

UDC 548.73:547.13:546.48

CRYSTAL ARCHITECTURE AND THERMAL DECOMPOSITION
OF TWO NEW ORGANICALLY TEMPLATED CADMIUM SULFATESR. Jlassi¹, W. Rekik¹, H. Naili¹, T. Mhiri¹, T. Bataille²¹Laboratoire Physico-Chimique de l'état Solide, Département de Chimie, Faculté des Sciences de Sfax, Université de Sfax, Sfax, Tunisia

E-mail: w_rekik@alinto.com

²Sciences Chimiques de Rennes (CNRS, UMR 6226), Université de Rennes 1, Rennes Cedex, France

Received April, 26, 2012

Revised — May, 25, 2012

Two organic-inorganic hybrid compounds $(C_5H_{14}N_2)[Cd(H_2O)_6](SO_4)_2$ (**I**) and $R-(C_5H_{14}N_2) \times [Cd(H_2O)_6](SO_4)_2$ (**II**) are synthesized by the slow evaporation method and characterized by single crystal X-ray diffraction, thermogravimetry, temperature-dependent X-ray diffraction, and infrared spectroscopy. The first compound crystallizes in the centrosymmetric space group $P2_1/n$ with the following unit cell parameters: $a = 6.6208(2) \text{ \AA}$, $b = 10.6963(3) \text{ \AA}$, $c = 12.9318(4) \text{ \AA}$, $V = 893.05(6) \text{ \AA}^3$, and $Z = 2$. Its structure is solved by direct methods and refined by the least-squares analysis [$R_1 = 0.0389$ and $wR_2 = 0.0821$]. This compound shows a crystallographic disorder **II** destroys the inversion symmetry and leads to a fully ordered structure. Indeed, compound **II** crystallizes in the non-centrosymmetric space group $P2_1$ with the following unit cell parameters: $a = 6.6306(1) \text{ \AA}$, $b = 10.7059(2) \text{ \AA}$, $c = 12.9186(1) \text{ \AA}$, $V = 894.67(2) \text{ \AA}^3$, and $Z = 2$. The crystal structure of both compounds is built from isolated SO_4^{2-} anions, disordered 2-methylpiperazinedium, $(C_5H_{14}N_2)^{2+}$ in compound **I** or R-2-methylpiperazinedium $R-(C_5H_{14}N_2)^{2+}$ in compound **II**, and divalent metal cations surrounded by six water molecules. These different entities are connected together only by a 3D hydrogen bond network. The thermodiffraction and the thermogravimetric analyses indicate that the decomposition of the supramolecular precursors proceeds through several stages leading to cadmium oxide.

Keywords: hybrid material, slow evaporation, X-ray diffraction, crystal structure, thermal decomposition, supramolecular.

INTRODUCTION

In recent years, hybrid organic-inorganic materials have increasingly attracted the attention of researchers in supramolecular chemistry thanks to the properties of various organic and inorganic species [1]. Great interest has been shown in some double sulfates of trivalent metals and monovalent aliphatic ammonium cations because of their ferroelastic and ferroelectric properties [2–6]. So far, there are few data on the double sulfates of divalent transition metal cations with mono- or divalent organic amine cations [7–19]. By analogy with trivalent metal sulfates showing a *para*-ferroelectric phase transition upon cooling [3–6], it was expected that such divalent metal sulfates would exhibit this feature. The use of non-centrosymmetric amine groups, instead of alkylamines, may help crystallize disordered phases at room temperature [19, 20]. Cation ordering at a low temperature would thus provide acentric structures that are the basic condition to have ferroelectricity. For this purpose, we have synthesized two new compounds using 2-methylpiperazine and R-2-methylpiperazine as tem-

plates and cadmium as divalent metal. In this paper, we report the chemical preparation, the structural study, the infrared spectroscopy analysis, and the thermal behavior of two compounds: $(C_5H_{14}N_2)[Cd(H_2O)_6](SO_4)_2$ and $R-(C_5H_{14}N_2)[Cd(H_2O)_6](SO_4)_2$.

EXPERIMENTAL

Synthesis. Single crystals of two compounds $(C_5H_{14}N_2)[Cd(H_2O)_6](SO_4)_2$ (**I**) and $R-(C_5H_{14}N_2) \times [Cd(H_2O)_6](SO_4)_2$ (**II**) were prepared by mixing $C_5H_{14}N_2$ or $R-C_5H_{14}N_2$ (3 mmol), H_2SO_4 (3 mmol), $3CdSO_4 \cdot 8H_2O$ (1 mmol), and 20 ml of distilled water. The mixture was then allowed to stand and evaporate slowly at room temperature. In 3 days time, colorless crystals were formed.

X-ray structure determination. A suitable single crystal of each compound was carefully selected under a polarizing microscope. Diffraction data were collected at room temperature by the ω -scan technique on an Oxford Diffraction supernova, dual, Cu at zero, four-circle diffractometer with an Atlas CCD detector and graphite-monochromatized MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). The data were corrected for Lorentz polarization. A numerical absorption correction based on the Gaussian integration over a multifaceted crystal model was applied using Oxford Diffraction CrysAlisPro [21]. The structure analyses were carried out with the monoclinic symmetry, space group $P2_1/n$ for compound **I** and $P2_1$ for compound **II**, according to the automated search for a space group available in WinGX [22]. Cadmium and sulfur atoms were located using the direct methods with the SHELXS-97 program [23]. Oxygen atoms and organic moieties were found from successive Fourier calculations using SHELXL-97 [24]. Aqua H atoms were located in a difference map and refined with O—H distance restraints of $0.85(1) \text{ \AA}$ and H—H restraints of $1.39(1) \text{ \AA}$ so that the H—O—H angle was fitted to the theoretical value of 104.5° . The H atoms bonded to C and N atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H and N—H bonds being fixed at 0.97 \AA and 0.89 \AA respectively. Crystallographic data and structural refinements are summarized in Table 1. The final fractional atomic coordinates are given in Table 2. Bond distances and angles calculated from the final atomic coordinates, as well as probable hydrogen bonds, are listed in Tables 3 and 4 respectively. The drawings were made with Diamond [25].

Further details of the crystal structure investigations can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The deposition numbers are CCDC 872127 and CCDC 872128 for **I** and **II** respectively.

Infrared spectroscopy. IR reflection spectra of compounds **I** and **II** were measured with a Perkin-Elmer BX FTIR spectrometer in the $4000\text{--}400 \text{ cm}^{-1}$ region at ambient temperature in KBr pellets.

Thermogravimetric analysis. Thermogravimetric analyses (TGA) were conducted using a SETARAM TG-DTA92 instrument under flowing air. Samples were contained within a platinum crucible and heated at $10 \text{ }^\circ\text{C min}^{-1}$ from ambient temperature to $900 \text{ }^\circ\text{C}$.

Temperature-dependent X-ray powder diffraction (TDXD) for compound **I** was performed with a powder diffractometer combining the curved-position-sensitive detector (CPS120) from INEL and a high temperature attachment from Rigaku. The detector was used in a semi-focusing arrangement by reflection ($CuK_{\alpha 1}$ radiation, $\lambda = 1.5406 \text{ \AA}$) as described elsewhere [26]. The thermal decomposition of compound **I** was carried out in flowing air with a heating rate of $7 \text{ }^\circ\text{C} \cdot \text{h}^{-1}$ from ambient temperature to $610 \text{ }^\circ\text{C}$. For compound **II** TDXD was performed with a D5005 powder diffractometer (Bruker AXS) using CuK_α radiation [$K(\alpha_1) = 1.5406 \text{ \AA}$, $K(\alpha_2) = 1.5444 \text{ \AA}$] selected with a diffracted-beam graphite monochromator and equipped with an Anton Paar HTK1200 high temperature oven camera. The thermal decomposition of compound **II** was carried out in air, with a heating rate of $14.4 \text{ }^\circ\text{C} \cdot \text{h}^{-1}$ from ambient to $870 \text{ }^\circ\text{C}$.

RESULTS AND DISCUSSION

Crystal structure. Compounds $(C_5H_{14}N_2)[Cd(H_2O)_6](SO_4)_2$ **I** and $R-(C_5H_{14}N_2)[Cd(H_2O)_6] \times (SO_4)_2$ **II** were found to crystallize in the centrosymmetric space group $P2_1/n$ and the non-

Table 1

Crystallographic data and structure refinement details for $(C_5H_{14}N_2)[Cd(H_2O)_6](SO_4)_2$
and $R-(C_5H_{14}N_2)[Cd(H_2O)_6](SO_4)_2$

	$C_5H_{26}CdN_2O_{14}S_2$ (I)	$C_5H_{26}CdN_2O_{14}S_2$ (II)
Empirical formula	$C_5H_{26}CdN_2O_{14}S_2$ (I)	$C_5H_{26}CdN_2O_{14}S_2$ (II)
Formula weight, g/mol	514.80	514.80
Temperature, K	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1$
$a, b, c, \text{\AA}$	6.6208(2), 10.6963(3), 12.9318(4)	6.6306(1), 10.7059(2), 12.9186(1)
β , deg.	102.800(3)	
$V, \text{\AA}^3$	893.05(6)	894.67(2)
Z	2	2
Calculated density, g/cm ³	1.911	1.911
Crystal size, mm	0.314×0.215×0.162	0.229×0.153×0.075
Habit-colour	Colourless	Colourless
$\lambda(\text{MoK}\alpha)$, \AA	0.71073	0.71073
μ , mm ⁻¹	1.525	1.523
Flack parameter	—	-0.05(2)
θ Range for data collection, deg.	3.23—32.92	3.68—32.98
Index ranges	$-8 \leq h \leq 8, -14 \leq k \leq 14, -16 \leq l \leq 15$	$-10 \leq h \leq 9, -16 \leq k \leq 16, -19 \leq l \leq 19$
Unique data	3204	6308
Observed data [$I > 2\sigma(I)$]	2838	5550
$F(000)$	522	524
Absorption correction	Numerical	Numerical
Transmission factors	0.676—0.800	0.899—0.947
Refinement method	Full matrix least-squares on $ F^2 $	Full matrix least-squares on $ F^2 $
R_1 , %	3.85	3.84
wR_2 , %	8.15	8.72
GOOF	1.048	1.004
No. parameters	140	265

centrosymmetric space group $P2_1$ respectively. They consist of divalent metal cations octahedrally coordinated by six water molecules, sulfate tetrahedra, and protonated diamines. Furthermore, their structures are composed of isolated entities interconnected by two types of hydrogen bonds OW—HW...O and N—H...O, giving rise to a three-dimensional aspect. While the anionic part is made up of the SO_4^{2-} sulfate group, the cationic part is mixed because it is composed not only of a protonated organic part $(C_5H_{14}N_2)^{2+}$ or $R-(C_5H_{14}N_2)^{2+}$, but also of divalent metal hexaaquacoordinated $[Cd(H_2O)_6]^{2+}$ (Fig. 1).

Within the structure of compound I, the divalent metal atoms are located in special positions on inversion centers and each of them is coordinated by six water molecule oxygen atoms, three of which are crystallographically independent. These $[Cd(H_2O)_6]^{2+}$ octahedra are slightly distorted. Indeed, the metal-oxygen distances vary from 2.253(2) \AA to 2.297(2) \AA and *cis*-OW—Cd—OW angles are comprised between 84.67(9)° and 95.33(9)° (Table 3). The metal octahedra are isolated of each other with the shortest distance Cd—Cd = 6.621 \AA . The $[Cd(H_2O)_6]^{2+}$ cations occupy the corners and the center of the unit cell while the (2-methylpiperazinediium) cations are located on the positions of the metal translated by 1/2 along the *b* axis: they are then placed in the middle of the edges parallel to [0 1 0] and the center of the faces defined in the (*ac*) plane. Thus, the organic and inorganic cations alternate along the [1 1 0] directions and form mixed cationic layers perpendicular to the crystallographic *c* axis

Table 2

Fractional atomic coordinates and equivalent isotropic temperature factor (\AA^2)
with e.s.d.'s in parentheses

Atomes	x	y	z	U_{eq}	Occupancy
(C ₅ H ₁₄ N ₂)[Cd(H ₂ O) ₆](SO ₄) ₂					
Cd	0	0	0	0.01439(8)	1
S	0.5670(1)	0.78927(7)	0.21435(5)	0.01912(14)	1
OW1	0.2838(3)	-0.0448(2)	-0.06218(17)	0.0200(4)	1
OW2	0.2296(4)	0.0758(3)	0.14342(18)	0.0337(6)	1
OW3	-0.0150(3)	0.1981(2)	-0.07000(17)	0.0208(4)	1
O1	0.5508(4)	0.9220(2)	0.2342(3)	0.0387(6)	1
O2	0.6392(4)	0.7719(4)	0.1156(2)	0.0502(9)	1
O3	0.7176(4)	0.7339(3)	0.3024(2)	0.0414(7)	1
O4	0.3659(3)	0.7250(2)	0.20270(17)	0.0223(4)	1
N	0.4276(10)	0.6192(6)	-0.0413(4)	0.099(3)	1
C1	0.2907(13)	0.5336(8)	-0.0001(5)	0.106(4)	1
C2	0.4086(12)	0.4475(7)	0.0877(4)	0.105(4)	1
C3	0.3126(13)	0.3794(8)	0.1233(6)	0.0358(17)	0.5
R-(C ₅ H ₁₄ N ₂)[Cd(H ₂ O) ₆](SO ₄) ₂					
Cd	0.26240(3)	0.05361(4)	0.752722(18)	0.01259(6)	1
S1	0.81739(11)	0.27202(8)	0.96403(6)	0.01175(15)	1
S2	0.68287(11)	-0.15113(8)	0.53477(6)	0.01195(15)	1
OW1	0.4996(4)	-0.0241(3)	0.8927(2)	0.0213(6)	1
OW2	0.2346(3)	-0.1477(3)	0.6888(2)	0.0158(5)	1
OW3	-0.0323(4)	0.0160(3)	0.8095(2)	0.0193(6)	1
OW4	0.0440(4)	0.1257(3)	0.6051(2)	0.0210(6)	1
OW5	0.2686(4)	0.2489(3)	0.8274(2)	0.0188(5)	1
OW6	0.5392(4)	0.1033(2)	0.6872(2)	0.0165(5)	1
O1	0.9784(4)	0.3339(3)	1.04429(19)	0.0190(5)	1
O2	0.6171(4)	0.3374(3)	0.9563(2)	0.0181(5)	1
O3	0.8010(4)	0.1410(3)	0.9925(2)	0.0209(5)	1
O4	0.8736(4)	0.2814(3)	0.85967(19)	0.0185(5)	1
O5	0.5880(4)	-0.1789(3)	0.6257(2)	0.0289(7)	1
O6	0.5473(4)	-0.1985(3)	0.4369(2)	0.0248(6)	1
O7	0.8844(3)	-0.2159(3)	0.55198(19)	0.0152(5)	1
O8	0.7049(4)	-0.0160(3)	0.5251(2)	0.0238(6)	1
N1	0.3654(4)	-0.0438(3)	0.2784(2)	0.0137(5)	1
N2	0.2196(4)	0.1946(3)	0.1947(2)	0.0165(5)	1
C1	0.2081(5)	0.0259(3)	0.3231(2)	0.0150(6)	1
C2	0.5046(4)	0.0418(4)	0.2354(3)	0.0173(6)	1
C3	0.0842(5)	0.1072(3)	0.2362(3)	0.0153(6)	1
C4	0.3808(5)	0.1268(3)	0.1517(3)	0.0172(6)	1
C5	0.0739(6)	-0.0641(4)	0.3677(3)	0.0209(7)	1

$$[U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j].$$

Table 3

Selected bond lengths (Å) and angles (deg.)

Octahedron around Cd		Tetrahedron around S		Within the organic moiety	
$(C_5H_{14}N_2)[Cd(H_2O)_6](SO_4)_2$					
Cd—OW1	2.253(2)	S1—O1	1.451(3)	N—C1	1.469(11)
Cd—OW2	2.271(2)	S1—O2	1.470(3)	N—C2 ⁱⁱ	1.527(8)
Cd—OW3	2.297(2)	S1—O3	1.463(2)	C1—C2	1.534(8)
OW1—Cd—OW2	84.67(9)	S1—O4	1.476(2)	C3—C2	1.130(11)
OW1—Cd—OW2 ⁱ	95.33(9)	O1—S1—O2	109.2(2)	C1—N—C2 ⁱⁱ	113.6(6)
OW1—Cd—OW3	91.27(8)	O1—S1—O3	108.84(17)	N—C1—C2	112.9(7)
OW1—Cd—OW3 ⁱ	88.73(8)	O1—S1—O4	111.90(15)	N ⁱⁱ —C2—C3	111.8(7)
OW2—Cd—OW3	87.44(9)	O2—S1—O3	109.2(2)	N ⁱⁱ —C2—C1	106.2(6)
OW2—Cd—OW3 ⁱ	92.56(9)	O2—S1—O4	108.17(14)	C3—C2—C1	116.7(9)
		O3—S1—O4	109.56(14)		
$R-(C_5H_{14}N_2)[Cd(H_2O)_6](SO_4)_2$					
Cd—OW1	2.277(3)	Tetrahedron around S(1)		N1—C1	1.498(4)
Cd—OW2	2.300(3)	S1—O1	1.472(2)	N1—C2	1.492(4)
Cd—OW3	2.269(3)	S1—O2	1.485(2)	N2—C3	1.477(5)
Cd—OW4	2.262(3)	S1—O3	1.460(3)	N2—C4	1.496(4)
Cd—OW5	2.300(3)	S1—O4	1.479(2)	C1—C5	1.509(5)
Cd—OW6	2.247(3)	O1—S1—O2	109.54(16)	C1—C3	1.513(4)
OW1—Cd—OW2	86.01(10)	O1—S1—O3	109.73(16)	C2—C4	1.510(5)
OW1—Cd—OW3	99.92(10)	O1—S1—O4	108.81(15)	C2—N1—C1	112.2(3)
OW1—Cd—OW4	175.37(11)	O2—S1—O3	110.78(17)	C3—N2—C4	111.6(3)
OW1—Cd—OW5	93.06(10)	O2—S1—O4	107.91(15)	N1—C1—C5	110.4(3)
OW1—Cd—OW6	84.66(10)	O3—S1—O4	110.03(17)	N1—C1—C3	108.1(3)
OW2—Cd—OW3	86.74(9)	Tetrahedron around S(2)		N1—C2—C4	110.7(2)
OW2—Cd—OW4	91.78(10)	S2—O5	1.479(3)	C3—N2—C4	111.1(3)
OW2—Cd—OW5	174.29(10)	S2—O6	1.472(3)	N2—C3—C1	110.77(23)
OW2—Cd—OW6	95.43(10)	S2—O7	1.478(2)	N2—C4—C2	110.3(3)
OW3—Cd—OW4	83.99(10)	S2—O8	1.462(3)	C5—C1—C3	112.4(3)
OW3—Cd—OW5	87.87(10)	O5—S2—O6	109.08(18)		
OW3—Cd—OW6	175.07(12)	O5—S2—O7	108.32(15)		
OW4—Cd—OW5	89.54(10)	O5—S2—O8	109.57(19)		
OW4—Cd—OW6	91.51(10)	O6—S2—O7	109.20(16)		
OW5—Cd—OW6	90.09(10)	O6—S2—O8	108.74(17)		
		O7—S2—O8	111.89(16)		

Symmetry codes: ⁱ $-x, -y+1, -z$; ⁱⁱ $-x, -y+1, -z$.

(Fig. 2). Each octahedron is H-bonded to six sulfate anions in a bidentate fashion (Fig. 3). The 2-methylpiperazinediium groups are located about inversion centers, while all their atoms are located in general positions. Their internal symmetry does not contain any inversion centre. Consequently, the molecule adopts two possible orientations: $(R-(C_5H_{14}N_2)^{2+})$ or $(S-(C_5H_{14}N_2)^{2+})$. The C3 atom is distributed between two positions related by the symmetry centre, with a refined site occupancy factor of 0.5 (Fig. 4). Within the organic moiety for **I**, the C—C and N—C distances and the C—N—C, N—C—C angles are in agreement with those reported for other compounds containing the same groups [27].

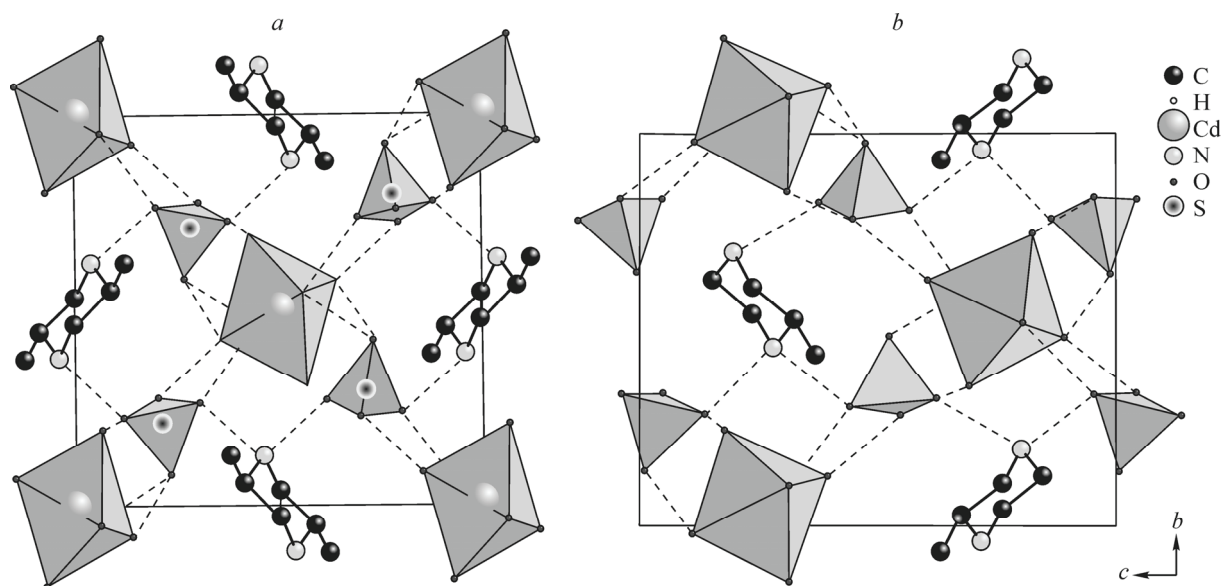


Fig. 1. Projection of the crystal structures of compound I (a), II (b) on the *a* axis

There is only one crystallographically independent S atom with a tetrahedral coordination geometry located in the general position. The sulfate groups are slightly distorted. Indeed, the S—O bond distances are comprised between 1.449(2) Å and 1.476(2) Å and the O—S—O bond angles are in the range 108.17(14)—111.90(15)° (Table 3). The sulfate groups are stacked in a manner that they form anionic layers parallel to the cationic ones and the crystal structure can be described as an alternation of cationic and anionic layers along [001] (Figs. 1 and 3). The sulfate anions play an important role in the cohesion of the crystal structure by linking the organic and inorganic cations via N—H...O and OW—HW...O hydrogen bonds. Indeed, all oxygen atoms of the sulfate groups participate in hydrogen bonds by accepting two hydrogen atoms linked to nitrogen atoms and all the hydrogen atoms of

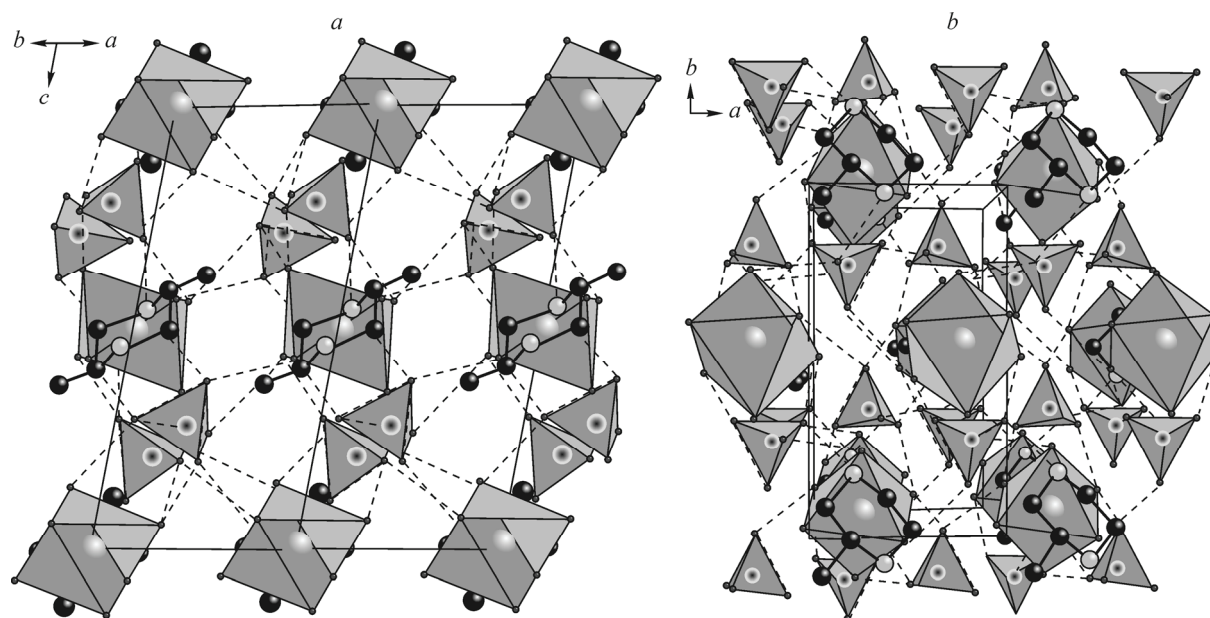


Fig. 2. Perspective view of compound I showing the alternation between organic and inorganic cations along the [110] direction (a), compound II showing the alternation between organic and inorganic cations along the *c* axis (b)

Table 4

Interatomic distances (Å) and bond angles (deg.) pertaining to the geometry of hydrogen bonds

D—H...A	<i>d</i> (D—H)	<i>d</i> (H...A)	<i>d</i> (D...A)	D—H...A
(C ₅ H ₁₄ N ₂)[Cd(H ₂ O) ₆](SO ₄) ₂				
N—HA...O2	0.90	1.84	2.737(5)	175.9
N—HB...O3 ⁱ	0.90	1.79	2.691(6)	174.6
OW1—H11...O3 ⁱⁱ	0.847(18)	1.82(2)	2.647(3)	167(4)
OW1—H12...O1 ⁱⁱⁱ	0.845(19)	2.31(4)	2.993(4)	138(4)
OW2—H21...O4 ^{iv}	0.839(19)	1.89(2)	2.732(3)	176(5)
OW2—H22...O1 ^v	0.841(18)	1.903(19)	2.738(3)	172(5)
OW3—H31...O4 ^{vi}	0.846(18)	1.86(2)	2.693(3)	169(5)
OW3—H32...O2 ⁱⁱⁱ	0.835(18)	1.89(2)	2.701(3)	162(4)

Symmetry codes: ⁱ $x-1/2, -y+3/2, z-1/2$; ⁱⁱ $x-1/2, -y+1/2, z-1/2$;
ⁱⁱⁱ $-x+1, -y+1, -z$; ^{iv} $-x+1/2, y-1/2, -z+1/2$; ^v $x, y-1, z$; ^{vi} $-x, -y+1, -z$.

R-(C ₅ H ₁₄ N ₂)[Cd(H ₂ O) ₆](SO ₄) ₂				
N1—H1A...O6	0.90	1.81	2.703(4)	168.7
N1—H1B...O4 ^v	0.90	1.94	2.820(4)	166.1
N2—H2A...O5 ⁱⁱ	0.90	1.86	2.747(4)	167.1
N2—H2B...O1 ^{vi}	0.90	1.78	2.682(4)	176.8
OW1—H11...O2 ⁱⁱⁱ	0.842(19)	1.86(2)	2.696(4)	172(6)
OW1—H12...O3	0.826(19)	1.947(19)	2.765(4)	171(4)
OW2—H22...O5	0.841(18)	1.849(19)	2.665(3)	163(4)
OW2—H21...O7 ⁱ	0.844(18)	1.89(2)	2.692(3)	158(5)
OW3—H31...O1 ⁱⁱⁱ	0.825(18)	1.93(3)	2.683(4)	152(5)
OW3—H32...O4 ^{iv}	0.836(19)	2.18(2)	3.010(4)	171(7)
OW4—H41...O7 ⁱⁱ	0.835(18)	1.930(19)	2.765(4)	177(5)
OW4—H42...O8 ⁱ	0.839(19)	1.89(2)	2.721(4)	168(7)
OW5—H52...O2	0.838(19)	1.88(2)	2.706(3)	171(5)
OW5—H51...O4 ^{iv}	0.832(19)	1.97(2)	2.763(3)	158(5)
OW6—H61...O6 ⁱⁱ	0.842(18)	1.804(19)	2.645(4)	178(5)
OW6—H62...O8	0.832(18)	2.11(3)	2.870(4)	152(5)

Symmetry codes: ⁱ $x-1, y, z$; ⁱⁱ $-x+1, y+1/2, -z+1$; ⁱⁱⁱ $-x+1, y-1/2, -z+2$;
^{iv} $x-1, y, z$; ^v $-x+1, y-1/2, -z+1$; ^{vi} $x-1, y, z-1$.

water molecules. Within the intermolecular bonds, the donor-acceptor distances are comprised between 2.647(3) Å and 2.993(4) Å with a mean distance $\langle D...O \rangle = 2.742$ Å. The D—H...O angles are comprised between 138(4)° and 176(5)° (Table 4).

Within the crystal structure of R-(C₅H₁₄N₂)[Cd(H₂O)₆](SO₄)₂] all atoms occupy general positions. The cadmium cation is octahedrally coordinated by six water molecules forming a slightly distorted octahedron [Cd(H₂O)₆]²⁺. In fact, the Cd—OW distance and OW—Cd—OW angles range from 2.247(3) Å to 2.300(3) Å and from 83.99(10)° to 175.37(11)° respectively (Table 3). The metal octa-

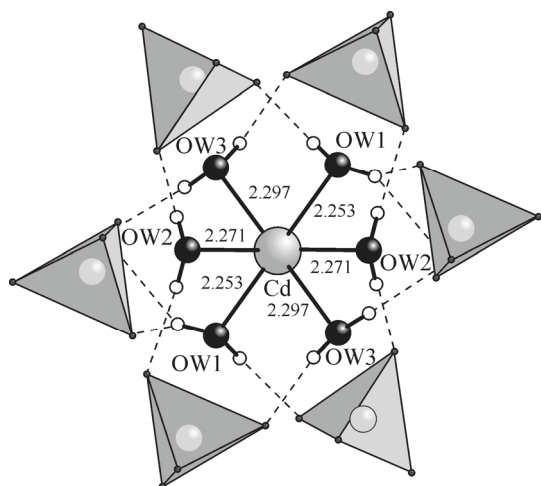


Fig. 3. Neighbouring sulfates in the environment of the cadmium octahedron for compound I

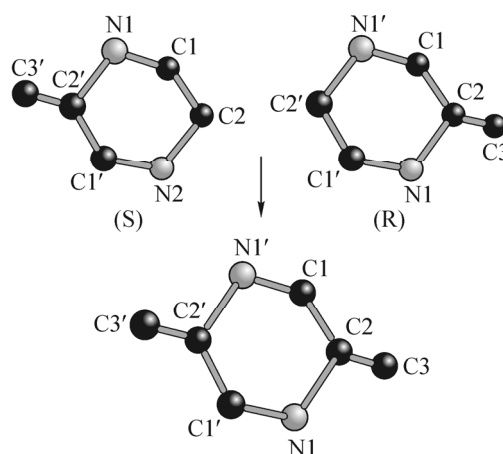


Fig. 4. Both R and S enantiomers present in the structure of the compound containing racemic amine ($C_5H_{14}N_2$)

hedra are separated from each other with the shortest Cd—Cd distance of 6.63 Å. As it was seen in compound I, each octahedron is H-bonded to six sulfate anions in a bidentate manner.

On the contrary to compound I, organic ($R-(C_5H_{14}N_2)^{2+}$) cations occupy general positions and they are ordered. Within protonated chiral diamine, the C—C and N—C distances range from 1.509(5) Å to 1.513(4) Å and from 1.477(5) Å to 1.498(4) Å respectively and the C—N—C angles are comprised between 111.1(3)° and 112.2(3)°. The single enantiomer plays two important roles: first, they assume the well-established role of protonated diamine which includes acting as a source of charge balance for the anionic inorganic architectures. The second, which is less well established, involves the effects of cation chirality on the extended symmetry. The presence or absence of each enantiomer can be chemically controlled; if $[(R)-C_5H_{14}N_2]^{2+}$ cations alone are present in a structure, they can never be related to one another through the centers of inversion because the required $[(S)-C_5H_{14}N_2]^{2+}$ cations are absent. Therefore, the formation of any inversion centers is prohibited, and the space group of the material is constrained to be non-centrosymmetric. The chirality of $[(R)-C_5H_{14}N_2]^{2+}$ is reflected in the enantiomorphic and polar crystal class of compound II. It is important to note here that the organic and inorganic cations alternate along the c crystallographic axis (Fig. 2, *b*) while they alternate along the $[110]$ direction in compound I. The two types of cations are stacked in the manner that they form cationic layers parallel to the (ab) plane. Within the structure of compound II there are two crystallographically independent sulfur atoms. Each of them is coordinated to four oxygen atom in a tetrahedral geometry. The sulfate groups are slightly distorted. Indeed, the S—O bond distances are comprised between 1.460(3) Å and 1.485(2) Å for the $S1O_4$ tetrahedron and between 1.462(3) Å and 1.479(3) Å for the $S2O_4$ tetrahedron and the O—S—O bond angles are in the range 107.91(15)—110.78(17)° and 108.32(15)—111.89(16)° in $S1O_4$ and $S2O_4$ respectively (Table 3). These tetrahedra are stacked one over another along the crystallographic a axis and they form anionic layers parallel to the (ab) plane. The two types of layers alternate along the crystallographic c axis (Fig. 1, *b*). The structure cohesion and stability are assured by two types of hydrogen bonds: OW—HW...O and N—H...O. Indeed, sulfate groups link the organic and inorganic cations via H-bonds; each oxygen atom of the anions accepts two hydrogen bonds with an exception for O3 and O4 which establish only one and three hydrogen bonds respectively. Within the intermolecular bonds, the N...O distances vary between 2.682(4) Å and 2.820(4) Å and the OW...O distances range from 2.645(4) Å to 3.010(4) Å and the D—H...O angles are comprised between 152(5)° and 177(5)° (Table 4).

Infrared spectroscopy. The presence of the template is confirmed by IR spectroscopy with C—H and N—H bands measured at 1559 cm^{-1} and 1601 cm^{-1} for $(C_5H_{14}N_2)[Cd(H_2O)_6](SO_4)_2$ and at 1455 cm^{-1} and 1617 cm^{-1} for $R-(C_5H_{14}N_2)[Cd(H_2O)_6](SO_4)$. C—H and N—H stretches are observed at

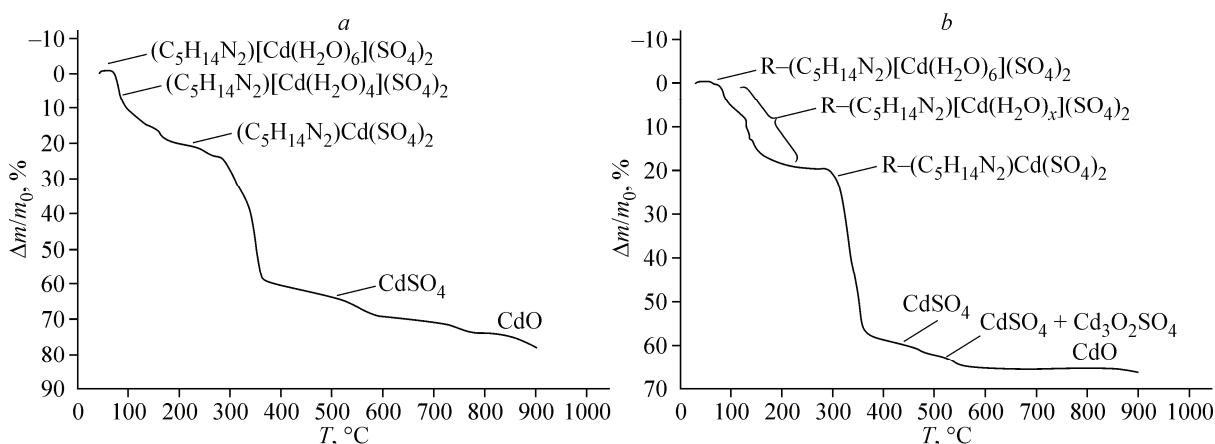


Fig. 5. TG curve for the decomposition of compound **I** (a), **II** (b) in air

about 3000 cm^{-1} and 2802 cm^{-1} for both compounds respectively. The presence of sulfate groups is confirmed by the bands observed at 617 cm^{-1} and 1116 cm^{-1} in the IR spectra. These data are also in agreement with the double protonation of the organic moiety.

Thermal behavior. The thermogravimetry curves and the three-dimensional representations of the powder diffraction patterns obtained during the decomposition of $(\text{C}_5\text{H}_{14}\text{N}_2)[\text{Cd}(\text{H}_2\text{O})_6](\text{SO}_4)_2$ and $\text{R}-(\text{C}_5\text{H}_{14}\text{N}_2)[\text{Cd}(\text{H}_2\text{O})_6](\text{SO}_4)_2$ under flowing air are shown in Figs. 5, and 6 respectively.

$(\text{C}_5\text{H}_{14}\text{N}_2)[\text{Cd}(\text{H}_2\text{O})_6](\text{SO}_4)_2$. The thermal decomposition of compound **I** takes place in several steps. At the first stage, the compound loses two water molecules in the temperature range $59\text{--}84\text{ }^\circ\text{C}$ (observed weight loss 7.03% ; calculated weight loss 6.99%). The TDXD plot shows that this transformation is accompanied by a change in the initial diffraction pattern. It can be concluded that the $(\text{C}_5\text{H}_{14}\text{N}_2)\text{Cd}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ tetrahydrate compound is a crystalline phase. The second step of the decomposition starts at $86\text{ }^\circ\text{C}$ and corresponds to the full dehydration of the compound by the loss of the remaining water molecule (observed weight loss 20.86% ; calculated weight loss 20.97%), thus leading to the anhydrous phase $(\text{C}_5\text{H}_{14}\text{N}_2)\text{Cd}(\text{SO}_4)_2$, amorphous to X-rays until $220\text{ }^\circ\text{C}$ (Fig. 6, a). At

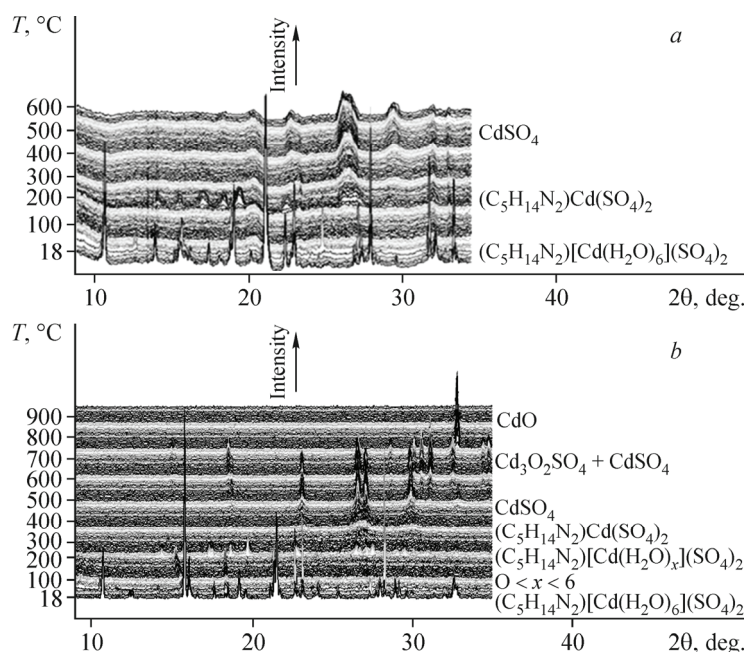


Fig. 6. TDXD plot for the decomposition of compound **I** (a), **II** (b) in air

this temperature, some diffraction lines emerge from the background in the TDXD plot and the TG curve does not show any weight loss. From these observations, it can be concluded that the anhydrous phase crystallizes. The next step corresponds to the decomposition of the anhydrous phase. The departure of amine sulfate $(C_5H_{14}N_2)(SO_4)$ appears on the TG curve by a slow gradual weight loss between 250 °C and 300 °C and more rapidly between 300 °C and 510 °C (observed weight loss 61.53 %; calculated weight loss 61.56 %). It leads to the formation of cadmium sulfate. The last stage corresponds to the transformation of cadmium sulfate into cadmium oxide (observed weight loss 73 %; calculated weight loss 71.78 %).

R-(C₅H₁₄N₂)[Cd(H₂O)₆](SO₄)₂. The TG analysis (Fig. 5, *b*) shows that the dehydration occurs in the temperature range 92—137 °C and corresponds to the gradual departure of the six water molecules (observed and theoretical weight losses 21.02 % and 20.79 %). Fig. 6, *b* shows the three-dimensional representation of the powder diffraction patterns obtained during the decomposition of R-(C₅H₁₄N₂)·[Cd(H₂O)₆](SO₄)₂ under flowing air in the temperature range 18—920 °C. This plot reveals that the precursor is stable until 92 °C and then transforms into the anhydrous phase $(C_5H_{14}N_2)Cd(SO_4)_2$, amorphous to X rays. The anhydrous compound, pointed out with the first plateau observed on the TG curve, is stable between 200 °C and 370 °C. The second transformation starts at 370 °C and corresponds to the decomposition of the amine entity and the partial decomposition of sulfate groups, giving rise to cadmium sulfate. At about 520 °C, the TDXD plot shows that some diffraction lines appear to coexist with CdSO₄. Interrogation of the ICDD Powder Diffraction File [28] revealed that this phase was Cd₃O₂SO₄. The end of the decomposition is marked by the last plateau observed on the TG curve and corresponds to the total decomposition of the CdSO₄ and Cd₃O₂SO₄ mixture product into CdO according to the observed weight loss of 66 % (calculated weight loss 67 %).

CONCLUSIONS

In the present study, the use of chiral amine is an effective means for the preparation of a new non-centrosymmetric organic-inorganic hybrid material. Structural studies show that the two compounds $(C_5H_{14}N_2)[Cd(H_2O)_6](SO_4)_2$ and R-(C₅H₁₄N₂)[Cd(H₂O)₆](SO₄)₂ are built from isolated ions: $[Cd(H_2O)_6]^{2+}$, SO_4^{2-} , and $(C_5H_{14}N_2)^{2+}$ or a single R-(C₅H₁₄N₂)²⁺ enantiomer. The cohesion is ensured by intermolecular OW—H...O and N—H...O hydrogen bonds. Further understanding of the role of enantiomorphically pure amines in determining the chiral structures will be helpful in the synthesis of new non-centrosymmetric functional materials.

Acknowledgements. Grateful thanks are expressed to Dr. Slimane Dahaoui (Université de Nancy I) for the respective assistance in single crystal X-ray diffraction data collection.

REFERENCES

1. Braga D., Desiraju G.R., Miller J.S., Orpen A.G., Price S.L. // *Cryst. Eng. Commun.* – 2002. – **4**. – P. 500.
2. Kirpichnikova L.F., Shuvalov L.A., Ivanov N.R., Prasolov B.N., Andreyev E.F. // *Ferroelectrics.* – 1989. – **96**. – P. 313.
3. Pietraszko A., Lukaszewicz K., Kirpichnikova L.F. // *Polish J. Chem.* – 1993. – **67**. – P. 1877.
4. Kirpichnikova L.F., Andreev E.F., Ivanov N.R., Shuvalov L.A., Varikash V.M. // *Kristallografiya.* – 1988. – **33**. – S. 1437.
5. Holden A.N., Matthias B.T., Merz W.J., Remeika J.P. // *Phys. Rev.* – 1955. – **98**. – P. 546.
6. Galesic N., Jordanovska V.B. // *Acta Crystallogr., Sect. C.* – 1992. – **48**. – P. 256.
7. Fleck M., Bohaty L., Tillmanns E. // *Solid State Sci.* – 2004. – **6**. – P. 469.
8. Pan J.-X., Yang G.-Y., Sun Y.-Q. // *Acta Crystallogr., Sect. E.* – 2003. – **59**. – P. m286.
9. Rujiwatra A., Limtrakul J. // *Acta Crystallogr., Sect. E.* – 2005. – **61**. – P. m1403.
10. Chaabouni S., Kamoun S., Daoud A., Mhiri T. // *Acta Crystallogr., Sect. C.* – 1996. – **52**. – P. 505.
11. Fu Y.-L., Xu Z.-W., Ren J.-L., Ng S.W. // *Acta Crystallogr., Sect. E.* – 2005. – **61**. – P. m1639.
12. Morimoto C.N., Lingafelter E.C. // *Acta Crystallogr., Sect. B.* – 1970. – **26**. – P. 335.
13. Jordanovska V., Aleksovska S., Siftar J. // *J. Thermal Anal.* – 1992. – **38**. – P. 1563.
14. Zhao Y.-J., Li X.-H., Wang S. // *Acta Crystallogr., Sect. E.* – 2005. – **61**. – P. m671.
15. Turel I., Leban I., Zupancic M., Bukovec P., Gruber K. // *Acta Crystallogr., Sect. C.* – 1996. – **52**. – P. 2443.

16. Rademeyer M. // Acta Crystallogr., Sect. E. – 2004. – **60**. – P. m993.
17. Rekik W., Naïli H., Mhiri T., Bataille T. // Acta Crystallogr., Sect. E. – 2005. – **61**. – P. m629.
18. Rekik W., Naïli H., Bataille T., Roisnel T., Mhiri T. // Inorg. Chim. Acta. – 2006. – **359**. – P. 3954.
19. Naïli H., Rekik W., Bataille T., Mhiri T. // Polyhedron. – 2006. – **25**. – P. 3543.
20. Yahyaoui S., Rekik W., Naïli H., Mhiri T., Bataille T. // J. Solid State Chem. – 2007. – **180**. – P. 3560.
21. Oxford diffraction, crysAlis Pro (version 1.171.33.41d). Oxford Diffraction Ltd; 2009.
22. Farrugia L.J. // J. Appl. Crystallogr. – 1999. – **32**. – P. 837.
23. Sheldrick G.M. SHELXS-97 Programs for Crystal Structure Solution, University of Göttingen, Germany, 1997.
24. Sheldrick G.M. SHELXL-97 Programs for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
25. Brandenburg K. Diamond version 2.0 Impact GbR, Bonn Germany, 1998.
26. Plévert J., Auffrédic J.P., Louër M., Louër D. // J. Mater. Sci. – 1989. – **24**. – P. 1913.
27. Hajlaoui F., Naïli H., Yahyaoui S., Norquist A.J., Mhiri T., Bataille T. // J. Organometallic Chem. – 2012. – **700**. – P. 110.
28. International Centre for diffraction Data, Powder Diffraction File, Newtown Square, PA, 2002.