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DOI: 10.1002/zaac.201300171

Synthesis and Characterization of Pillared Metal Sulfates (Diamine)MeSO₄, (Me = Zn, Cd)

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Keywords: Layered compounds; X-ray diffraction; Electron microscopy; Organic-inorganic hybrid composites

Abstract. Hybrid organic-inorganic materials of the type (diamine)-MeSO₄ (Me = Cd, Zn) [diamine = *p*-xylylenediamine (PXDA) or *m*xylylenediamine (MXDA)] have not been described in the literature to date. Four compounds of this type, namely, (MXDA)ZnSO₄ (1), (MXDA)CdSO₄ (2), (PXDA)ZnSO₄ (3), and (PXDA)CdSO₄ (4), were synthesized by solvothermal methods. Since all compounds crystallized as very fine powders, crystal structure studies were performed using powder diffraction methods. All compounds crystallize in the orthorhombic crystal system and the cell parameters are: *a* = 9.8004(4) Å, *b* = 10.7829(3) Å, *c* = 4.88473(19) Å for 1; 9.8824(10),

Introduction

As has been recently found, even simple inorganic salts (e.g. sulfates) create interesting layered or linear structures under solvothermal conditions in the presence of amines. A number of compounds, which belong to this class, have been described in the literature.^[1–4] These materials are interesting because of their potential applications in catalysis, as sorption or ion exchange materials, etc.

While studying the MeSO₄-diamine system (Me = Zn or Cd), a new group of compounds was obtained. These materials with the formula (diamine)MeSO₄ formed using solvothermal methods. Their diffraction patterns and unit cell parameters are similar to typical MeQ(amine)_{1/2} compounds (Q = S, Se, Te).^[5–10] Because these new materials crystallize as very fine, greasy powders, the formation of a novel type of complexes was proved by X-ray powder diffraction data analysis.

The new compounds feature a unique structural architecture. They are built of parallel monolayers consisted of Zn^{2+} or Cd^{2+} and sulfate anions. Amines, MXDA, or PXDA, are connecting adjacent layers, by the covalent bonds with metal atoms from the 2D inorganic slabs –Me–SO₄–, forming a 3D network.

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11.0907(7), 4.9663(5) Å for **2**; 9.8496(3), 21.2419(5), 4.89556(17) Å for **3**; and 10.1136(4), 21.6625(3), 4.9562(2) Å for **4**. The compounds with MXDA as a linker, crystallize in the space group $P2_1ma$, those with PXDA in *Pnma*. These hybrid materials are built of inorganic monolayers [–Me–(SO₄)–] joined by organic linkers created by diamines (PXDA or MXDA). Me metal ions and SO₄^{2–} anions form layers with a honeycomb structure. In addition to crystal structure, chemical analyses and SEM investigations were performed. Thermal stability of the compounds was also investigated using TG-DSC methods and XRD as a function of temperature.

The obtained materials were the subject of wide-range research aimed at their full structural characterization based on powder diffraction data. Their morphology and thermal stability were also investigated.

Results and Discussion

X-ray Powder Diffraction

Since all compounds crystallize as very fine powders, structural investigations were performed using X-ray powder diffraction (XRPD). Firstly, XRPD data were recorded using a diffractometer working in Bragg-Brentano geometry, if further studies indicate the presence of texture, for purpose of structural studies, additional measurements were performed in DSH geometry (samples loaded into capillaries).

XRPD patterns for (MXDA)ZnSO₄ (1) and (MXDA)CdSO₄ (2) were recorded with a diffractometer working in Debye-Scherrer geometry (capillary size 2r = 0.7 mm). Cell parameters were found using the WinPLOTR program package.^[11] space group was obtained with the program The EXPO2009,^[12] which calculates normalized structure factors, prepares intensity statistics; subsequently the program suggests space groups ranked in the order of their probability. Positions of heavy atoms and atoms of organic parts were found using direct methods and global optimization techniques. Calculations were performed using the EXPO2009 and FOX^[12,13] programs. The structure models were refined with the Rietveld method (JANA2006 program^[14]). Using LeBail fitting, the background, zero shift, unit cell, and profile parameters, including asymmetry, were refined one by one. Afterwards, the

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positions of atoms were fitted. For all atoms isotropic thermal displacement parameters were applied. The absorption correction was introduced, assuming a cylindrical sample shape. Geometric restraints on bond lengths and angles and constraints on atomic displacement parameters were used to improve the stability of the refinement. Figure 1 and Figure 2 show the Rietveld plots of compounds 1 and 2.



Figure 1. Rietveld refinement plots for (MXDA)ZnSO₄ (1).



Figure 2. Rietveld refinement plots for (MXDA)CdSO₄ (2).

Compounds 1 and 2 with MXDA as ligand crystallize in the space group $P2_1ma$. Selected crystallographic data of (MXDA)MeSO₄ are summarized in Table 1, selected interatomic distances in Table 2 and Table 3, respectively.

Table 1. Crystallographic data for $(MXDA)ZnSO_4$ (1) and $(MXDA)CdSO_4$ (2).

Empirical formula	$ZnSO_{4} \cdot C_{8}H_{12}N_{2}$ (1)	$CdSO_4 \cdot C_8 H_{12} N_2$ (2)
Formula weight /g·mol ⁻¹	297.65	344.57
Crystal system	orthorhombic	orthorhombic
Space group	$P2_1ma$	$P2_1ma$
a /Å	9.8004(4)	9.8645(9)
b /Å	10.7829(3)	11.0854(6)
c /Å	4.88473(2)	4.9572(4)
V /Å ³	516.21(3)	542.08(7)
R _p	6.9	7.2
$\hat{R_{wp}}$	9.2	9.2
R _F	6.1	6.8
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Table 2. Selected interatomic distances of compound 1.

Atom 1	Atom 2 (symm. code)	d /Å	
Zn1	01	2.111(16)	
Zn1	O2	2.199(15)	
Zn1	N1	2.203(12)	
Zn1	N1 $(x, -y+2, z)$	2.203(12)	
Zn1	O3	2.427(9)	
Zn1	O3 $(x, -y+2, z)$	2.427(9)	

Table 3. Selected interatomic distances of compound 2.

		-	
Atom 1	Atom 2 (symm. code)	d /Å	
Cd1	01	2.400(9)	
Cd1	O2	2.400(5)	
Cd1	N1	2.275(2)	
Cd1	N1 $(x, -y+2, z)$	2.275(2)	
Cd1	O3(x, y, z+1)	2.400(1)	
Cd1	O3 $(x, -y+2, z+1)$	2.400(1)	

Diffraction patterns of (PXDA)ZnSO₄ (**3**) and (PXDA)-CdSO₄ (**4**) were recorded using a diffractometer working in Bragg-Brentano geometry. The diffraction patterns of **3** and **4** were indexed as in cases **1** and **2** using the WinPLOTR program package. The compounds with PXDA as ligand crystallize in the space group *Pnma*. All steps in the refining procedure were essentially the same as in the case of compounds **1** and **2**. In these cases, only small preferred orientation was detected and taken into account in Rietveld refinement (March-Dollase texture function, direction [010]). The Rietveld plots for (PXDA)ZnSO₄ and (PXDA)CdSO₄ are shown in Figure 3 and Figure 4, respectively.



Figure 3. Rietveld refinement plots for (PXDA)ZnSO₄ (3).

Basic crystallographic data of $(PXDA)MeSO_4$ are summarized in Table 4, selected interatomic distances in Table 5 and Table 6.

Structure Description

Compounds 1–4 crystallize in the orthorhombic crystal system. They have three-dimensional structures built of $-Me-(SO_4)-$ layers, connected by diamines (MXDA or PXDA) through covalent bonds with the metal atoms (Me)

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Figure 4. Rietveld refinement plots for (PXDA)CdSO₄ (4).

Table 4. Crystallographic data for $(PXDA)ZnSO_4$ (3) and $(PXDA)CdSO_4$ (4).

Empirical formula	$ZnSO_4 \cdot C_8 H_{12}N_2$ (3)	$CdSO_4 \cdot C_8H_{12}N_2$ (4)
Formula weight /g•mol ⁻¹	297.65	344.57
Crystal system	orthorhombic	orthorhombi
Space group	Pnma	Pnma
a /Å	9.8496(3)	10.1136(4)
b /Å	21.2419(5)	21.6625(3)
c /Å	4.8956(2)	4.9562(2)
V/Å ³	1024.27(5)	1086.83(7)
R _p	6.8	9.6
R _{wp}	9.1	12.3
R _F	5.1	6.5
Color	white	white

 Table 5. Selected interatomic distances of compound 3.

Atom 1	Atom 2 (symm. code)	d /Å
Zn1	01	2.250(8)
Zn1	O2	2.399(4)
Zn1	O2 $(x-1/2, y, -z-1/2)$	2.399(4)
Zn1	N1	2.112(6)
Zn1	N1 $(x, -y+1/2, z)$	2.112(6)
Zn1	03	2.263(9)

Table 6. Selected interatomic distances of compound 4.

Atom 1	Atom 2 (symm. code)	d /Å
Cd1	01	2.432(15)
Cd1	O2	2.469(10)
Cd1	O2 $(x-1/2, y, -z-1/2)$	2.469(10)
Cd1	N1	2.368(14)
Cd1	N1 $(x, -y+1/2, z)$	2.368(14)
Cd1	03	2.414(17)

from the layer. Compounds 1, 2 and 3, 4 are isostructural, and all compounds show significant similarities. This is demonstrated clearly in Figure 5A and B, where basic structures' fragments are presented.



Figure 5. Basic fragments of structure: (A) (MXDA)MeSO₄ (1, 2), (B) (PXDA)MeSO₄ (3, 4).

In each compound, the atoms Me (Zn, Cd) are surrounded by six ligands, two nitrogen atoms (in *cis* position to each other) and four oxygen atoms, forming a distorted octahedron. The sulfur atoms are tetrahedrally coordinated by oxygen atoms.

The $-Me-SO_4$ - layers in all compounds are essentially similar; they are flat as being located exactly on the crystallographic mirror plane. A $-Cd-SO_4$ - layer is shown in Figure 6A. Interestingly, from the viewpoint of topology, the layers $-Me-SO_4$ - are similar to the layers in $MeQ(amine)_{1/2}$ compounds.^[5] In both cases, there exist fused six-membered rings, their vertices are alternately occupied by the three Me atoms and by three anions (SO_4^{2-} in our studies). Each vertex is common to three rings. Inorganic layers can be described by topological index 6³. However, in the presented cases, each Me atom is coordinated by two amine groups; this results in different stoichiometry, octahedrally coordinated central metal atoms can be more easily accommodated in flat $Me-SO_4$ layers, whereas in $MeQ(amine)_{1/2}$ such layers are puckered.

The use of different amines determines the space group, in which these type of compounds [(amine)MeSO₄] crystallize. All compounds with MXDA as an organic linker crystallize in the space group $P2_1ma$, whereas compounds with PXDA crystallize in *Pnma*. This could be related to the arrangement of the linking fragment and the preference of terminal –CH₂– NH₂ groups to adopt *cis* or *trans* conformation (mutual orientation). Such a phenomenon was observed in the case of MeQ(diamine)_{1/2},^[5] where two different space groups according to an even or odd number of carbon atoms in aliphatic diamine NH₂–(CH2)_n–NH₂ were found. Figure 6B and C show layered structures, the alignment of the diamines, and linking fragments in the structures of (MXDA)ZnSO₄ and (PXDA)ZnSO₄.

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Figure 7. The orthogonal alignment of MXDA molecules (black bars represent aromatic rings) seen through $-Me-SO_4-$ layers.



Figure 6. Structure of (amine)MeSO₄, (A) layer of –Zn–SO₄–. View along layers: (B) (MXDA)ZnSO₄, (C) (PXDA)ZnSO₄.

In all structures the diamine rings are perpendicular to each other. The arrangement of amines is shown in Figure 7. Moreover, in compounds 1 and 2 the MXDA molecules are arranged orthogonally to $-Me-SO_4$ - layers (lying exactly on the plane of symmetry *m*), in contrast to compounds 3 and 4 (Figure 8). In these compounds the LS planes of diamines are perpendicular, but their long axes are arranged obliquely to the $-Me-SO_4$ - layers. This is the result of the different mutual positions of $-CH_2$ -NH₂ groups in both amines (*p*-xylylenediamine and *m*-xylylenediamine).



Figure 8. The alignment of amines between inorganic layers in (A) (1, 2) (amine – MXDA), (B) (3, 4) (amine – PXDA).

The materials obtained are similar to reported recently reported open-framework sulfates.^[1-4] Nevertheless, some differences can be observed. The most important is the way of connection of the organic components. In case of the new compounds, the amine molecules are linked directly by covalent bonds to the metal atoms, whereas in the open-framework compounds^[1-4] ammonium fragments are connected by ionic forces and hydrogen bonds. Also, only the new compounds

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were obtained as three-dimensional hybrid inorganic-organic materials. An interesting representative of such a kind of open-framework compound is $[H_3N(CH_2)_3NH_3][Cd_2(H_2O)_2-(SO_4)_3]$.^[4] It is a lamellar material with a 4⁴ topology of the Cd–SO₄– layer. In this case fused rings in the layer are built of two octahedrally coordinated cadmium atoms and two sulfate groups, whereas in our compounds three metal atoms and three sulfate groups are involved.

Chemical Analyses

The obtained compounds provided good diffraction images, but they were greasy materials, difficult to properly wash and drain. The chemical analyses are in general agreement with the results of the structure solution, but indicate also that samples (particularly MXDA complexes) are significantly contaminated by amorphous or liquid admixtures.

 $(PXDA)ZnSO_4$: ZnSO₄C₈H₁₂N₂ (297.65 g·mol⁻¹): C 33.92 (calcd. 32.28), H 4.22 (4.06), N 9.61 (9.41), S 9.79 (10.77)%. This result indicates a small excess of amine.

(MXDA)ZnSO₄: $ZnSO_4C_8H_{12}N_2$ (297.65 g·mol⁻¹): C 38.95 (calcd. 32.28), H 4.16 (4.06), N 9.63 (9.41), S 10.70 (10.77)%. In this case the chemical analysis also indicates an excess of amine, but in larger quantities.

 $(PXDA)CdSO_4: CdSO_4N_2H_{12}C_8 (344.57 \text{ g} \cdot \text{mol}^{-1}): C 29.88 (calcd. 27.88), H 3.59 (3.48), N 8.29 (8.12), S 9.02 (9.31)%. These slight differences can be explained by an excess of amine.$

(MXDA)CdSO₄: CdSO₄N₂H₁₂C₈ (344.57 g·mol⁻¹): C 24.31 (calcd. 27.88), H 3.15 (3.48), N 7.07 (8.12), S 10.03 (9.31)%. That indicates the presence of impurities (synthesis substrates).

SEM

(MXDA) $ZnSO_4$ (1): SEM images of 1 (Figure 9A) show that the obtained crystallites share uniform morphology. Dominant are thin plates (thickness from 10 to 50 nm) with very uneven surfaces. The crystallites are complex aggregates.

(MXDA)CdSO₄ (2): SEM images show aggregates of plate-like crystallites with irregular edges and heterogeneous surfaces. Their shape and thickness vary greatly (from 0.1 μ m to 1 μ m). The crystallites are shown in Figure 9B.

(PXDA)ZnSO₄ (3): The crystallites are rectangular and of different sizes, with a thickness of about 0.1 μ m. The edges of the crystallites are regular and the surfaces are homogeneous (Figure 9C).

(**PXDA**)**CdSO**₄ (4): SEM images show that the crystallites are of different sizes, from 0.1 μ m to several μ m, and with thicknesses of about 1 μ m or less. The surfaces are quite homogeneous and the edges are rather regular (Figure 9D).

TG-DSC and XRPD versus Temperature

Using TG-DSC, thermal stability of the compounds was investigated. For all compounds, the results obtained through TG-DSC exhibit multi-step weight losses.



Figure 9. SEM images of compounds (amine)MeSO₄: (A) (MXDA)-ZnSO₄ (B) (MXDA)CdSO₄ (C) (PXDA)ZnSO₄ (D) (PXDA)CdSO₄.

(MXDA)ZnSO₄: Three weight loss steps, 21.04 %, 14.79 %, and 22.81 % (in the range 210 °C to 520 °C), correspond to releases of amine. It is also possible that in the last mass loss (22.81 %), two combined effects occur: the release of amine and the first step of decomposition of ZnSO₄ to ZnO. Total loss of weight is 81.64 % and the product is ZnO. TG-DSC results of (MXDA)ZnSO₄ are shown in Figure 10.



Figure 10. TG-DSC analysis of (MXDA)ZnSO₄.

(MXDA)CdSO₄: The weight loss steps (16.55%, 16.96%, 3%) can be explained by the sequential release of two nearly equal amounts of amines. The total weight loss is 38.72% and the final product is CdSO₄. TG-DSC results of (MXDA)-CdSO₄ are shown in Figure 11.

(**PXDA**)**ZnSO**₄: The weight loss steps around 300 °C to 510 °C, connected with the first two exothermic peaks, correspond to the loss of amines pertaining to (PXDA)ZnSO₄ as a result of its decomposition 48.96 (calcd. 46%). The last exothermic peak (at 559 °C) is a consequence of zinc sulfate decomposition with release of SO₃ (19.00% loss of mass). The total mass loss in is between 72–74% (cal. 73%) and the final product is ZnO. TG-DSC results of (PXDA)ZnSO₄ are shown in Figure 12.

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Figure 12. TG-DSC analysis of (PXDA)ZnSO4.

(**PXDA**)**CdSO**₄: The two weight loss steps (20.33% and 21.09%) in the range 300 °C to 650 °C correspond to the complete loss of amine belonging to the (PXDA)CdSO₄ (calcd. 39.5%). In turn, the two exothermic peaks that appear at 800 and 854 °C may be caused by the melting of some products of thermal decomposition, such as CdSO₄. The final product of the TG-DSC analysis is cadmium sulfate (CdSO₄). TG-DSC results of (PXDA)CdSO₄ are shown in Figure 13.





Summing up the TG-DSC experiments, the obtained compounds are stable to about 300 °C. Next, two-step removal of

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amine is observed. Nearly equal amounts of released amine suggest the formation of intermediate compounds with the formula $(diamine)_{1/2}MeSO_4$. In the case of zinc compounds 1 and 3, final decomposition leads to formation of ZnO (ca. 670 °C), whereas CdSO₄ is formed (500–550 °C) in the case of cadmium-amine sulfates 2 and 4.

The TG-DSC results were verified by temperature-dependent XRPD measurements. (PXDA)ZnSO4 and (PXDA)CdSO4 were investigated in this way (see Figure 14 and Figure 15). High temperature XRPD data indicate that the samples are stable until ca. 300 °C and proved the type of final products of thermal decomposition (ZnO, CdSO₄). They also indicate that the intermediate product formed with one amine per formal molecule (ca. 300-400 °C) is different from the initial product. The cell parameters of those intermediate products are: a = b = 10.074(4) Å, c = 21.864(8) Å for (PXDA)CdSO₄ and a = b = 9.961(5) Å, c = 21.181(9) Å for (PXDA)ZnSO₄. It seems that the initial orthorhombic structure with formula (PXDA)Me]SO₄ recrystallized to a tetragonal material with the formula (PXDA)_{1/2}MeSO₄. It was tried to isolate and examine the intermediate phase. However, our efforts have yielded in complex two-phase mixtures, leading to difficulties in determination of the space group, which prevented structural studies. The temperature-dependent XRPD patterns are shown in Figure 14 and Figure 15.



Figure 14. XRPD pattern vs. temp. for (PXDA)CdSO₄.



Figure 15. XRPD pattern vs. temp. for (PXDA)ZnSO₄.

Conclusions

Four new hybrid compounds (diamine)MeSO₄, (Me = Cd, Zn) were synthesized under solvothermal conditions (2 d, 160 °C). All materials crystallize in the orthorhombic crystal system: (PXDA)MeSO₄ in space group *Pnma* and

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(MXDA)MeSO₄ in $P2_1ma$. The cell parameters for compounds with the same amine but varied metal atoms are slightly different because of the different zinc and cadmium ionic radii. These three-dimensional hybrid materials are built of infinite parallel layers –Me–(SO₄)–, connected by diamines (MXDA, PXDA) forming coordination bonds with metal ions. SEM images showed that the obtained compounds are aggregates of plate-shaped crystals. TG-DSC analyses showed that all compounds are stable to about 300 °C, after which a two-step release of amine is observed. In the case of (MXDA)ZnSO₄ and (PXDA)ZnSO₄ the final product is ZnO, whereas for (PXDA)CdSO₄ and (MXDA)CdSO₄ the final product is CdSO₄. Although they comprise of more complicated building blocks, the inorganic layers in MeQ(amine)_{1/2} and (amine)MeSO₄ are similar from a topological point of view.

Experimental Section

Materials: Zinc sulfate hydrate ($ZnSO_4$ ·7H₂O) and cadmium sulfate hydrate (CdSO₄·8H₂O) were purchased from Fabryka Odczynników Chemicznych Gliwice (POCH); *p*-xylylenediamine and *m*-xylylenediamine were purchased from Sigma-Aldrich. All chemicals were used as received without further purification.

Synthesis of (MXDA)MeSO₄ (1, 2): (MXDA)ZnSO₄ was obtained by solvothermal route using ZnSO₄·7H₂O (0.01 mol) and *m*-xylylenediamine (MXDA) (0.01 mol). Zinc sulfate hydrate was thoroughly ground and placed into a 63-mL Teflon-lined stainless steel autoclave and the amine (MXDA) was added. The mixture was heated at 160 °C for 2 d and cooled naturally to room temperature. The product 1 was washed with a mixture of 2-propanol and water (2:1) and finally dried at room temperature for 24 h. Similar conditions were used for the synthesis of [(MXDA)Cd]SO₄ (2), but in this case the source of Me atoms was CdSO₄·8H₂O.

Synthesis of (PXDA)MeSO₄ (3, 4): The synthesis was performed using $ZnSO_4$ ·7H₂O (0.01 mol) and *p*-xylylenediamine (PXDA) (0.0125 mol). Zinc sulfate hydrate and *p*-xylylenediamine were ground, mixed, and placed in a 63-mL Teflon-lined stainless steel autoclave. The mixture was heated at 160 °C for 2 d and cooled naturally to room temperature. The product **3** was washed with a mixture of 2-propanol and water (2:1) and finally dried at room temperature. A similar method was used to synthesize (PXDA)CdSO₄ (4), however CdSO₄·8H₂O was used instead of zinc sulfate.

Crystal Structure Determination: X-ray powder diffraction patterns (XRPD) of the samples were recorded with a X'PERT PRO MPD diffractometer, working in Bragg-Brentano or Debye-Scherrer geometry; incident and antiscatter slits were 1/4 and 1/2°, respectively (detector X'CELERATOR, radiation Cu- K_a , X-ray tube working conditions 40 kV and 30 mA). The measurement range was from 4° to 65° 2θ with interpolated step size 0.02°.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-901450 (1), -901449 (2), -9006899 (3), and -900688 (4) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http:// www.ccdc.cam.ac.uk).

Methods for Characterization: The simultaneous Thermogravimetry and Differential Scanning Calorimetry (TG-DSC) studies were performed with a computer-controlled STA 409 PC Luxx system. The measurements were performed in an air atmosphere. The heating rate was 10 °C·min⁻¹; the initial temperature was 20 °C, the final 1000 °C.

The morphology of the samples was investigated with a JEOL JSM-7500F Scanning Electron Microscope. The samples were applied on brass stubs and sputter-coated with chrome. The accelerating voltage was 15 kV.

Chemical analysis was performed with a Euro Vector EA 300 Elemental Analyzer.

Thermal analysis was performed in air, or helium using an XRK chamber produced by Anton Paar. The heat rate was 10 °C·min⁻¹. After reaching the desired temperature the sample was stabilized for 10 min. The initial temperature was equal to room temperature; subsequent temperatures were 100 °C, 200 °C, 300 °C, etc. up to 700 °C.

Acknowledgements

This work was supported by the Krakow Interdisciplinary PhD-Project in Nanoscience and Advanced Nanostructures, operated within the Foundation for Polish Science MPD Programme co-financed by the EU European Regional Development Fund. The support of the Polish Government Program MNiSW, grant NN204546439, is also kindly acknowledged.

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Received: March 25, 2013 Published Online:

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schrift für rganische Ilgemeine Chemie ZAAAC Journal of General

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Job/Unit: **Z13171** /KAP1

ARTICLE

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Synthesis and Characterization of Pillared Metal Sulfates (Diamine) $MeSO_4$, (Me = Zn, Cd)



Z. Anorg. Allg. Chem. 0000, 0-0