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Suppression of Realgar Cage Degradation during Complexation: Formation of Hybrid Coordination Polymers with As_4S_4, PAs_3S_3, and Cu(I) Halide Building Blocks

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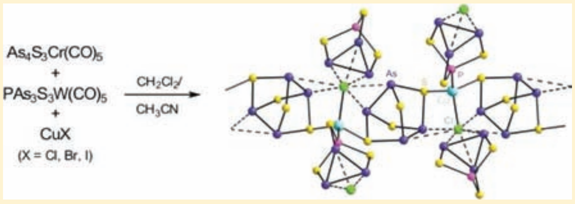
S *Supporting Information*

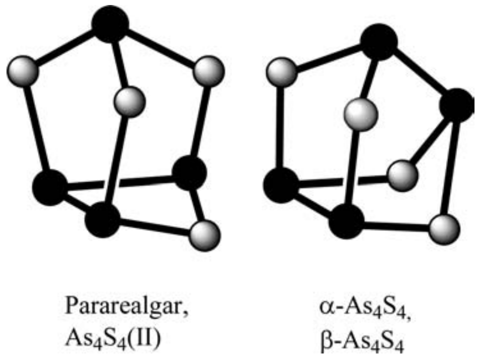
ABSTRACT: Realgar, As_4S_4, reacts with $Cr(CO)_5THF$ under cage degradation to give $As_4S_3{\cdot}Cr(CO)_5$ (**1**). The reverse structural change is found if solutions of **1** in CH_2Cl_2 react with equimolar amounts of $PAs_3S_3{\cdot}W(CO)_5$ and CuX (X = Cl, Br, I) in CH_3CN under biphasic diffusion conditions. The resulting coordination polymers **2**−**4** contain a reconstituted realgar molecule along with the PAs_3S_3 cage. The crystal structures of $(CuX)(As_4S_4)(PAs_3S_3)$ (X = Cl: **2**; Br: **3**) are characterized by one-dimensional (1D) $(CuX)(As_4S_4)$ strands, which are formed by alternating As_4S_4 cages and CuX dumbbells. Terminal PAs_3S_3 molecules are coordinated to copper by apical phosphorus and bridging realgar through sulfur. The As_3 triangles of the resulting $(CuX)(As_4S_4)(PAs_3S_3)$ strands interact with halides of neighbored strands to give a folded three-dimensional (3D) network. The structure of $(CuI)_3(As_4S_4)(PAs_3S_3)$ (**4**) contains 1D $(Cu_3I_3)_n$ strands as backbones, which are bridged by sulfur atoms of two $\eta^{1:2}$-As_4S_4 molecules while PAs_3S_3 confines the resulting sheet. The As_3 triangles at the surface of the layers interact with iodide of the next layer to form a layered 3D network.



INTRODUCTION

Among arsenic sulfide minerals realgar, α-As_4S_4, is distinguished by a unique light-induced structural change to pararealgar (Scheme 1).[1,2] While the solid-state chemistry of realgar has been well explored[3−7] its solution chemistry is poorly developed. A recent exception includes dissolution of α-As_4S_4 in ethylendiamine and its transfer into nanocrystals exhibiting interesting photochemical properties.[8]

Scheme 1. Structures of As_4S_4 Polymorphs (As, black; S, gray)



Efforts to integrate the intact realgar cage in the coordination sphere of organometallic complexes led in most cases to excision of small As/S fragments.[9] Attempts to improve the very low solubility of realgar by reacting it with $Cr(CO)_5THF$ in tetrahydrofuran (THF) led to the postulation of an $As_4S_4{\cdot}2[Cr(CO)_5]$ diadduct.[10] A new strategy for implementation of intact inorganic cage molecules in polymeric copper(I) halide assemblies has been recently developed for P_4S_3 in kinetically controlled biphasic diffusion experiments.[11,12] This method has been successfully adapted for As_4S_3 and, with still better results, for its adduct $As_4S_3{\cdot}Cr(CO)_5$.[13,14] Recently, we have found that the PAs_3S_3 cage plays a crucial role in the construction of copper halide coordination polymers not only because of the availability of P and S coordination sites but also for the important contribution of As-X interactions leading even to the cleavage of CuX (X = Cl, Br, I) bonds.[15] In this work we report on the degradation of the realgar cage in its reaction with $Cr(CO)_5THF$ and its reconstitution in inorganic hybrid polymers containing As_4S_4, PAs_3S_3 and copper halide building blocks.

RESULTS AND DISCUSSION

1. Reaction of Realgar with $Cr(CO)_5THF$. The reaction of a suspension of realgar in THF with $Cr(CO)_5THF$ (18 h, room temperature) gives an orange-brown solid. Relatively pure **1** is obtained after chromatography on SiO_2 as a yellow-orange amorphous powder in 33−40% yield. The composition $As_4S_3{\cdot}Cr(CO)_5$ is based on IR, Raman, and field desorption (FD) mass spectra. The IR spectrum of **1** shows intense ν(CO) frequencies at 1943 and 2072 cm^{-1} typical of the $Cr(CO)_5$ fragment. FD mass spectrometry reveals the base peak at m/z =

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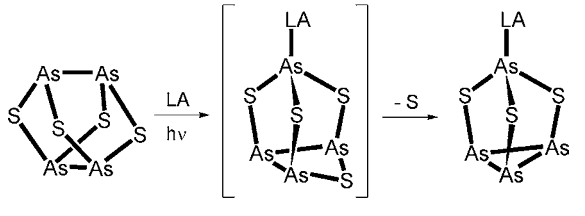
395.5 ([As_4S_3]$^+$), which may be formed by loss of $Cr(CO)_5$ from **1** under mass spectroscopic conditions, and a very weak peak at $m/z = 619.5$ (intensity <1). The latter may be assigned to the composition [$As_4S_4{\cdot}Cr(CO)_5$]$^+$ and may arise from adducts of residual realgar or pararealgar.

It is important to note that the formation of **1** requires the presence of light, for in the dark the yield of **1** drops below 4%. This observation parallels the transformation of realgar into pararealgar in the solid state suggesting the participation of adducts of intermediate pararealgar[2] or As_4S_4(II)[16] (Scheme 2).

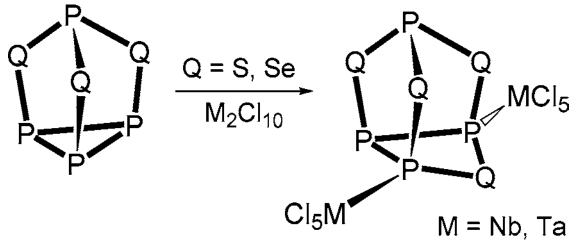
Scheme 2. LA = $Cr(CO)_5$



1

Attempts to recrystallize **1** from toluene or other solvents gave a mixture of two polymorphs of As_4S_3 (dimorphite-I and dimorphite-II[17]), β-As_4S_4,[18] alacranite (As_8S_9),[19] and uzonite (As_4S_5)[20] according to single crystal X-ray determinations. An amorphous yellow powder cannot be analyzed. These findings show that the stability of the As_4S_3 cage is considerably reduced by attached $Cr(CO)_5$ when compared to the crystalline phase. A similar cage enlargement has been observed for P_4Q_3 (Q = S, Se), which gives $(MCl_5)_2$(β-P_4Q_4) upon reaction with M_2Cl_{10} (M = Nb, Ta) in CS_2/hexane (Scheme 3).[21]

Scheme 3



Because of the lack of single crystal or powder X-ray diffraction data, the structure of **1** can be deduced by comparison of its Raman spectrum with that of $As_4S_3{\cdot}Cr(CO)_5$ previously prepared from As_4S_3 and $Cr(CO)_5$THF.[13] For the latter compound the coordination of $Cr(CO)_5$ at the apical arsenic atom has been established crystallographically.[9] Both spectra are similar so that they may belong to the same compound. A comparison with the spectra of realgar,[22] pararealgar,[22] and As_4S_3 shows most similarities with the pattern observed for As_4S_3.[23] A characteristic shift from 282 to 270 cm^{-1} is observed for one of the ν(As−S) modes, while the other one at 232 cm^{-1} may be part of the frequencies around 200 cm^{-1} (Figure 1). The Raman active ν_1 (358 cm^{-1}) and ν_6 (378 cm^{-1}) modes of the free cage[23] may be split into a couple of frequencies between 335 and 384 cm^{-1} as a consequence of symmetry reduction. There is also strong chemical evidence for the identity of **1** with that of directly prepared $As_4S_3{\cdot}Cr(CO)_5$ (see above), for both compounds form identical polymers in their reactions with copper(I) halides.[13]

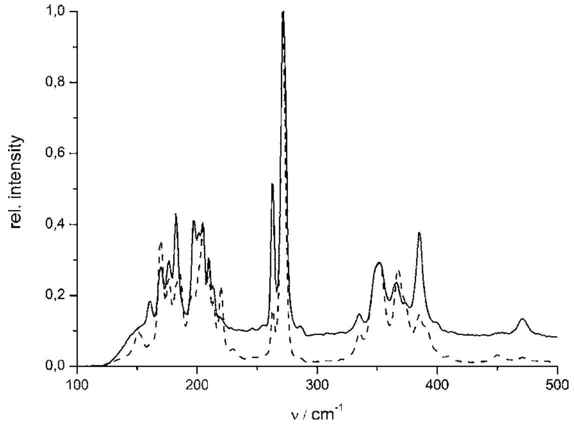


Figure 1. Comparison of Raman spectra of **1** (dashed line) and $As_4S_3{\cdot}Cr(CO)_5$ (solid line) synthesized from As_4S_3 and $Cr(CO)_5$THF.

2. Synthesis and Structures of Coordination Polymers. Layering an equimolar mixture of $PAs_3S_3{\cdot}W(CO)_5$, **1**, and CH_2Cl_2 with the solution of CuX (X = Cl, Br, I) in CH_3CN gave after complete interdiffusion yellow prisms of $(CuX)(As_4S_4)(PAs_3S_3)$ (X = Cl, **2**; Br, **3**) and orange platelets of $(CuI)_3(As_4S_4)(PAs_3S_3)$ (**4**). These were characterized by single crystal X-diffraction analysis, while other yellow crystalline material was not suitable for X-ray diffraction experiments. Accompanying red crystals were identified as realgar[18] and As_8S_9.[19] Variation of stoichiometry or concentration did not influence the product distribution. For comparison purposes reactions of saturated solutions of PAs_3S_3 and As_4S_4 in CS_2 with CuX solutions in CH_3CN were carried out, but produced crystals of realgar,[18] As_8S_9,[19] and As_4S_5.[20] Note that reactions of **1** with copper(I) halides give polymers $(CuX)(As_4S_3)$.[13,24]

The characteristic structural features of **2** and isostructural **3** are one-dimensional (1D) $(CuX)(As_4S_4)$ strands (X = Cl, Br) bearing attached PAs_3S_3 molecules. The latter coordinate via their apical P atoms to pseudotetrahedral coordinated Cu atoms (Figures 2, 3). The realgar cages are linked by CuX dumbbells through the sulfur atoms S4 and S6, the concerned Cu−S distances are 0.1 Å longer than those, for example, in $(CuCl)(As_4S_3)$.[13] The mean As−As distances (2.557(1) Å) within the realgar cage are slightly shorter than those in the free

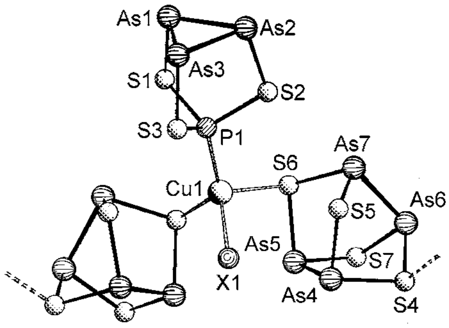


Figure 2. Section of the structures of $(CuX)(As_4S_4)(PAs_3S_3)$ (X = Cl (**2**), Br (**3**)). Selected distances (Å) for **2**: Cu1−Cl1 2.320(2), Cu1−P1 2.207(2), Cu1−S4 2.393(2), Cu1−S6 2.348(2), P−S_{mean} 2.091(2), As−As $(PAs_3S_3)_{mean}$ 2.456(1), As−As $(As_4S_4)_{mean}$ 2.557(1), As−S $(PAs_3S_3)_{mean}$ 2.235(2), As−$S_{Cu(mean)}$ 2.266(2), As−S $(As_4S_4)_{mean}$ 2.235(2).

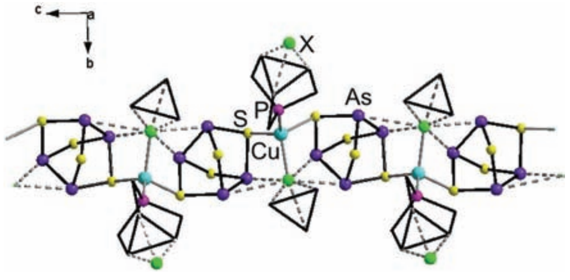


Figure 3. Section of the crystal structures of **2** (X = Cl) and **3** (X = Br) showing the 1D-strand of $(CuX)(As_4S_4)$ with attached PAs_3S_3 cages (black). The PAs_3S_3 molecules coordinated at X are represented by As_3 triangles and the As···X interactions by dashed lines.

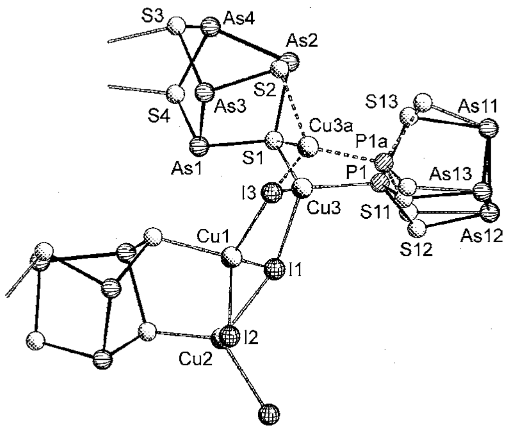


Figure 4. Section of the structure of **4**. The disorder ratio of Cu3/Cu3a, P1/P1a, S11/S11a, S12/S12a, and S13/S13a is ca. 67:33. Selected distances (Å): Cu1–Cu2 2.598(2), I–Cu 2.564(3)–2.706(2), S1–Cu3 2.279(2), S3–Cu2 2.303(2), S4–Cu1 2.310(2), Cu3–P1 2.239(7), $P{-}S_{mean}$ 2.072(12), As–As $(As_4S_4)_{mean}$ 2.547(2), As–As $(PAs_3S_3)_{mean}$ 2.468(2), As1–S1 2.238(2), As1–S4 2.632(2), As2–S1 2.280(2), As2–S2 2.230(2), As3–S3 2.253(2), As4–S3 2.284(2), As4–S4 2.255(2), As–S $(PAs_3S_3)_{mean}$ 2.252(6).

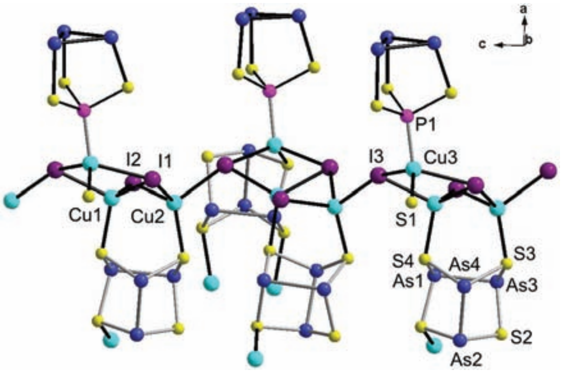


Figure 5. Section of the structure of **4A**, showing the $(Cu_3I_3)_n$ backbone with attached cage molecules. Monodentate As_4S_4 is represented by "S1".

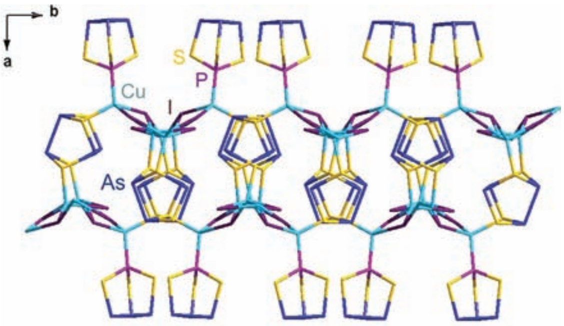


Figure 6. Section of the structure of **4A**, view down the *c* axis. As···I interactions are not shown.

molecule [*d*(As–As) = 2.59 Å].[25] A slight deformation of the As_4S_4 cage is observed, for the As–S distances in the vicinity to copper [mean 2.266(2) Å] are longer by 0.03–0.04 Å than the other ones [mean 2.235(2) Å].

The observed slight deformation may be explained by Cu coordination to sulfur, but also by As···X interactions. These may be divided into weak intrastrand interactions between realgar atoms As4 and As5 with, for example, Cl1 [*d*(As···Cl1) 3.10–3.40 Å] and interstrand interactions between the arsenic rich basis of PAs_3S_3 cages and Cl1 of the next chain [*d*(As···Cl1) 3.13–3.34 Å] (Figure 3). Thus, stacks of $(CuX)(As_4S_4)$ strands running down the *c* axis are mutually connected by PAs_3S_3 molecules to give a three-dimensional network (Supporting Information, Figure S1). The corresponding As···Br distances in **3** range between 3.18 and 3.47 Å.

Compounds **2** and **3** are first examples of coordination polymers of intact realgar obtained from solution. Related high temperature phases have been synthesized recently from d^{10} metal halides and As_4S_4.[26] While the Hg(II) compounds can be described as adducts with very weak metal–sulfur contacts, Raman spectroscopy proves cage deformation in $(CuI)_3(As_4S_4)_2$.[26c]

Compound **4** crystallizes as twins in the space group $P2_1/c$. Refinement of the structure gives two partially disordered polymeric strands. Each strand is characterized by a 1D $(Cu_3I_3)_n$ backbone bearing a PAs_3S_3 cage and two $\mu,\eta^{1:2}$-As_4S_4 cage molecules. The difference between both strands is a 67:33 occupancy of Cu3/Cu3a giving rise to the formation of two isomers **4A** and **4B** (Figure 4). In **4A** bicyclic Cu_3I_3 rings are linked via their corners Cu2–I3. The Cu1–I1–Cu2–I2 ring is folded giving rise to a relatively short Cu1–Cu2 distance of 2.60 Å,[27] while the ring Cu1–I1–Cu3–I3 is nearly planar (Figure 5). Such a looped-chain structural motif seems to be unusual in the coordination chemistry of copper(I) halides.[28] The coordination sphere of Cu3 is completed by P1 of an exo PAs_3S_3 cage and S1 of one of the As_4S_4 cradles. The edge Cu1–Cu2 is bridged by another realgar molecule. The resulting averaged Cu–S distances of 2.306 Å are significantly shorter than those in **2** or **3**, which may explain slight distortions in both realgar ligands.

As a result of weak Cu–S and As–I bonding (see below) stacks of $(Cu_3I_3)(PAs_3S_3)$ strands are connected by As_4S_4 giving a two-dimensional (2D) layer with exo-As_3 triangles as nearly coplanar surfaces (Figure 6). The appropriate triangles interact with I2 of the next layer to form a layered 3D-network (Figure 7).

In the structure of **4B** Cu(3a) is ligated by I3, by S1 and S2 of an As_4S_4 ligand, and P1a of the exo-PAs_3S_3 ligand, which also shows a 33% disorder. As a consequence of the altered coordination geometry around Cu3a the ring Cu3–I3–Cu1–I1 is opened [*d*(Cu3a–I1) = 3.972 Å] (Figure 4), but without severe consequences for the polymeric nature of the (Cu_3I_3) chain. This is also the case for the concerned realgar cage which now provides all sulfur atoms for coordination in the 2D-network (Supporting Information, Figure S2).

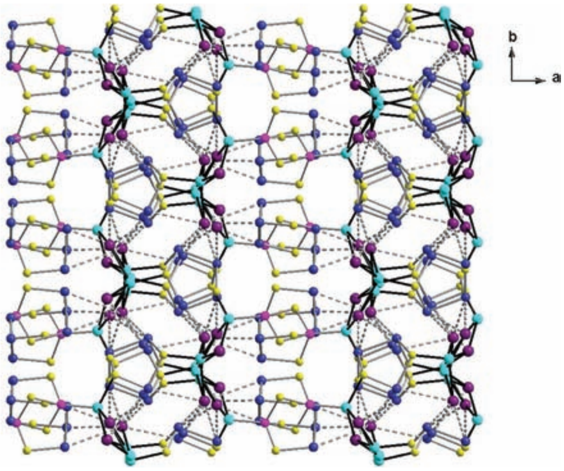


Figure 7. 3D network of the structure of **4A**. As···X interactions are represented by dashed lines.

As already mentioned As−I distances between 3.49 and 3.76 Å, which are significantly shorter than the sum of the van der Waals radii of As and I (4.15 Å) are observed within and between the 2D layers. According to the steric situation of the iodine atoms different coordination numbers exist. While I(2) is surrounded by seven As atoms (Supporting Information, Figure S3) of three As_4S_4 ligands and one PAs_3S_3 cage, I1 interacts with As2 and As4 and I3 with As3 of two As_4S_4 ligands.

CONCLUSIONS

This study reports on the formation of a novel type of inorganic hybrid polymer by assembling different inorganic cage molecules of multifunctional character, for example, As_4S_4 and PAs_3S_3, and copper(I) halide building blocks. It is also a contribution to the long sought complexation of the intact realgar cage in solution. The incorporation of the intact realgar cage in polymeric d^{10} metal halide compounds has been a privilege of high temperature solid-state chemistry thus far.[26,29]

EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out under nitrogen by using Schlenk techniques; the tube diameter in diffusion experiments was 3 cm. β-As_4S_4[30] and PAs_3S_3[31] were obtained by melting together the elements in stoichiometric amounts. $PAs_3S_3\cdot W(CO)_5$ was synthesized from PAs_3S_3 and $W(CO)_5THF$ in THF.[15] The Raman spectra were recorded on a Varian FTS 7000e spectrometer containing a FT Raman unit. The excitation of the microcrystalline samples was carried out with a Nd:YAG laser (λ = 1064 nm) and detection was performed with a liquid N_2 cooled Ge detector.

Synthesis of 1. A 274 mg portion (0.64 mmol) of As_4S_4 was added to 35 mL (c = 0.028 mol L^{-1}) of $Cr(CO)_5THF$[32] in THF. The suspension was stirred for 18 h at room temperature. After evaporation of the solvent the dark brown solid was suspended in 20 mL of toluene and transferred to the top of a column with SiO_2 (15 × 3 cm). With toluene an orange band was eluted containing **1** in 33−40% yield. **1:** IR (KBr, cm^{-1}): 1943s, 2072 m [ν(CO)].

(CuX)(As_4S_4)(PAs_3S_3) (X = Cl, 2; Br, 3) and (CuI)$_3$(As_4S_4)-(PAs_3S_3) (4). The yellow solutions of $PAs_3S_3\cdot W(CO)_5$ (0.044 mmol) and $As_4S_3\cdot Cr(CO)_5$ (0.044 mmol) in CH_2Cl_2 (20 mL) were carefully layered with the solution of the corresponding copper(I) halide (0.048 mmol) in acetonitrile (15 mL). At the end of this process a fine powder precipitated and then yellow to orange crystals appeared. These were separated from the powder by repeated washing and decantation with pentane. According to X-ray diffraction analysis the yellow prisms have composition (CuX)(As_4S_4)(PAs_3S_3) (X = Cl, **2**; Br, **3**) and the orange-red platelets have composition (CuI)$_3$(As_4S_4)-(PAs_3S_3) (**4**).

X-ray Structure Determination of Compounds 1−4. Crystallographic data of the crystal structure determinations for **1−4** are given in Table 1. The structures were solved by direct methods (SIR-97 program) and refined by full-matrix anisotropic least-squares (SHELXL97 program) with all reflections. Compound **4**: All examined

Table 1. Crystallographic Data of Compounds 2−4

	2	3	4
formula	$As_7ClCuPS_7$	$As_7BrCuPS_7$	$As_7Cu_3I_3PS_7$
M_w	878.90	923.35	1351.25
crystal size [mm]	0.9 × 0.05 × 0.03	0.08 × 0.06 × 0.05	0.11 × 0.05 × 0.015
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [Å]	9.531(1)	9.630(1)	15.233(1)
b [Å]	13.201(1)	13.295(1)	10.887(1)
c [Å]	13.563(1)	13.738(1)	13.332(1)
β [deg]	96.2(1)	96.6(1)	91.5(1)
V [Å^3]	1696.5(1)	1747.4(1)	2206.1(1)
Z	4	4	4
σ_{calcd} [g cm^{-3}]	3.441	3.510	4.068
μ [Cu$_{K\alpha}$, mm^{-1}]	27.212	27.692	54.795
instrument	Oxf. Diff. Gemini Ultra	Oxf. Diff. Gemini Ultra	Oxf. Diff. SuperNova
T [K]	123	123	123
scan range	$4.67 < \Theta < 66.51$	$4.62 < \Theta < 66.57$	$5.00 < \Theta < 73.76$
reflns collected	6144	6815	8870
unique observed [$I > 2\sigma(I)$]	2651	2724	7784
parameters refined	154	154	201
absorption correction	analytical	analytical	analytical
transmission	0.477/0.201	0.381/0.197	0.433/0.047
max/min residual density [e/Å^{-3}]	0.895/−1.546	0.818/−0.958	1.858/−1.409
R_1, wR_2 ($I > 2\sigma$)	0.031, 0.083	0.026, 0.067	0.041, 0.122
R_1, wR_2 (all data)	0.035, 0.086	0.030, 0.069	0.048, 0.125

crystals obviously were nonmerohedral two-domain twins, a single crystal could not be found, and therefore we must collect the data from such a twin. It was possible to index all reflections with two orientation matrices, and the twin law then was identified as (100, 0−10, 00−1). The software (CrysAlisPro)[33] enabled us to integrate the intensities of the two domains. In the next step, it is possible to generate one data set of the major component only with those reflections that do not overlap with any reflection of the second domain. From this data set the structure clearly could be solved. In the last step the HKLF5 format file with all reflections and their required batch number was generated by the program, including all unaffected reflections, all exactly overlapped, and all partially overlapped reflections. The subsequent structure refinement led to a very satisfactory result and refined the ratio of the twin components to 0.616(2) to 0.384.

ASSOCIATED CONTENT

Supporting Information

Crystal structure of **2**, section of the structure of **4B**, coordination sphere around I2 in **4A**. This material is available free of charge via the Internet at http://pubs.acs.org.

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