

Substitution of Conventional High-temperature Syntheses of Inorganic Compounds by Near-room-temperature Syntheses in Ionic Liquids

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The high-temperature syntheses of the low-valent halogenides P_2I_4 , Te_2Br , $\alpha\text{-Te}_4I_4$, $Te_4(Al_2Cl_7)_2$, $Te_4(Bi_6Cl_{20})$, $Te_8(Bi_4Cl_{14})$, $Bi_8(AlCl_4)_2$, Bi_6Cl_7 , and Bi_6Br_7 , as well as of $WSCl_4$ and $WOCl_4$ have been replaced by resource-efficient low-temperature syntheses in room temperature ionic liquids (RTILs). The simple one-pot syntheses generally do not require elaborate equipment such as two-zone furnaces or evacuated silica ampoules. Compared to the published conventional approaches, reduction of reaction time (up to 80 %) and temperature (up to 500 K) and, simultaneously, an increase in yield were achieved. In the majority of cases, the solid products were phase-pure. X-Ray diffraction on single crystals (redetermination of 11 crystal structures) has demonstrated that the quality of the crystals from RTILs is comparable to that of products obtained by chemical transport reactions.

Key words: Cluster Compounds, Ionic Liquids, Low-valent Compounds, Resource-efficient Synthesis, Sustainable Chemistry

Introduction

Chemical synthesis of materials is facing enormous challenges: Energy turnaround for sustainability requires completely new materials with outstanding properties on the one hand, while there is the imperative for resource-efficient use of raw materials and energy through more efficient production of well-known and already used materials on the other hand. Sustainable chemical processes must be conceived and developed, which are working at lower temperature, allow for higher purity and yield, and produce less waste. A promising option is the use of ionic liquids (ILs) – organic salts that are liquid below 100 °C or, for some examples, even at room temperature (room-temperature ionic liquids, RTILs) [1–7] – as unique reaction media. The features of these solvents can be widely adapted by variation of their chemical composi-

tion. Promising first results have demonstrated that various inorganic materials (metals, alloys, semiconductors, refractory and functional materials) can be produced in ILs near ambient conditions [8–18]. Hence, this approach enables an enormous reduction of energy usage and technical efforts compared to the so far applied high-temperature processes. At the same time, chemical material syntheses become better controllable, also increasing the energy and resource efficiency. Syntheses in ILs also provide great opportunities to discover completely new low-temperature compounds with potentially outstanding and useful chemical and physical properties [19–25].

In this contribution, we want to show some of our own examples from inorganic solid-state chemistry that demonstrate the validity of the low-temperature approach for replacing classical high-temperature synthesis even for compounds with rather complex com-

positions and/or unusual oxidation states. We compare the reaction conditions, the obtained yields, and the purity of the products when using RTILs with those of the corresponding conventional syntheses reported in literature. The eleven showcases comprise main-group as well as transition metal chemistry, structures with discrete groups, such as molecules or cationic clusters, as well as network structures.

Results and Discussion

We utilized Lewis-acidic RTILs of the type [BMIm]Cl· x AlCl₃ with $x = 1.3–4.8$ ([BMIm]⁺ = 1-butyl-3-methylimidazolium) to synthesize the discussed compounds. Due to the sensitivity of aluminum halides and some of the products to humid air, all manipulations were carried out under inert conditions in an argon-filled glove box, and the reactions under Schlenk conditions or, in two cases, in ampoules. In a first step, the liquid RTILs were formed by reaction of solid [BMIm]Cl with solid AlCl₃. Subsequently, the reactants were added to the RTIL under argon counter current. After stirring the reaction mixture, typically for about 16 h (overnight), the solution was filtered into a screw cap septum vial to separate unreacted starting material. To promote crystallization by decreasing the Lewis acidity, dry sodium chloride was added to the solution in some cases ($\text{AlCl}_3 + \text{Cl}^- \rightarrow \text{AlCl}_4^-$). The purity of the isolated materials was checked by visual inspection and powder X-ray diffraction. In case of single-phase products, the yields ranged from 39 to 64 %. X-Ray diffraction on single crystals demonstrated that the quality of the crystals from RTILs is comparable to those obtained by slow deposition in high-temperature chemical gas-phase transport reactions. However, using RTILs for the synthesis of materials can also have some disadvantages, such as the coverage of the surface of the product with solvent

molecules or hindered crystallization due to the high viscosity of the solutions at room temperature.

In the following, we compare the performances of RTIL-based and conventional syntheses for eleven inorganic compounds in detail. The synopsis (see Table 12) also includes five syntheses in RTILs that were previously published by us.

P_2I_4

Baudler synthesized P_2I_4 by a modified version of the method of Germann and Traxler as follows [26]: A solution of white phosphorus in CS₂ and a solution of iodine in CS₂ were gradually combined. After 12 h in the dark and quick evaporation of the solvent, orange-red crystals were isolated. We obtained bright-red crystals of P_2I_4 by reacting red phosphorus and iodine in the Lewis-acidic RTIL [BMIm]Cl·4.8AlCl₃ at 120 °C within 3 days (yield 30 %). Thereby, the pyrophoric solution of white phosphorus in highly toxic CS₂ was substituted by a much more convenient and safe alternative. The atomic coordinates (Table 1) correspond well with published data [27]. The triclinic unit cell contains one P_2I_4 molecule in the shape of a phosphorus dumbbell with terminal iodine atoms.

Te_2Br

Te_2Br was formerly synthesized by Rabenau *et al.* from the elements at 220 to 260 °C with subsequent annealing at 350 °C, quenching, and again annealing at 165 °C for several weeks. To obtain phase pure material, the product had to be extracted from the solid solution by organic solvents in several steps [28]. In contrast, we synthesized phase pure Te_2Br (Fig. 1) at room temperature by synproportionation of tellurium and TeBr₄ in the RTIL [BMIm]Cl·1.3AlCl₃ within five days. The atomic coordinates correspond to the published data with a maximum deviation of 4 σ (Table 2).

Table 1. Atomic parameters for a P_2I_4 single crystal synthesized in RTIL. ICSD data determined using a conventionally synthesized crystal is given in *italics*.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
P	0.601(1) <i>0.603</i>	0.1370(6) <i>0.139</i>	0.4613(8) <i>0.463</i>	350(60)	510(30)	280(70)	40(30)	−40(70)	−70(20)	400(30)
I1	0.4416(4) <i>0.423</i>	0.2290(2) <i>0.230</i>	0.1654(3) <i>0.165</i>	570(20)	477(7)	340(20)	−3(8)	−130(20)	−7(6)	472(8)
I2	0.1814(4) <i>0.180</i>	0.3023(2) <i>0.303</i>	0.6944(3) <i>0.695</i>	560(20)	514(8)	460(20)	100(9)	−180(20)	−183(7)	502(9)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₃	<i>U</i> _{eq}
Te1	0.4250(1) <i>0.4251(3)</i>	1/4	0.7346(1) <i>0.7352(3)</i>	200(10)	220(10)	275(9)	−29(9)	234(5)
Te2	0.0893(1) <i>0.0889(3)</i>	1/4	0.0794(1) <i>0.0792(3)</i>	240(10)	170(10)	226(9)	−27(8)	213(5)
Te3	0.2823(1) <i>0.2823(3)</i>	1/4	0.0445(1) <i>0.0440(3)</i>	290(10)	140(10)	191(8)	11(8)	210(5)
Te4	0.1792(2) <i>0.1788(3)</i>	1/4	0.6916(1) <i>0.6904(3)</i>	210(10)	140(10)	250(10)	31(8)	200(5)
Br1	0.0533(2) <i>0.0533(5)</i>	1/4	0.3968(2) <i>0.3970(5)</i>	600(30)	140(20)	210(10)	50(10)	315(9)
Br2	0.3446(2) <i>0.3446(5)</i>	1/4	0.3649(2) <i>0.3638(5)</i>	550(30)	180(20)	240(10)	−40(10)	326(9)

Table 2. Atomic parameters for a Te₂Br single crystal synthesized in RTIL. ICSD data determined using a conventionally synthesized crystal is given in *italics*. *U*₁₂ = *U*₂₃ = 0.

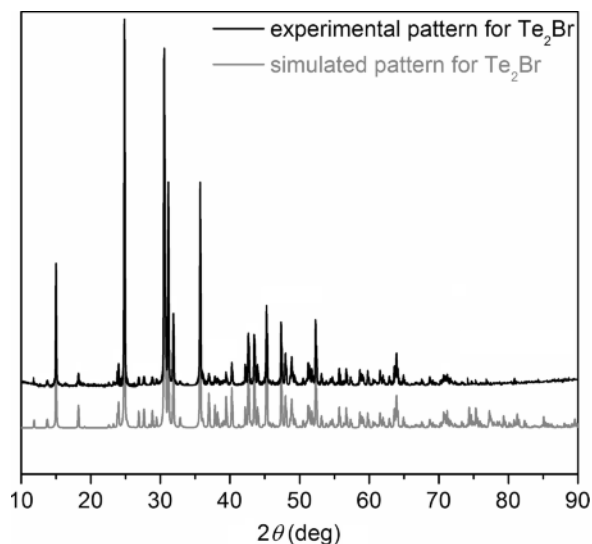


Fig. 1. Experimental (black) and calculated (grey) powder pattern of Te₂Br (CuK α ₁).

The crystal structure of Te₂Br consists of condensed infinite double zig-zag chains of tellurium which form a ribbon of boat-shaped rings. These ribbons are saturated by bridging bromine atoms.

α -Te₄I₄

α -Te₄I₄ was conventionally synthesized first by Kniep *et al.* from the elements at 200 °C [29]. By using a hydrothermal approach in concentrated HI acid at the same temperature, Kniep could improve the synthesis and obtained a single-phase product within eight days [30]. We obtained phase pure α -Te₄I₄ (Fig. 2) within two days at room temperature by reacting tellurium with TeI₄ in [BMIm]Cl·1.3AlCl₃. The crystal structure consists of slightly folded Te₄ rings that are saturated with two iodine atoms perpendicular to the

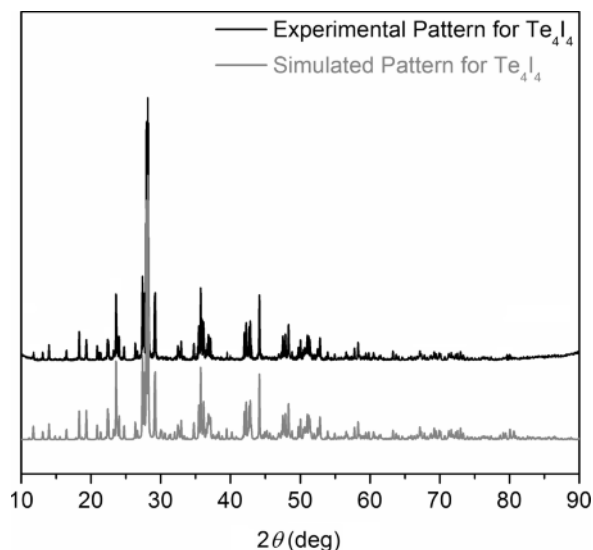


Fig. 2. Experimental (black) and calculated (grey) powder pattern of α -Te₄I₄ (CuK α ₁).

ring and two iodine atoms in the plane of the ring. The atomic coordinates correspond to the published data of a structural redetermination [31] with a maximum deviation of 5 σ (Table 3).

Te₄(Al₂Cl₇)₂

Corbett *et al.* synthesized Te₄(Al₂Cl₇)₂ by heating a mixture of tellurium, TeCl₄, and AlCl₃ in the molar proportions 3 : 1 : 4 to about 250 °C in a sealed evacuated Pyrex tube [32]. We obtained Te₄(Al₂Cl₇)₂ by reacting tellurium, TeI₄, and red phosphorus (attempt to synthesize phosphorus-tellurium polycations) in the Lewis-acidic RTIL [BMIm]Cl·4.8AlCl₃ at 80 °C within four days. The yield was about 70%. Phosphorus and a fraction of the tellurium remained. The structure of Te₄(Al₂Cl₇)₂ consists of square Te₄²⁺ cations

Table 3. Atomic parameters for a twinned α -Te₄I₄ crystal synthesized in RTIL. ICSD data determined using a conventionally synthesized crystal is given in *italics*.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃	<i>U</i> _{eq}
Te1	0.5049(2) <i>0.5043(2)</i>	0.0041(1) <i>0.0046(1)</i>	0.19334(9) <i>0.1931(2)</i>	348(8)	274(4)	298(5)	104(4)	71(5)	55(4)	303(3)
Te2	0.7729(2) <i>0.7727(2)</i>	0.3150(1) <i>0.3147(1)</i>	0.2886(1) <i>0.2884(2)</i>	312(7)	327(4)	322(6)	105(4)	66(5)	56(4)	317(3)
Te3	0.5006(2) <i>0.5008(2)</i>	0.4779(1) <i>0.4776(1)</i>	0.1999(1) <i>0.1999(2)</i>	384(8)	266(4)	331(5)	105(4)	94(5)	61(4)	321(3)
Te4	0.2310(2) <i>0.2310(2)</i>	0.1852(1) <i>0.1848(1)</i>	0.1902(1) <i>0.1898(2)</i>	279(7)	332(4)	345(6)	111(4)	72(5)	74(4)	313(3)
I1	0.2006(2) <i>0.2003(2)</i>	0.6904(1) <i>0.6905(1)</i>	0.0678(1) <i>0.0676(2)</i>	342(8)	355(4)	407(6)	108(4)	66(5)	72(4)	368(3)
I2	0.1977(2) <i>0.1977(2)</i>	0.1569(1) <i>0.1566(1)</i>	0.8284(1) <i>0.8285(2)</i>	316(8)	351(4)	400(6)	120(5)	76(5)	83(4)	351(3)
I3	0.2121(2) <i>0.2118(2)</i>	0.6810(1) <i>0.6810(1)</i>	0.43382(9) <i>0.4336(2)</i>	425(8)	346(5)	343(6)	135(5)	78(5)	73(4)	366(3)
I4	0.2129(2) <i>0.2129(2)</i>	0.1824(1) <i>0.1826(1)</i>	0.4614(1) <i>0.4613(2)</i>	443(9)	352(5)	381(6)	137(5)	159(6)	89(4)	375(3)

Table 4. Atomic parameters for a Te₄(Al₂Cl₇)₂ single crystal synthesized in RTIL. ICSD data determined using a conventionally synthesized crystal is given in *italics*.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃	<i>U</i> _{eq}
Te1	0.0635(4) <i>0.0643(2)</i>	0.1553(2) <i>0.1559(1)</i>	0.0315(4) <i>0.0329(1)</i>	460(20)	430(20)	750(60)	10(20)	−140(30)	−100(20)	550(20)
Te2	0.1796(4) <i>0.1800(1)</i>	0.5626(3) <i>0.5626(1)</i>	0.5449(4) <i>0.5455(1)</i>	450(20)	590(20)	880(70)	−10(20)	−220(30)	30(30)	640(20)
Al1	0.383(2) <i>0.3818(6)</i>	0.175(1) <i>0.1779(5)</i>	0.295(2) <i>0.2946(4)</i>	500(100)	490(80)	200(200)	30(60)	−100(100)	230(90)	400(70)
Al2	0.233(1) <i>0.2387(6)</i>	0.5800(9) <i>0.5778(5)</i>	0.151(2) <i>0.1554(4)</i>	260(90)	350(70)	600(200)	−120(60)	100(100)	10(90)	400(70)
Cl1	0.410(2) <i>0.4073(6)</i>	0.171(1) <i>0.1718(5)</i>	0.130(2) <i>0.1332(3)</i>	800(100)	690(80)	600(200)	−50(70)	500(100)	150(90)	710(70)
Cl2	0.170(2) <i>0.1727(6)</i>	0.122(1) <i>0.1223(5)</i>	0.336(2) <i>0.3371(5)</i>	600(100)	1000(100)	700(200)	10(60)	200(200)	100(100)	780(80)
Cl3	0.449(1) <i>0.4524(6)</i>	0.3338(9) <i>0.3350(4)</i>	0.361(1) <i>0.3677(4)</i>	700(100)	480(70)	800(200)	90(60)	0(100)	50(80)	660(80)
Cl4	0.523(1) <i>0.5256(5)</i>	0.0312(8) <i>0.0286(4)</i>	0.353(2) <i>0.3554(4)</i>	410(90)	260(70)	800(200)	70(40)	−100(100)	−90(70)	500(70)
Cl5	0.191(2) <i>0.1869(7)</i>	0.6367(9) <i>0.6370(5)</i>	0.008(2) <i>0.0061(4)</i>	1000(100)	540(70)	700(200)	330(70)	0(100)	150(90)	730(70)
Cl6	0.222(2) <i>0.2186(6)</i>	0.7174(9) <i>0.7171(5)</i>	0.261(2) <i>0.2616(4)</i>	800(100)	430(70)	900(200)	−80(60)	0(100)	−140(80)	710(70)
Cl7	0.136(1) <i>0.1314(6)</i>	0.4177(8) <i>0.4194(5)</i>	0.199(2) <i>0.1990(5)</i>	700(100)	360(70)	800(200)	50(60)	−100(100)	210(80)	610(60)

and pairs of corner-sharing chlorido-aluminate(III) tetrahedra. The atomic coordinates correspond to the published data [32] with a maximum deviation of 7σ (Table 4).

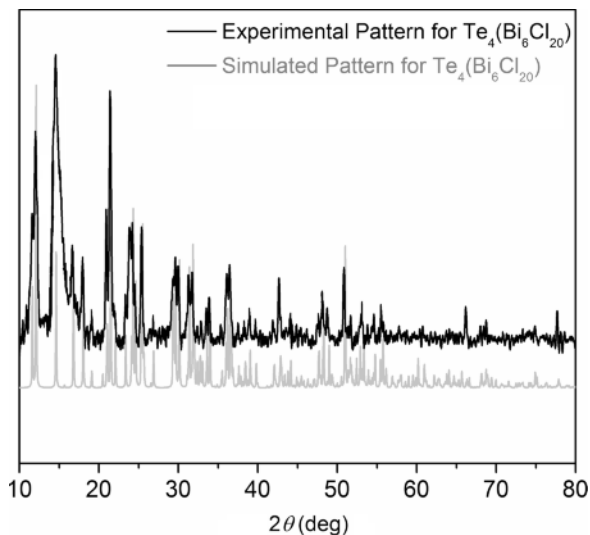
Te₄(Bi₆Cl₂₀)

Crystals of Te₄(Bi₆Cl₂₀) were first synthesized by Beck *et al.* using a chemical gas-phase transport reac-

tion in the temperature gradient of 160 to 140 °C. In the course of several days, they obtained single crystals with 40 % yield [33]. We accomplished the synproportionation of elemental tellurium with tellurium(IV) in the presence of BiCl₃ in the Lewis-acidic RTIL [BMIm]Cl·1.3AlCl₃ at room temperature. Addition of anhydrous NaCl to the dark colored filtrate resulted in the precipitation of black crystals in only two days (yield: 54 %, Fig. 3). The structure consists of discrete

Table 5. Atomic parameters for a $\text{Te}_4(\text{Bi}_6\text{Cl}_{20})$ single crystal synthesized in RTIL. ICSD data determined using a conventionally synthesized crystal is given in *italics*.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃	<i>U</i> _{eq}
Te1	0.4015(2) <i>0.3995(2)</i>	0.1622(2) <i>0.1637(1)</i>	0.4265(1) <i>0.42800(8)</i>	670(10)	469(8)	512(9)	−104(7)	−199(8)	39(6)	538(4)
Te2	0.6744(2) <i>0.6741(1)</i>	0.1310(1) <i>0.1313(1)</i>	0.5369(1) <i>0.53813(7)</i>	590(10)	483(8)	495(8)	−193(7)	−153(7)	−21(6)	513(4)
Bi1	0.0750(1) <i>0.07354(6)</i>	0.02661(7) <i>0.02700(5)</i>	0.16681(5) <i>0.16704(3)</i>	349(5)	346(4)	331(4)	−9(3)	−63(3)	−73(3)	338(2)
Bi2	0.1043(1) <i>0.10461(6)</i>	0.48091(8) <i>0.48065(5)</i>	0.74054(5) <i>0.73992(3)</i>	451(5)	389(4)	364(4)	−67(3)	−50(3)	−126(3)	397(2)
Bi3	0.5931(1) <i>0.59293(5)</i>	0.26431(7) <i>0.26427(4)</i>	0.03268(5) <i>0.03244(3)</i>	322(5)	328(4)	354(4)	5(3)	−79(3)	−66(3)	330(2)
Cl1	0.2600(6) <i>0.2597(4)</i>	0.0383(4) <i>0.0398(3)</i>	0.9778(3) <i>0.9765(2)</i>	430(30)	230(20)	270(20)	40(20)	−40(20)	−50(20)	310(10)
Cl2	0.5862(7) <i>0.5868(5)</i>	0.5442(4) <i>0.5444(3)</i>	0.1031(3) <i>0.1035(2)</i>	560(40)	240(20)	430(30)	40(20)	−250(20)	−120(20)	390(10)
Cl3	0.2226(7) <i>0.2216(4)</i>	0.2894(4) <i>0.2894(3)</i>	0.1586(3) <i>0.1570(3)</i>	460(30)	300(20)	480(30)	−30(20)	30(20)	−170(20)	420(10)
Cl4	0.1953(7) <i>0.1955(5)</i>	0.2031(5) <i>0.2036(4)</i>	0.7319(3) <i>0.2685(3)</i>	550(40)	340(20)	470(30)	−40(20)	90(20)	90(20)	470(10)
Cl5	0.7151(7) <i>0.7140(4)</i>	0.2120(4) <i>0.2128(3)</i>	0.2008(3) <i>0.2006(2)</i>	400(30)	250(20)	410(30)	30(20)	−180(20)	−70(20)	340(10)
Cl6	0.3615(7) <i>0.3594(5)</i>	0.8835(5) <i>0.8845(4)</i>	0.1981(3) <i>0.1981(3)</i>	410(30)	460(30)	430(30)	130(20)	−120(20)	−90(20)	430(10)
Cl7	0.0920(6) <i>0.0924(4)</i>	0.6769(4) <i>0.6785(4)</i>	0.0501(3) <i>0.0506(3)</i>	310(30)	350(20)	470(30)	−30(20)	80(20)	−50(20)	380(10)
Cl8	0.3434(8) <i>0.3400(6)</i>	0.5285(4) <i>0.5280(4)</i>	0.5972(3) <i>0.5974(3)</i>	660(40)	290(20)	400(30)	−150(20)	160(30)	−80(20)	470(10)
Cl9	0.1423(8) <i>0.1391(7)</i>	0.5408(5) <i>0.5424(5)</i>	0.3649(4) <i>0.3631(4)</i>	510(40)	460(30)	580(30)	20(20)	−350(30)	−170(20)	490(10)
Cl10	0.0271(8) <i>0.0290(5)</i>	0.0918(7) <i>0.0911(6)</i>	0.3519(3) <i>0.3515(3)</i>	380(40)	1130(40)	250(30)	−50(30)	−50(20)	−290(30)	580(20)

Fig. 3. Experimental (black) and calculated (grey) powder pattern of $\text{Te}_4(\text{Bi}_6\text{Cl}_{20})$ ($\text{CuK}\alpha_1$).

Te_4^{2+} polycations and chlorido-bismuthate(III) anions $[\text{Bi}_6\text{Cl}_{20}]^{2-}$. The atomic coordinates correspond to the published data [33] with a maximum deviation of 15σ (Table 5).

$\text{Te}_8(\text{Bi}_4\text{Cl}_{14})$

$\text{Te}_8(\text{Bi}_4\text{Cl}_{14})$ was also synthesized by Beck *et al.* using a chemical gas-phase transport reaction in the temperature gradient of 160 to 140 °C in two days with 30 % yield [34]. Contrary to the higher temperature method, we obtained $\text{Te}_8(\text{Bi}_4\text{Cl}_{14})$ by reacting tellurium, TeCl_4 , and BiCl_3 in the Lewis-acidic RTIL $[\text{BMIm}]\text{Cl} \cdot 1.3\text{AlCl}_3$ at room temperature (63 % yield, Fig. 4). The orthorhombic unit cell contains an infinite chain of $[\text{Te}_8]^{2+}$ polycations and two-dimensional chlorido-bismuthate(III) anions $[\text{Bi}_4\text{Cl}_{14}]^{2-}$. The atomic coordinates [34] correspond to the published data with a maximum deviation of 5σ (Table 6).

Table 6. Atomic parameters for a Te₈(Bi₄Cl₁₄) single crystal synthesized in RTIL. ICSD data determined using a conventionally synthesized crystal is given in *italics*.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃	<i>U</i> _{eq}
Bi1	0.33265(6) <i>0.33253(5)</i>	0.12500(4) <i>0.12501(2)</i>	0.01439(3) <i>0.01439(3)</i>	180(3)	115(4)	191(3)	3(3)	11(2)	−5(3)	162(2)
Bi2	0.36231(6) <i>0.36227(5)</i>	0.39576(4) <i>0.39577(2)</i>	0.06779(3) <i>0.06775(3)</i>	225(3)	198(4)	162(3)	−22(3)	22(3)	−3(3)	195(2)
Bi3	0.33210(6) <i>0.33203(5)</i>	0.40271(4) <i>0.40268(2)</i>	0.43935(3) <i>0.43931(3)</i>	210(3)	186(4)	181(3)	−33(3)	−7(3)	17(3)	192(2)
Bi4	0.30746(6) <i>0.30768(5)</i>	0.12446(5) <i>0.12444(2)</i>	0.46996(3) <i>0.46998(3)</i>	212(3)	209(4)	261(4)	−3(3)	21(3)	74(3)	227(2)
Te1	0.1192(1) <i>0.1192(1)</i>	0.56127(8) <i>0.56129(5)</i>	0.29728(6) <i>0.29725(6)</i>	397(7)	255(7)	400(8)	−11(6)	−41(6)	148(7)	350(3)
Te2	0.6299(1) <i>0.6302(1)</i>	0.10965(8) <i>0.10946(5)</i>	0.27097(6) <i>0.27093(6)</i>	325(6)	187(7)	660(10)	−23(6)	89(6)	63(7)	390(3)
Te3	0.5947(1) <i>0.5948(1)</i>	0.25875(8) <i>0.25878(4)</i>	0.22530(6) <i>0.22532(5)</i>	338(6)	223(7)	302(7)	48(5)	−94(5)	−19(6)	288(3)
Te4	0.2518(1) <i>0.2518(1)</i>	0.17743(8) <i>0.17738(4)</i>	0.68130(5) <i>0.68129(5)</i>	353(6)	195(7)	175(6)	29(5)	−21(5)	−34(6)	241(3)
Te5	0.0463(1) <i>0.0464(1)</i>	0.27401(9) <i>0.27397(5)</i>	0.28780(6) <i>0.28777(7)</i>	320(7)	393(9)	388(8)	26(6)	−95(6)	−146(8)	367(3)
Te6	0.0057(1) <i>0.0055(1)</i>	0.21531(9) <i>0.21528(4)</i>	0.18025(6) <i>0.18024(6)</i>	494(8)	378(9)	253(7)	−64(7)	168(6)	−61(7)	375(3)
Te7	0.2145(1) <i>0.2142(1)</i>	0.01586(8) <i>0.01578(5)</i>	0.72144(6) <i>0.72141(6)</i>	341(7)	218(7)	531(9)	−19(6)	−106(6)	29(7)	363(3)
Te8	0.0561(2) <i>0.0567(1)</i>	0.0056(1) <i>0.00582(5)</i>	0.29528(6) <i>0.29534(7)</i>	671(9)	500(10)	237(8)	175(8)	148(7)	−3(8)	468(4)
Cl1	0.7578(6) <i>0.7583(5)</i>	0.2453(3) <i>0.2461(2)</i>	0.0351(2) <i>0.0351(2)</i>	660(30)	140(30)	360(30)	−110(20)	20(20)	50(30)	390(10)
Cl2	0.3959(5) <i>0.3965(4)</i>	0.2159(3) <i>0.2166(2)</i>	0.1078(2) <i>0.1078(2)</i>	380(20)	300(30)	290(30)	60(20)	−40(20)	−190(30)	330(10)
Cl3	0.0677(4) <i>0.0692(3)</i>	0.1065(3) <i>0.1065(2)</i>	0.0542(2) <i>0.0537(2)</i>	230(20)	460(30)	310(30)	−20(20)	80(20)	−60(30)	330(10)
Cl4	0.3325(5) <i>0.3326(4)</i>	0.5502(3) <i>0.5501(2)</i>	0.0596(2) <i>0.0598(2)</i>	330(20)	200(30)	300(20)	0(20)	−80(20)	100(20)	270(10)
Cl5	0.3677(5) <i>0.3678(4)</i>	0.4131(3) <i>0.4133(1)</i>	0.1771(2) <i>0.1768(2)</i>	570(30)	230(30)	130(20)	30(20)	−40(20)	−60(20)	310(10)
Cl6	0.0759(4) <i>0.0777(3)</i>	0.3758(4) <i>0.3756(1)</i>	0.0826(2) <i>0.0828(2)</i>	320(20)	440(30)	210(20)	−60(20)	−50(20)	50(30)	320(10)
Cl7	0.6897(4) <i>0.6898(4)</i>	0.0560(3) <i>0.0558(2)</i>	0.0621(2) <i>0.0623(2)</i>	310(20)	160(20)	380(30)	−30(20)	−20(20)	80(20)	280(10)
Cl8	0.3778(4) <i>0.3778(4)</i>	0.4072(3) <i>0.4071(1)</i>	0.3298(2) <i>0.3297(2)</i>	270(20)	410(30)	160(20)	30(20)	20(20)	−70(20)	280(10)
Cl9	0.0494(4) <i>0.0493(3)</i>	0.3869(3) <i>0.3870(2)</i>	0.4144(2) <i>0.4145(2)</i>	170(20)	450(30)	290(20)	−20(20)	0(20)	−20(30)	300(10)
Cl10	0.2430(6) <i>0.2433(5)</i>	0.2520(3) <i>0.2523(2)</i>	0.5250(3) <i>0.5252(2)</i>	750(30)	140(30)	460(30)	20(30)	0(30)	0(30)	450(10)
Cl11	0.0459(4) <i>0.0460(4)</i>	0.1198(4) <i>0.1193(2)</i>	0.4304(2) <i>0.4304(3)</i>	270(20)	650(40)	270(20)	70(20)	−50(20)	−90(30)	400(10)
Cl12	0.3889(7) <i>0.3901(6)</i>	0.2118(5) <i>0.2123(2)</i>	0.3815(3) <i>0.3821(4)</i>	570(30)	1050(60)	650(40)	90(40)	230(30)	700(50)	760(20)
Cl13	0.1522(4) <i>0.1530(3)</i>	0.0468(3) <i>0.0470(1)</i>	0.5652(2) <i>0.5654(2)</i>	240(20)	220(30)	230(20)	−30(20)	40(20)	−50(20)	230(10)
Cl14	0.6928(4) <i>0.6922(4)</i>	0.4492(3) <i>0.4494(1)</i>	0.0844(2) <i>0.0846(2)</i>	290(20)	290(30)	270(20)	50(20)	10(20)	−60(20)	290(10)

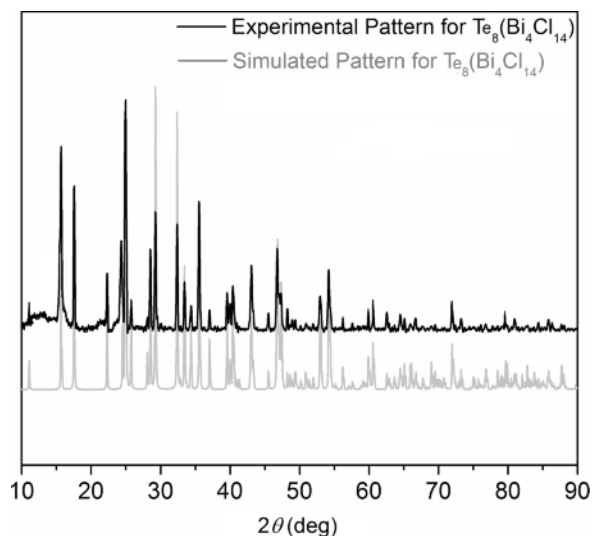


Fig. 4. Experimental (black) and calculated (grey) powder pattern of $\text{Te}_8(\text{Bi}_4\text{Cl}_{14})$ ($\text{CuK}\alpha_1$).

$\text{Bi}_8(\text{AlCl}_4)_2$

Corbett *et al.* synthesized $\text{Bi}_8(\text{AlCl}_4)_2$ conventionally from elemental bismuth, BiCl_3 , and AlCl_3 [35, 36]. Later, Beck *et al.* modified the synthesis in order to improve crystal quality and to finally solve

the crystal structure [37]. The starting materials were heated to 350 °C for a period of seven days and subsequently rapidly cooled to 160 °C, then slowly cooled to 130 °C. At this temperature, they decanted the supernatant melt from black crystals of $\text{Bi}_8(\text{AlCl}_4)_2$. The decanted melt solidified to $\text{Bi}_8(\text{AlCl}_4)_2$ and an unidentified by-product. The classical synthesis is very difficult due to kinetic and subcooling problems [37]. We obtained well-shaped crystals of $\text{Bi}_8(\text{AlCl}_4)_2$ as the main product by reducing BiCl_3 with sodium in $[\text{BMIm}]\text{Cl}\cdot 3.6\text{AlCl}_3$ at 140 °C. Bismuth, NaAlCl_4 , and $\text{Bi}_5(\text{AlCl}_4)_2$ were formed as by-products. By reducing the reaction temperature to 80 °C and using a less Lewis-acidic RTIL ($[\text{BMIm}]\text{Cl}\cdot 1.3\text{AlCl}_3$), we obtained $\text{Bi}_8(\text{AlCl}_4)_2$ with elemental bismuth and NaAlCl_4 as the only by-products. The crystals of $\text{Bi}_8(\text{AlCl}_4)_2$ showed two morphologies: hexagonal rods (up to 0.5 mm) as well as hexagonal platelets. The crystal structure consists of square-antiprismatic Bi_8^{2+} polycations and tetrahedral AlCl_4^- anions. The results of the structure determination (Table 7) showed no significant difference to the published ones in terms of shape and position of the structural motifs. However, the examined crystal from the IL approach featured a fully ordered crystal structure in the polar space group $P6_3$, while Beck *et al.* had found $\text{Bi}_8(\text{AlCl}_4)_2$ to crystallize in $P6_3/m$ with orientational disorder of the AlCl_4^-

Table 7. Atomic parameters for a $\text{Bi}_8(\text{AlCl}_4)_2$ single crystal synthesized in RTIL (ordered structure in space group $P6_3$).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃	<i>U</i> _{eq}
Bi1	0.2640(2)	0.3164(2)	−0.0563(1)	530(10)	610(20)	480(10)	310(10)	−132(9)	8(9)	532(6)
Bi2	0.4673(2)	0.4278(2)	0.2227(1)	530(20)	510(10)	500(10)	130(10)	−138(8)	−105(9)	574(7)
Bi3	0.3713(2)	0.2272(2)	0.2304(1)	660(20)	540(10)	440(10)	410(10)	−27(9)	59(9)	500(6)
Bi4	0.3667(2)	0.2208(2)	−0.0060(1)	880(20)	520(10)	410(10)	450(10)	27(9)	−77(8)	558(7)
Bi5	0.2717(2)	0.3263(2)	0.2750(1)	700(20)	700(20)	450(10)	430(10)	207(9)	52(9)	579(7)
Bi6	0.33745(9)	0.46473(8)	0.1037(2)	819(8)	472(7)	609(6)	444(7)	90(10)	40(10)	579(3)
Bi7	0.4612(2)	0.4204(2)	−0.0174(1)	460(10)	520(10)	476(9)	180(10)	125(8)	66(9)	510(6)
Bi8	0.19967(8)	0.17762(8)	0.1165(2)	456(7)	478(7)	705(8)	63(6)	−20(10)	80(10)	622(4)
Al1	0	0	0.371(1)	400(50)	400(50)	390(90)	200(30)	0	0	400(40)
Al2	0.6379(6)	0.6935(6)	0.0869(6)	510(60)	460(60)	400(60)	290(50)	−80(40)	−60(40)	440(30)
Al3	2/3	1/3	0.279(1)	560(80)	560(80)	460(70)	280(40)	0	0	530(50)
Al4	2/3	1/3	−0.188(1)	380(70)	380(70)	550(80)	190(30)	0	0	440(40)
Cl1	0.662(1)	0.443(1)	0.334(1)	500(100)	370(90)	1100(80)	160(80)	−10(70)	110(60)	700(40)
Cl2	0.6547(5)	0.5829(5)	0.096(1)	370(50)	450(50)	1290(80)	190(40)	−30(80)	−30(80)	710(30)
Cl3	0.660(1)	0.443(1)	−0.1335(8)	800(100)	610(90)	560(60)	520(80)	70(50)	60(50)	570(40)
Cl4	0.5453(7)	0.6762(8)	−0.0215(7)	590(70)	790(80)	410(40)	390(60)	−100(40)	20(40)	570(30)
Cl5	0.407(1)	0.290(1)	−0.2697(7)	2000(200)	1400(100)	380(50)	1200(100)	50(70)	30(60)	1090(60)
Cl6	2/3	1/3	−0.3515(7)	590(70)	590(70)	480(70)	290(30)	0	0	550(40)
Cl7	0	0	0.5340(8)	570(70)	570(70)	470(60)	290(30)	0	0	540(40)
Cl8	0.0216(7)	0.1217(6)	0.3150(6)	1020(90)	620(70)	750(50)	460(70)	180(50)	200(40)	770(30)
Cl9	2/3	1/3	10.124(1)	3000(200)	3000(200)	200(100)	1500(100)	0	0	2100(100)
Cl10	0.7607(8)	0.7993(7)	0.0469(8)	530(70)	410(70)	1810(90)	190(60)	−150(50)	−30(60)	940(30)

Table 8. Atomic parameters for a Bi_6Cl_7 single crystal (at 100(5) K) synthesized in RTIL.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
Bi1	0.04637(2)	0.22154(2)	0.18773(4)	142(1)	127.3(9)	108(1)	−26.0(7)	39(1)	−17.9(9)	125.7(6)
Bi2	0.20146(2)	0.15441(2)	0.18278(4)	147(1)	97.3(8)	114(1)	−26.2(7)	−49(1)	34.8(9)	119.2(6)
Bi3	0.41000(2)	0.45429(2)	0	87(1)	68(1)	93(2)	18.6(9)	0	0	82.5(7)
Bi4	0.09936(2)	0.06723(2)	0	114(1)	70(1)	130(2)	−33.9(9)	0	0	104.4(8)
Bi5	0.07201(2)	0.39766(2)	0	213(2)	80(1)	247(2)	66(1)	0	0	179.9(9)
Bi6	0.41391(2)	0.10081(2)	0	322(2)	244(2)	60(2)	−227(2)	0	0	209(1)
Bi7	0.85840(2)	0.30867(2)	0	82(1)	58(1)	101(2)	14.3(9)	0	0	80.4(7)
Bi8	0.23955(2)	0.33026(2)	0	112(1)	82(1)	140(2)	−34(1)	0	0	111.5(8)
Bi9	0.15313(2)	0.34276(2)	0.26861(4)	151(1)	174.0(9)	144(2)	−20.8(8)	8(1)	−96(1)	156.4(7)
Cl1	0	0	0.2826(3)	125(9)	147(7)	110(10)	−37(7)	0	0	126(4)
Cl2	0.5492(1)	0.0820(1)	0	129(9)	119(7)	160(10)	−42(7)	0	0	136(4)
Cl3	0.6111(1)	0.3745(1)	0	140(9)	104(7)	90(10)	−14(7)	0	0	110(4)
Cl4	0.7649(1)	0.2103(1)	0	139(9)	182(8)	160(10)	−68(7)	0	0	159(5)
Cl5	0.7890(1)	0.4478(1)	0	190(10)	99(7)	220(10)	69(7)	0	0	168(5)
Cl6	0.3126(1)	0.0137(1)	0	107(8)	72(6)	200(10)	−16(6)	0	0	125(4)
Cl7	0.33887(7)	0.21375(8)	0.1920(2)	146(6)	104(5)	85(8)	37(4)	−18(7)	−1(5)	112(3)
Cl8	0.33281(8)	0.44389(8)	0.2154(2)	161(6)	91(5)	94(8)	−27(4)	6(7)	2(5)	115(3)
Cl9	0.9331(1)	0.1618(1)	0	100(8)	105(7)	230(10)	5(6)	0	0	143(5)
Cl10	0.44374(8)	0.08286(9)	0.3059(2)	168(7)	164(5)	72(8)	95(5)	3(7)	11(6)	135(3)
Cl11	0.4653(1)	0.2787(1)	0	170(10)	143(7)	110(10)	−63(7)	0	0	144(4)

tetrahedra [37]. Since the crystallization in both synthesis routes occurs in the same temperature region, the presence of the IL seems to influence the crystal growth.

Bi_6Cl_7 and Bi_6Br_7

Bi_6Cl_7 was previously synthesized by Corbett and co-workers by reacting elemental bismuth with molten BiCl_3 or with mixtures of BiCl_3 and KCl at temperatures above 250 °C [38, 39]. The severe problems associated with slowly established equilibria and concomitant metal contaminations of the final product experienced in the former synthetic route are only partially relieved by adding KCl . Later, Beck *et al.* applied two alterations to Corbett's methods to minimize these problems [37]. In the first method, a reaction between elemental bismuth and BiCl_3 (1 : 2) was performed using a temperature gradient of 265 to 240 °C for one week to get crystals of Bi_6Cl_7 . In the second method, Bi_6Cl_7 was conveniently synthesized from a melt of elemental bismuth, BiCl_3 , and SbCl_3 (2 : 1 : 4), keeping the temperature at 300 °C for several days to get well-shaped single crystals. We obtained phase-pure Bi_6Cl_7 by reduction of BiCl_3 with indium metal in the Lewis-acidic IL $[\text{BMIm}]\text{Cl} \cdot 2\text{AlCl}_3$ at room temperature after two days (yield: 63 %).

Bi_6Br_7 was first synthesized by von Benda *et al.* by annealing a mixture of elemental bismuth and

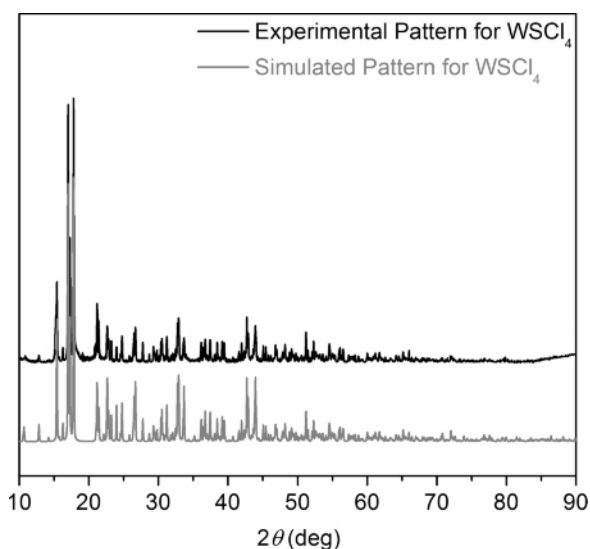
BiBr_3 at 272 °C for two days with subsequent cooling to room temperature. Owing to demixing problems, a single-phase product was not achieved [40]. In contrast, we obtained phase-pure Bi_6Br_7 by reacting Bi and BiBr_3 in $[\text{BMIm}]\text{Cl} \cdot 2\text{AlCl}_3$ at room temperature with a yield of 71 %. The isotypic crystal structures consist of distorted, tricapped trigonal prismatic Bi_9^{5+} polycations and halogenido-bismuthate(III) anions. The atomic coordinates correspond to the published data for Bi_6Cl_7 [37] and Bi_6Br_7 [40], yet a direct comparison is not applicable with respect to the large temperature differences of the measurements (Tables 8 and 9).

WSCl_4

WSCl_4 crystallizes in two modifications which have been reported to be formed under different conditions [41–44]. The triclinic polymorph was first synthesized by Fowles *et al.* in 1970 from WCl_6 and sulfur at 120 °C with 100 % yield [41]. To obtain suitable crystals for structural analysis, the product had to be recrystallized from CS_2 [42]. In 1989, Cotton *et al.* synthesized a monoclinic modification from tungsten, sulfur und S_2Cl_2 at 425 °C with an excess of the elemental educts within more than two days [43]. One year later, Gibson *et al.* published a low temperature synthesis of WSCl_4 . They let $(\text{Me}_3\text{Si})_2\text{S}_2$ react with WCl_6 in CH_2Cl_2 at −30 °C and obtained phase pure

Table 9. Atomic parameters for a Bi₆Br₇ single crystal (at 100(5) K) synthesized in RTIL.

Atom	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃	U _{eq}
Bi1	0.04532(2)	0.22509(2)	0.18226(4)	167(2)	195(1)	128(1)	−44(2)	52(2)	−28(1)	163.4(8)
Bi2	0.19704(2)	0.15740(2)	0.17544(3)	164(2)	127(1)	135(1)	−19(2)	−50(2)	37(1)	141.8(7)
Bi3	0.40871(2)	0.45848(3)	0	95(2)	79(2)	93(2)	10(2)	0	0	88.9(9)
Bi4	0.09642(2)	0.07595(3)	0	137(3)	112(2)	167(2)	−48(2)	0	0	138(1)
Bi5	0.07362(3)	0.39421(3)	0	293(3)	131(2)	225(2)	100(2)	0	0	216(1)
Bi6	0.40847(3)	0.09820(3)	0	318(3)	287(2)	82(2)	−207(3)	0	0	229(1)
Bi7	0.85586(2)	0.31150(3)	0	107(2)	87(2)	116(2)	19(2)	0	0	103.4(9)
Bi8	0.23429(2)	0.32989(3)	0	127(2)	103(2)	143(2)	−23(2)	0	0	125(1)
Bi9	0.15085(2)	0.33949(2)	0.26123(3)	154(2)	193(1)	152(1)	−21(2)	6(2)	−86(1)	166.2(8)
Br1	0	0	0.2771(1)	111(6)	133(5)	103(5)	−18(5)	0	0	116(2)
Br2	0.55060(6)	0.08605(7)	0	116(6)	122(5)	135(5)	−29(5)	0	0	125(2)
Br3	0.61267(6)	0.36487(7)	0	133(7)	104(5)	92(5)	−2(5)	0	0	110(2)
Br4	0.75876(6)	0.20988(7)	0	104(6)	171(5)	122(5)	−54(5)	0	0	132(3)
Br5	0.78715(7)	0.45379(7)	0	191(8)	113(5)	256(6)	68(5)	0	0	187(3)
Br6	0.30716(6)	0.00766(7)	0	129(7)	85(4)	199(5)	−11(5)	0	0	138(3)
Br7	0.33371(4)	0.21374(5)	0.18984(8)	124(4)	120(3)	61(3)	28(3)	−3(3)	3(3)	102(2)
Br8	0.33093(4)	0.44540(5)	0.22316(8)	123(4)	104(3)	113(4)	−21(3)	12(3)	1(3)	114(2)
Br9	0.93315(6)	0.16241(7)	0	110(6)	120(5)	175(5)	19(5)	0	0	135(2)
Br10	0.44312(4)	0.08236(5)	0.30783(9)	151(5)	179(3)	61(3)	75(4)	−1(3)	7(3)	130(2)
Br11	0.46264(6)	0.28188(7)	0	119(6)	140(5)	140(5)	−45(5)	0	0	133(2)

Fig. 5. Experimental (black) and calculated (grey) powder pattern of WSCl₄ (CuK α_1).

WSCl₄ with 80 % yield after several steps of processing of the solution [44]. However, they performed no X-ray analysis on their product. Therefore, it remains unclear which polymorph was formed. We obtained the monoclinic modification of WSCl₄ by reacting stoichiometric amounts of elemental sulfur and WCl₆ in [BMIm]Cl·1.3AlCl₃ at room temperature with a yield

of 55 %. The atomic coordinates of the molecular compound correspond to the published data with a maximum deviation of 4 σ (Table 10) [43]. Compared to the published synthesis route of monoclinic WSCl₄, we were able to reduce the reaction temperature tremendously and attained a phase-pure product (Fig. 5).

WOCl₄

Hess and Hartung synthesized needle-shaped crystals of WOCl₄ by reacting WO₂ and SOCl₂ at 200 °C [45]. We obtained needles of tetragonal WOCl₄ as a by-product of an attempt to synthesize phosphorus-sulfur polycations by reacting elemental sulfur and phosphorus with WCl₆ in [BMIm]Cl·1.3AlCl₃. The initially undesired oxygen content is probably a consequence of traces of phosphoric acid. The atomic coordinates in the molecular crystal structure correspond to the published data [45] with a maximum deviation of 5 σ (Table 11).

Conclusion

Lewis-acidic, redox-stable RTILs proved to be suitable reaction media for convenient and resource-efficient near-room-temperature syntheses of low-valent compounds. We have resynthesized various halogenides of main-group elements and transition

Table 10. Atomic parameters for a WSCl₄ single crystal synthesized in RTIL. ICSD data determined using a conventionally synthesized crystal is given in *italics*.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃	<i>U</i> _{eq}
W1	0.86828(5) <i>0.8683(2)</i>	0.40937(4) <i>0.4092(2)</i>	0.16070(4) <i>0.1609(1)</i>	252(3)	312(3)	261(3)	6(2)	101(2)	−8(2)	274(2)
W2	0.44660(6) <i>0.4455(3)</i>	0.14070(4) <i>0.1407(2)</i>	0.07344(4) <i>0.0726(2)</i>	302(3)	309(3)	397(3)	−20(2)	186(2)	−32(2)	320(2)
Cl1	0.1125(4) <i>0.114(1)</i>	0.8087(3) <i>0.8072(9)</i>	0.1762(3) <i>0.1766(8)</i>	430(20)	500(20)	290(10)	−50(20)	160(10)	−70(10)	399(7)
Cl2	0.2132(4) <i>0.212(1)</i>	0.5537(3) <i>0.5539(9)</i>	0.0378(3) <i>0.0372(8)</i>	470(20)	510(20)	310(10)	10(20)	170(10)	80(10)	424(8)
Cl3	0.0636(4) <i>0.062(1)</i>	0.3018(3) <i>0.3016(9)</i>	0.1398(3) <i>0.1396(9)</i>	380(20)	490(20)	540(20)	110(20)	240(20)	20(20)	446(8)
Cl4	0.6136(3) <i>0.613(1)</i>	0.4557(3) <i>0.4546(9)</i>	0.1455(3) <i>0.1450(8)</i>	310(20)	440(20)	430(20)	50(10)	160(10)	−30(20)	385(7)
Cl5	0.3104(4) <i>0.309(1)</i>	0.2303(2) <i>0.2279(9)</i>	0.4472(3) <i>0.4478(9)</i>	420(20)	400(20)	410(20)	−50(20)	110(20)	−90(20)	422(8)
Cl6	0.6772(3) <i>0.679(1)</i>	0.1925(2) <i>0.1917(9)</i>	0.0425(3) <i>0.0404(9)</i>	320(20)	390(20)	350(20)	−40(10)	190(10)	−20(10)	338(7)
Cl7	0.2157(3) <i>0.217(1)</i>	0.0505(2) <i>0.0498(9)</i>	0.0478(3) <i>0.0452(9)</i>	270(10)	410(20)	420(20)	−40(10)	150(10)	40(10)	362(7)
Cl8	0.4103(4) <i>0.411(1)</i>	0.4753(2) <i>0.4733(9)</i>	0.3550(2) <i>0.3547(8)</i>	350(20)	410(20)	320(10)	−10(10)	110(10)	−70(10)	365(7)
S1	0.0011(4) <i>0.001(2)</i>	0.0454(3) <i>0.046(1)</i>	0.2619(3) <i>0.262(1)</i>	430(20)	410(20)	520(20)	90(20)	140(20)	80(20)	465(8)
S2	0.4929(4) <i>0.492(2)</i>	0.2123(3) <i>0.212(1)</i>	0.2368(3) <i>0.237(1)</i>	490(20)	530(20)	340(20)	10(20)	190(20)	10(20)	445(8)

Table 11. Atomic parameters for a WOCl₄ single crystal synthesized in RTIL. ICSD data determined using a conventionally synthesized crystal is given in *italics*.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃	<i>U</i> _{eq}
W	0 <i>0</i>	0 <i>0</i>	0 <i>0</i>	322(4)	322(4)	230(4)	0	0	0	291(3)
Cl	0.0665(4) <i>0.0669(6)</i>	0.2574(4) <i>0.2584(6)</i>	0.0847(8) <i>0.079(1)</i>	430(20)	320(20)	470(20)	−20(10)	20(10)	−10(10)	406(9)
O	0 <i>0</i>	0 <i>0</i>	0.562(7) <i>0.55(3)</i>	480(70)	480(70)	700(300)	0	0	0	540(80)

metals (Table 12) at reaction temperatures that were up to 500 K lower than for the conventional syntheses reported in literature. Further advantages are the comparatively fast formation of the products, their high purity and good yield. The latter is also owed to the option that undissolved starting materials can easily be separated by filtration before the crystallization of products starts.

The low-temperature syntheses in RTILs can be controlled more accurately than many high-temperature syntheses. For example, the conventional synthesis of Te₄(Bi₆Cl₂₀) and Te₈(Bi₄Cl₁₄) by gas-phase transport necessitates knowledge about and precise control of the proper temperature gradient. The yield depends on the volatility of the transport species,

which makes optimization tedious. In RTILs, the stoichiometric ratio of the starting material simply controls the product, while the synthetic protocol remains the same.

Compared to classical crystallization from a high-temperature melt, the formation of by-products by local inhomogeneity or temperature-dependent change of the composition (precipitation of neighboring phases or eutectic mixtures) and by partial evaporation of components (deposition of volatile components during cooling) is avoided. These advantages hold especially for incongruently melting compounds and compounds with high vapor pressure. RTILs can also substitute toxic room-temperature solvents, such as benzene and CS₂, or solvents that need permanent cool-

Compound	Conventional synthesis	Synthesis in RTIL
P ₂ I ₄	in CS ₂ at 20 °C, 12 h [26]	3d, 120 °C, small amount
Te ₂ Br	CM, 350 °C, 2–3 weeks [28]	5d, 20 °C, yield 39 %, phase-pure
α-Te ₄ I ₄	a) from elements, ~ 200 °C, ~3 weeks [29] b) HYD in conc. HI acid, 8d [30]	2d, 20 °C, yield 64 %, phase-pure
Te ₄ (AlCl ₄) ₂	CM, 250 °C [32]	2d, 20 °C, yield 66 %, phase-pure [46]
Te ₄ (Al ₂ Cl ₇) ₂	CM, 250 °C [32]	4d, 80 °C, major crystalline phase
Te ₄ (Bi _{0.67+δ} Cl ₄)	CTR, 160 °C, yield 10 %, 1 week [24]	3d, 20 °C, yield 63 %, phase-pure [24]
Te ₄ (Bi ₆ Cl ₂₀)	CTR, 170 °C, several days [33]	2d, 20 °C, yield 54 %, phase-pure
Te ₆ (WOCl ₄) ₂	CTR, 200 °C, 2 weeks [47]	3d, 20 °C, yield 39 %, phase-pure [46]
Te ₈ (Bi ₄ Cl ₁₄)	CTR, 160 °C, 2d [34]	2d, 20 °C, yield 63 %, phase-pure
Bi ₅ (AlCl ₄) ₃	a) CM, 180 °C [36]; b) in liquid SO ₂ , –78 °C, > 3d [48]	3d, 20 °C, yield 68 %, phase-pure [49]
Bi ₈ (AlCl ₄) ₂	CM, 350 °C; phase-pure synthesis difficult, > 8d [37]	4d, 80 °C, by-product Bi 5d, 140 °C, main product
Bi ₆ Cl ₇	CM; inhomogeneous melt; phase-pure synthesis difficult, > 1 week [37]	2d, 20 °C, yield 63 %, phase-pure
Bi ₆ Br ₇	CM; inhomogeneous melt; phase-pure synthesis difficult, 2d [40]	2d, 20 °C, yield 71 %, phase-pure
BiCl(Mo ₆ Cl ₁₄)	CM, 550 °C, 10 days [50]	2d, 20 °C, yield 56 %, phase-pure [51]
WOCl ₄	HYD, 200 °C, 6h [45]	3d, 20 °C, by-product
WSCI ₄	CM, 425 °C, > 2d [43]	3d, 20 °C, yield 55 %, phase-pure

Table 12. Synopsis of the reaction conditions of known compounds which have been resynthesized in RTILs by us. Some of the syntheses in RTILs have been published elsewhere. CTR = chemical transport reaction, CM = crystallization from melt, HYD = hydrothermal synthesis.

ing, such as liquid SO₂. The quality of single crystals appears to be competitive to that of the in general well-grown crystals obtained by slow deposition in a chemical gas-phase transport reaction. No attempts to grow large crystals from ILs were made yet.

A further exploration of the fascinating possibilities given by the substitution of classical synthesis routes with the RTIL approach could lead to tremendous energy savings and provide more efficient use of starting materials in the synthesis of inorganic materials. Thus, ILs are expected to play a significant role on the road towards a more sustainable chemical industry.

Experimental Section

All manipulations and reactions were performed with exclusion of air in an UNILab glove box (MBraun; $p(\text{O}_2)/p_0 < 3$ ppm, $p(\text{H}_2\text{O})/p_0 < 3$ ppm) or under dry argon atmosphere (Alphagaz, 99.999 %) in Schlenk tubes. The RTILs were synthesized by mixing [BMIm]Cl (Merck, 98 %) and AlCl₃ (Fluka, 98 % or technical, sublimated three times). In order to remove the ILs, the products were washed with dry CH₂Cl₂, except the single crystals, which were directly taken from the IL. Bismuth (Riedel de Haën, chemical pure) was treated twice with H₂ at 220 °C. BiBr₃ (Alfa Aesar, 98 %) and BiCl₃ (Alfa Aesar, 99.999 %) were sublimed prior to use. TeCl₄ was synthesized from the elements (Te: Aldrich, 99.999 %; Cl₂: Air Liquide, 99.8 %) according to literature [52]. TeBr₄ (Strem, 99.9 %) was sublimed twice. TeI₄ was synthesized by reacting the elements in a fused evacuated silica ampoule at 500 °C. Sulfur (Alfa Aesar 99.99 %) was distilled

prior to the reactions. WCl₆ (ABCR, 99.9 %) and indium (Aldrich, 99.999 %) were used without further purification. Iodine (Grüssing, 99.5 %) was sublimed twice before its use. Red phosphorus was washed with NaOH to remove phosphoric acid and dried in dynamic vacuum. Sodium was freshly cut.

P₂I₄

Red phosphorus and I₂ (molar ratio = 1 : 2, total mass = 270 mg) were sealed together with the Lewis-acidic RTIL [BMIm]Cl·4.8AlCl₃ (mass = 320 mg) in an evacuated quartz ampoule. The red solution was heated for three days at 120 °C. After cooling to room temperature orange plate-like crystals of P₂I₄ could be obtained besides a dark-brown powder.

Te₂Br

Tellurium and TeBr₄ (molar ratio = 7 : 1, total mass = 268 mg) were added to 1.5 mL of the Lewis-acidic RTIL [BMIm]Cl·1.3AlCl₃. The reaction mixture was stirred overnight at room temperature, then filtered to separate unreacted material. Addition of a small amount of anhydrous NaCl to the filtrate led to the precipitation of dark-grey block-shaped crystals of Te₂Br within five days. Yield: 39 %.

α-Te₄I₄

Te and TeI₄ (molar ratio = 3 : 1, total mass = 254 mg) were added to 1.5 mL of the Lewis-acidic RTIL [BMIm]Cl·1.3AlCl₃. The orange-red reaction mixture was

stirred overnight at room temperature, then filtered to separate unreacted material. Addition of a small amount of anhydrous NaCl to the filtrate led to the precipitation of black column-shaped crystals of α -Te₄I₄ within two days. Yield: 64 %.

Te₄(Al₂Cl₇)₂

Tellurium, TeCl₄ and red phosphorus (molar ratio = 1 : 1 : 1, total mass = 208 mg) were combined in the Lewis-acidic RTIL [BMIm]Cl·4.8AlCl₃ and heated to 80 °C for four days. Dark-red crystals of Te₄(Al₂Cl₇)₂ were obtained. Yield: 70 %.

Te₄(Bi₆Cl₂₀)

Tellurium, TeCl₄, and BiCl₃ (molar ratio = 3.5 : 0.5 : 6, total mass = 275 mg) were reacted in 1.5 mL of the Lewis-acidic RTIL [BMIm]Cl·1.3AlCl₃. The reaction mixture was stirred overnight at room temperature, then filtered to separate unreacted material. Addition of a small amount of anhydrous NaCl to the filtrate led to the precipitation of black crystals in the course of two days. Yield: 54 %.

Te₈(Bi₄Cl₁₄)

The same procedure as described for Te₄(Bi₆Cl₂₀) was applied, but the molar ratio of the reactants was taken according to Te₈(Bi₄Cl₁₄) (total mass = 285 mg). After two days, black, irregularly shaped crystals were isolated. Yield: 63 %.

Bi₈(AlCl₄)₂

For powder: Na and BiCl₃ (molar ratio 2.8 : 1, total mass 115 mg) were added to 1.5 mL of the Lewis-acidic RTIL [BMIm]Cl·1.3AlCl₃. After heating the mixture to 80 °C, the solution turned dark brown while all starting material was dissolved, and black fine powders of Bi₈(AlCl₄)₂ and elemental bismuth precipitated. *For crystals:* Na and BiCl₃ (molar ratio 2.8 : 1, total mass 115 mg) were mixed with 250 mg AlCl₃ and 90 mg [BMIm]Cl in a glass ampoule and heated to 140 °C for 4 days with subsequent cooling with a 6 K h⁻¹ gradient. Yield (powder synthesis): 40 %.

Bi₆Cl₇

In and BiCl₃ (molar ratio 2 : 3, total mass = 284 mg) were added to the Lewis-acidic IL [BMIm]Cl·2AlCl₃ (volume ≈ 1.5 mL) at room temperature, which immediately turned into a dark-brown solution. The reaction mixture was stirred overnight and then filtered to separate unreacted material. After two days, black needle-shaped crystals were obtained. Yield with respect to BiCl₃: 63 %.

Bi₆Br₇

Black shiny needles of Bi₆Br₇ were synthesized from Bi and BiBr₃ (molar ratio 1 : 1, total mass = 328 mg) in [BMIm]Cl·2AlCl₃ using the same methodology as for Bi₆Cl₇. Yield with respect to bismuth: 71 %.

WSCl₄

Equimolar amounts of elemental sulfur and WCl₆ (total mass = 231 mg) were added to 1.5 mL of the Lewis-acidic RTIL [BMIm]Cl·1.3AlCl₃. The dark-red reaction mixture was stirred overnight at room temperature, then filtered to separate unreacted material. Addition of a small amount of anhydrous NaCl to the red filtrate led to the precipitation of ruby-red platelets of WSCl₄ in the course of three days. Yield: 55 %. Evolution of Cl₂ has not been observed, but soluble sulfur chlorides might have formed in the IL.

WOCl₄

Red phosphorus, sulfur, and WCl₆ (molar ratio = 8 : 1 : 8, total mass = 280 mg) were combined in the Lewis-acidic acid [BMIm]Cl·1.3AlCl₃ (total mass = 320 mg) at 60 °C. Orange needles of WOCl₄ were obtained in small quantities using a chemical gas-phase transport reaction in the temperature gradient of 60 °C (temperature of the IL) to 30 °C (upper part of the Schlenk tube) within three days. The formation of WOCl₄ is a sign for oxidative contamination probably of the phosphorus. In addition crystals of WSCl₄ were formed above the meniscus of the IL.

X-Ray structure determinations

The powder diffraction patterns were measured using a Stoe STADI P powder diffractometer equipped with a position sensitive detector covering 90° in 2θ and using CuK_{α1} radiation. The sample were sealed in 0.3 mm glass capillaries and kept spinning during the data collection at 296(1) K. Because of the high moisture and air sensitivity of the isolated substances, crystals were selected in an argon filled glove box and sealed in glass capillaries of 0.2 mm diameter. Intensity data of the single crystals were recorded using an imaging plate diffraction system IPDS-I or IPDS-II (Stoe & Cie., Darmstadt) with graphite-monochromated MoK_α radiation at 296(1) K or 100(5) K. The raw data were corrected for background, polarization, and the Lorentz factor. The microscopically determined description of the crystal shape was optimized [53], based on sets of equivalent reflections and then utilized for a numerical absorption correction [54]. In case of P₂I₄ a spherical absorption correction with $\mu r = 1$ was applied. The structures were solved with Direct Methods and subsequent difference Fourier syntheses and refined by full-matrix least-squares on F_o^2 (SHELX-97 [55, 56]) using anisotropic displacement parameters for all atoms. The

Table 13. Crystal structure data.

	P₂I₄	Te₂Br	α-Te₄I₄	Te₄(Al₂Cl₇)₂	Te₄(Bi₆Cl₂₀)	Te₈(Bi₄Cl₁₄)
M_m , g mol ⁻¹	569.54	335.11	1018.00	1114.62	2473.28	2353.02
T , K	296(1)	296(1)	296(1)	296(1)	296(1)	296(1)
Crystal system	triclinic	orthorhombic	triclinic	monoclinic	triclinic	orthorhombic
Space group	$P\bar{1}$	$Pnma$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$
a , pm	453.8(1)	1497.8(1)	799.2(2)	915(2)	739.9(2)	879.2(2)
b , pm	709.2(1)	401.2(3)	819.8(2)	1119(2)	876.6(2)	1641.2(1)
c , pm	738.2(1)	1294.5(2)	994.6(2)	1309(3)	1391.7(3)	2268.3(2)
α , deg	80.49(2)	90	90.03(2)	90	87.79(2)	90
β , deg	73.07(2)	90	103.06(2)	90.0(2)	83.06(2)	90
γ , deg	81.81(2)	90	104.37(2)	90	87.93(2)	90
V , 10 ⁶ pm ³	223.0(1)	777.9(6)	613.8(2)	1340(5)	894.9(4)	3273.0(8)
Z	1	8	2	2	1	4
$\rho_{\text{calcd.}}$, g cm ⁻³	4.24	5.72	5.51	2.76	4.59	4.78
μ (MoK α), mm ⁻¹	14.2	25.0	19.4	5.8	34.1	29.6
$F(000)$, e	242	1112	840	996	1046	3944
hkl range	$-6 \leq h \leq 3$ $-8 \leq k \leq 8$ $-4 \leq l \leq 9$	$-11 \leq h \leq 15$ $-3 \leq k \leq 4$ $-13 \leq l \leq 13$	$-9 \leq h \leq 9$ $-9 \leq k \leq 9$ $-11 \leq l \leq 11$	$-8 \leq h \leq 5$ $-10 \leq k \leq 8$ $-11 \leq l \leq 6$	$-7 \leq h \leq 7$ $-9 \leq k \leq 9$ $-15 \leq l \leq 15$	$-9 \leq h \leq 9$ $-18 \leq k \leq 18$ $-25 \leq l \leq 25$
$((\sin \theta)/\lambda)_{\text{max}}$, Å ⁻¹	0.683	0.531	0.595	0.481	0.563	0.563
Refl. measured	267	1410	4127	581	7100	26 482
Refl. unique	267	545	1916	530	2418	4775
$R_{\text{int}}/R_{\sigma}$	0.000/0.067	0.102/0.109	0.104/0.104	0.142/0.496	0.095/0.080	0.090/0.048
Parameters	29	37	73	100	137	236
R_1 (all F)/ wR_2 (all F^2) ^a	0.074/0.032	0.095/0.049	0.085/0.072	0.146/0.086	0.064/0.075	0.043/0.052
Inversion twin ratio	—	—	—	—	—	1 : 1
GooF(F^2) ^a	0.92	0.94	1.96	0.34	1.34	1.35
$\Delta\rho_{\text{fin}}$ (max/min), e Å ⁻³	+0.36/−0.34	+0.94/−1.27	+5.41/−2.52	+0.20/−0.22	+1.75/−1.31	+1.18/−1.83
	Bi₈(AlCl₄)₂	Bi₆Cl₇	Bi₆Br₇	WSCl₄	WOCl₄	
M_m , g mol ⁻¹	2009.40	1502.03	1813.25	357.71	341.65	
T , K	296(1)	100(5)	100(5)	296(1)	296(1)	
Crystal system	hexagonal	orthorhombic	orthorhombic	monoclinic	tetragonal	
Space group	$P6_3$	$Pnmm$	$Pnmm$	$P2_1/c$	$I4$	
a , pm	1789.5(3)	2289.2(1)	2366.5(1)	891.5(1)	847.8(3)	
b , pm	1789.5(3)	1495.5(1)	1550.4(1)	1244.5(1)	847.8(3)	
c , pm	1309.5(3)	871.9(1)	905.4(1)	1210.8(3)	397.0(2)	
β , deg	90	90	90	111.79(3)	90	
V , 10 ⁶ pm ³	3631.6(1)	2985.2(1)	3321.9(1)	1247.3(3)	285.3(2)	
Z	6	8	8	8	2	
$\rho_{\text{calcd.}}$, g cm ⁻³	5.51	6.68	7.25	3.81	3.98	
μ (MoK α), mm ⁻¹	58.9	71.7	80.2	20.4	22.0	
$F(000)$, e	4956	4936	5944	1264	300	
hkl range	$-19 \leq h \leq 19$ $-19 \leq k \leq 19$ $-14 \leq l \leq 14$	$-33 \leq h \leq 33$ $-22 \leq k \leq 22$ $-12 \leq l \leq 12$	$-32 \leq h \leq 32$ $-21 \leq k \leq 21$ $-11 \leq l \leq 12$	$-10 \leq h \leq 10$ $-14 \leq k \leq 14$ $-13 \leq l \leq 13$	$-13 \leq h \leq 13$ $-6 \leq k \leq 13$ $-6 \leq l \leq 3$	
$((\sin \theta)/\lambda)_{\text{max}}$, Å ⁻¹	0.538	0.744	0.690	0.573	0.800	
Refl. measured	35060	32983	27317	7494	1035	
Refl. unique	3147	5337	4723	1933	496	
$R_{\text{int}}/R_{\sigma}$	0.119/0.058	0.072/0.034	0.084/0.043	0.084/0.055	0.082/0.076	
Parameters	164	139	139	110	17	
R_1 (all F)/ wR_2 (all F^2) ^a	0.057/0.035	0.037/0.055	0.054/0.036	0.052/0.057	0.061/0.062	
Inversion twin ratio	1 : 0.02(2)	—	—	—	1 : 0.01(3)	
GooF(F^2) ^a	0.90	2.21	1.33	1.38	1.74	
$\Delta\rho_{\text{fin}}$ (max/min), e Å ⁻³	+0.80/−0.89	+4.92/−6.14	+3.82/−3.77	+3.27/−3.08	+2.80/−2.79	

^a $R_1 = \Sigma \|F_o\| - |F_c| / \Sigma |F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$ and A and B are constants adjusted by the program; $\text{GoF} = S = [\Sigma w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$, where n_{obs} is the number of data and n_{param} the number of refined parameters.

settings of the structures were chosen in accordance with the standardized versions of the ICSD dataset. For details see Table 13.

Further details of the crystal structure investigations may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; E-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition numbers CSD-426518 (P₂I₄), CSD-426519 (Te₂Br), CSD-426522

(α -Te₄I₄), CSD-426520 (Te₄(Al₂Cl₇)₂), CSD-426521 (Te₄(Bi₆Cl₂₀)), CSD-426523 (Te₈(Bi₄Cl₁₄)), CSD-426517 (Bi₈(AlCl₄)₂), CSD-426516 (Bi₆Cl₇), CSD-426515 (Bi₆Br₇), CSD-426525 (WSCl₄), CSD-426524 (WOCl₄).

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