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Synthesis, crystal structures and thermal behaviour of organic—inorganic hybrids incorporating a chiral diamine

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A series of noncentrosymmetric metal sulfates $[R-C_5H_{14}N_2][M^{II}(H_2O)_6](SO_4)_2$ and $[S-C_5H_{14}N_2][M^{II}(H_2O)_6](SO_4)_2$ ($M^{II} = Mn (1, 2)$, Fe (3, 4), Co (5, 6) and Ni (7, 8)) have been synthesized by slow evaporation conditions through the use of enantiomorphically pure sources of either R-2-methylpiperazine (R)-C_5H_{12}N_2 or S-2-methylpiperazine (S)-C_5H_{12}N_2. These materials crystallize in the polar, noncentrosymmetric space group $P2_1$ (No. 4), crystal class 2 (C_2). Isolated $[M^{II}(H_2O)_6]^{2+}$, $[(R)-C_5H_{14}N_2]^{2+}$ or $[(S)-C_5H_{14}N_2]^{2+}$ cations and $(SO_4)^{2-}$ anions linked together via two types of hydrogen bonds, $O_w-H_w\cdots O$ and $N-H\cdots O$, from which supramolecular structures are formed. The use of single enantiomer of either R-2-methylpiperazine or S-2-methylpiperazine precludes inversion symmetry within the crystal lattices and forces crystallization in noncentrosymmetric structures. Compounds **1–8** were characterized using single crystal X-ray diffraction, infrared spectroscopy and thermal analyses. The structural arrangements and the intermolecular interactions such as hydrogen-bonding are discussed.

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1. Introduction

The chemistry of noncentrosymmetric sulfate materials has been the focus of significant interest for several years, owing to the great structural diversity such compounds exhibit [1-9] and the desirable physical properties that such compounds can exhibit, including magnetic, catalysis, fluorescent materials, optical activity and ferroelectric materials [10-13]. As all these properties require crystallographic noncentrosymmetry, several strategies [14-16]are currently employed to deter inversion symmetry in new compounds, including the use of chiral organic amines [17-19].

During the last two decades, specific interest in noncentrosymmetric organic—inorganic materials has been focused on the possibility of combining excellent features from both types of constituents within a single material [20–22]. In addition, a fundamental understanding of how specific connectivities and compositions affect these symmetry dependent properties is critical for the development of new technologies. As such, the strategy employed in this study involves the synthesis of four pairs of polar, noncentrosymmetric hexaaqua-metal sulfates using Mn^{II}, Fe^{II}, Co^{II} or Ni^{II} and enantiomerically pure sources of either R-2-methylpiperazine or S-2-methylpiperazine. The synthesis, crystal structures and the thermal behaviour of these new compounds are discussed in the context of amine symmetry and M^{II} size.

2. Experimental section

2.1. Materials

MnSO₄·H₂O (99%, Merck), FeSO₄·**7**H₂O (99%, Merck), CoSO₄·7H₂O (99%, Merck), NiSO₄· 6H₂O (99%, Merck), (R)-(-)-2-methylpiperazine (99%, Aldrich), (S)-(+)-2-methylpiperazine (99%, Aldrich) and H₂SO₄ (96%, Carlo Erba) were used as received. Deionized water was used in these syntheses.

2.2. Chemical preparation

Single crystals of $[R-C_5H_{14}N_2][Mn(H_2O)_6](SO_4)_2$ (1), $[S-C_5H_{14}N_2][Mn(H_2O)_6](SO_4)_2$ (2), $[R-C_5H_{14}N_2][Fe(H_2O)_6](SO_4)_2$ (3), $[S-C_5H_{14}N_2][Fe(H_2O)_6](SO_4)_2$ (3), $[S-C_5H_{14}N_2][Fe(H_2O)_6](SO_4)_2$ (4), $[R-C_5H_{14}N_2][Co(H_2O)_6](SO_4)_2$ (5), $[S-C_5H_{14}N_2][Co(H_2O)_6](SO_4)_2$ (6), $[R-C_5H_{14}N_2][Ni(H_2O)_6](SO_4)_2$ (7), $[S-C_5H_{14}N_2][Ni(H_2O)_6](SO_4)_2$ (8) were grown from solutions containing 1 mmol



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of the appropriate metal sulfate hydrate $M^{II}SO_4 \cdot nH_2O$, 3 mmol of either R-2-methylpiperazine or S-2-methylpiperazine and 1 mmol of H₂SO₄, in 10 mL of distilled water. Initial solution pHs were between 1.5 and 3 for all reactions. Prismatic crystals were observed after a few days for each reaction. The experimental powder X-ray diffraction patterns for these compounds match well with those simulated from single crystal structure data, indicating that the eight compounds were isolated as single phases.

2.3. Single-crystal X-ray diffraction and structure determination

A suitable single crystal of each compound was carefully selected under a polarizing microscope and glued to a glass fibre mounted on a four-circle Nonius Kappa CCD area-detector diffractometer. Intensity data sets were collected using MoKa radiation through the program COLLECT [23]. Corrections for Lorentzpolarisation effect, peak integration and background determination were carried out with the program DENZO [24]. Frame scaling and unit cell parameters refinement were performed with the program SCALEPACK [23]. Analytical absorption corrections were performed by modeling the crystals faces [25]. The structures analyses were carried out with the monoclinic symmetry, space group $P2_1$ (No. 4), according to the automated search for space group available in WinGX [26]. Transition metal atoms (M^{II}: Mn, Fe, Co and Ni) and sulfur atoms were located using the direct methods with program SHELXS-97 [27]. The oxygen atoms and the organic moieties were found from successive Fourier calculations using SHELXL-97 [28]. The drawings were made with Diamond [29]. The aqua H atoms were located in a difference map and refined with O-H distance restraints of 0.85(1) Å and H-H restraints of 1.39(1) Å. Hydrogen atoms on the organic amines were positioned geometrically and allowed to ride on their parent atom, with C-H and N-H bonds were fixed at 0.97 and 0.90 Å, respectively. Crystallographic data and structural refinements are summarized in Table 1. Selected bond distances are provided in Table 2. Full tables of bond lengths, bond angles and hydrogen bonds are available in CIF format from the CambridgeCrystallographic Data Center (see Supplementary Data).

2.4. Thermal analyses

DTA-TG investigations were performed using a "multi-module 92 SETARAM" analyser operating from room temperature up to 1000 °C at a constant rate of 5 °C min⁻¹ under flowing air.

2.5. Infrared spectroscopy

Infrared measurements were obtained using a Perkin–Elmer FT-IR Spectrum. Samples were diluted with spectroscopic grade KBr and pressed into a pellet. Scans were run over the range of 400-4000 cm⁻¹.

3. Results

Compounds **1–8** are all constructed from octahedrally coordinated transition metal cations coordinated by six water molecules $[M^{II}(H_2O)_6]^{2+}$, isolated sulfate anions $(SO_4)^{2-}$, and either $[(R)-C_5H_{14}N_2]^{2+}$ or $[(S)-C_5H_{14}N_2]^{2+}$ cations, all of which are held together through extensive hydrogen-bonding networks. Mn–O_w bond lengths range by the transition metal with averages of 2.182(2), 2.128(3), 2.096(2) and 2.062(2) Å observed for Mn, Fe, Co and Ni, respectively. Variations in the bond lengths between enantiomeric pairs are small, with deviations of between 0.0153 and 0.125%.

Strong similarities in both structure and composition are observed in compound 1-8. The asymmetric units in each compound consists of one $[R-C_5H_{14}N_2]^{2+}$ or $[S-C_5H_{14}N_2]^{2+}$ cation, two distinct $(SO_4)^{2-}$ anions and one M^{II} $(M = Mn^{2+}, Fe^{2+}, Co^{2+}$ and Ni^{2+}) cation octahedrally coordinated by six water molecules. which is similar to the well known Tutton's salt. $A_2M(H_2O)_6(XO_4)_2$ (A = monovalent cation, M = bivalent cation, X = hexavalentcation) [30–33]. Extensive hydrogen-bonding networks are observed between the $[C_5H_{14}N_2]^{2+}$ and $[M(H_2O)_6]^{2+}$ cations and $(SO_4)^{2-}$ anions in each compound, with the $[C_5H_{14}N_2]^{2+}$ and $[M(H_2O)_6]^{2+}$ cations acting as donor with sulfate acceptors. Similar structures have been observed in other organically templated metal sulfates [1–5,32,34,35]. In addition, all eight compounds crystallize in the noncentrosymmetric space group $P2_1$ (No. 4), in which only 2₁ screw axes are present. However, despite the similarities in compositions in compounds 1-8, distinct differences in threedimensional packing are observed between the Mn^{II} compounds $(1 \text{ and } 2) \text{ and } \text{Fe}^{\text{II}}$ (3 and 4), Ni^{II} $(5 \text{ and } 6) \text{ and } \text{Co}^{\text{II}}$ (7 and 8)analogues. The three-dimensional packing of compounds 1 and 2 are shown in Fig. 1, while packing images of compounds 3-8 are shown in Fig. 2.

The local coordination environment around the $[Mn(H_2O)_6]^{2+}$ cations in compounds **1** and **2** is shown in Fig. 3. The octahedra environment of Mn^{II} cations are not regular, see Table 2, as seen in other isostructural metal sulfates [1,36]. The M–O_w bond distances

Table 1

Crystal data and structure refinement for $[C_5H_{14}N_2][M^{II}(H_2O)_6](SO_4)_2$ (M = Mn, Fe, Co, Ni) (1–8).

Compound	1	2	3	4	5	6	7	8
Empirical formula	C5H26MnN2O14S2	C5H26MnN2O14S2	C5H26FeN2O14S2	C5H26FeN2O14S2	C ₅ H ₂₆ CoN ₂ O ₁₄ S ₂	C ₅ H ₂₆ CoN ₂ O ₁₄ S ₂	C5H26NiN2O14S2	C5H26NiN2O14S2
Formula weight	457.34	457.34	458.25	458.25	461.33	461.33	461.11	461.11
Temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Space group	P2 ₁ (No. 4)	P2 ₁ (No. 4)	P2 ₁ (No. 4)	P2 ₁ (No. 4)				
a (Å)	6.62720(10)	6.6276(2)	10.9270(10)	10.9444(4)	10.8770(3)	10.8707(5)	10.8343(2)	10.8320(10)
b (Å)	11.0877(2)	11.0852(3)	7.8540(10)	7.8602(3)	7.8576(2)	7.8521(3)	7.8405(2)	7.84220(10)
c (Å)	12.6073(2)	12.6084(2)	11.7870(10)	11.8020(4)	11.7446(2)	11.7389(5)	11.6769(3)	11.6735(2)
β (deg)	101.9720(10)	101.974(2)	116.235(10)	116.170(2)	116.2890(10)	116.3950(10)	116.3890(10)	116.3880(10)
V (Å ³)	906.24(3)	906.16(4)	907.36(16)	911.19(6)	899.96(4)	897.55(7)	888.55(4)	888.30(2)
Ζ	2	2	2	2	2	2	2	2
$\rho_{\rm calc}$, (g cm ⁻³)	1.676	1.676	1.677	1.670	1.702	1.725	1.723	1.724
Λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
$\mu (mm^{-1})$	1.027	1.027	1.129	0.0345	1.254	1.272	1.396	1.396
Flack parameter	-0.016(15)	-0.016(17)	-0.04(2)	0.020(9)	-0.015(10)	-0.013(13)	-0.036(15)	-0.001(9)
R_1^a	0.0294	0.0353	0.0388	0.0345	0.0353	0.0309	0.0313	0.0218
WR_2^b	0.0695	0.0955	0.0932	0.0775	0.0864	0.0818	0.0727	0.0551

^a $R_1 = \Sigma ||F_0| - F_c || / \Sigma |F_0|.$

^b $wR_2 = [\Sigma w (F_0^2 - F_c^2)^2 / [\Sigma w (F_0^2)^2]^{1/2}.$

Table 2

Compound	1	2	3	4	5	6	7	8
$M(1) - O_w(1)$	2.1639(2)	2.150(2)	2.110(3)	2.1443(1)	2.1179(2)	2.119(2)	2.054(2)	2.0518(2)
$M(1) - O_w(2)$	2.1880(2)	2.214(2)	2.144(3)	2.1494(1)	2.0693(2)	2.069(2)	2.071(2)	2.0663(1)
$M(1) - O_w(3)$	2.214(2)	2.188(2)	2.128(2)	2.1314(1)	2.0922(1)	2.0972(2)	2.047(3)	2.0732(1)
$M(1) - O_w(4)$	2.1521(2)	2.163(2)	2.131(3)	2.1358(2)	2.1218(2)	2.118(2)	2.072(2)	2.0552(2)
$M(1) - O_w(5)$	2.1790(2)	2.195(2)	2.101(3)	2.1121(1)	2.0778(2)	2.075(2)	2.065(2)	2.0684(1)
$M(1) - O_w(6)$	2.1930(2)	2.182(2)	2.145(3)	2.1019(2)	2.0969(2)	2.0923(2)	2.059(3)	2.0596(1)

Selected bond lengths (Å) in compounds 1-8.

range between 2.152(2) and 2.214(2) Å and between 2.150(2) and 2.214(2) Å for **1** and **2**, respectively. These values are in agreement with the values calculated from the bond valence program VALENCE [37] for a six-fold oxygen coordinated manganese atom, 2.211 Å in compounds **1** and **2**, respectively. The *cis*-O–Mn–O angles range from 86.21(8)° to 95.77(8)° in **1** and between 86.31(9)° to 95.89(9)° in **2**. While the *trans*-O–Mn–O angles deviate from the ideal value by approximately 3° for the two compounds.



Fig. 1. Three-dimensional packing in (a) **1** and (b) **2**. Selected hydrogen-bonding interactions are shown as dashed lines. Purple, yellow, red, blue, black and white represent manganese, sulphur, oxygen, nitrogen, carbon and hydrogen atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Both **1** and **2** contain $[Mn(H_2O)_6]^{2+}$ cations stacked along the [100] and [010] directions and are separated by SO_4^{2-} anions and either $[R-C_5H_{14}N_2]^{2+}$ or $[S-C_5H_{14}N_2]^{2+}$ cations, in **1** and **2**, respectively. Each $[Mn(H_2O)_6]^{2+}$ cation donates hydrogen bonds to six adjacent $(SO_4)^{2-}$ groups, each of which accepts hydrogen bonds from at least two H₂O ligands on the same Mn center. The $[R-C_5H_{14}N_2]^{2+}$ and $[S-C_5H_{14}N_2]^{2+}$ cations also donate hydrogen bonds to nearby $(SO_4)^{2-}$ groups, creating an extended, supramolecular structure. The cation-anion distances range between 2.680(3) and 2.800(3) Å for N-H…O interactions and between 2.666(3) and 2.982(3) Å for O_w -H…O interactions in **1** and **2**, respectively.

The $[Mn(H_2O)_6]^{2+}$ cations are separated from one another through two short, four intermediate and four long distances, with approximate values of 6.627 × 2, 8.486 × 2, 8.577 × 2, 9.493 Å × 4. These Mn···Mn distances are both shorter and longer than those find in others analogous phases containing other diammonium cations, 7.303 Å for diazabicyclo[2.2.2]octaneH₂]²⁺ [36], and 6.544 Å for [piperazineH₂]²⁺ [1]. The trend in these distances mirrors the sizes of the included organic cations. The Flack parameters for these compounds refined to -0.016(15) and -0.016(17), indicating absolute configurations. The enantiomeric structures are inverses of one another and are isostructural with a related copper phase [5].

The presences of the $[R-C_5H_{14}N_2]^{2+}$ and $[S-C_5H_{14}N_2]^{2+}$ cations in compounds **1** and **2** were confirmed using infrared spectroscopy. C–H bands were observed at 1405 and 2955 cm⁻¹, while N–H bands were present 1612 and 3110 cm⁻¹. A S–O band was centered at 1105 cm⁻¹ for compound **1**. Analogous C–H (1409 and 2953 cm⁻¹), N–H (1627 and 3213 cm⁻¹), S–O (1109 cm⁻¹) bands were observed in **2**.

Compounds **3**–**8** are all isostructural, with **3** and **4**, **5** and **6** and **7** and **8** existing as enantiomeric pairs. Each contains a single unique transition metal ($M^{II} =$ Fe, Co and Ni), a single organic cation and two sulfate tetrahedra, all of which lie on general positions. The M^{II} cations exhibit irregular, largely octahedral coordination environments, as shown in Fig. 4. The average $M-O_w$ bond lengths decrease from 2.128(3) to 2.062(2) Å, as one moves from iron to nickel. This reflects a decrease in the ionic radius of nickel versus iron. These $M-O_w$ distances are provided in Table 2. These values agree with calculated distances, based upon bond valence sums, in which the values of the Fe²⁺–Ow, Co²⁺–Ow and Ni²⁺–Ow distances are equal to 2.135 Å, 2.075 Å and 2.047 Å for **3**, **4**, **5**, **6**, **7** and **8**, respectively.

The $[M^{II}(H_2O)_6]^{2+}$ cations stack along the [010] and [001] directions in **3**–**8**, and form inorganic pseudo-layers with the $(SO_4)^{2-}$ in the *bc* plane. See Fig. 2. The $[M(H_2O)_6]^{2+}$ cations in **3**–**8** donate hydrogen bonds to six adjacent $(SO_4)^{2-}$ tetrahedra, as shown in Fig. 4. The geometries of these interactions differ from compounds **1** and **2**, as each $[M(H_2O)_6]^{2+}$ cation is surrounded by one monodentate two bidentate and two tridentate $(SO_4)^{2-}$ anions. As in compounds **1** and **2**, the $[R-C_5H_14N_2]^{2+}$ and $[S-C_5H_14N_2]^{2+}$ cations also donate hydrogen bonds to neighboring $(SO_4)^{2-}$ tetrahedra. The N–H…O distances range between 2.733(3) and 2.925(4) Å, while the O_w –H…O distances range between 2.664(3) and



Fig. 2. Three-dimensional packing in (a) for **3**, **5** and **7** and (b) **4**, **6** and **8**. Selected hydrogen-bonding interactions are shown as dashed lines. Green, yellow, red, blue, black and white represent metal (M^{II} = Fe, Co and Ni), sulphur, oxygen, nitrogen, carbon and hydrogen atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.834(2) Å. These values agree with those currently observed in inorganic salts containing the organic groups used in this work [5,7,38]. One again, extended, supramolecular structures are constructed from these molecular units by hydrogen-bonding.



S1 S2 M^{II} S1 S2 S2 S1

\$2

Fig. 3. Neighbouring sulfates in the environment of $[Mn(H_2O)_6]$ in 1 and 2. Purple, yellow, red and white represent manganese, sulphur, oxygen and hydrogen atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. Neighbouring sulfates in the environment of $[M^{II}(H_2O)_6]$ in **3**, **4**, **5**, **6**, **7** and **8**. Green, yellow, red and white represent manganese, sulphur, oxygen and hydrogen atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Each $[M^{II}(H_2O)_6]^{2+}$ octahedron is separated from six other $[M^{II}(H_2O)_6]^{2+}$ cations through two short, two intermediate and two long distances. The average values of these distances are 7.035(3), 7.091(3) and 7.851(3) Å. The Flack parameters are refined to -0.04(2), 0.020(9), -0.015(10), -0.013(13), -0.036(15) and -0.001(9) for **3–8**, respectively.

The presence of $[R-C_5H_{14}N_2]^{2+}$ and $[S-C_5H_{14}N_2]^{2+}$ cations was confirmed using infrared spectroscopy with average positions of 1453 and 2849 cm⁻¹ for C–H bands, 3155 cm⁻¹ for N–H and O–H bands and 1113 cm⁻¹ for S–O bands.

The thermal properties of compounds 1-8 were probed using thermogravimetric (TG) and differential thermal analyses (DTA). Data were collected on one compound in each enantiomeric pair was studied, as little or no variability is expected between analogous compounds. See Fig. 5.

 $[S-C_5H_{14}N_2][Mn(H_2O_6](SO_4)_2$ (2). Fig. 5a shows the TG-DTA curves obtained during the decomposition of compound 2 in the temperature range 25–1000 °C. The TG curve shows that the first weight loss of 6.734% starts at about 90 °C and corresponds to the departure of 1.75 · H₂O molecules (calculated weight loss, 6.8887%). The second weight loss, observed on the TG curve between 128 and 203 °C, is attributed to departure of the remaining water molecules to form the anhydrous compound $[S-C_5H_{14}N_2]Mn(SO_4)_2$. These phenomena are accompanied by two endothermic peaks on the DTA curve, with a maximum at 211 °C. The amine decomposition together with loss of one sulfate group $([S-C_5H_{14}N_2]\cdot SO_4)$ gives rise to the manganese sulfate at $\sim 401 \,^{\circ}\text{C}$ (observed weight loss, 42.932%; theoretical, 43.308%). This phenomenon is accompanied by two endothermic peaks on the DTA curve, at 334 °C and 370 °C, respectively. The last step takes place between 410 and 910 °C and corresponds to the decomposition of MnSO₄ to Mn₂O₃.

This transformation is accompanied by three peaks on the DTA curve, i. e. two exothermic peaks observed at 416 and 525 $^\circ$ C and one endothermic peak at 871 $^\circ$ C.

 $[S-C_5H_{14}N_2][Fe(H_2O)_6](SO_4)_2$ (4). The results of TG-DTA measurements for [S-C₅H₁₄N₂][Fe(H₂O)₆](SO₄)₂ are illustrated in Fig. 5b. The TG curve shows that the compound is stable to approximately 105 °C. The first transformation occurs in the temperature range 105–145 °C. The weight loss of 5.834% is in agreement with the departure of 1.5 · H₂O molecules (calculated weight loss, 5.892%). This phenomenon is accompanied with an endothermic peak on the DTA curve, at 125 °C. The second weight loss of 17.532%, observed between 145 and 215 °C, (endothermic peak at 171 °C on the DTA curve) corresponds to the departure of the last water molecules (calculated weight loss, 17.676%), leading to the anhydrous phase [S-C₅H₁₄N₂]Fe(SO₄)₂. The decomposition of the anhydrous phase starts at about 280 °C and leads to crystalline $Fe_2(SO_4)_3$ (PDF N° 01-073-0148). This result is evidenced by a weight loss of 48.033% (calculated weight loss, 47.771%). The decomposition of Fe₂(SO₄)₃ leads to stage observed between 500 and 670 °C, in agreement with the global formula Fe₂O₂(SO₄). These phenomena are accompanied by several endothermic peaks on the DTA curve between 300 and 690 °C). The last transformation starts at about 700 °C and corresponds to the formation of iron oxide Fe₂O₃.

 $[S-C_5H_{14}N_2][Co(H_2O)_6](SO_4)_2$ (6). The TG-DTA curves of $[S-C_5H_{14}N_2][Co(H_2O)_6](SO_4)_2$, between room temperature and 1000 °C, are shown in Fig. 5c. According to the TG curve the dehydration of the precursor occurs in two stages. First, an immediate weight loss of 3.866% observed at 139 °C corresponds to the departure of only one water molecule (calculated weight loss, 3.901%). The second stage of the dehydration takes place between



Fig. 5. DTA-TG curves of thermal decomposition of $[S-C_5H_{14}N_2][M^{II}(H_2O)_6](SO_4)_2$, $M^{II} = Mn$ (2), Fe (4), Co (6) and Ni (8).

154 and 219 °C, and corresponds to the loss of the remaining water molecules (observed weight loss, 19.735%; calculated weight loss, 19.508%) giving rise to the anhydrous compound $[S-C_5H_{14}N_2]$ Co(SO₄)₂. These phenomena are accompanied by two endothermic peaks on the DTA curve, maximum at 180 °C. The next transformation starts at ~295 °C and corresponds to the decomposition of the amine entity and partial decomposition of the sulfate groups leading to the CoSO₄ phase (observed weight loss, 41.988%; calculated weight loss, 42.933%). This transformation is accompanied, on the DTA curve, by two endothermic peaks and one exothermic peak observed at 326 °C, 365 °C and 387 °C, respectively. The last stage corresponds to the decomposition of the cobalt sulfate, starting at about 780 °C, and gives rise to the cobalt oxide Co₃O₄.

 $[S-C_5H_{14}N_2][Ni(H_2O)_6](SO_4)_2$ (8). Coupled TG-DTA curves for compound 8 are shown in Fig. 5d. The first two weight losses of 9.723 and 13.594, observed at 155 and 223 °C, are accompanied by to endothermic peaks. They are ascribed to the release of $2.5 \cdot H_2O$ (calculated weight loss, 9.759%) and $3.5H_2O$ (calculated weight loss, 13.663%) molecules found in the structure. The degradation of the organic part with one sulfate group occurs between 277 and 485 °C (observed weight loss, 42.654%, calculated weight loss, 42.955%). This transformation is evidenced by high exothermic peak observed on DTA, in the range 284–400 °C. Above this temperature NiSO₄ is formed. The last stage corresponds to the decomposition of nickel sulfate to NiO, starting at about 548 °C.

4. Discussion

Compounds **1–8** were obtained by slow evaporation of solutions containing either R-2-methylpiperazine or S-2-methylpiperazine, in an effort to force crystallization in a noncentrosymmetric space group. This technique has been used with success in a variety of systems [5,17,38]. The role of 2-methylpiperazinediium cations in these reactions is three-fold. First, they assume the well-established role of protonated amines in which they help achieve charge neutrality with the other charged inorganic moieties.

Second, they act as hydrogen bond donors and participate in the supramolecular extended structures of compounds **1–8**. Third, the chirality of $[R-C_5H_{14}N_2]^{2+}$ and $[S-C_5H_{14}N_2]^{2+}$ cations is reflected in the extended symmetry of the resulting compound. The presence of such cations precludes the cancellation of the local distortions via formation of inversion centers because inversion symmetry would require the presence of both [R-C5H14N2]2+ and [S- $C_5H_{14}N_2$]²⁺ cations in the structures. 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 structures, they can never be related to one another through centers of inversion because the required $[S-C_5H_{14}N_2]^{2+}$ cations are absent. In addition, the mild conditions used in the experiments described above preclude inversion of the amine chiralities. Therefore the formation of any inversion centers is prohibited and the space group of these materials is constrained to be noncentrosymmetric, as shown in Fig. 6. The chirality of the $[R-C_5H_{14}N_2]^{2+}$ and $[S-C_5H_{14}N_2]^{2+}$ cations is reflected in the enan-tiomorphic and polar crystal class of these compounds, 2 (C_2).

The possibility of pseudosymmetry in compounds **1–8** was investigated. The organic cations were removed from the crystallographic models, and PLATON [39] was used to probe for missing symmetry. The ADDSYM command suggests the possibility of a missing additional symmetry leading to the $P2_1/c$ space group (No. 14), with inversion symmetry directly between the metal centers. The position of the methyl groups on the 2-methylpiperazinediium cations rings violates the pseudosymmetry found by PLATON, does not recognize the contribution of a single –CH₃ group over the rest of the structure. In addition, the systematic absences are not correct for $P2_1/c$. Specifically, the expected l = 2n+1 absences in hol reflections are not present. These results confirm the crystallographic noncentrosymmetry in compounds **1–8**.

Despite the clear similarities between compounds **1–8**, distinct differences exist. Notably, the local hydrogen-bonding around the $[M(H_2O)_6]^{2+}$ centers differs between structure types. In compounds **1** and **2**, six $(SO_4)^{2-}$ anions coordinate to each $[Mn(H_2O)_6]^{2+}$ cation



Fig. 6. Cation structures in 1–8. The symmetry element is shown. Blue and black represent nitrogen and carbon atoms, respectively. Transition metal, oxygen, sulphur and hydrogen atoms have been removed for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in a bidentate fashion. In contrast, the six $(SO_4)^{2-}$ anions that coordinate to each $[M(H_2O)_6]^{2+}$ (M = Fe, Ni, Co) cation in compounds **3–8** include two $(SO_4)^{2-}$ anions that accept just a single hydrogen bond from the cation. See Figs. 3 and 4. This change in the hydrogen-bonding structure affects the threedimensional packings of the compounds. Indeed, Compounds 1 and **2** adopt a distinctly different packing arrangement with respect to compounds **3–8**. See Figs. 1 and 2. Both differences can be attributed to a gradual decrease in the ionic radius of the metal as one move from Mn to Ni. Compounds 1 and 2 contain the largest transition metal cations, Mn^{II}, from which the longest M–O_w bonds are observed, see Table 2. In these compounds, six $(SO_4)^{2-}$ anions are able to fit around each cation. As the ionic radius of the metal centers decrease in Fe, Co and Ni, a corresponding decrease in $M-O_w$ bond lengths is observed. As the $[M(H_2O)_6]^{2+}$ cations become smaller, the six $(SO_4)^{2-}$ anions are no longer able to adopt the same hydrogen-bonding structure and a shift in connectivity is observed. This correlation between $[M(H_2O)_6]^{2+}$ cation size and three-dimensional packing is also manifested in the distances between neighboring cations. While two short Mn…Mn distances of 6.627(3) Å are observed in both compounds **1** and **2**, the other eight Mn...Mn distances are significantly larger, at distances of approximately 8.5 or 9.5 Å. In contrast, the $[M(H_2O)_6]^{2+}$ (M = Fe, Co, Ni) exhibit both fewer, and, on average shorter M…M distances. Each $[M(H_2O)_6]^{2+}$ (M = Fe, Co, Ni) cation has six nearest neighbors at distances of approximately 7.03, 7.09 and 7.85 Å. This clearly indicates the role of cation size in the determination of the supramolecular structure.

In compounds **1–8**, the S–O distances range from 1.462(2) to 1.481(2) Å with an average of 1.471(1) Å. Slight differences in the S-O bond lengths together with the slight deformation of the anions reflect the how the ionic radii of the M^{II} cations affects the supramolecular structures. The chemical formula of these materials resembles that of the Tutton's salts [30-33]. Indeed, although replacing monovalent metals by divalent organic cations, there are strong similarities between the two families, with difference resulting from the size, shape and charge of the amino group involved in the present structures.

The thermogravimetric analysis (DTA-TG) curves for compounds 1-8 show that there are similar changes in the decomposition of precursors with somewhat small differences, which could be associated with the structural variations. Specifically, the dehydration temperatures are affected by both the strengths and topologies of the extensive hydrogen-bonding structures.

5. Conclusion

The use of chiral amines is an effective method for the preparation of new noncentrosymmetric organic-inorganic hybrid materials. These directed syntheses resulted in the formation of eight noncentrosymmetric metal sulfate compounds using a chiral source of 2-methylpiperazine, either R-2-methylpiperazine or S-2methylpiperazine. The crystal structures consist of isolated entities linked by hydrogen bonds only, namely, two anionic sulfate groups, a chiral source of $[C_5H_{14}N_2]^{2+}$ and bivalent transition metal surrounded by six water molecules $[M^{II}(H_2O)_6]$, with $(M^{II} = Mn^{2+},$ Fe^{2+} , Co^{2+} and Ni^{2+}) playing the role of cations. The hydrogenbonding plays an important role in the formation of this kind of materials. The facile formation of high quality noncentrosymmetric single crystals makes them potential candidates for future practical applications. The thermal behaviour of the precursors, as studies by TG-DTA, 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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Appendix A. Supplementary material

CCDC 823970-823977; contain the supplementary crystallographic data for tables of hydrogen bond details for all compounds. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_ request/cif.

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