
Ni–Ow3	2.061(2)	Ow1-Ni-Ow4	93.10(6)	Ow3-Ni-Ow4	85.99(6)
Ni–Ow4	2.062(1)	Ow1–Ni–Ow5	92.97(6)	Ow3–Ni–Ow5	177.73(6)
Ni–Ow5	2.077(1)	Ow1-Ni-Ow6	177.36(5)	Ow3-Ni-Ow6	92.83(6)
Ni–Ow6	2.085(1)	Ow2-Ni-Ow3	93.65(7)	Ow4–Ni–Ow5	93.08(6)
		Ow2-Ni-Ow4	179.41(6)	Ow4-Ni-Ow6	85.20(6)
				Ow5–Ni–Ow6	89.15(6)
$(C_4H_{12}N_2)/Fe(H$	$(20)_{6} l(SO_{4})_{2} (III)$				
Fe-Owl	2.095(1)	Ow1–Fe–Ow1 ^I	180.00(8)	Ow1 ^I -Fe-Ow3	90.98(5)
Fe-Ow1 ^I	2.095(1)	Ow1-Fe-Ow2	92.66(4)	Ow1 ^I -Fe-Ow3 ^I	89.02(5)
Fe–Ow2	2.1291(9)	Ow1-Fe-Ow2 ^I	87.34(4)	Ow2–Fe–Ow2 ^I	180.00(7)
Fe–Ow2 ^I	2.1291(9)	Ow1-Fe-Ow3	89.02(5)	Ow2–Fe–Ow3	87.97(4)
Fe–Ow3	2.134(1)	Ow1-Fe-Ow3 ^I	90.98(5)	Ow2–Fe–Ow3 ^I	92.03(4)
Fe–Ow3 ^I	2.134(1)	Ow1 ^I -Fe-Ow2	87.34(4)	Ow2 ^I -Fe-Ow3	92.03(4)
		Ow1 ^I -Fe-Ow2 ^I	92.66(4)	Ow2 ^I -Fe-Ow3 ^I	87.97(4)
				Ow3–Fe–Ow3 ^I	180.00(6)
$(C_4H_{12}N_2)/Cu(H_1)$	$(SO_A)_{\mathcal{S}}(SO_A)_{\mathcal{S}}(IV)$				
Cu–Ow1	1.960(2)	Ow1–Cu–Ow1 ^I	180.0(1)	Ow1 ^I –Cu–Ow3	92.43(8)
Cu–Ow1 ^I	1.960(2)	Ow1–Cu–Ow2	86.20(7)	Ow1 ^I –Cu–Ow3 ^I	87.57(8)
Cu–Ow2	1.963(2)	Ow1–Cu–Ow2 ^I	93.80(7)	Ow2–Cu–Ow2 ^I	180.00
Cu–Ow2 ^I	1.963(2)	Ow1–Cu–Ow3	87.57(8)	Ow2–Cu–Ow3	92.78(7)
Cu–Ow3	2.397(2)	Ow1–Cu–Ow3 ^I	92.43(8)	Ow2–Cu–Ow3 ^I	87.22(7)
Cu–Ow3 ^I	2.397(2)	Ow1 ^I -Cu-Ow2	93.80(7)	Ow2 ^I –Cu–Ow3	87.22(7)
		Ow1 ^I -Cu-Ow2 ^I	86.20(7)	Ow2 ^I -Cu-Ow3 ^I	92.78(7)
				Ow3–Cu–Ow3 ^I	180.00(9)

Symmetry code: $^{I} -x, -y + 1, -z$.

Thermogravimetric (TG) measurements were performed with a Rigaku Thermoflex instrument under flowing air, with a heating rate of 15 °C h^{-1} for the four compounds. The powdered samples (79.82 mg for I, 95.07 mg for II, 89.48 mg for III and 109.46 mg for IV) were spread evenly in a large platinum crucible to avoid mass effects.

3. Results and discussion

3.1. Description of the structures

The crystal structures of $(C_4H_{12}N_2)[M^{II}(H_2O)_6](SO_4)_2$ $[M^{II} = Mn (I)$, Ni (II), Fe (III) and Cu (IV)] belong to the centro-symmetric space group $P2_1/n$. They consist of transition metal cations octahedrally coordinated by six water molecules, $[M(H_2O)_6]^{2+}$, isolated sulfate anions, SO_4^{2-} , and diprotonated piperazine moieties, $C_4H_{12}N_2^{2+}$. The cohesion is ensured by hydrogen bonds between the cationic groups and the sulfate O atoms only. The resulting H-bonding networks can be alternatively described by three-dimensional supramolecular frameworks belonging to two structure types, thus forming channels in which the piperazinediium cation plays a templating role (Fig. 1).

Compounds I (Mn) and II (Ni) are isostructural with the related cobalt [19] and zinc [25] phases. In the present structure type, transition metal atoms and sulfate tetrahedra occupy general positions (Wyckoff site 4e), while the two crystallographically independent piperazine molecules lie in centers of symmetry (Wyckoff sites 2a and 2b). Such an arrangement gives rise to a second type of channels, made of inorganic moieties, running along the *b*-axis (Fig. 2). The octahedral environment of these M^{II} cations is not regular (Table 2), as seen in other isostructural templated metal sulfates [19,25]. Indeed, metal–oxygen distances vary from 2.147(2) to 2.206(1) Å and from 2.031(1) to 2.085(1) Å for Mn and Ni, respectively. Bond angles are comprised in the range 84.71(7)–93.12(6)° for O–Mn–O and 85.02(6)–94.35(6)° for O–Ni–O. The mean

Table 3 Hydrogen-bonding geometry (Å, °)

D–HA	d(D-H)	<i>d</i> (HA)	d(DA)	∠D-HA	
	(Å)	(Å)	(Å)	(°)	
$(C \parallel N) (M_{\pi}(\parallel O))$	1(50) (1)				
$(C_4 \Pi_{12} N_2) [Mn(\Pi_2 O)]$	$_{6}(SO_{4})_{2}(\mathbf{I})$	1.01	2 770(2)	1(2.0	
NI-HIC04	0.90	1.91	2.779(2)	163.0	
NI-HID06	0.90	1.92	2.747(2)	151.2	
N2–H2CO7	0.90	1.84	2.726(2)	169.6	
N2–H2DO4	0.90	1.85	2.749(2)	171.7	
$OW1-H11O7^{II}$	0.84(2)	1.87(2)	2.708(2)	177(3)	
OW1- H1201 ^{III}	0.86(2)	1.86(2)	2.710(2)	170(3)	
OW2-H21O2	0.85(2)	1.85(2)	2.701(2)	177(3)	
$OW_{2}H_{22}O1_{IV}$	0.88(2)	1.85(2)	2.719(2)	169(3)	
OW_2 H31 $O5^V$	0.87(2)	1.05(2) 1.85(2)	2.719(2) 2.708(2)	171(3)	
$OW_2 H_2 O_{\text{ell}}$	0.87(2)	1.05(2)	2.708(2)	171(3) 178(2)	
OW3-H3208	0.88(2)	1.80(2)	2.745(2)	178(3)	
OW4- H41O2"	0.85(2)	1.88(2)	2.734(2)	1/5(3)	
OW4–H42O6 ^{V1}	0.88(2)	1.86(2)	2.706(2)	165(3)	
OW5–H51O3 ^{III}	0.84(2)	2.01(2)	2.84(2)	172(3)	
OW5–H52O8 ^V	0.85(2)	1.89(2)	2.734(2)	176(3)	
$OW6-H61O5^{VI}$	0.86(2)	2.20(2)	2.989(3)	151(3)	
OW6–H62O3	0.89(2)	1.92(2)	2.802(2)	172(3)	
Symmetry codes: $I - r$	-1/2 v - 1/2	$\frac{1}{2} - \frac{1}{2} + \frac{1}{2} \cdot \frac{1}{2}$	$r_{v+1} = 1$	$\frac{11}{11} r = 1/2$	
$y \pm 1/2$ z $1/2$ IV	$x \pm 1/2$, $y = 1/2$	$\frac{1}{2}, \frac{1}{2}, \frac$	V = 1/2	$y \pm 1/2$	
-y + 1/2, 2 - 1/2, -	-x + 1/2, y + 1/2 = 1	1/2, -2 + 1/2	-x - 1/2,	y + 1/2,	
-z + 1/2; x + 1/2, -	-y + 1/2, z +	1/2.			
$(C_4H_{12}N_2)[Ni(H_2O)_6]$	$[(SO_4)_2 (II)]$				
N1-H1C07 ^I	0.90	1.83	2.726(2)	170.6	
$N1-H1D O4^{II}$	0.90	1 84	2 733(2)	170.2	
N2 H2C O^{II}	0.90	1.80	2.755(2)	163.2	
N2_H2C04	0.90	1.05	2.762(2)	105.2	
$N_2 - H_2 D_{\dots} O_0$	0.90	1.95	2.700(2)	150.7	
OWI-HIIOI	0.839(9)	1.86(1)	2.688(2)	1/1(3)	
OW1- H1207 ^{IV}	0.841(9)	1.87(1)	2.711(2)	176(3)	
$OW2-H21O2^{II}$	0.85(1)	1.88(1)	2.724(2)	175(3)	
OW2-H22O1	0.852(9)	1.88(1)	2.710(2)	163(3)	
OW3-H31O2	0.846(9)	1.92(1)	2.755(2)	171(3)	
OW3-H3206 ^V	0 857(9)	1.86(1)	2 693(2)	163(2)	
OW4- H41 05	0.853(9)	1.88(1)	2.000(2) 2.723(2)	169(3)	
$OW4 H42 O8^{IV}$	0.055(7)	1.00(1)	2.723(2)	107(3) 172(2)	
OW4-114208	0.80(1)	1.91(1)	2.739(2)	1/3(3)	
0w5-H5103	0.843(9)	2.10(1)	2.9222)	165(2)	
OW5–H52O8	0.845(9)	1.89(1)	2.735(2)	173(3)	
OW6–H61O3 ¹¹	0.856(9)	1.97(1)	2.822(3)	174(3)	
OW6–H62O5 ^V	0.86(1)	2.33(2)	3.086(3)	146(2	
Symmetry codes: $I - x$	-1/2, v - 1/2	$^{\prime}2, -z + 1/2; ^{I}$	$x^{1} - x + 1/2, v$	-1/2,	
-z + 1/2. III $-x - v +$	1 - 7. IV - x	-1/2 v + 1/2	$2^{-7} + 1/2^{-7}$	-r	
y + 1, z, y + 1	1, 2, ,	1/2, y 11/	2, 2 1, 1, 2,	л,	
-y + 1, -2 + 1.					
$(C_4H_{12}N_2)[Fe(H_2O)_6]$	$[(SO_4)_2 (III)]$)			
N—H1AO3	0.90	1.89	2.780(2)	168.1	
$N - H1B - O4^{I}$	0.90	2.06	2.946(2)	168.6	
OW1_H11_01	0.85(2)	1.93(2)	2.764(2)	168(3)	
$OW1$ H12 $O3^{II}$	0.89(2)	1.99(2)	2.701(2)	157(3)	
$OW2$ $U21$ $O1^{III}$	0.07(2)	1.05(2)	2.077(2)	177(3)	
	0.87(2)	1.00(2)	2.751(1)	173(3)	
0w2–H2204 ¹⁰	0.87(2)	1.91(2)	2.780(2)	1/2(2)	
OW3–H31O2 ¹ v	0.85(2)	1.86(2)	2.695(2)	168(2)	
OW3–H32O4 ^{III}	0.88(2)	1.89(2)	2.760(2)	169(2)	
Symmetry codes: $I - x$	+1, -y, -z	+1; II - x + 1	/2, y - 1/2, -	z + 1/2;	
III $x - 1, y, z; W - x +$	1/2, y + 1/2,	-z + 1/2.			
$(C_4H_{12}N_2)[C_4(H_2O)]$	$[(SO_4)_2 (IV)_3]$)			
$N-H1AO1^{1}$	0.90	1.86	2.726(3)	161.9	
N-H1B04	0.90	2.04	2.880(3)	155.2	
$OW1-H11O3^{II}$	0.85(1)	1.81(1)	2.651(2)	169(3)	
$OW1-H12$ $O4^{III}$	0.87(1)	1.88(2)	2.685(2)	157(4)	
OW2_H21 O3 ^{IV}	0.84(2)	2 01(5)	2.687(2)	137(7)	
OW2 H22 O2V	0.07(2)	1.94(2)	2.007(2)	166(4)	
$OW2 - \Pi ZZ \dots OZ^T$	0.05(1)	1.04(2)	2.070(2)	100(4)	
OW3-H3102"	0.85(1)	2.05(2)	2.863(3)	101(3)	
OW3-H32O4 ^{v1}	0.85(1)	2.05(1)	2.901(3)	176(4)	
Symmetry codes: $^{1}-x+2, -y, -z; ^{11}x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}; ^{111}-x+1, -x + 1, -$					
$-y + 1, -z; {}^{1}-x, -y + 1, -z; {}^{1V}-x + 3/2, y + 1/2, -z - 1/2; {}^{V}x - 1, y, z;$					
$v_{I} - x + 1/2, y + 1/2, -$	-z - 1/2.				

planes of the two piperazine groups are about parallel to $(2 \ 0 \ -2)$ and $(4 \ 4 \ -1)$, respectively, with a dihedral angle between them of 56.6°. The sulfate anions play a major role in the formation of the 3D supramolecular arrangement. In I and II, there are two crystallographically independent SO₄ groups, both interconnect three metal complexes and two piperazinium cations. Within S1O₄, each of O1, O2 and O3 oxygen atoms is bonded to two metal complexes, while O4 is only H-bonded to two N atoms. Within S2O₄, O5 and O8 connect two metal complexes, while O6 and O7 are bonded to one complex and one piperazinium cation.

In the crystal structure of III (Fe) and IV (Cu), transition metal and piperazinediium cations are located in the centres of symmetry (Wyckoff sites 2c and 2d, respectively), while the sulfate tetrahedron lies in a general position (Wyckoff site 4e). Then, Fe²⁺/Cu²⁺ octahedra alternate with the diprotonated amine along the *c*-axis. The octahedral environment of Fe is quite regular in III. On the contrary, in IV, the Cu–OW1 and Cu–OW2 distances are 1.960(2) and 1.963(2) Å, respectively, and the Cu–OW3 distance of 2.397(2) Å is strongly elongated (Table 2). Thus, Cu^{2+} ions display the so-called (4+2)coordination type that has often been observed [32-34]. It is consistent with the well-known Jahn-Teller distortion of the 3d cation. Contrary to the structures of I and II, which are strictly identical, the structures of III and IV differ from each other by the position and the orientation of the sulfate groups (Fig. 3). As a consequence (Fig. 4), the Fe^{2+} complex is hydrogen-bonded to four sulfate groups sharing two O atoms and four sulfate groups sharing one O atom. On the contrary, the Cu^{2+} octahedron is surrounded by six sulfate tetrahedra only, connected via H bonds in a bidentate fashion to the octahedron. In the same manner, the sulfate connectivity differs from the two structures, i.e., SO₄ interconnects four complexes and two piperazines in III, while it connects three complexes and two piperazines in IV. In III, O1 is bonded to one metal complex, O2 is surrounded by one complex and two piperaziniums, O3 is connected to one complex and one piperazinium and O4 is bonded to two complexes and one piperazinium cation. In IV, the hydrogen-bonding scheme is similar to that observed in compounds I and II, except that there is one additional bond between O4 and a piperazinium group.

3.2. Thermal behaviour of the precursors

The thermal decomposition of phases **I**–**IV** proceeds through three main stages. The first step corresponds to the full dehydration of the precursor, the second stage coincides with the decomposition of the organic moiety, together with the partial release of sulfate groups, and the third stage is characterised by the removal of remaining sulfates to form the final oxide product. Within these decompositions, some peculiarities have to be noticed, as also indicated in Table 4.



Fig. 1. Projection of the crystal structures of (a) compounds I (Mn) and II (Ni), (b) III (Fe) and IV (Cu), showing the piperazinium cations in the cavities formed by the supramolecular metal-sulfate frameworks. Light grey octahedra: $[M(H_2O)_6]^{2+}$, dark grey tetrahedra: SO_4^{2-} , light grey spheres: C, black spheres: N. The hydrogen bonds are represented by the dashed lines.



Fig. 2. Projection of the structure of I and II along the *b*-axis, showing $(C_4H_{12}N_2)^{2+}$ located a second type of channels, as well as the environment of $[M(H_2O)_6]^{2+}$ octahedra.

Fig. 5 shows the three-dimensional representation of the powder diffraction patterns obtained during the decomposition of $(C_4H_{12}N_2)[Mn(H_2O)_6](SO_4)_2$ (I) in air in the temperature range 19–850 °C. This plot reveals that the anhydrous sulfate is amorphous to X-rays. Furthermore, the end of the decomposition is marked by the slow formation of Mn_2O_3 from ~590 °C. This compound appears as a lone phase in the range 590–840 °C. From this temperature, the diffraction lines of Mn_3O_4 emerge from the background, in addition to those of Mn_2O_3 . Such a reduction of Mn_2O_3 into Mn_3O_4 is well known in non-oxidising atmospheres, as described for example by Zaki et al. [35].

As it is shown for compound I, the anhydrous phase, $(C_4H_{12}N_2)Ni(SO_4)_2$, is amorphous to X-rays. NiSO₄ is completely formed at 420 °C, and starts to decompose into NiO at 450 °C. The decomposition is slow and leads to the pure final oxide at 710 °C only.

The anhydrous phase $(C_4H_{12}N_2)Fe(SO_4)_2$ (III) is stable in the temperature range 135–210 °C (Fig. 6). It appears amorphous to X-rays up to 190 °C. Then, two successive poorly crystalline phases are observed between 190 and 260 °C on the TDXD plot. Unfortunately, they could not



Fig. 3. Projection of the structures of III and IV on the (*ab*) plane, showing the neighbouring sulfates in the environment of (a) $[Fe(H_2O)_6]^{2+}$, (b) $[Cu(H_2O)_6]^{2+}$.



Fig. 4. Hydrogen bonding geometry between SO_4^{2-} and (a) $[Fe(H_2O)_6]^{2+}$, (b) $[Cu(H_2O)_6]^{2+}$.

Table 4	
Successive stages of the thermal decomposition of compounds I–IV in air (heating rate $15 ^{\circ}\text{C}$ h	1^{-1})

		Temperature range (°C)/[Δm/m ₀ (%)]			
		I (Mn)	II (Ni)	III (Fe)	IV (Cu)
1	$\begin{array}{l} (C_4H_{12}N_2)[M(H_2O)_6](SO_4)_2 \rightarrow (C_4H_{12}N_2)M(SO_4)_2\text{-am}^a \\ (C_4H_{12}N_2)M(SO_4)_2\text{-am} \rightarrow (C_4H_{12}N_2)M(SO_4)_2\text{-cr}^b \end{array}$	68-125/[-24.0]	92-180/[-23.8]	78–135/[–23.6] 190	66–135/[–23.2] 180
2	$\begin{array}{l} (C_4H_{12}N_2)M(SO_4)_2 \to M(SO_4) \\ (C_4H_{12}N_2)Fe(SO_4)_2 \to 1/2Fe_2(SO_4)_3 \end{array}$	230-430/[-65.0]	245-420/[-64.4]	210-370/[-54.3]	210-350/[-64.7]
3	$\begin{array}{l} Mn(SO_4) \to 1/2Mn_2O_3 \\ Mn_2O_3 \to (1-x)Mn_2O_3 + 2x/3Mn_3O_4 \\ Ni(SO_4) \to NiO \\ Fe_2(SO_4)_3 \to Fe_2O_2(SO_4) \\ Fe_2O_2(SO_4) \to Fe_2O_3 \\ Cu(SO_4) \to 1/2Cu_2O(SO_4) \\ Cu_2O(SO_4) \to CuO \end{array}$	590–770/[–77.8] 840	450–710/[—80.9]	480–590/[–73.2] 650–>950/[–82.0]	520–590/[–72.8] 590–660/[–79.3]

^a am: amorphous to X-rays.

^b cr: crystallised.



Fig. 5. TDXD plot for the decomposition of $(C_4H_{12}N_2)[Mn(H_2O)_6](SO_4)_2$ (I) in air (14.4 °C h⁻¹, counting time of 1800 s per pattern).



Fig. 6. TG curve for the decomposition of $(C_4H_{12}N_2)[Fe(H_2O)_6](SO_4)_2$ (III) in air (15 °C $h^{-1}).$

be identified on the lone basis of their powder data. Since no weight loss is observed at 190 °C, it was assumed that $(C_4H_{12}N_2)Fe(SO_4)_2$ crystallises at this temperature, and then decomposes into the second badly crystallised phase. This hypothesis is formulated from a similar result obtained for the Cu compound (**IV**), as described below. While decomposing, the oxidation of Fe²⁺ into Fe³⁺ is observed, leading to $Fe_2(SO_4)_3$ being stable in the temperature range 370–480 °C. This result is evidenced by the weight loss of 54.3 % (calc. 54.9 %) and the diffraction patterns obtained from a subsequent thermodiffractometry measurement. The decomposition of $Fe_2(SO_4)_3$ leads to a small plateau observed between 590 and 650 °C, for which the weight loss of 73.2 % is in agreement with the global formula " $Fe_2O_2(SO_4)$ " (calc. 73.0 %). This compound appears amorphous to X-rays. It decomposes slowly between 650 and 950 °C into α - Fe_2O_3 .

Fig. 7 shows the successive powder patterns obtained during the thermal decomposition of (C₄H₁₂N₂)[Cu- $(H_2O)_6$ (SO₄)₂ (IV) upon heating. The TG curve appears in Fig. 8. The first transformation occurs in the temperature range 68–125 °C. The weight loss of 23.2 % is in agreement with the departure of the six water molecules (calc. weight loss, 23.9%), thus leading to the anhydrous phase, (C₄H₁₂N₂)Cu(SO₄)₂, amorphous to X-rays (Fig. 7). At 180 °C, some diffraction lines emerge from the background. At this temperature, no weight loss is observed in the TG curve. From these observations, it was concluded that the anhydrous phase crystallises. High quality powder diffraction data for this phase were collected in situ at 172 °C, using the Bruker D5005 diffractometer. The first 20 lines of the powder pattern of $(C_4H_{12}N_2)Cu(SO_4)_2$ were indexed using the dichotomy-method program DICVOL04 [36], on the basis of a triclinic solution, and the complete review



Fig. 7. TDXD plot for the decomposition of $(C_4H_{12}N_2)[Cu(H_2O)_6](SO_4)_2$ (IV) in air (14.4 °C h⁻¹, counting time of 1800 s per pattern). (am) amorphous to X-rays, (cr) crystallised.



Fig. 8. TG curve for the decomposition of $(C_4H_{12}N_2)[Cu(H_2O)_6](SO_4)_2$ (IV) in air (15 °C $h^{-1}).$

and least-squares refinements of the 28 diffraction lines available led to the unit cell dimensions a = 6.201(1) Å, b = 11.476(2) Å, c = 12.352(3) Å, $\alpha = 66.46(2)^{\circ}$, $\beta = 80.70(2)^{\circ}$, $\gamma = 84.60(2)^{\circ}$ and V = 794.81 Å³ [M₂₀ = 57.5, $F_{28} = 121(0.0050, 46)$, refined zero-shift 0.047° (2 θ)]. Unfortunately, high background contribution and instability of diffracted intensities did not allow further structural investigations of the compound.

 $(C_4H_{12}N_2)Cu(SO_4)_2$ is not stable and decomposes into $CuSO_4$ (weight loss 64.7%). As shown in Fig. 7, some diffraction lines appear to coexist with $CuSO_4$ in the temperature range 530–590 °C. These are attributed to Cu_2OSO_4 , as also evidenced by the weight loss of 72.8% (calc. 73.5%) observed on the TG curve at the inflection. The final transformation corresponds to the formation of copper oxide, CuO, which crystallises immediately after Cu_2OSO_4 starts to decompose.

3.3. Discussion

These studies show that there are similar changes in the decomposition of precursors with somewhat small differences, which could be associated with the structural variations. The first noticeable point is related to the difference of the dehydration temperatures that could be explained by the nature of the metal as well as the hydrogen bonds involved in the structures. For compound II (Ni), dehydration takes place at higher temperature than the three other compounds, while its crystal structure is similar to that of I (Mn). It has often been shown that Ni complexes are generally more stable than other transition metal complexes [37], as also observed for example for NiSO₄ \cdot 6H₂O [38] and NiSeO₄ · 6H₂O [39]. Compared to the related Cu compound (IV), III (Fe) dehydrates at higher temperature. This is certainly due to the fact that $[Fe(H_2O)_6]^{2+}$ forms hydrogen bonds with eight sulfate anions, instead of six SO_4^{2-} for the Cu complex. The lower temperature observed for IV may also be explained by the elongated Cu–Ow3 distance while the octahedron around Fe is quite regular, as shown in transition metal selenates [40]. The structure of IV (Cu) differs from that of I (Mn), but the onsets of dehydration are similar for the two compounds. Indeed, the hydrogen bonds formed with the sulfate groups are comparable in the two structures. In addition, the amorphous anhydrous phases obtained from compounds III and IV, which have similar structures, crystallise at high temperature. Since no crystal structure is available for (C₄H₁₂N₂)Cu(SO₄)₂, no explanation can be given for that phenomenon.

The second feature is that the Mn, Co [19], Ni and Zn [25] phases belong to one structure type, while Fe and Cu compounds belong to a second one, with a unit-cell volume about half of the first-cited compounds. It is surprising since there is no relation between the increase of ionic radius of the cation from Mn^{2+} to Zn^{2+} and the structural arrangement observed for these supramolecular sulfates. On the contrary, the use of NH_4^+ instead of piperazinediium with all transition metal sulfates gives rise to the isostructural Tutton's salts structures [41–46]. Further studies to understand the templating role of diamines in the presence of transition metal sulfates are under way.

4. Conclusion

Four metal sulfate compounds templated by piperazine have been synthesised and characterised by single crystal X-ray diffraction, powder thermodiffractometry and thermogravimetric analyses. The four structures consist of isolated M^{II} octahedrally coordinated by six water molecules, diprotonated piperazinium cations and sulfate anions linked by hydrogen bonds only. Two structure types were distinguished and described. The thermal behaviour of the precursors is shown to be dependent not only on the structure type but also on the transition metal atom involved in the structure.

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