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Antimonato polyoxovanadates with structure directing transition metal complexes: pseudopolymorphic ${Ni(dien)_2}_3[V_{15}Sb_6O_{42}(H_2O)] \cdot nH_2O$ compounds and ${Ni(dien)_2}_4[V_{16}Sb_4O_{42}(H_2O)]^{\dagger}$

Elena Antonova, Christian Näther and Wolfgang Bensch*

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Three new poloxovanadates were synthesized under solvothermal conditions and were structurally characterized. The two compounds with composition {Ni(dien)₂}₃[V₁₅Sb₆O₄₂(H₂O)]·*n*H₂O (*n* = 12 and 8; dien = bis(2-aminoethyl)amine or diethylenetriamine) are pseudopolymorphs crystallizing in different space groups. The compounds were obtained by applying identical reaction slurries but using different reaction temperatures. Both compounds feature the [V₁₅Sb₆O₄₂(H₂O)]⁶⁻ anion which is the antimony analogue to the single molecule magnet [V₁₅As₆O₄₂(H₂O)]⁶⁻. Crystal data: **1** tetragonal space group $P\bar{4}$, *a* = 46.9378(3), *c* = 16.51300(10) Å and *V* = 36380.7(4) Å³. **2** rhombohedral space group *R*3c with *a* = 23.0517(4), *c* = 28.6216(5) Å and *V* = 13171.3(4) Å³. In **1** several unusual short inter-cluster Sb··· O contacts lead to the formation of three different super-clusters with composition V₆₀Sb₂₄O₁₆₈. The 12 unique {Ni(dien)₂}²⁺ complexes adopt all three possible configurations. In **2** the special arrangement of the {Ni(dien)₂}²⁺ complexes around the cluster anion prevents inter-cluster Sb··· O contacts. The main structural motif of the third compound {Ni(dien)₂}₄[V₁₆Sb₄O₄₂(H₂O)] (**3**) is the [V₁₆Sb₄O₄₂(H₂O)]⁸⁻ cluster anion consisting of two perpendicular eight-membered rings of VO₅ pyramids. Two additional VO₅ polyhedra are located on opposite sides. Crystal data: **3** triclinic space group $P\bar{1}$, *a* = 13.5159(4), *b* = 14.2497(5), *c* = 14.9419(4) Å, α = 98.322(2), β = 114.080(2), γ = 110.130(2)° and *V* = 2326.35(12) Å³.

Introduction

The chemistry of polyoxometalates (POMs) is a fast growing field of active research due to the fascinating diversity of crystal structures and interesting properties. Many applications are envisaged in areas like catalysis, supramolecular, analytical and clinical chemistry, medicine, electronic and protonic conductors, batteries and sorption.¹⁻⁵ Although the interest in POM chemistry is enormous, the number of publications on antimony substituted polyoxovanadates (POVs) is comparably small. On the other hand, arsenato POVs with the general formula $[V_{18-x}As_{2x}O_{42}] \cdot nH_2O(x =$ 2-4)6-10 have been intensively studied owing to their attractive magnetic properties^{11,12} like *e.g.* spin frustration,^{13,14} and their potential applications in nanoscale magnetism.¹⁵ In contrast to arsenato POVs, the antimony based POVs are less explored although the antimony cations have a stabilizing effect on polyoxometalates at high temperatures.¹⁶ Therefore, antimony POVs may find applications in many areas like heterogeneous oxidation

catalysis,¹⁷ selective oxidation reactions,¹⁸ sorption applications¹⁹ or as deNO_x catalysts.²

While the arsenic substituted polyoxovanadates can be chemically modified by other elements like Cd or Zn,^{20,21} there are only three known types of antimony substituted clusters with shell structures ($[V_{14}Sb_8O_{42}]^{4-}$, $[V_{15}Sb_6O_{42}]^{6-}$, and $[V_{16}Sb_4O_{42}]^{8-22-26}$), which are either extended by the transition metal complexes^{17,19} or being functionalized by Sb–N bonding to amine molecules.²⁷

Very recently we successfully modified the shells of antimonato polyoxovanadate clusters with Co^{2+} and Ni^{2+} complexes $((Co(N_3C_5H_{15})_2)_2[\{Co(N_3C_5H_{15})_2\}V_{15}Sb_6O_{42}(H_2O)]\cdot 5H_2O$ and $(Ni(N_3C_5H_{15})_2)_2[\{Ni(N_3C_5H_{15})_2\}V_{15}Sb_6O_{42}(H_2O)])^{28}$ and with 1-(2-aminoethyl)piperazine $([V_{14}Sb_8(C_6H_{15}N_3)_4O_{42}(H_2O)]\cdot 4H_2O$ and $(C_6H_{17}N_3)_2[V_{15}Sb_6(C_6H_{15}N_3)_2O_{42}(H_2O)]\cdot 2.5H_2O).^{27}$

Here we report the syntheses and X-ray crystal structures of new antimonato polyoxovanadates with the isolated spherical $[V_{15}Sb_6O_{42}(H_2O)]^{6-}$ and $[V_{16}Sb_4O_{42}(H_2O)]^{8-}$ cluster anions and additional $\{Ni(dien)_2\}^{2+}$ complexes, which were obtained under solvothermal conditions by variation of temperature and reactants.

Results and discussion

Compound 1 crystallizes in the tetragonal space group $P\bar{4}$ with 16 formula units per unit cell, compound 2 crystallizes in

Christian-Albrechts-Universität zu Kiel, Institut für Anorganische Chemie, D-24098, Kiel, Germany. E-mail: wbensch@ac.uni-kiel.de; Fax: +49 431 880 1520; Tel: +49 431 880 2091

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	Compound 1	Compound 2	Compound 3
Crystal system	Tetragonal	Hexagonal	Triclinic
Sum formula	C ₂₄ H ₁₀₄ N ₁₈ Ni ₃ -	$C_{24}H_{96}N_{18}Ni_{3}$ -	C32H106N24Ni4-
	$O_{55}Sb_6V_{15}$	$O_{51}Sb_6V_{15}$	$O_{43}Sb_4V_{16}$
Formula weight	3195.8699	3123.8087	3052.1526
Space group	$P\bar{4}$	R3c	$P\overline{1}$
a(Å)	46.9378(3)	23.0517(4)	13.5159(4)
$b(\mathbf{A})$	46.9378(3)	23.0517(4)	14.2497(5
$c(\mathbf{A})$	16.5130(10)	28.6216(5)	14.9419(4)
$\alpha(\circ)$	90	90	98.322(2)
β(°)	90	90	114.080(2)
γ(°)	90	120	110.130(2)
Volume (Å ³)	36380.7(4)	13171.3(4)	2326.35(12)
Z	16	6	2
Density (g cm ⁻³)	2.163	2.357	2.269
Refl. collected	200 212	64 789	31 328
Independ.	31 512	6231	12 535
reflections			
$R_{\rm int}$	0.0560	0.0500	0.0403
R_1 for $[I > 2\sigma(I)]$	0.0306	0.0396	0.0483
GOOF	1.039	1.146	1.141
wR_2 for all	0.0768	0.085	0.0866
reflections			
T (K)	293	293	293

 Table 1
 Selected crystal data and details of the structure determination of the new compounds

the rhombohedral space group R3c with 6 formula units, and compound 3 crystallizes in the triclinic space group $P\overline{1}$ with 2 formula units per unit cell. Selected crystal data and details of the structure determination of the compounds are summarized in Table 1.

As mentioned above, the composition of compounds 1 and 2 is identical but the crystal structures are different.

While the asymmetric unit of **2** comprises only a third of the cluster anion and one Ni²⁺ complex, the asymmetric unit of **1** consists of four crystallographically independent $[V_{15}Sb_6O_{42}]^{6-}$ clusters and 12 unique $\{Ni(dien)_2\}^{2+}$ complexes.

The central structural motif of 1 and 2 is a spherical $[V_{15}Sb_6O_{42}]^{6-}$ cluster anion. The centre of the cluster anion is occupied by one H₂O molecule and the diameter of the clusters in both compounds is approximately 11 Å.

The spherical $[V_{15}Sb_6O_{42}]^{6-}$ cluster shell is easily derived from the $\{V_{18}O_{42}\}$ archetype cluster by substituting three VO₅ square pyramids by three Sb₂O₅ moieties. The resulting cluster shell is identical with that of the most studied arsenato analogue $[V_{15}As_6O_{42}]^{6-}$ consisting of 15 VO₅ square pyramids and 3 Sb₂O₅ handle-like moieties (Sb–O bond lengths: 1.912(7)–1.988(7) Å for 1 and 1.935(5)–1.945(5) for **2**) (Tables S1 and S2;† Fig. 1). A central $\{V_3\}$ triangle is capped above and below by $\{V_6\}$ rings. The V–O bonds in the VO₅ polyhedra exhibit the typical pattern of relatively long V- μ -O (1.867(7) to 2.040(7) Å for **1** and 1.897(6)–2.032(6)



Fig. 1 The $[V_{15}Sb_6O_{42}(H_2O)]^{6-}$ cluster anion in compounds 1 and 2.

for **2**) and short V=O (1.586(8)–1.642(8) Å for **1** and 1.599(6)– 1.610(5) for **2**) distances (Tables S1 and S2[†]). The shortest V–V distances are between 2.839(3) and 3.068(2) Å (average: 2.95 Å) for **1** and 2.8303(15) to 3.0728(15) (average: 2.98 Å) for **2**. All geometric parameters agree with those reported in literature for structurally related POVs.^{22–24,27} In the well characterized arsenato POV cluster $[V_{15}As_6O_{42}(H_2O)]^6$ - slightly smaller V–O and V–V distances (V-µ–O: 1.912(5) to 2.006(5), V=O: 1.610(5) to 1.618(5) and V–V: 2.870(1) to 3.049(1) Å) are observed,²⁹ which may be due to the presence of the smaller As(III).

In 1 several unusual short Sb–O distances of only 2.678, 2.691 Å and 2.704 Å (sum of van der Waals radii: 3.52 Å) are found between the cluster anions besides longer Sb–O distances from 2.817 to 2.969 Å (Table 2) which are either between Sb₂O₅ moieties (short) or between Sb₂O₅ and a terminal O atom of the neighboured cluster (long). The former distances are significantly shorter than those observed in different antimony modified POVs like $(C_6H_{17}N_3)_4[V_{16}Sb_4O_{42}]\cdot 2H_2O$ (2.85 Å), $[trenH_3]_2[tren]_{0.33}[V_{15}Sb_6O_{42}]\cdot H_2O$ (x: 3–5) (tren = tris(2-aminoethyl)amine) (2.88 Å), $[(C_2N_2H_{10})_2-\beta-\{V_{14}Sb_8O_{42}(H_2O)\}]-(C_2N_2H_8)\cdot 4H_2O$ (2.79 Å) and $[V_{14}Sb_8(C_6H_{15}N_3)_4O_{42}(H_2O)]\cdot 4H_2O$ (2.73 Å) indicating weak bonding interactions.^{22,23,25,27}

Taking the inter-cluster Sb–O interactions into account three super-clusters of composition $V_{60}Sb_{24}O_{168}$ are formed consisting of four $[V_{15}Sb_6O_{42}]^{6-}$ anions (Fig. 2 right). Two of the three super-clusters consist of only one crystallographically independent anion (type A: Sb1–Sb6; type B: Sb31–Sb36) and one is formed by two crystallographically independent cluster shells (type C: Sb11–Sb16 and Sb21–Sb26 atoms).

The super-clusters show two alternating orientations in the *ab* plane yielding a layer-like arrangement (Fig. 2 left).

The formation of super-clusters has been reported before. However, the inter-cluster Sb–O separation of 2.884(8) Å in [trenH₃]₂[tren]_{0.33}[V₁₅Sb₆O₄₂] interconnects the anions into [V₄₅Sb₁₈O₁₂₆] super-clusters forming Sb₃O₃ rings displaying a pattern being different to that in 1.²³

Table 2 Sb–O distances (Å) between the neighbouring clusters in compound 1. O_t = terminal O atoms of the cluster anions

Super-cluster A		Super-cluster B		Super-cluster C	
Bond	Distance/Å	Bond	Distance/Å	Bond	Distance/Å
Sb1–O5 _t Sb4–O15	2.912 2.691	Sb31–O178 _t Sb36–O154	2.931 2.704	Sb16–O115 _t Sb24–O72	2.678 2.948
				Sb22–O60 Sb12–O103 _t	2.817 2.969



Fig. 2 Arrangement of the super-clusters A, B, and C in compound **1** in the *ab* plane. The red lines (left) clarify the different orientations of these structural motifs.

The values of the bond-valence sums (BVS) yield values for the Sb atoms in the range from 3.09 (Sb31) to 3.38 (Sb4, Sb16) (average: 3.26) (Table 3).³⁰ In tendency, the values for the Sb atoms involved in inter-cluster Sb–O interactions (Sb4, Sb16 and Sb36) are larger than for the remaining Sb atoms. However, one should keep in mind that the BVS method is not very accurate for "soft" atoms and those with a lone electron pair like Sb(III).

The water molecules and the Ni²⁺ centred complexes occupy the free voids between these cluster quartets. In compounds **1** and **2** Ni²⁺ is coordinated by six N atoms from two dien ligands. The resulting octahedra are strongly distorted with Ni–N bonds from 2.025(19) to 2.33(3) Å for **1** and from 2.059(9) to 2.169(6) for **2** (Table S1, S2†) which are in agreement with data reported in literature.³¹⁻⁴⁰ Around Ni12 the Ni–N bonds are significantly longer (from 2.13 to 2.33 Å) than in the other complexes. This elongation is caused by a slight positional disorder which could not be resolved during structure refinement. Two of 12 {Ni(dien)₂}²⁺ complexes (Ni12, Ni11) adopt the *mer*-, Ni1, Ni7 the *s*-fac, and the remaining complexes (Ni2–Ni6, Ni8–Ni10) the *u*-facconfiguration (Fig. 3). The maximum diameter of the complexes is in the range of 5.468 to 5.947 Å (Table 4).

 Table 3
 Bond valence sums of the antimony atoms in 1

Sb1 3.31	Sb11 3.17	Sb21 3.22	Sb31 3.09
Sb2 3.22	Sb12 3.25	Sb22 3.16	Sb32 3.37
Sb3 3.19	Sb13 3.22	Sb23 3.29	Sb33 3.31
Sb4 3.38	Sb14 3.27	Sb24 3.21	Sb34 3.24
Sb5 3.16	Sb15 3.28	Sb25 3.30	Sb35 3.36
Sb6 3.29	Sb16 3.38	Sb26 3.23	Sb36 3.24

Table 4 The diameter (Å) of the ${Ni(dien)_2}^{2+}$ complexes in compound 1

Complex	Min. diameter/Å	Max. diameter/Å
Nil - s-fac	4.153	5.891
Ni2 - u-fac	4.185	5.875
Ni3 - u-fac	4.199	5.947
Ni4 - u-fac	4.218	5.750
Ni5 - u-fac	4.207	5.821
Ni6 - u-fac	4.215	5.854
Ni7 - s-fac	4.140	5.908
Ni8 - u-fac	4.182	5.924
Ni9 - u-fac	4.178	5.783
Ni10 - u-fac	4.169	5.811
Nill - mer	4.066	5.730
Ni12 - mer	4.262	5.468



Fig. 3 Representation of the transition metal complexes: *s-fac*- ${Ni(dien)_2}^{2+}$ (left), *mer*- ${Ni(dien)_2}^{2+}$ (middle) and *u-fac*- ${Ni(dien)_2}^{2+}$ complex (right).

Fig. 4 shows the arrangement of the ${Ni(dien)_2}^{2+}$ complexes in the unit cell. In the center of the cell, symmetry related Ni6 centred complexes occupy the corners of a square. The Ni1, Ni10, Ni2, and Ni7 containing complexes are arranged in a ring-like fashion (denoted as ring 2) separating the super-cluster B from the other clusters. Another ring-like arrangement is observed for the complexes centered by Ni3, Ni5, Ni8, Ni11, Ni12 (ring 3). The remaining complexes (Ni4 and Ni9) are located at the corners of unit cell.



Fig. 4 Arrangement of the cluster shells (red balls) and Ni^{2+} centred complexes in the unit cell of compound 1. H atoms and H₂O molecules are not shown.

The cluster shells in **2** alternate in an \dots ABC \dots fashion along the *b*-axis and in an \dots ABAB \dots manner along the *c*-axis (Fig. 5). Neighboring clusters being directed along the *c*-axis are rotated by about 20 degrees against each other (Fig. 6). In contrast to **1** no short inter-cluster Sb–O separations are observed and the shortest distance is 5.21 Å. However, one relatively short Sb–O distance is found to the O atom of a water molecule (2.9524(0) Å). In the (001) plane the Ni²⁺ complexes are located between the anions



Fig. 5 Arrangement of the constituent in the structure of 2 in the *bc* plane. Atoms of the complexes are not displayed.



Fig. 6 View of two clusters along *c*-axis in the structure of 2.

forming a triangular-like arrangement around the cluster shells thus isolating the $[V_{15}Sb_6O_{42}]^{6-}$ anions preventing inter-cluster Sb– O interactions (Fig. 7). The $\{Ni(dien)_2\}^{2+}$ cation in **2** adopts the *mer*-configuration (see Fig. 3 and 7). In contrast to compound **1** the complex in compound **2** exhibits a smaller diameter (max. 5.585 Å).



Fig. 7 Representation of the clusters and Ni^{2+} complexes in compound **2** in the *ab* plane. The clusters are shown as red balls.

The *mer*-configuration of the complex allows denser packing, but the shielding of the clusters by the complexes leads to larger distances between the Sb₂O₅ units (Fig. 7). In total 24 N–H \cdots O bonds in the range from 2.0627(0) Å to 2.9213(0) Å are identified leading to a three-dimensional network structure.

The central structural motif of compound **3** can also be derived from the { $V_{18}O_{42}$ } archetype cluster. Substitution of two of the VO₅ square pyramids by two Sb₂O₅ moieties (Sb–O 1.934(3)–1.955(3) Å) generates the spherical [$V_{16}Sb_4O_{42}$]⁸⁻ cluster anion consisting of two eight-membered rings of VO₅ (V–O: 1.9008(3)–2.000(3) and V=O: 1.607(4)–1.639(3) Å) perpendicular to each other (Fig. 8). Two additional VO₅ pyramids are located on opposite sides and these polyhedra share two edges with the two rings (Fig. 8). In the



Fig. 8 $[V_{16}Sb_4O_{42}]^{8-}$ cluster as the central fragment in compound 3.

centre of the cluster a H_2O molecule is encapsulated. All geometric parameters match well with those of compounds **1** and **2** and with literature data.^{14–16,27} Bond-valence sum calculations reveal that the oxidation state of the Sb atoms is close to III (Sb1: 3.19; Sb2: 3.27).

There are 3 crystallographically independent Ni²⁺ ions in **3**. One is located on a general position and two on special positions. Like in compounds **1** and **2** the {Ni(dien)₂}²⁺ octahedron is strongly distorted. The Ni–N bonds (Table S3[†]) and N–Ni–N angles are comparable with those in **1** and **2** and agree with literature data.³²⁻⁴¹ Two of three {Ni(dien)₂}²⁺ complexes adopt the *s*-fac- and one occurs in the *u*-fac-configuration (see Fig. 3). The minimum diameter of the complexes varies from 4.196 Å (Ni2) to 4.246 Å (Ni1) and the maximum extension varies from 5.865 Å (Ni2) to 5.928 (Ni1) Å. The anionic clusters in compound **3** are arranged in layers in the (100) plane with intervening water molecules and complex cations (Fig. 9).



Fig. 9 Arrangement of the cluster anions and Ni^{2+} centred complexes in compound 3. H atoms are not shown.

Bond-valence sum calculations reveal that the oxidation state of all the vanadium atoms in the studied compound is around +4 (Σ s = 4.07–4.33 for 1, Σ s = 4.15– 4.22 for 2 and Σ s = 4.09– 4.17 for 3), which is consistent with the overall charge balance in the formula. This is also proven in compounds 1 and 2 by IR spectra, where the typical vibration of V⁴⁺ (V=O)_s appears as a very strong band at 968 cm⁻¹ (Fig. 10).



Fig. 10 IR spectra of compounds 1 and 2. Some important absorption modes are marked.

In the IR spectra of **1** and **2** the v(O-H) = 3431 (s), v(N-H) = 3268 (s) and v(C-H) = 2927, 2871 (m) cm⁻¹ vibrations and also the asymmetric $v_{as}(V-O-V)$ at 726 cm⁻¹ are observed besides further absorptions that can be assigned to the organic molecules. The characteristic terminal $v_s(V=O)$ stretching vibration occurs at 968 cm⁻¹. The assignment of the vibrational modes are in good agreement with literature data.⁴¹

DTA-TG investigations reveal that compounds 1 and 2 decompose in two steps with a total mass loss of $\Delta m_{\rm exp} = 37.4$ wt%. The first process in the temperature range from 30 to 300 °C corresponds to the loss of water molecules ($\Delta m_{\rm exp} = 5.4$ wt %). After 400 °C an almost smooth decrease of the sample mass is observed with a mass loss of $\Delta m_{\rm exp} = 32$ wt%. Crystalline powders were obtained as the products of the decomposition reaction of both compounds which were identified as mixtures of NiSb, NiSb₂, Sb and V₂O₃.

Both, compounds 1 and 2 readily dissolve in methanol and ethanol. In contrast the solubility of the two compounds in water is significantly different as becomes apparent by the color of the solutions (Fig. 11), *i.e.*, compound 1 is significantly less soluble in H_2O than 2.



Fig. 11 Aqueous solutions of compound 1 (left) and compound 2 (right).

The absorption maximum in the UV spectra is at 255 for **1** and at 265 nm for **2**.

Conclusions

Polymorphs or pseudopolymorphs of antimonato polyoxovanadate compounds have not been reported in literature until now. Applying identical starting material ratios but varying the reaction temperature afforded crystallization of compounds 1 and 2. The main difference between the two compounds is the occurrence of Ni2+ centred complexes adopting three different configurations in 1 while only one configuration is observed in 2. The special arrangement of the complex cations around the spherical $[V_{15}Sb_6O_{42}]^{6-}$ clusters in 1 allows short intermolecular $Sb \cdots O$ interactions whereas the location of the complexes in 2 prevents such interactions. Currently investigations of the magnetic properties are under way to probe whether the intercluster interactions in 1 influence the magnetic properties of the single molecule magnet behaviour. Compound 3 was synthesized using the bimetallic precursor Sb₂VO₅ which is a promising source for further syntheses.

Syntheses of the compounds

For compound **1** 1.34 mmol NH₄VO₃, 1.06 mmol Sb₂O₃ and 0.66 mmol NiCl₂·6H₂O in a mixture of 1.7 mL bis(2-aminoethyl)amine (or diethylenetriamine = dien) and 2.3 mL water were sealed in a 30 mL Teflon lined stainless steel autoclave and heated at 150 °C for 7 days. After cooling to room temperature the product was filtered off and washed with water and acetone. The brown crystals were dried under vacuum. Yield: 36% based on antimony. Elemental analysis: C 9.8, H 2.6, N 8.8%, calc. C 9.02, H 3.28, N 7.89%.

Compound **2** was synthesized applying the same starting materials in identical ratio but the temperature was kept at 130 °C for 7 days. The main product consisted of red-brown needles, which were washed with water and acetone and dried in vacuum. Yield: 37% based on antimony. Elemental analysis of the needles: C 9.4, H 3.1, N 8.1%, calc. C 9.23, H 3.1 N 8.07%. SEM images of crystals are shown in Fig. 12.



Compound 3

Fig. 12 SEM micrographs and images of crystals.

The product of the synthesis at 130 °C (**2**) contained brown needles of **2** and black crystals that were identified as $[V_5O_{11}(dien)_3]$.⁴² In order to avoid the formation of the byproduct the synthesis parameters such as temperature, reactants and concentration of amine were varied, but the variation of temperature and concentration of amine led mainly to the formation of $[V_5O_{11}(dien)_3]$. Often the water to amine ratio played a crucial role and further syntheses were carried out with 5, 10 and 20 mL water keeping the amount of the other educts constant. The product of these reactions was a green powder which was identified as Sb_2VO_5 (Stibivanite). Unfortunately, the variation of the syntheses did not increase the yield of compound **2**. For compound **3** a mixture of 1 mmol Sb₂VO₅, 0.66 mmol NH₄VO₃, 0.66 mmol NiCl₂·6H₂O was treated with an amine–water solution analogous to compound **1**. X-ray powder diffractometry showed reflections of at least two different compounds. Because the black crystals grow in chunks a manual separation of the different compounds was not possible (Fig. 12). For this reason chemical analyses were not possible, and only the X-ray structure is reported here.

Crystal structure determination

The X-ray intensity data of a single crystal of compound 1 with dimensions $0.0542 \times 0.1027 \times 0.1476$ mm³, of a crystal of compound 2 with dimensions $0.057 \times 0.0728 \times 0.1325$ mm³ and of a crystal of **3** with dimensions $0.0395 \times 0.0588 \times 0.0686 \text{ mm}^3$, were collected at room temperature using a STOE-1 Imaging Plate Diffraction System (IPDS-1) with Mo-K α radiation (λ = 0.71073 Å). The raw intensities were treated in the usual way applying Lorentz polarization as well as absorption correction. Selected crystal data and details of the structure determination are summarized in Table 1. The structures were solved with direct methods with SHELXS-97.43 Crystal structure refinements were done against F² using SHELXL-97 for 2 and 3.43 For 1 a special version of SHELXL for the refinement of very large structures (SHELXH) was used.43 The crystal of 1 was racemically twinned and therefore a twin refinement was performed (BASF: 0.21 (1)). The CH and NH hydrogen atoms were positioned with idealized geometry and refined using a riding model. The H atoms from water could not be located in difference Fourier maps. Numerical absorption corrections were performed (for compound 1 T_{\min}/T_{\max} 0.3990, 0.7064; for compound 2 T_{\min}/T_{\max} 0.3864, 0.5805, and for compound 3 T_{min}/T_{max} 0.5243, 0.6284). After structure refinement of compound 1 there were several residual peaks in the electron density map indicating the presence of disordered solvent for which no reasonable structure model could be found. Therefore, the data were corrected for disordered solvent molecules using the SQUEEZE option in PLATON.³⁰ During the squeezing procedure 1476 electrons were collected. Calculation of the accessible free space using the program suite PLATON yields 6725.9 Å³ as potential solvent area for 1.

Elemental analysis

CHN analyses were done using an EURO EA Elemental Analyzer, fabricated by EURO VECTOR Instruments and Software. Note that experimental CHN data for 1 indicate smaller water content which may be explained by water loss during sample preparation.

IR spectroscopy

IR spectroscopy investigations were done at room temperature using a Genesis FTIRTM spectrometer from ATI Mattson. The IR spectra were measured from 400 to 4000 cm⁻¹. The powdered samples were mixed with dry KBr and were pressed into transparent pills.

Thermal analysis

The DTA-TG investigations were carried out in a nitrogen atmosphere (purity: 5.0; heating rate 4 K min⁻¹; flow rate: 75 mL

min⁻¹; Al₂O₃ crucibles) using a Netzsch STA-409CD instrument. To determine the water content of 1 several TG measurements were performed using products of different syntheses. For all products the weight loss corresponded to 12 H_2O molecules per formula unit.

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