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Polyoxomolybdate-Supported Bismuth Trihalides $[Mo_8O_{26}(BiX_3)_2]^{4-}$ (X = Cl, Br, I): Syntheses and Study of Polymorphism

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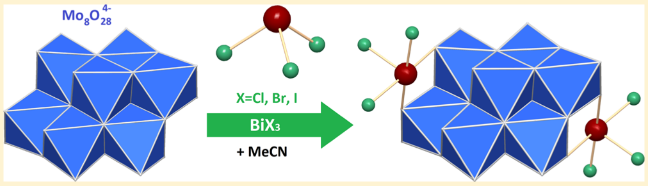
Supporting Information

ABSTRACT: Octamolybdate complexes $TBA_4[Mo_8O_{26}(BiX_3)_2]$ (TBA = *n*-tetrabutylammonium, X = Cl (**1**), Br (**2**), I (**3**)) were obtained by straightforward syntheses from $TBA_4[Mo_8O_{26}]$ and corresponding Bi(III) halides in MeCN. All compounds were structurally characterized; in all cases, $\{BiX_3\}$ fragments are coordinated by two oxygen atoms of polyoxometalate core. Occurring polymorphism is also discussed.



INTRODUCTION

Polyoxometalates (POM) represent a large class of metal−oxide polynuclear complexes. Its main feature is a huge structural diversity both in connectivity and in size (reaching to nanoscale objects with hundreds of transition metal atoms), which is, in turn, reflected in a high variety of chemical properties.[1−3] This area attracts attention due to multiple aspects, such as catalysis[4] (in particular photocatalysis[5]), materials science and nanodevices,[6] molecular magnetism,[7] etc.

Among the whole palette of possible heteroatoms in POM frameworks, there is a group of complexes containing Sb and Bi. These elements act as central atoms in the well-known family of trilacunary polyoxoanions ($[SbW_9O_{33}]^{9-}$, $[BiW_9O_{33}]^{9-}$ etc.), which constitute building blocks for numerous heterometallic complexes, for example, with a sandwich structure.[8] It is noteworthy that in this case Sb or Bi atoms are "enclosed" by metal−oxide shell and, therefore, are prevented from direct involvement in chemical processes (e.g., catalytic) occurring on the POM "surface" (or in accessible coordination sphere of a heterometal). On the other hand, both Sb and Bi may also play a role of POM "external" atoms, but this class of compounds is significantly less studied. For antimony, there are examples of sandwich-type complexes with Sb located in the heterometallic "belt" between the POM moieties,[9] a family of $[NaSb_9W_{21}O_{86}]^{18-}$-based polyoxoanions[10] and several other compounds of various structures.[11]

POM complexes of bismuth not being the central atom are especially rare. In fact, all known structurally characterized examples belong to three families, specifically, (1) Lindqvist-type polyoxoanions $[Bi(Mo_5O_{13}(OMe)_4(NO))_2]^{3-}$ and $[Bi(W_5O_{13}(OMe)_4Mo(NO))_2]^{3-}$,[12] (2) products of their derivatization on the Mo−NO site,[13] and (3) a Keggin-type polyoxovanadate $[(Bi(DMSO)_3)_4V_{13}O_{40}]^{3-}$, which catalyzes visible-light photooxidation.[14] An obvious reason for this scarcity is the limitation imposed by the basic chemistry of bismuth: most of available Bi(III) compounds are hydrolytically unstable, especially beyond acidic pH range, with a pronounced tendency to form insoluble products such as "oxosalts" and, therefore, are hardly compatible with POMs when water is used as solvent (which is still most common solvent in the POM chemistry). This gap is to be filled both in terms of fundamental development of POM chemistry and in terms of its applied aspects. First, Bi(III) compounds are well-known catalysts for a wide spectrum of organic reactions (oxidation, amination, alkylation, cycloizomerisation, etc.);[15] we may expect that Bi-POM complexes may also possess catalytic activity, at very least in oxidation reactions where POMs themselves are well-known to be efficient. Second, complexes of POM with "grafted" BiX_3 (X = halide) may be considered as molecular models of supported BiOX phases, which are extensively studied as photocatalysts.[16] Third, catalytic activity has been shown for related Sb-containing POMs.[17] Thus, obtaining and studies of Bi-containing POMs is interesting both as synthetic challenge and for further applications in catalysis.

Here we report synthesis and characterization of a new family of polyoxomolybdate complexes containing bismuth trihalogenide fragments—$TBA_4[Mo_8O_{26}(BiX_3)_2]$ (TBA = *n*-tetrabutylammonium, X = Cl (**1**), Br (**2**), and I (**3**)). All these complexes were obtained by a simple and convenient procedure, which may be expanded both on other POMs and on other poor metal halogenides.

RESULTS AND DISCUSSION

Synthesis of $TBA_4[Mo_8O_{26}(BiX_3)_2]$. One of the common properties of Bi(III) is its ability to extend the coordination number at least up to 10.[18] Hence, considering also the

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favorable energetics for Bi−O bonds, we could predict that Bi(III) halide would react with POMs, becoming coordinated by nucleophilic oxygen atoms. However, there are a number of restrictions mentioned above (hydrolytic instability of Bi(III) vs instability of many POMs in acidic media) that, from the synthetic point of view, significantly complicate the preparation of Bi(III)-containing POMs in water. To prevent the hydrolysis of BiX_3 as well as possible pH-triggered rearrangements of POM frameworks, we decided to carry out reactions in CH_3CN, with an easily available TBA salt of $[Mo_8O_{26}]^{4-}$ as POM precursor. This idea has worked, and we found that $[Mo_8O_{26}]^{4-}$ polyoxoanion coordinates two BiX_3 fragments by three terminal oxo-ligands (Figure 1a).

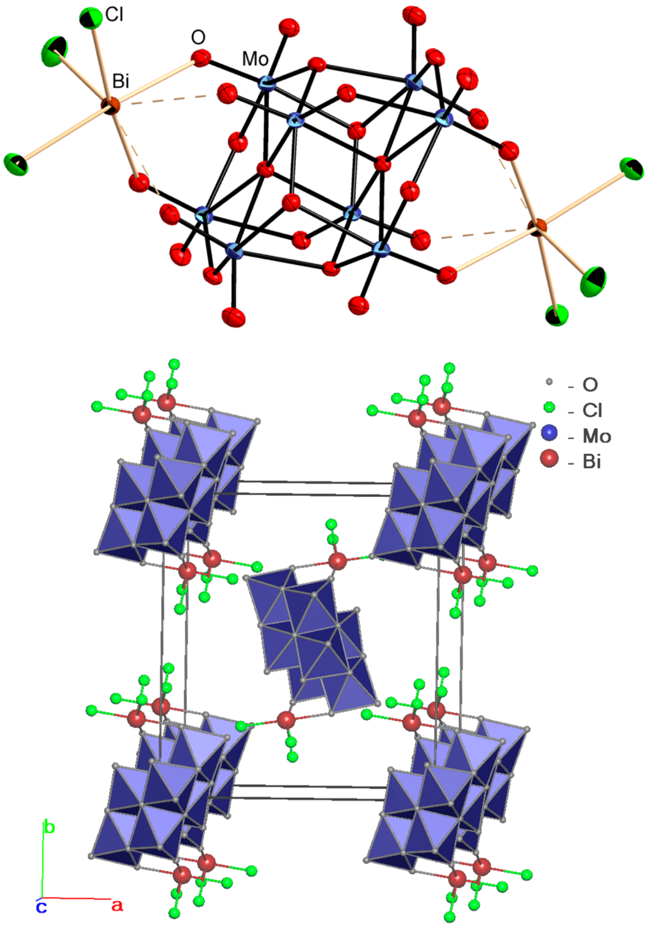

Figure 1. (a) The anion $[Mo_8O_{26}(BiCl_3)_2]^{4-}$ (ellipsoids of 50% probability) and crystal packing (b) in **1**. The additional elongated contacts Bi···O are shown by dashed lines. The TBA cations are not shown for clarity.

It is noteworthy that complexes of this type are relatively rare. There has been reported a large number of hybrid compounds where a heterometal (typically Cu or Zn with various organic ligands) is coordinated via one or, at best, two oxygen atoms,[19] but examples where $[Mo_8O_{26}]^{4-}$ acts as ligand of higher denticity are rather exotic, being limited to several complexes with four-coordinated Ag reported by Cronin, Kögerler, and Hu[20] and a few lanthanide compounds.[21]

Structures of $TBA_4[Mo_8O_{26}(BiX_3)_2]$. The compounds **1**−**3** are characterized as seven distinct crystalline phases (Tables 1 and 2), of the general formula $TBA_4[Mo_8O_{26}(BiX_3)_2]\cdot n$MeCN, X being Cl, Br, or I, and *n* is 0 or 2. All of them comprise decanuclear $[Mo_8O_{26}(BiX_3)_2]^{4-}$ anions formed by eight molybdenum atoms joined via edge-sharing of the MoO_6 octahedra (Figure 1a). In all structures the POM anions feature similar geometrical parameters (Supporting Information, Tables 5S and 6S) that are expectable in comparison to known $[Mo_8O_{26}]^{4-}$ geometries. Two $\{Bi^{III}X_3\}$ fragments coordinate β-$[Mo_8O_{26}]^{4-}$ anions, via two terminal oxygen atoms each. Coordination polyhedron of Bi^{3+} is a distorted square pyramid (ψ-octahedron) formed by two halides and by two oxygen atoms in the equatorial plane (Figure 1a). The Bi−O bond lengths vary from 2.58 to 2.65 Å, depending on the crystalline phase. The coordination of the BiX_3 group does not influence the Mo═O bond length, which is comparable with that of noncoordinate Mo═O. The lone electron pair of Bi(III) is stereochemically active and causes elongation of additional Bi···O contacts of 2.9−3.1 Å with two terminal oxygen atoms of POM anion (Supporting Information, Table 2S). The effect of the lone electron pair decreases in the series Cl > Br > I with the decrease in the electronegativity of X that is followed by diminishing of the difference between lengths of Bi−O and Bi···O contacts. For X = Cl or Br, the difference achieves 0.35 Å, while for X = I it is only 0.10−0.20 Å. As a result, the coordination polyhedron of Bi becomes more uniform in the halide series.

Solvatomorphism in 1 and 2. Upon exposure to air the crystals of isostructural salts $(TBA)_4[Mo_8O_{26}(BiX_3)_2]\cdot 2$MeCN, X = Cl (**1**·2MeCN) and Br (**2**·2MeCN), lose their MeCN of solvation, but retain the crystallinity, despite significant rearrangement of unit cell parameters, and transform into the solvent-free $(TBA)_4[Mo_8O_{26}(BiX_3)_2]$ (**1** and **2**). The colorless crystals become slightly milky, but no significant change in appearance occurs. The X-ray diffractometry (XRD) pattern from freshly prepared polycrystalline sample of **1** and **2** showed that both phases coexist (Supporting Information, Figures 1S−3S), but after two weeks almost complete transformation of **2**·2MeCN into **2** occurs. The same phenomenon was observed on single crystals of **1** and **2**, as manifested by decrease of the unit cell volumes by 219 and 237 Å^3, respectively, and by slight increase of calculated densities D_{calc} (Table 1). In crystal structures **1** and **2** (Supporting Information, Figure 8S) the position vacated by leaving MeCN molecule becomes available for occupation by the nearest *n*-Bu groups of a TBA cation. This leads to the change in conformations of TBA and a disordering of one of the *n*-Bu groups that was ordered in solvated phase, over two positions (with relative weight of 0.7/0.3), one being closer to the former position in the solvated crystal, the other taking place of MeCN (Figures 2 and 3). The anionic sublattice does not change, nor does the geometry of the anion. Only slight rearrangement of the Bi−X bond lengths within 0.02−0.03 Å range and slight systematic shortening of Bi−O bond lengths from 2.59 to 2.65 to 2.56−2.70 Å takes place (Supporting Information, Table 1S, Figures 5S and 6S). The angular distortion of the $Bi(III)X_3O_2$ tetragonal pyramid is minor; the polyhedron becomes marginally more regular in the nonsolvated phase, by ~3° (in **1**) and ~2° (in **2**) (Supporting Information, Tables 2S and 3S).

In the crystals of solvatomorphs **1** and **2** the anions are packed according to the topological motif of face-centered cubic (*f.c.c.*) lattice (Supporting Information, Figure 9S); the TBA cations and MeCN molecules occupy the voids in this packing. Therefore, we can conclude that the solvatomorphism is obviously caused by conformational flexibility of TBA cations that adapt both to the presence of small solvent molecules and

Table 1. Crystal Data, Data Collection, and Structure Refinement Parameters for **1** and **2**

compound	**1**·2MeCN	**1**	**2**·2MeCN	**2**
CCDC code	990 359	990 360	990 361	990 362
empirical formula	$C_{68}H_{150}Bi_2Cl_6Mo_8N_6O_{26}$	$C_{64}H_{144}Bi_2Cl_6Mo_8N_4O_{26}$	$C_{68}H_{150}Bi_2Br_6Mo_8N_6O_{26}$	$C_{64}H_{144}Bi_2Br_6Mo_8N_4O_{26}$
molecular weight	2866.12	2784.01	3132.88	3050.77
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	16.1078(3)	15.5263(3)	16.2030(2)	15.7271(3)
b, Å	16.8850(3)	17.2193(3)	16.9342(3)	17.0654(3)
c, Å	19.3604(3)	18.7055(3)	19.4793(3)	18.8408(3)
β, deg	102.184(2)	99.763(2)	102.250(2)	99.593(2)
V, Å^3	5147.03(15)	4928.53(15)	5223.13(14)	4985.96(15)
Z	2	2	2	2
D_{calc}, g/cm^3	1.849	1.876	1.992	2.032
μ, mm^{-1}	16.242	4.765	6.641	6.953
$2\theta_{max}$, deg	147.7	75.1	69.5	58.4
temperature, K	123.0(2)	123.0(2)	123.0(2)	123.0(2)
wavelength, Å	Cu Kα (1.541 78)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
crystal size, mm	0.32 × 0.25 × 0.10	0.32 × 0.25 × 0.10	0.33 × 0.24 × 0.06	0.11 × 0.08 × 0.06
range h, k, l	$-19 \leq h \leq 19$, $-20 \leq k \leq 14$, $-22 \leq l \leq 24$	$-24 \leq h \leq 25$, $-28 \leq k \leq 24$, $-17 \leq l \leq 31$	$-24 \leq h \leq 25$, $-28 \leq k \leq 24$, $-17 \leq l \leq 31$	$-17 \leq h \leq 20$, $-21 \leq k \leq 22$, $-24 \leq l \leq 12$
reflns measured	22 877	42 262	35 460	20 390
unique reflns	10 020	24 496	20 591	11 298
R_{int}	0.0256	0.0366	0.0327	0.0419
observed ($I > 2\sigma(I)$)	8998	11 944	12 751	6676
refined parameters	533	504	532	504
restraints	0	0	0	0
R_1, wR_2 ($I > 2\sigma(I)$)	$R_1 = 0.0304$, $wR_2 = 0.0778$	$R_1 = 0.0332$, $wR_2 = 0.0567$	$R_1 = 0.0313$, $wR_2 = 0.0513$	$R_1 = 0.0347$, $wR_2 = 0.0400$
R_1, wR_2 (all data)	$R_1 = 0.0348$, $wR_2 = 0.0798$	$R_1 = 0.0866$, $wR_2 = 0.0603$	$R_1 = 0.0594$, $wR_2 = 0.0532$	$R_1 = 0.0727$, $wR_2 = 0.0433$
goodness-of-fit on F^2	1.004	0.723	0.780	0.670
largest diff. peak, hole (e Å^{-3})	1.022/−2.129	2.529/−3.023	3.525/−1.629	0.893/−0.687

to packing of large building blocks as $[Mo_8O_{26}(BiX_3)_2]^{4-}$ anions.

Polymorphism in 3. The crystal structure of **3** (Figure 4) was established for three polymorphous modifications $(TBA)_4[Mo_8O_{26}(BiX_3)_2]$ (**3a**–**3c**), all being solvent-free despite the fact that **3a** polymorph possesses cell parameters similar to those of **1**·2MeCN and **2**·2MeCN (Table 1). We expected that **3a** polymorph could be a result of desolvation of a hypothetic solvatomorph "**3a**·2MeCN" analogously to **1** and **2**. However, this **3a**·2MeCN phase was not detected even in freshly prepared samples. All three polymorphs crystallize in the form of yellow or orange truncated square bipyramids (**3a**), thin goldish-yellow plates for (**3b**), and thin rhombic plates (**3c**) (Supporting Information, Figure 10S).

Compound **3c** was obtained and, with XRD, characterized as a major product of the reaction, while **3b** and **3a** were obtained as minor products. In some crystallizations **3a** appeared as major crystalline phase with a few crystals of **3b** and no trace of **3c** (Supporting Information, Figure 4S). At that we did not observe all three polymorphs to appear concomitantly, despite the fact that they possess very similar densities and, according to the well-known density rule, are expected to cocrystallize readily. Formally, we can assign **3c** to α-phase according to the highest density (at 123 K), **3a** and **3b** to β and γ-phases, respectively, but the relative thermodynamic stability of these three modifications is not obvious. In the $Bi^{III}I_3O_2$ tetragonal pyramid, the angular distortions do not exceed 4° among polymorphs (Supporting Information, Table 4S, Figure 7S).

The lower density correlates with relatively more disorder of the cationic sublattice. One of two independent TBA cations is ordered in all **3a**–**c** structures, while the other demonstrates different modes of disorder involving one or two *n*-Bu fragments. In **3a** and **3c** one of the terminal CH_3-CH_2- group is disordered over two parallel positions with 0.6/0.4 probability in **3a**, and crosswise with 0.5/0.5 probability in **3c**. The densities of these polymorphs deviate only by 0.002 g/cm^3. The **3b** polymorph shows the disorder in $CH_3-CH_2-CH_2-$ and CH_3- fragments of two *n*-Bu groups (Supporting Information, Figure 11S), and the density is lower by ~0.02 g/cm^3. It is worth noting that no reliable evidence for polymorphism in **1** and **2** that would yield the same polymorphs as in **3** was found. The fact of cationic disorder in **3** might give a chance for **3a**·2MeCN to exist, since in solvated structures of **1** and **2** embedding of MeCN molecules leads to ordering of TBA cations. Similar embedding could still occur also for **3**. However, we investigated the behavior of crystals of **3** down to 123 K, but could not find any interconversion between these modifications despite rather minor differences between the structures.

Packing in crystals of three polymorphs of **3** is generally different from solvatomorphs **1** and **2**, and this difference is reflected in anionic packing. In **3a** it is similar to solvatomorphs **1** and **2** and has the same topology of *f.c.c.* lattice. The **3b** and

Table 2. Crystal Data, Data Collection, And Structure Refinement Parameters for 3a−c

compound	3a	3b	3c
CCDC Code	990 363	990 364	990 365
empirical formula	$C_{68}H_{144}Bi_2I_6Mo_8N_6O_{26}$	$C_{64}H_{144}Bi_2I_6Mo_8N_4O_{26}$	$C_{68}H_{150}Bi_2I_6Mo_8N_6O_{26}$
molecular weight	3332.71	3332.71	3332.71
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a, Å	16.4558(10)	17.3860(3)	18.4441(6)
b, Å	16.7492(8)	17.3957(2)	16.4254(5)
c, Å	19.4562(14)	17.0461(2)	18.4370(5)
β, deg	107.579(2)	90.1720(10)	113.8610(10)
V, Å^3	5112.1(5)	5155.43(12)	5108.1(3)
Z	2	2	2
D_{calc}, g/cm^3	2.165	2.147	2.167
μ, mm^{-1}	6.249	6.197	6.254
$2\theta_{max}$, deg	69.0	69.0	56.4
temperature, K	123.0(2)	123.0(2)	123.0(2)
wavelength, Å	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
crystal size, mm	0.21 × 0.19 × 0.11	0.23 × 0.10 × 0.05	0.38 × 0.19 × 0.05
range h, k, l	$-16 \leq h \leq 22$, $-25 \leq k \leq 14$, $-25 \leq l \leq 19$	$-15 \leq h \leq 27$, $-27 \leq k \leq 21$, $-27 \leq l \leq 23$	$-22 \leq h \leq 25$, $-20 \leq k \leq 22$, $-16 \leq l \leq 23$
reflns measured	26 067	33 989	40 619
unique reflns	12 782	20 251	11 555
R_{int}	0.0384	0.0239	0.0396
observed ($I > 2\sigma(I)$)	8948	11 975	8985
refined parameters	523	518	502
restraints	0	0	0
R_1, wR_2 ($I > 2\sigma(I)$)	R_1 = 0.0409, wR_2 = 0.0752	R_1 = 0.0283, wR_2 = 0.0611	R_1 = 0.0305, wR_2 = 0.0537
R_1, wR_2 (all data)	R_1 = 0.0683, wR_2 = 0.0780	R_1 = 0.0486, wR_2 = 0.0463	R_1 = 0.0532, wR_2 = 0.0607
goodness-of-fit on F^2	0.995	0.778	1.012
largest diff. peak, hole (e Å^{-3})	2.482/−1.011	1.483/−1.419	3.525/−1.629

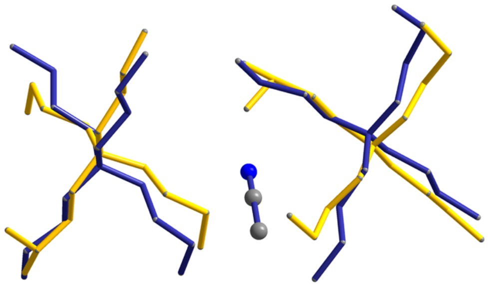

Figure 2. Comparison of the cationic TBA (blue) and solvate MeCN portion of **2** (blue) and **2** (yellow).

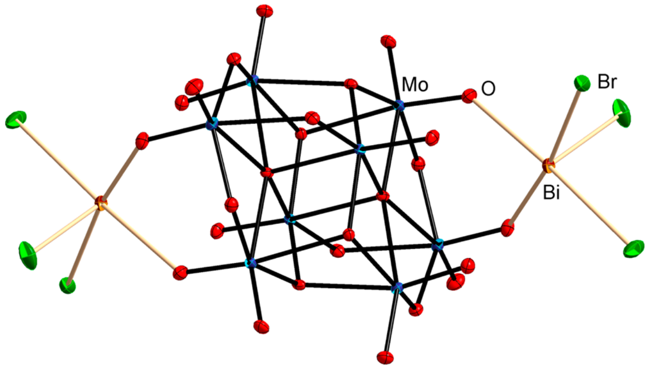

Figure 3. Anion $[Mo_8O_{26}(BiBr_3)_2]^{4-}$ (ellipsoids of 50% probability) in **2**·2MeCN. Longer Bi···O contacts are not shown.

3c polymorphs possess primitive cubic (α-Po) and body-centered cubic (*b.c.c.*) motifs of anionic packing (Supporting Information, Figure 12S). The difference exists also in mutual orientation of the polyoxomolybdate anions (Figure 5). In **3a** and **3c** the anionic parts are isolated by TBA cations, and X···X specific interactions that are quite characteristic of halogen atoms do not occur. In **3b** there are I···I contacts of 4.690 Å found, but they refer to weak van der Waals interactions (>4.30 Å).

■ CONCLUSIONS

A new family of polyoxomolybdate complexes containing coordinated BiX_3 (X = Cl, Br, I) was discovered. All compounds were synthesized in high yield by a very simple and convenient method. In all cases, there appears solvato- or polymorphism, which must be taken into account when checking the purity of complexes by routine X-ray powder diffractometry (XPRD). This synthetic approach may be expanded on numerous POMs soluble in organic media, as well as on several other post-transition metal halides.

■ EXPERIMENTAL SECTION

General Comments. $TBA_4[Mo_8O_{26}]$ was obtained according to the published procedure.[22] All other reagents, including anhydrous Bi

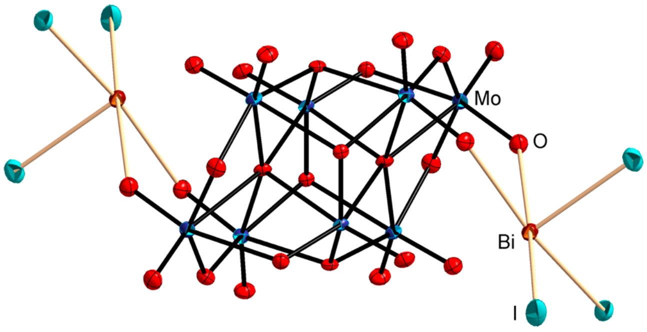

Figure 4. Anion $[Mo_8O_{26}(BiI_3)_2]^{4-}$ (ellipsoids of 50% probability) in **3c**. Longer Bi···O contacts are now shown.

halides, were available from commercial sources and used as purchased; CH_3CN was dried by distillation over P_4O_{10}.

Synthesis of TBA$_4$*[Mo*$_8$*O*$_{26}$*(BiX*$_3$*)*$_2$*] (X = Cl (**1**), Br (**2**), I (**3**)).* 400 mg (0.185 mmol) of $TBA_4[Mo_8O_{26}]$ was dissolved in 20 mL of CH_3CN. Then 0.37 mmol of BiX_3 (117 mg of $BiCl_3$, 167 mg of $BiBr_3$, or 219 mg of BiI_3) was added under stirring. The solution was refluxed. After dissolving BiX_3, the solution remains slightly cloudy; after a few minutes, however, it becomes clear again (being colorless (**1**), very light yellow (**2**), or light orange (**3**)). After 10 min, refluxing was stopped, and the solution was cooled to room temperature. During the cooling, crystals of **1**, **2**, or **3** begin to appear on the flask surface; the process completes in approximately 30 min. Additional portion of **1**, **2**, or **3** may be obtained by cooling of mother liquor (4 °C, overnight). Total yields up to 90%. For $C_{64}H_{144}N_4O_{26}Mo_8Bi_2Cl_6$ calcd, %: C, 27.5; H, 5.19; N, 2.00; found, %: C, 27.6; H, 5.22; N, 2.05. For $C_{64}H_{144}N_4O_{26}Mo_8Bi_2Br_6$ calcd, %: C, 25.1; H, 4.74; N, 1.83; found, %: C, 25.2; H, 4.78; N, 1.89. For $C_{64}H_{144}N_4O_{26}Mo_8Bi_2I_6$ calcd, %: C, 22.9; H, 4.34; N, 1.67; found, %: C, 23.0; H, 4.38; N, 1.70. IR (KBr, cm^{-1}): (**1**) 2961 s, 2932 s, 2874 s,1896 w, 1481 s, 1463 m, 1381 m, 1152 w, 1107 w, 1060 w, 1028 w, 946 s, 933 s, 883 s, 821 s, 721 m, 690 s, 648 m, 577 w, 556 w, 523 m, 480 w, 454 w, 414 m; (**2**) 2960 s, 2931 s, 2872 s, 1894 w, 1481 s, 1462 m, 1380 m, 1153 w, 1106 w, 1058 w, 1028 w, 946 s, 930 s, 889 s, 875 s, 825 s, 722 m, 689 s, 649 m, 577 w, 555 w, 523 m, 480 w, 453 w, 415 m; (**3**) 2958 s, 2930 m, 2872 s, 1896 w, 1481 s, 1463 m, 1379 m, 1152 w, 1106 w, 1055 w, 1026 w, 947 s, 928 s, 893 s, 877 s, 828 s, 721 m, 689 s, 650 m, 579 w, 557 m, 523 m, 482 w, 451 w, 415 m.

X-ray Diffractometry. Crystallographic data and details of structure **1**−**3** refinement are given in Table 1. The diffraction data were collected on an Agilent Technologies SuperMova (**2**·2MeCN, **2**,

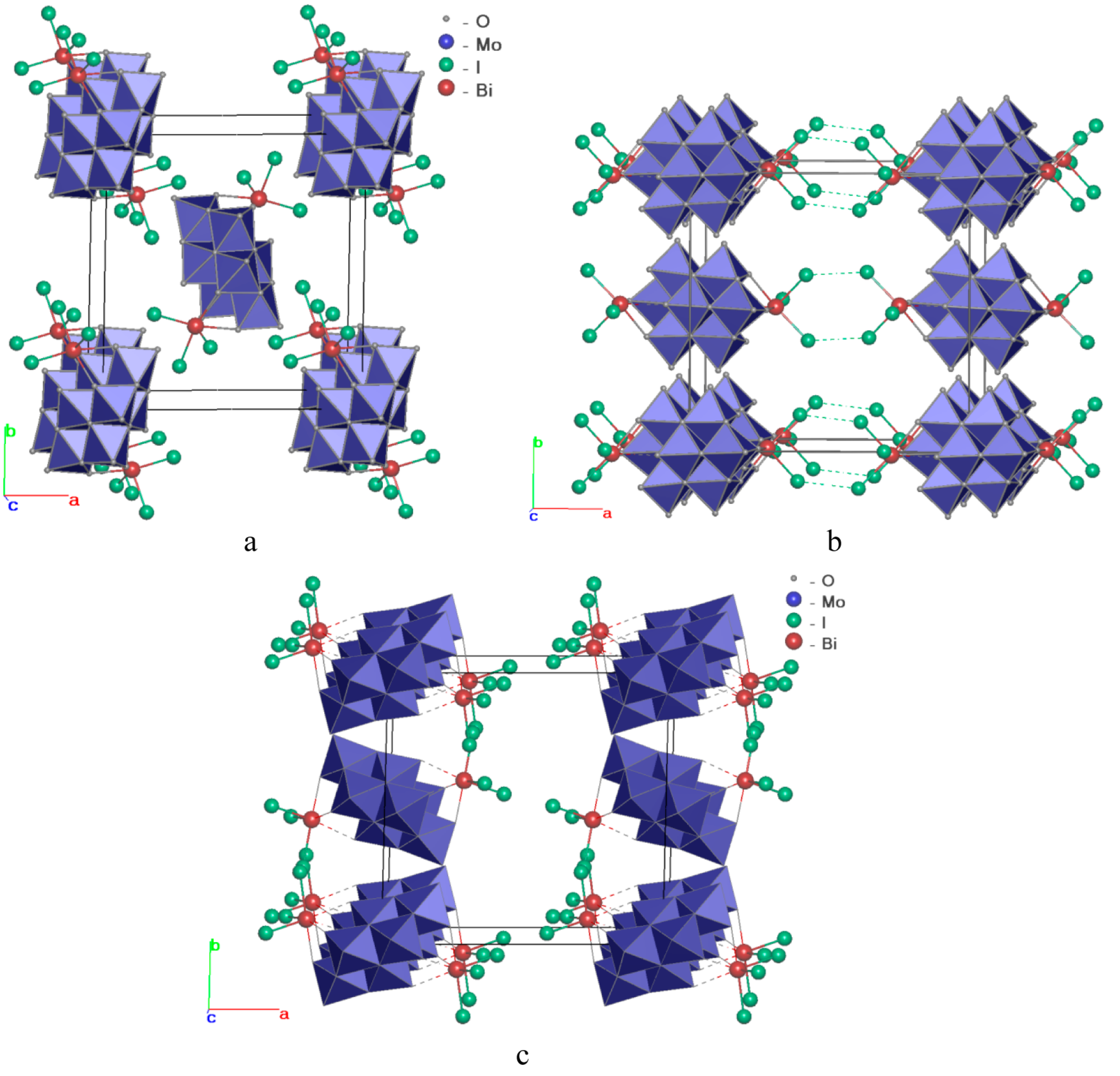

Figure 5. Packing of the anions $[Mo_8O_{26}(BiI_3)_2]^{4-}$ (in polyhedral view) in the polymorphs with motifs of *f.c.c.* (**3a**), primitive cubic (**3b**), and *b.c.c* (**3c**).

3b), Gemini R-Ultra (**1**) with Mo Kα radiation (λ = 0.710 73 Å) using ω scans of 0.5° frames at 123 K, and SuperNova with Cu Kα radiation (λ = 1.541 78 Å) using ω scans of 1° frames (**1**·2MeCN) at 123 K (University of Regensburg). The diffraction data for **3a** and **3c** were collected on a Bruker Apex DUO diffractometer with Mo Kα radiation (λ = 0.710 73 Å) using φ and ω scans of 0.5° frames at 123 K. All structures were solved by direct methods and refined by full-matrix least-squares method against $|F|^2$ in anisotropic approximation using *SHELXTL* programs set.[23] For **1**·2MeCN, **2**·2MeCN, **2**, and **3b** absorption corrections were applied numerically based on multifaceted crystal model using *CrysAlis PRO* software.[24] Absorption corrections were applied empirically using *SADABS* program[25] for **3a** and **3c**. All non-hydrogen atoms were refined anisotropically. Some TBA cations are partly disordered in all structures of **3a**−**c**. Carbon atoms with site occupancy factors less than 0.5 were refined in isotropic approximation. Hydrogen atoms were refined in calculated positions riding on pivot atoms.

The crystal structures of polymorphs **3a** and **3b**/**3c** were solved in different cell choices of monoclinic space group $P2_1/n$ (**3a**, cell choice 2) or $P2_1/c$ (**3b**/**3c**, cell choice 1). The structures **3b** and **3c** in $P2_1/n$ (cell choice 2) would have unit cell parameters a = 17.386, b = 17.396, c = 24.385, β = 135.65 and a = 18.444, b = 16.425, c = 30.907 Å, β = 146.94° of the same volume, respectively; therefore, the unit cell of **3a** can be derived from neither **3b** nor **3c** via this unit cell transformation.

Packing motif was analyzed with TOPOS 4.0 Professional program suite for crystal chemical analysis.[26] Bond lengths and bond angles are summarized in Table 2. Additional crystallographic data are available in the Supporting Information

XRD powder analysis for **1**−**3** was performed on Shimadzu XRD-7000 diffractometer (Cu Kα radiation, Ni filter, 5−60° 2θ range, 0.03° 2θ step, 1 s per step, room temperature). All polycrystalline samples were slightly ground with hexane in an agate mortar, and the resulting suspension was deposited on the polished side of a standard quartz sample holder; a smooth thin layer formed after drying. Indexing of the diffraction patterns was carried out using single-crystal data. Using Powder Cell 2.4 program[27] we estimated cell parameters of **1**: a = 15.5, b = 17.5, c = 19.0 Å, and β = 100.5°.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

XPRD data for **1**−**3**, detail of crystal structures in poly- and solvatomorphs of **1**−**3**, TGA data for **1**·2MeCN and **2**·2MeCN. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC-990359 (compound **1**·2MeCN), −990360 (compound **1**), −990361 (compound **2**·2MeCN), −990362 (compound **2**), −990363 (compound **3a**), −990364 (compound **3b**), and −990365 (compound **3c**) contain the supplementary crystallographic data for this publication. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44−1223−336−033; e-mail: deposit@ccdc.cam.ac.uk).

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Miras, H. N.; Yan, J.; Long, D.-L.; Cronin, L. *Chem. Soc. Rev.* **2012**, *41*, 7403.

(2) Cronin, L.; Müller, A. *Chem. Soc. Rev.* **2012**, *41*, 7333.

(3) Long, D.-L.; Cronin, L. *Dalton Trans.* **2012**, *41*, 9815.

(4) (a) Mizuno, N.; Yamaguchi, K.; Kamata, K. *Coord. Chem. Rev.* **2005**, *249*, 1944. (b) Kozhevnikov, I. V. *Chem. Rev.* **1998**, *98*, 171. (c) Bonchio, M.; Carraro, M.; Sartorel, A.; Scorrano, G.; Kortz, U. *J. Mol. Catal. A: Chem.* **2006**, *25*, 93−99. (d) Antonova, N. S.; Carbo, J. J.; Kortz, U.; Kholdeeva, O. A.; Poblet, J. M. *J. Am. Chem. Soc.* **2010**, *132*, 7488. (e) Maksimchuk, N. V.; Kovalenko, K. A.; Arzumanov, S. S.; Chesalov, Y. A.; Melgunov, M. S.; Stepanov, A. G.; Fedin, V. P.; Kholdeeva, O. A. *Inorg. Chem.* **2010**, *49*, 2920. (f) Kamata, K.; Nakagawa, Y.; Yamaguchi, K.; Mizuno, N. *J. Am. Chem. Soc.* **2008**, *130*, 15304. (g) Zhao, P.; Wang, J.; Chen, G.; Zhou, Y.; Huang, J. *Catal. Sci. Technol.* **2013**, *3*, 1394. (h) Besson, C.; Schmitz, S.; Capella, K. M.; Kopilevich, S.; Weinstock, I. A.; Kögerler, P. *Dalton Trans.* **2012**, 9852. (i) Kholdeeva, O. A. *Eur. J. Inorg. Chem.* **2013**, *10−11*, 1595 and references therein.

(5) (a) Sartorel, A.; Bonchio, M.; Campaqna, S.; Scandola, F. *Chem. Soc. Rev.* **2013**, *42*, 2262. (b) Li, S.; Liu, S.; Liu, S.; Liu, S.; Tang, Q.; Shi, Z.; Ouyang, S.; Ye, J. *J. Am. Chem. Soc.* **2012**, *134*, 19716. (c) Huang, P.; Qin, C.; Su, Z.-M.; Xing, Y.; Wang, X.-L.; Shao, K.-Z.; Lan, Y.-Q.; Wang, E.-B. *J. Am. Chem. Soc.* **2012**, *134*, 14004. (d) Sartorel, A.; Carraro, M.; Toma, F. M.; Prato, M.; Bonchio, M. *Energy Environ. Sci.* **2012**, *5*, 5592. (e) Streb, C. *Dalton Trans.* **2012**, *41*, 1651. (f) Orlandi, M.; Argazzi, R.; Sartorel, A.; Carraro, M.; Scorrano, G.; Bonchio, M.; Scandola, F. *Chem. Commun.* **2010**, *46*, 3152. (g) Wang, Z.-L.; Tan, H.-Q.; Chen, W.-L.; Li, Y.-G.; Wang, E.-B. *Dalton Trans.* **2012**, 9882. (h) Geletii, Y. V.; Botar, B.; Kögerler, P.; Hillesheim, D. A.; Musaev, D. G.; Hill, C. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 3896 and references therein.

(6) (a) Song, Y.-F.; Tsunagashima, R. *Chem. Soc. Rev.* **2012**, *41*, 7384. (b) Li, S.; Liu, R.; Ngo Biboum, R.; Lepoittevin, B.; Zhang, G.; Dolbecq, A.; Mialane, P.; Keita, B. *Eur. J. Inorg. Chem.* **2013**, *10−11*, 1882. (c) Wang, H.; Kawasaki, N.; Yokoyama, T.; Yoshikawa, H.; Awaga, K. *Dalton Trans.* **2012**, 9863. (d) Neves, C. S.; Granadeiro, C. M.; Cunha-Silva, L.; Ananias, D.; Gago, S.; Feio, G.; Carvalho, P. A.; Eaton, P.; Balula, S. S.; Pereira, E. *Eur. J. Inorg. Chem.* **2013**, *16*, 2877. (e) Pinto, R. J. B.; Granadeiro, C. M.; Freire, C. S. R.; Silvestre, A. J. D.; Pascoal Neto, C.; Ferreira, R. A. S.; Carlos, L. D.; Cavaleiro, A. M. V.; Trindade, T.; Nogueira, H. I. S. *Eur. J. Inorg. Chem.* **2013**, *10−11*, 1890. (f) Cardona-Serra, S.; Clemente-Juan, J. M.; Coronado, E.; Marti-Gastaldo, C.; Navarro-Moratalla, E. *Eur. J. Inorg. Chem.* **2013**, *10−11*, 1903 and references therein.

(7) (a) Clemente-Juan, J. M.; Coronado, E.; Gaita-Arino, A. *Chem. Soc. Rev.* **2012**, *41*, 7464. (b) Luo, Z.; Kögerler, P.; Cao, R.; Hill, C. L. *Inorg. Chem.* **2009**, *48*, 7812. (c) Forment-Aliaga, A.; Coronado, E.; Feliz, M.; Gaita-Arino, A.; Llusar, R.; Romero, F. M. *Inorg. Chem.* **2003**, *42*, 8019. (d) Botar, B.; Kögerler, P.; Hill, C. L. *Inorg. Chem.* **2007**, *46*, 5398. (e) AlDamen, M. A.; Clemente-Juan, J. M.; Coronado, E.; Marti-Gastaldo, C.; Gaita-Arino, A. *J. Am. Chem. Soc.* **2008**, *130*, 8874. (f) Wang, N.; Li, F.; Wang, Y.; Xu, L.; Cui, K.; Xu, B. *Eur. J. Inorg. Chem.* **2013**, *10−11*, 1699 and references therein.

(8) (a) Kortz, U.; Al-Kassem, N. K.; Savelieff, M. G.; Al Kadi, N. A.; Sadakane, M. *Inorg. Chem.* **2001**, *40*, 4742. (b) Sokolov, M. N.; Kalinina, I. V.; Peresypkina, E. V.; Cadot, E.; Tkachev, S. V.; Fedin, V. P. *Angew. Chem., Int. Ed.* **2008**, *47*, 1465. (c) Volkmer, D.; Bredenkotter, B.; Tellenbroker, J.; Kögerler, P.; Kurth, D. G.; Lehmann, P.; Schnablegger, H.; Schwahn, D.; Piepenbrink, M.; Krebs, B. *J. Am. Chem. Soc.* **2002**, *124*, 10489. (d) Ibrahim, M.; Mal, S. S.; Bassil, B. S.; Banerjee, A.; Kortz, U. *Inorg. Chem.* **2011**, *50*, 956 and references therein.

(9) (a) Ni, L.; Patzke, G. *CrystEngComm* **2012**, *14*, 6778. (b) Assran, A. S.; Izarova, N. V.; Banerjee, A.; Rabie, U. M.; Abou-El-Wafa, M. H. M.; Kortz, U. *Dalton Trans.* **2012**, *41*, 9914.

(10) (a) Liu, J.; Liu, S.; Qu, L.; Pope, M. T.; Rong, C. *Transition Met. Chem.* **1992**, *17*, 311. (b) Michelon, M.; Herve, G.; Leytrie, M.; Inorg, *J. Nucl. Chem.* **1980**, *42*, 1583.

(11) (a) Hu, X.-X.; Xu, J.-Q.; Cui, X.-B.; Song, J.-F.; Wang, T.-G. *Inorg. Chem. Commun.* **2004**, *7*, 264. (b) Khenkin, A. M.; Shimon, L. J. W.; Neumann, R. *Eur. J. Inorg. Chem.* **2001**, 789. (c) Lu, Y.-K.; Xu, J.-N.; Cui, X.-B.; Jin, J.; Shi, S.-Y.; Xu, J.-Q. *Inorg. Chem. Commun.* **2010**, *13*, 46. (d) Xiao, L.-N.; Peng, Y.; Wang, Y.; Xu, J.-N.; Gao, Z.-M.; Liu, Y.-B.; Zheng, D.-F.; Cui, X.-B.; Xu, J.-Q. *Eur. J. Inorg. Chem.* **2011**, 1997 and references therein.

(12) Villanneau, R.; Proust, A.; Robert, F.; Gouzerh, P. *J. Chem. Soc., Dalton Trans.* **1999**, 421.

(13) Bustos, C.; Carey, D.M.-L.; Boubekeur, K.; Thouvenot, R.; Proust, A.; Gouzerh, P. *Inorg. Chim. Acta* **2010**, *363*, 4262.

(14) Tucher, J.; Nye, L. C.; Ivanovic-Burmazovic, I.; Notarnicola, A.; Streb, C. *Chem.—Eur. J.* **2012**, *18*, 10949.

(15) Ollevier, T. *Org. Biomol. Chem.* **2013**, *11*, 2740 and references therein.

(16) (a) Cheng, H.; Huang, B.; Dai, Y. *Nanoscale* **2014**, *6*, 2009. (b) Liu, J.; Ruan, L.; Adeloju, S. B.; Wu, Y. *Dalton Trans.* **2014**, *43*, 1706. (c) Dash, A.; Sarkar, S.; Adusumalli, V. N. K. B.; Mahalingam, V. *Langmuir* **2014**, *30*, 1401. (d) Shang, J.; Hao, W.; Lv, X.; Wang, T.; Wang, X.; Du, Y.; Dou, S.; Xie, T.; Wang, D.; Wang, J. *ACS Catal.* **2014**, *4*, 954.

(17) Ni, L.; Patscheider, J.; Baldridge, K. K.; Patzke, G. R. *Chem.—Eur. J.* **2012**, *18*, 13293.

(18) Sokolov, M. N.; Mitkina, T. V.; Gerasko, O. A.; Fedin, V. P.; Virovets, A. V.; Llusar, R. *Z. Anorg. Allg. Chem.* **2003**, *629*, 2440.

(19) (a) Li, S.-L.; Lan, Y.-Q.; Ma, J.-F.; Yang, J.; Wang, X.-H.; Su, Z.-M. *Inorg. Chem.* **2007**, *46*, 8283. (b) Zhang, L.; Zhao, Y.; You, W.; Zhu, Z.; Huang, C. *J. Cluster Sci.* **2010**, *21*, 93. (c) Burkholder, E.; Heitzler, F.; Orian, L.; Ouellette, W.; Zubieta, J. *Polyhedron* **2008**, *27*, 3700. (d) Jin, H.; Qi, Y.; Wang, E.; Li, Y.; Qin, C.; Wang, X.; Song, C. *Eur. J. Inorg. Chem.* **2006**, 4541. (e) Hagrman, D.; Zapf, P. J.; Zubieta, J. *Chem. Commun.* **1998**, 1283. (f) Gil-Garcia, R.; Zichner, R.; Diez-Gomez, V.; Donnadieu, B.; Madariaga, G.; Insausti, M.; Lezama, L.; Vitoria, P.; Pedrosa, M. R.; Garcia-Tojal, J. *Eur. J. Inorg. Chem.* **2010**, 4513. (g) Armatas, N. G.; Quellette, W.; Pelcher, J.; Zubieta, J. *Inorg. Chem. Commun.* **2009**, *12*, 747 and numerous references therein.

(20) (a) Abbas, H.; Pickering, A. L.; Long, D.-L.; Kögerler, P.; Cronin, L. *Chem.—Eur. J.* **2005**, *11*, 1071. (b) Abbas, H.; Streb, C.; Pickering, A. L.; Neil, A. R.; Long, D.-L.; Cronin, L. *Cryst. Growth Des.* **2008**, *8*, 635. (c) Han, Z.; Gao, Y.; Hu, C. *Cryst. Growth Des.* **2008**, *8*, 1261. (d) Song, Y.-F.; Abbas, H.; Ritchie, C.; McMillian, N.; Long, D.-L.; Gadegaard, N.; Cronin, L. *J. Mater. Chem.* **2007**, *17*, 1903.

(21) (a) Kitamura, A.; Ozeki, T.; Yagasaki, A. *Inorg. Chem.* **1997**, *36*, 4275. (b) Chen, S.-M.; Lu, C.-Z.; Yu, Y.-Q.; Zhang, Q.-Z.; He, X. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2006**, *60*, m549.

(22) Ginsberg, A. P. *Inorg. Synth.* **1990**, *27*, 78.

(23) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

(24) *APEX2 (Version 1.08), SAINT (Version 7.03), SADABS (Version 2.11);* Bruker Advanced X-Ray Solutions, Madison, WI, 2004.

(25) *CrysAlisPro, Version 1.171.36.21;* Agilent Technologies: Santa Clara, CA, 2012

(26) Blatov, V. A. *IUCr CompComm Newsletter* **2006**, *7*, 4 http://www.topos.ssu.samara.ru.

(27) Kraus, W.; Nolze, G. *J. Appl. Crystallogr.* **1996**, *29*, 301.