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, α-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$Te_8(Bi_4Cl_{14})$, $Bi_8(AlCl_4)_2$, Bi_6Cl_7, and Bi_6Br_7, as well as of $WSCl_4$ and $WOCl_4$ have been replaced by resource-efficient low-temperature syntheses in room temperature ionic liquids (RTILs).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 composition. 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 compositions 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 $[\mathrm{BMIm}]\mathrm{Cl}\cdot x\mathrm{AlCl_3}$ with $x = 1.3-4.8$ ($[\mathrm{BMIm}]^+ =$ 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 $\mathrm{AlCl_3}$. 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 ($\mathrm{AlCl_3} + \mathrm{Cl^-} \rightarrow \mathrm{AlCl_4}^-$). 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 $\mathrm{P_2I_4}$ by a modified version of the method of Germann and Traxler as follows [26]: A solution of white phosphorus in $\mathrm{CS_2}$ and a solution of iodine in $\mathrm{CS_2}$ 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 $\mathrm{P_2I_4}$ by reacting red phosphorus and iodine in the Lewis-acidic RTIL $[\mathrm{BMIm}]\mathrm{Cl}\cdot4.8\mathrm{AlCl_3}$ at 120 °C within 3 days (yield 30 %). Thereby, the pyrophoric solution of white phosphorus in highly toxic $\mathrm{CS_2}$ 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 $\mathrm{P_2I_4}$ molecule in the shape of a phosphorus dumbbell with terminal iodine atoms.

Te_2Br

$\mathrm{Te_2Br}$ 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 $\mathrm{Te_2Br}$ (Fig. 1) at room temperature by synproportionation of tellurium and $\mathrm{TeBr_4}$ in the RTIL $[\mathrm{BMIm}]\mathrm{Cl}\cdot1.3\mathrm{AlCl_3}$ 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 $\mathrm{P_2I_4}$ 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)	0.1370(6)	0.4613(8)	350(60)	510(30)	280(70)	40(30)	−40(70)	−70(20)	400(30)
	0.603	*0.139*	*0.463*							
I1	0.4416(4)	0.2290(2)	0.1654(3)	570(20)	477(7)	340(20)	−3(8)	−130(20)	−7(6)	472(8)
	0.423	*0.230*	*0.165*							
I2	0.1814(4)	0.3023(2)	0.6944(3)	560(20)	514(8)	460(20)	100(9)	−180(20)	−183(7)	502(9)
	0.180	*0.303*	*0.695*							

Table 2. Atomic parameters for a Te_2Br single crystal synthesized in RTIL. ICSD data determined using a conventionally synthesized crystal is given in *italics*. $U_{12} = U_{23} = 0$.

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

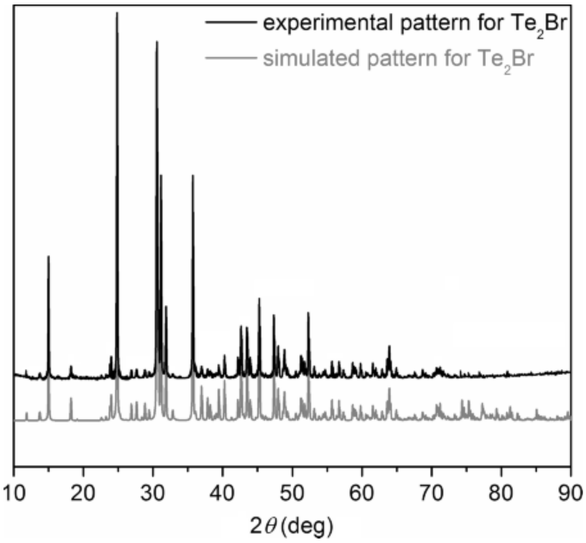

Fig. 1. Experimental (black) and calculated (grey) powder pattern of Te_2Br (CuK_{α_1}).

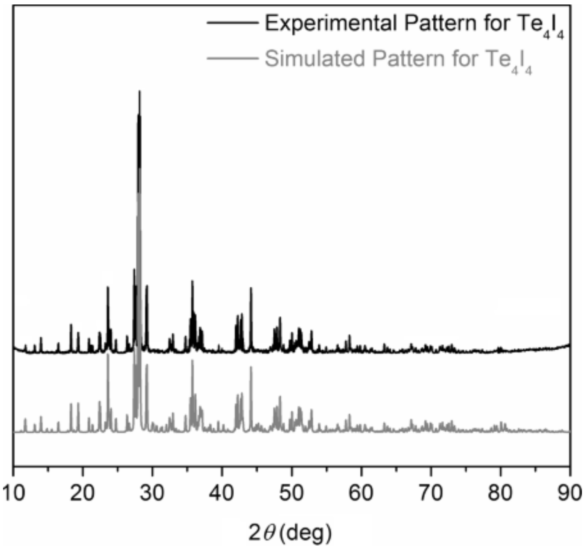

Fig. 2. Experimental (black) and calculated (grey) powder pattern of α-Te_4I_4 (CuK_{α_1}).

The crystal structure of Te_2Br 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-Te_4I_4

α-Te_4I_4 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-Te_4I_4 (Fig. 2) within two days at room temperature by reacting tellurium with TeI_4 in [BMIm]Cl·1.3$AlCl_3$. The crystal structure consists of slightly folded Te_4 rings that are saturated with two iodine atoms perpendicular to the 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 5σ (Table 3).

$Te_4(Al_2Cl_7)_2$

Corbett *et al.* synthesized $Te_4(Al_2Cl_7)_2$ by heating a mixture of tellurium, $TeCl_4$, and $AlCl_3$ in the molar proportions 3 : 1 : 4 to about 250 °C in a sealed evacuated Pyrex tube [32]. We obtained $Te_4(Al_2Cl_7)_2$ by reacting tellurium, TeI_4, and red phosphorus (attempt to synthesize phosphorus-tellurium polycations) in the Lewis-acidic RTIL [BMIm]Cl·4.8$AlCl_3$ at 80 °C within four days. The yield was about 70 %. Phosphorus and a fraction of the tellurium remained. The structure of $Te_4(Al_2Cl_7)_2$ consists of square $Te_4{}^{2+}$ cations

Table 3. Atomic parameters for a twinned α-Te_4I_4 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}
Te1	0.5049(2)	0.0041(1)	0.19334(9)	348(8)	274(4)	298(5)	104(4)	71(5)	55(4)	303(3)
	0.5043(2)	*0.0046(1)*	*0.1931(2)*							
Te2	0.7729(2)	0.3150(1)	0.2886(1)	312(7)	327(4)	322(6)	105(4)	66(5)	56(4)	317(3)
	0.7727(2)	*0.3147(1)*	*0.2884(2)*							
Te3	0.5006(2)	0.4779(1)	0.1999(1)	384(8)	266(4)	331(5)	105(4)	94(5)	61(4)	321(3)
	0.5008(2)	*0.4776(1)*	*0.1999(2)*							
Te4	0.2310(2)	0.1852(1)	0.1902(1)	279(7)	332(4)	345(6)	111(4)	72(5)	74(4)	313(3)
	0.2310(2)	*0.1848(1)*	*0.1898(2)*							
I1	0.2006(2)	0.6904(1)	0.0678(1)	342(8)	355(4)	407(6)	108(4)	66(5)	72(4)	368(3)
	0.2003(2)	*0.6905(1)*	*0.0676(2)*							
I2	0.1977(2)	0.1569(1)	0.8284(1)	316(8)	351(4)	400(6)	120(5)	76(5)	83(4)	351(3)
	0.1977(2)	*0.1566(1)*	*0.8285(2)*							
I3	0.2121(2)	0.6810(1)	0.43382(9)	425(8)	346(5)	343(6)	135(5)	78(5)	73(4)	366(3)
	0.2118(2)	*0.6810(1)*	*0.4336(2)*							
I4	0.2129(2)	0.1824(1)	0.4614(1)	443(9)	352(5)	381(6)	137(5)	159(6)	89(4)	375(3)
	0.2129(2)	*0.1826(1)*	*0.4613(2)*							

Table 4. Atomic parameters for a $Te_4(Al_2Cl_7)_2$ 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}
Te1	0.0635(4)	0.1553(2)	0.0315(4)	460(20)	430(20)	750(60)	10(20)	−140(30)	−100(20)	550(20)
	0.0643(2)	*0.1559(1)*	*0.0329(1)*							
Te2	0.1796(4)	0.5626(3)	0.5449(4)	450(20)	590(20)	880(70)	−10(20)	−220(30)	30(30)	640(20)
	0.1800(1)	*0.5626(1)*	*0.5455(1)*							
Al1	0.383(2)	0.175(1)	0.295(2)	500(100)	490(80)	200(200)	30(60)	−100(100)	230(90)	400(70)
	0.3818(6)	*0.1779(5)*	*0.2946(4)*							
Al2	0.233(1)	0.5800(9)	0.151(2)	260(90)	350(70)	600(200)	−120(60)	100(100)	10(90)	400(70)
	0.2387(6)	*0.5778(5)*	*0.1554(4)*							
Cl1	0.410(2)	0.171(1)	0.130(2)	800(100)	690(80)	600(200)	−50(70)	500(100)	150(90)	710(70)
	0.4073(6)	*0.1718(5)*	*0.1332(3)*							
Cl2	0.170(2)	0.122(1)	0.336(2)	600(100)	1000(100)	700(200)	10(60)	200(200)	100(100)	780(80)
	0.1727(6)	*0.1223(5)*	*0.3371(5)*							
Cl3	0.449(1)	0.3338(9)	0.361(1)	700(100)	480(70)	800(200)	90(60)	0(100)	50(80)	660(80)
	0.4524(6)	*0.3350(4)*	*0.3677(4)*							
Cl4	0.523(1)	0.0312(8)	0.353(2)	410(90)	260(70)	800(200)	70(40)	−100(100)	−90(70)	500(70)
	0.5256(5)	*0.0286(4)*	*0.3554(4)*							
Cl5	0.191(2)	0.6367(9)	0.008(2)	1000(100)	540(70)	700(200)	330(70)	0(100)	150(90)	730(70)
	0.1869(7)	*0.6370(5)*	*0.0061(4)*							
Cl6	0.222(2)	0.7174(9)	0.261(2)	800(100)	430(70)	900(200)	−80(60)	0(100)	−140(80)	710(70)
	0.2186(6)	*0.7171(5)*	*0.2616(4)*							
Cl7	0.136(1)	0.4177(8)	0.199(2)	700(100)	360(70)	800(200)	50(60)	−100(100)	210(80)	610(60)
	0.1314(6)	*0.4194(5)*	*0.1990(5)*							

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).

$Te_4(Bi_6Cl_{20})$

Crystals of $Te_4(Bi_6Cl_{20})$ were first synthesized by Beck *et al.* using a chemical gas-phase transport reaction 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 $BiCl_3$ in the Lewis-acidic RTIL [BMIm]Cl·1.3$AlCl_3$ 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 $Te_4(Bi_6Cl_{20})$ 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}
Te1	0.4015(2)	0.1622(2)	0.4265(1)	670(10)	469(8)	512(9)	−104(7)	−199(8)	39(6)	538(4)
	0.3995(2)	*0.1637(1)*	*0.42800(8)*							
Te2	0.6744(2)	0.1310(1)	0.5369(1)	590(10)	483(8)	495(8)	−193(7)	−153(7)	−21(6)	513(4)
	0.6741(1)	*0.1313(1)*	*0.53813(7)*							
Bi1	0.0750(1)	0.02661(7)	0.16681(5)	349(5)	346(4)	331(4)	−9(3)	−63(3)	−73(3)	338(2)
	0.07354(6)	*0.02700(5)*	*0.16704(3)*							
Bi2	0.1043(1)	0.48091(8)	0.74054(5)	451(5)	389(4)	364(4)	−67(3)	−50(3)	−126(3)	397(2)
	0.10461(6)	*0.48065(5)*	*0.73992(3)*							
Bi3	0.5931(1)	0.26431(7)	0.03268(5)	322(5)	328(4)	354(4)	5(3)	−79(3)	−66(3)	330(2)
	0.59293(5)	*0.26427(4)*	*0.03244(3)*							
Cl1	0.2600(6)	0.0383(4)	0.9778(3)	430(30)	230(20)	270(20)	40(20)	−40(20)	−50(20)	310(10)
	0.2597(4)	*0.0398(3)*	*0.9765(2)*							
Cl2	0.5862(7)	0.5442(4)	0.1031(3)	560(40)	240(20)	430(30)	40(20)	−250(20)	−120(20)	390(10)
	0.5868(5)	*0.5444(3)*	*0.1035(2)*							
Cl3	0.2226(7)	0.2894(4)	0.1586(3)	460(30)	300(20)	480(30)	−30(20)	30(20)	−170(20)	420(10)
	0.2216(4)	*0.2894(3)*	*0.1570(3)*							
Cl4	0.1953(7)	0.2031(5)	0.7319(3)	550(40)	340(20)	470(30)	−40(20)	90(20)	90(20)	470(10)
	0.1955(5)	*0.2036(4)*	*0.2685(3)*							
Cl5	0.7151(7)	0.2120(4)	0.2008(3)	400(30)	250(20)	410(30)	30(20)	−180(20)	−70(20)	340(10)
	0.7140(4)	*0.2128(3)*	*0.2006(2)*							
Cl6	0.3615(7)	0.8835(5)	0.1981(3)	410(30)	460(30)	430(30)	130(20)	−120(20)	−90(20)	430(10)
	0.3594(5)	*0.8845(4)*	*0.1981(3)*							
Cl7	0.0920(6)	0.6769(4)	0.0501(3)	310(30)	350(20)	470(30)	−30(20)	80(20)	−50(20)	380(10)
	0.0924(4)	*0.6785(4)*	*0.0506(3)*							
Cl8	0.3434(8)	0.5285(4)	0.5972(3)	660(40)	290(20)	400(30)	−150(20)	160(30)	−80(20)	470(10)
	0.3400(6)	*0.5280(4)*	*0.5974(3)*							
Cl9	0.1423(8)	0.5408(5)	0.3649(4)	510(40)	460(30)	580(30)	20(20)	−350(30)	−170(20)	490(10)
	0.1391(7)	*0.5424(5)*	*0.3631(4)*							
Cl10	0.0271(8)	0.0918(7)	0.3519(3)	380(40)	1130(40)	250(30)	−50(30)	−50(20)	−290(30)	580(20)
	0.0290(5)	*0.0911(6)*	*0.3515(3)*							

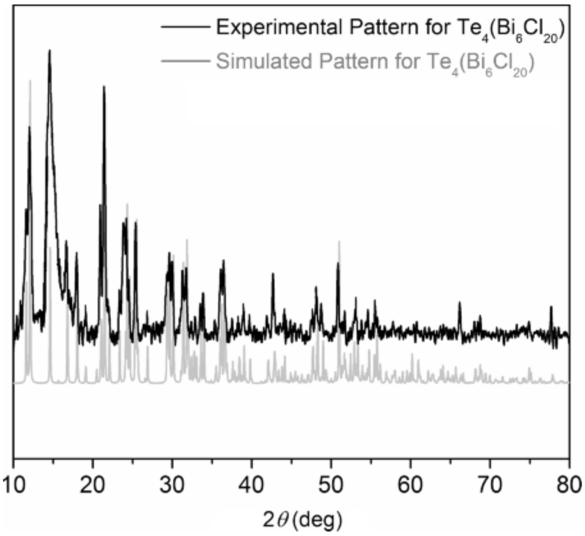

Fig. 3. Experimental (black) and calculated (grey) powder pattern of $Te_4(Bi_6Cl_{20})$ (CuK_{α_1}).

Te_4^{2+} polycations and chlorido-bismuthate(III) anions $[Bi_6Cl_{20}]^{2-}$. The atomic coordinates correspond to the published data [33] with a maximum deviation of 15σ (Table 5).

$Te_8(Bi_4Cl_{14})$

$Te_8(Bi_4Cl_{14})$ 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 $Te_8(Bi_4Cl_{14})$ by reacting tellurium, $TeCl_4$, and $BiCl_3$ in the Lewis-acidic RTIL $[BMIm]Cl\cdot1.3AlCl_3$ at room temperature (63 % yield, Fig. 4). The orthorhombic unit cell contains an infinite chain of $[Te_8]^{2+}$ polycations and two-dimensional chlorido-bismuthate(III) anions $[Bi_4Cl_{14}]^{2-}$. The atomic coordinates [34] correspond to the published data with a maximum deviation of 5σ (Table 6).

Table 6. Atomic parameters for a $Te_8(Bi_4Cl_{14})$ 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}
Bi1	0.33265(6)	0.12500(4)	0.01439(3)	180(3)	115(4)	191(3)	3(3)	11(2)	−5(3)	162(2)
	0.33253(5)	*0.12501(2)*	*0.01439(3)*							
Bi2	0.36231(6)	0.39576(4)	0.06779(3)	225(3)	198(4)	162(3)	−22(3)	22(3)	−3(3)	195(2)
	0.36227(5)	*0.39577(2)*	*0.06775(3)*							
Bi3	0.33210(6)	0.40271(4)	0.43935(3)	210(3)	186(4)	181(3)	−33(3)	−7(3)	17(3)	192(2)
	0.33203(5)	*0.40268(2)*	*0.43931(3)*							
Bi4	0.30746(6)	0.12446(5)	0.46996(3)	212(3)	209(4)	261(4)	−3(3)	21(3)	74(3)	227(2)
	0.30768(5)	*0.12444(2)*	*0.46998(3)*							
Te1	0.1192(1)	0.56127(8)	0.29728(6)	397(7)	255(7)	400(8)	−11(6)	−41(6)	148(7)	350(3)
	0.1192(1)	*0.56129(5)*	*0.29725(6)*							
Te2	0.6299(1)	0.10965(8)	0.27097(6)	325(6)	187(7)	660(10)	−23(6)	89(6)	63(7)	390(3)
	0.6302(1)	*0.10946(5)*	*0.27093(6)*							
Te3	0.5947(1)	0.25875(8)	0.22530(6)	338(6)	223(7)	302(7)	48(5)	−94(5)	−19(6)	288(3)
	0.5948(1)	*0.25878(4)*	*0.22532(5)*							
Te4	0.2518(1)	0.17743(8)	0.68130(5)	353(6)	195(7)	175(6)	29(5)	−21(5)	−34(6)	241(3)
	0.2518(1)	*0.17738(4)*	*0.68129(5)*							
Te5	0.0463(1)	0.27401(9)	0.28780(6)	320(7)	393(9)	388(8)	26(6)	−95(6)	−146(8)	367(3)
	0.0464(1)	*0.27397(5)*	*0.28777(7)*							
Te6	0.0057(1)	0.21531(9)	0.18025(6)	494(8)	378(9)	253(7)	−64(7)	168(6)	−61(7)	375(3)
	0.0055(1)	*0.21528(4)*	*0.18024(6)*							
Te7	0.2145(1)	0.01586(8)	0.72144(6)	341(7)	218(7)	531(9)	−19(6)	−106(6)	29(7)	363(3)
	0.2142(1)	*0.01578(5)*	*0.72141(6)*							
Te8	0.0561(2)	0.0056(1)	0.29528(6)	671(9)	500(10)	237(8)	175(8)	148(7)	−3(8)	468(4)
	0.0567(1)	*0.00582(5)*	*0.29534(7)*							
Cl1	0.7578(6)	0.2453(3)	0.0351(2)	660(30)	140(30)	360(30)	−110(20)	20(20)	50(30)	390(10)
	0.7583(5)	*0.2461(2)*	*0.0351(2)*							
Cl2	0.3959(5)	0.2159(3)	0.1078(2)	380(20)	300(30)	290(30)	60(20)	−40(20)	−190(30)	330(10)
	0.3965(4)	*0.2166(2)*	*0.1078(2)*							
Cl3	0.0677(4)	0.1065(3)	0.0542(2)	230(20)	460(30)	310(30)	−20(20)	80(20)	−60(30)	330(10)
	0.0692(3)	*0.1065(2)*	*0.0537(2)*							
Cl4	0.3325(5)	0.5502(3)	0.0596(2)	330(20)	200(30)	300(20)	0(20)	−80(20)	100(20)	270(10)
	0.3326(4)	*0.5501(2)*	*0.0598(2)*							
Cl5	0.3677(5)	0.4131(3)	0.1771(2)	570(30)	230(30)	130(20)	30(20)	−40(20)	−60(20)	310(10)
	0.3678(4)	*0.4133(1)*	*0.1768(2)*							
Cl6	0.0759(4)	0.3758(4)	0.0826(2)	320(20)	440(30)	210(20)	−60(20)	−50(20)	50(30)	320(10)
	0.0777(3)	*0.3756(1)*	*0.0828(2)*							
Cl7	0.6897(4)	0.0560(3)	0.0621(2)	310(20)	160(20)	380(30)	−30(20)	−20(20)	80(20)	280(10)
	0.6898(4)	*0.0558(2)*	*0.0623(2)*							
Cl8	0.3778(4)	0.4072(3)	0.3298(2)	270(20)	410(30)	160(20)	30(20)	20(20)	−70(20)	280(10)
	0.3778(4)	*0.4071(1)*	*0.3297(2)*							
Cl9	0.0494(4)	0.3869(3)	0.4144(2)	170(20)	450(30)	290(20)	−20(20)	0(20)	−20(30)	300(10)
	0.0493(3)	*0.3870(2)*	*0.4145(2)*							
Cl10	0.2430(6)	0.2520(3)	0.5250(3)	750(30)	140(30)	460(30)	20(30)	0(30)	0(30)	450(10)
	0.2433(5)	*0.2523(2)*	*0.5252(2)*							
Cl11	0.0459(4)	0.1198(4)	0.4304(2)	270(20)	650(40)	270(20)	70(20)	−50(20)	−90(30)	400(10)
	0.0460(4)	*0.1193(2)*	*0.4304(3)*							
Cl12	0.3889(7)	0.2118(5)	0.3815(3)	570(30)	1050(60)	650(40)	90(40)	230(30)	700(50)	760(20)
	0.3901(6)	*0.2123(2)*	*0.3821(4)*							
Cl13	0.1522(4)	0.0468(3)	0.5652(2)	240(20)	220(30)	230(20)	−30(20)	40(20)	−50(20)	230(10)
	0.1530(3)	*0.0470(1)*	*0.5654(2)*							
Cl14	0.6928(4)	0.4492(3)	0.0844(2)	290(20)	290(30)	270(20)	50(20)	10(20)	−60(20)	290(10)
	0.6922(4)	*0.4494(1)*	*0.0846(2)*							

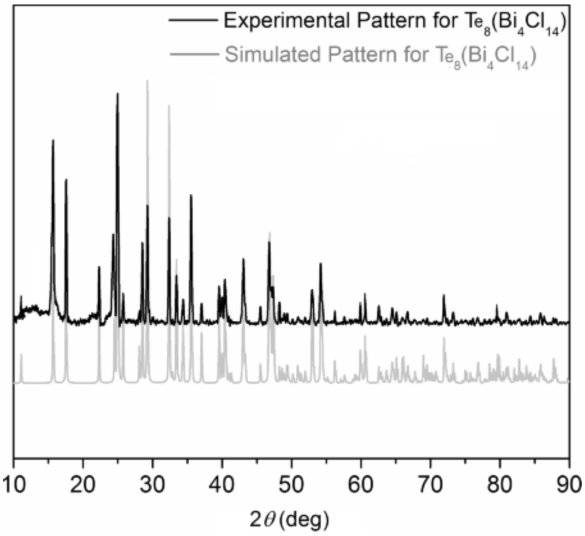

Fig. 4. Experimental (black) and calculated (grey) powder pattern of $Te_8(Bi_4Cl_{14})$ (CuK_{α_1}).

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 $Bi_8(AlCl_4)_2$. The decanted melt solidified to $Bi_8(AlCl_4)_2$ and an unidentified by-product. The classical synthesis is very difficult due to kinetic and subcooling problems [37]. We obtained well-shaped crystals of $Bi_8(AlCl_4)_2$ as the main product by reducing $BiCl_3$ with sodium in [BMIm]Cl·3.6AlCl$_3$ at 140 °C. Bismuth, $NaAlCl_4$, and $Bi_5(AlCl_4)_2$ were formed as by-products. By reducing the reaction temperature to 80 °C and using a less Lewis-acidic RTIL ([BMIm]Cl·1.3AlCl$_3$), we obtained $Bi_8(AlCl_4)_2$ with elemental bismuth and $NaAlCl_4$ as the only by-products. The crystals of $Bi_8(AlCl_4)_2$ 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 $Bi_8(AlCl_4)_2$ to crystallize in $P6_3/m$ with orientational disorder of the $AlCl_4^-$

$Bi_8(AlCl_4)_2$

Corbett *et al.* synthesized $Bi_8(AlCl_4)_2$ 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

Table 7. Atomic parameters for a $Bi_8(AlCl_4)_2$ single crystal synthesized in RTIL (ordered structure in space group $P6_3$).

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{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	x	y	z	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_6C1_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_6C1_7. In the second method, Bi_6Cl_7 was conveniently synthesized from a melt of elemental bismuth, $BiCl_3$, and $SbC1_3$ (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 [BMIm]Cl·2AlCl$_3$ 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 [BMIm]Cl·2AlCl$_3$ 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 $(Me_3Si)S_2$ react with WCl_6 in CH_2Cl_2 at −30 °C and obtained phase pure

Table 9. Atomic parameters for a Bi_6Br_7 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)

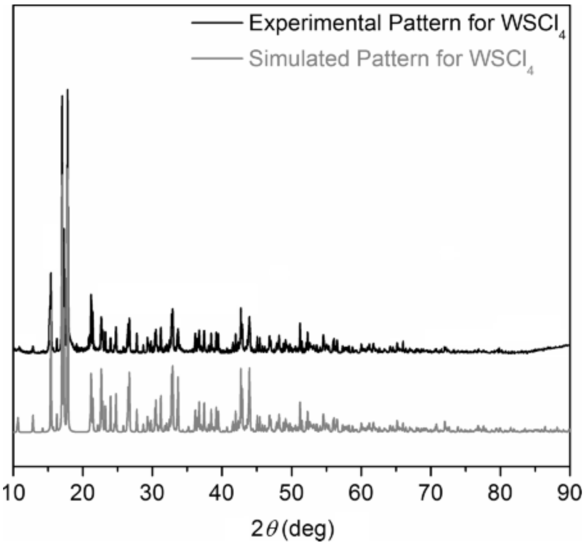

Fig. 5. Experimental (black) and calculated (grey) powder pattern of $WSCl_4$ (CuK_{α_1}).

$WSCl_4$ 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 $WSCl_4$ by reacting stoichiometric amounts of elemental sulfur and WCl_6 in [BMIm]Cl·1.3$AlCl_3$ 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 4σ (Table 10) [43]. Compared to the published synthesis route of monoclinic $WSCl_4$, we were able to reduce the reaction temperature tremendously and attained a phase-pure product (Fig. 5).

$WOCl_4$

Hess and Hartung synthesized needle-shaped crystals of $WOCl_4$ by reacting WO_2 and $SOCl_2$ at 200 °C [45]. We obtained needles of tetragonal $WOCl_4$ as a by-product of an attempt to synthesize phosphorus-sulfur polycations by reacting elemental sulfur and phosphorus with WCl_6 in [BMIm]Cl·1.3$AlCl_3$. 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 5σ (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 $WSCl_4$ 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}
W1	0.86828(5)	0.40937(4)	0.16070(4)	252(3)	312(3)	261(3)	6(2)	101(2)	−8(2)	274(2)
	0.8683(2)	*0.4092(2)*	*0.1609(1)*							
W2	0.44660(6)	0.14070(4)	0.07344(4)	302(3)	309(3)	397(3)	−20(2)	186(2)	−32(2)	320(2)
	0.4455(3)	*0.1407(2)*	*0.0726(2)*							
Cl1	0.1125(4)	0.8087(3)	0.1762(3)	430(20)	500(20)	290(10)	−50(20)	160(10)	−70(10)	399(7)
	0.114(1)	*0.8072(9)*	*0.1766(8)*							
Cl2	0.2132(4)	0.5537(3)	0.0378(3)	470(20)	510(20)	310(10)	10(20)	170(10)	80(10)	424(8)
	0.212(1)	*0.5539(9)*	*0.0372(8)*							
Cl3	0.0636(4)	0.3018(3)	0.1398(3)	380(20)	490(20)	540(20)	110(20)	240(20)	20(20)	446(8)
	0.062(1)	*0.3016(9)*	*0.1396(9)*							
Cl4	0.6136(3)	0.4557(3)	0.1455(3)	310(20)	440(20)	430(20)	50(10)	160(10)	−30(20)	385(7)
	0.613(1)	*0.4546(9)*	*0.1450(8)*							
Cl5	0.3104(4)	0.2303(2)	0.4472(3)	420(20)	400(20)	410(20)	−50(20)	110(20)	−90(20)	422(8)
	0.309(1)	*0.2279(9)*	*0.4478(9)*							
Cl6	0.6772(3)	0.1925(2)	0.0425(3)	320(20)	390(20)	350(20)	−40(10)	190(10)	−20(10)	338(7)
	0.679(1)	*0.1917(9)*	*0.0404(9)*							
Cl7	0.2157(3)	0.0505(2)	0.0478(3)	270(10)	410(20)	420(20)	−40(10)	150(10)	40(10)	362(7)
	0.217(1)	*0.0498(9)*	*0.0452(9)*							
Cl8	0.4103(4)	0.4753(2)	0.3550(2)	350(20)	410(20)	320(10)	−10(10)	110(10)	−70(10)	365(7)
	0.411(1)	*0.4733(9)*	*0.3547(8)*							
S1	0.0011(4)	0.0454(3)	0.2619(3)	430(20)	410(20)	520(20)	90(20)	140(20)	80(20)	465(8)
	0.001(2)	*0.046(1)*	*0.262(1)*							
S2	0.4929(4)	0.2123(3)	0.2368(3)	490(20)	530(20)	340(20)	10(20)	190(20)	10(20)	445(8)
	0.492(2)	*0.212(1)*	*0.237(1)*							

Table 11. Atomic parameters for a $WOCl_4$ 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}
W	0	0	0	322(4)	322(4)	230(4)	0	0	0	291(3)
	0	*0*	*0*							
Cl	0.0665(4)	0.2574(4)	0.0847(8)	430(20)	320(20)	470(20)	−20(10)	20(10)	−10(10)	406(9)
	0.0669(6)	*0.2584(6)*	*0.079(1)*							
O	0	0	0.562(7)	480(70)	480(70)	700(300)	0	0	0	540(80)
	0	*0*	*0.55(3)*							

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 $Te_4(Bi_6Cl_{20})$ and $Te_8(Bi_4Cl_{14})$ 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 CS_2, or solvents that need permanent cool-

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.

Compound	Conventional synthesis	Synthesis in RTIL
P_2I_4	in CS_2 at 20 °C, 12 h [26]	3d, 120 °C, small amount
Te_2Br	CM, 350 °C, 2 – 3 weeks [28]	5d, 20 °C, yield 39 %, phase-pure
α-Te_4I_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]
$Te_4(Al_2Cl_7)_2$	CM, 250 °C [32]	4d, 80 °C, major crystalline phase
$Te_4(Bi_{0.67+\delta}Cl_4)$	CTR, 160 °C, yield 10 %, 1 week [24]	3d, 20 °C, yield 63 %, phase-pure [24]
$Te_4(Bi_6Cl_{20})$	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]
$Te_8(Bi_4Cl_{14})$	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_6Cl_7	CM; inhomogeneous melt; phase-pure synthesis difficult, > 1 week [37]	2d, 20 °C, yield 63 %, phase-pure
Bi_6Br_7	CM; inhomogeneous melt; phase-pure synthesis difficult, 2d [40]	2d, 20 °C, yield 71 %, phase-pure
$BiCl(Mo_6Cl_{14})$	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
$WSCl_4$	CM, 425 °C, > 2d [43]	3d, 20 °C, yield 55 %, phase-pure

ing, such as liquid SO_2. 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; $p(O_2)/p_0 <$ 3 ppm, $p(H_2O)/p_0 <$ 3 ppm) or under dry argon atmosphere (Alphagaz, 99.999 %) in Schlenk tubes. The RTILs were synthesized by mixing [BMIm]Cl (Merck, 98 %) and $AlCl_3$ (Fluka, 98 % or technical, sublimated three times). In order to remove the ILs, the products were washed with dry CH_2Cl_2, except the single crystals, which were directly taken from the IL. Bismuth (Riedel de Haën, chemical pure) was treated twice with H_2 at 220 °C. $BiBr_3$ (Alfa Aesar, 98 %) and $BiCl_3$ (Alfa Aesar, 99.999 %) were sublimed prior to use. $TeCl_4$ was synthesized from the elements (Te: Aldrich, 99.999 %; Cl_2: Air Liquide, 99.8 %) according to literature [52]. $TeBr_4$ (Strem, 99.9 %) was sublimed twice. TeI_4 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. WCl_6 (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.

P_2I_4

Red phosphorus and I_2 (molar ratio = 1 : 2, total mass = 270 mg) were sealed together with the Lewis-acidic RTIL [BMIm]Cl·4.8$AlCl_3$ (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 P_2I_4 could be obtained besides a dark-brown powder.

Te_2Br

Tellurium and $TeBr_4$ (molar ratio = 7 : 1, total mass = 268 mg) were added to 1.5 mL of the Lewis-acidic RTIL [BMIm]Cl·1.3$AlCl_3$. 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 Te_2Br within five days. Yield: 39 %.

α-Te_4I_4

Te and TeI_4 (molar ratio = 3 : 1, total mass = 254 mg) were added to 1.5 mL of the Lewis-acidic RTIL [BMIm]Cl·1.3$AlCl_3$. 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-Te_4I_4 within two days. Yield: 64 %.

$Te_4(Al_2Cl_7)_2$

Tellurium, $TeCl_4$ and red phosphorus (molar ratio = 1 : 1 : 1, total mass = 208 mg) were combined in the Lewis-acidic RTIL [BMIm]Cl·4.8$AlCl_3$ and heated to 80 °C for four days. Dark-red crystals of $Te_4(Al_2Cl_7)_2$ were obtained. Yield: 70 %.

$Te_4(Bi_6Cl_{20})$

Tellurium, $TeCl_4$, and $BiCl_3$ (molar ratio = 3.5 : 0.5 : 6, total mass = 275 mg) were reacted in 1.5 mL of the Lewis-acidic RTIL [BMIm]Cl·1.3$AlCl_3$. 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 %.

$Te_8(Bi_4Cl_{14})$

The same procedure as described for $Te_4(Bi_6Cl_{20})$ was applied, but the molar ratio of the reactants was taken according to $Te_8(Bi_4Cl_{14})$ (total mass = 285 mg). After two days, black, irregularly shaped crystals were isolated. Yield: 63 %.

$Bi_8(AlCl_4)_2$

For powder: Na and $BiCl_3$ (molar ratio 2.8 : 1, total mass 115 mg) were added to 1.5 mL of the Lewis-acidic RTIL [BMIm]Cl·1.3$AlCl_3$. After heating the mixture to 80 °C, the solution turned dark brown while all starting material was dissolved, and black fine powders of $Bi_8(AlCl_4)_2$ and elemental bismuth precipitated. *For crystals:* Na and $BiCl_3$ (molar ratio 2.8 : 1, total mass 115 mg) were mixed with 250 mg $AlCl_3$ 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 %.

Bi_6Cl_7

In and $BiCl_3$ (molar ratio 2 : 3, total mass = 284 mg) were added to the Lewis-acidic IL [BMIm]Cl·2$AlCl_3$ (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 $BiCl_3$: 63 %.

Bi_6Br_7

Black shiny needles of Bi_6Br_7 were synthesized from Bi and $BiBr_3$ (molar ratio 1 : 1, total mass = 328 mg) in [BMIm]Cl·2$AlCl_3$ using the same methodology as for Bi_6Cl_7. Yield with respect to bismuth: 71 %.

$WSCl_4$

Equimolar amounts of elemental sulfur and WCl_6 (total mass = 231 mg) were added to 1.5 mL of the Lewis-acidic RTIL [BMIm]Cl·1.3$AlCl_3$. 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 $WSCl_4$ in the course of three days. Yield: 55 %. Evolution of Cl_2 has not been observed, but soluble sulfur chlorides might have formed in the IL.

$WOCl_4$

Red phosphorus, sulfur, and WCl_6 (molar ratio = 8 : 1 : 8, total mass = 280 mg) were combined in the Lewis-acidic acid [BMIm]Cl·1.3$AlCl_3$ (total mass = 320 mg) at 60 °C. Orange needles of $WOCl_4$ 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 $WOCl_4$ is a sign for oxidative contamination probably of the phosphorus. In addition crystals of $WSCl_4$ 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_{α_1} 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 P_2I_4 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.

	P_2I_4	**Te_2Br**	**α-Te_4I_4**	**$Te_4(Al_2Cl_7)_2$**	**$Te_4(Bi_6Cl_{20})$**	**$Te_8(Bi_4Cl_{14})$**
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
$\rho_\mathrm{calcd.}$, g cm^{-3}	4.24	5.72	5.51	2.76	4.59	4.78
$\mu(\mathrm{Mo}K_\alpha)$, 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	$-6 \le h \le 3$	$-11 \le h \le 15$	$-9 \le h \le 9$	$-8 \le h \le 5$	$-7 \le h \le 7$	$-9 \le h \le 9$
	$-8 \le k \le 8$	$-3 \le k \le 4$	$-9 \le k \le 9$	$-10 \le k \le 8$	$-9 \le k \le 9$	$-18 \le k \le 18$
	$-4 \le l \le 9$	$-13 \le l \le 13$	$-11 \le l \le 11$	$-11 \le l \le 6$	$-15 \le l \le 15$	$-25 \le l \le 25$
$((\sin\theta)/\lambda)_\mathrm{max}$, 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_int/R_σ	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
$\Delta\rho_\mathrm{fin}$ (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

	$Bi_8(AlCl_4)_2$	**Bi_6Cl_7**	**Bi_6Br_7**	**$WSCl_4$**	**$WOCl_4$**
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	$P6_3$	$Pnnm$	$Pnnm$	$P2_1/c$	$I4$
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
$\rho_\mathrm{calcd.}$, g cm^{-3}	5.51	6.68	7.25	3.81	3.98
$\mu(\mathrm{Mo}K_\alpha)$, mm^{-1}	58.9	71.7	80.2	20.4	22.0
$F(000)$, e	4956	4936	5944	1264	300
hkl range	$-19 \le h \le 19$	$-33 \le h \le 33$	$-32 \le h \le 32$	$-10 \le h \le 10$	$-13 \le h \le 13$
	$-19 \le k \le 19$	$-22 \le k \le 22$	$-21 \le k \le 21$	$-14 \le k \le 14$	$-6 \le k \le 13$
	$-14 \le l \le 14$	$-12 \le l \le 12$	$-11 \le l \le 12$	$-13 \le l \le 13$	$-6 \le l \le 3$
$((\sin\theta)/\lambda)_\mathrm{max}$, 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_int/R_σ	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
$\Delta\rho_\mathrm{fin}$ (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] $R_1 = \Sigma \| F_\mathrm{o}| - |F_\mathrm{c} \| / \Sigma |F_\mathrm{o}|$; $wR_2 = [\Sigma w(F_\mathrm{o}^2 - F_\mathrm{c}^2)^2 / \Sigma w(F_\mathrm{o}^2)^2]^{1/2}$, $w = [\sigma^2(F_\mathrm{o}^2) + (\mathrm{A}P)^2 + \mathrm{B}P]^{-1}$, where $P = (\mathrm{Max}(F_\mathrm{o}^2, 0) + 2F_\mathrm{c}^2)/3$ and A and B are constants adjusted by the program; GoF $= S = [\Sigma w(F_\mathrm{o}^2 - F_\mathrm{c}^2)^2 / (n_\mathrm{obs} - n_\mathrm{param})]^{1/2}$, 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 (P_2I_4), CSD-426519 (Te_2Br), CSD-426522 (α-Te_4I_4), CSD-426520 ($Te_4(Al_2Cl_7)_2$), CSD-426521 ($Te_4(Bi_6Cl_{20})$), CSD-426523 ($Te_8(Bi_4Cl_{14})$), CSD-426517 ($Bi_8(AlCl_4)_2$), CSD-426516 (Bi_6Cl_7), CSD-426515 (Bi_6Br_7), CSD-426525 ($WSCl_4$), CSD-426524 ($WOCl_4$).

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