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Preparation and structure of soluble complexes of the ternary compounds GaSBr and GaSeBr

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[GaSBr] and [GaSeBr] can be prepared from $Ga[GaBr_4]$ and elemental sulfur/selenium in toluene or tetrahydrofuran, respectively. $GaBr_3(thf)_2$ is a by-product of these reactions. Its structure (a trigonal-bipyramidal array of ligands with the bromine atoms in equatorial positions) has been determined. The two ternary gallium bromides are insoluble in most common organic solvents, but are readily dissolved in pyridine and substituted pyridines (L) to give trinuclear complexes $[GaSBr(L)]_3$ with L = 3,5-dimethylpyridine (**1**), 4-*tert*-butylpyridine (**2**) and 4-dimethylaminopyridine, and $[GaSeBr(L)]_3$ with L = 3,5-dimethylpyridine (**5**), respectively. The molecular structures of **1**, **2** and **5** have been determined. The core units are six-membered rings with different substitution patterns depending largely on the steric requirements of the ligands L, and on the mode of crystallization. The reaction of [GaSBr] with the strongly basic $4\text{-}Me_2NC_5H_4N$ in refluxing acetonitrile leads to partial degradation of the trinuclear units to give an ionic product $[Ga_4S_5(L)_4]^{2+}2Br^-$ (**4**). The dications have a bicyclic structure of the well-known borax-type. The reactions and structures are discussed in the light of previous findings in the corresponding chloride series $[GaSCl(L)]_3$ and $[GaSeCl(L)]_3$. For comparison the structure of $[GaSCl(L)]_3$ with L = 3,5-dimethylpyridine has also been determined for the solvate-free crystal and for a tetrahydrofuran solvate, where different conformations are observed.

Introduction

Owing to the extensive application of binary and ternary compounds of gallium with elements of Groups 15 and 16 in semiconductor and related technologies[1] there is great current interest in the general chemistry of pertinent systems. It is immediately obvious from the complexity of the phase diagrams[2,3] that the preparation of pure ternary compounds is a synthetic challenge especially in solid state reactions.[3–5] Therefore there is a need for well-defined volatile or soluble derivatives which can be used as precursors for the target compounds.[6,7]

Ternary gallium(III) compounds with a chalcogen Y (S, Se, Te) and a halogen X (Cl, Br, I) of the type $[GaYX]_n$ may be particularly useful intermediates in the preparation of other gallium chalcogenides with hydride or organic substituents, $[GaYH]_n$ or $[GaYR]_n$. However, these ternary compounds are difficult to prepare from the elemental components, and other synthetic routes are required.[1–5]

In studies of the *chloride* system, we have shown that dichlorogallane $[HGaCl_2]$ is readily accessible from anhydrous $[GaCl_3]_2$ and trimethylsilane Me_3SiH or triethylsilane Et_3SiH.[6–10] The components undergo a quantitative conversion at −13 °C with Me_3SiCl/Et_3SiCl as the only by-products. Moreover, $[HGaCl_2]_2$ can be thermolyzed quantitatively at only slightly elevated temperature to give $Ga[GaCl_4]$ and hydrogen. Finally, $Ga[GaCl_4]$ can be reacted with elemental *sulfur* to give [GaSCl] and $GaCl_3$. The [GaSCl] thus obtained is soluble in pyridine[7] with formation of a trinuclear complex $[GaSCl(pyr)]_3$ which can be purified by crystallization. The structures of this complex and the *selenium* analogue have been determined.[7,8]

We now describe a facile preparation of new complexes of the *bromine* compounds $[GaSBr]_n$ and $[GaSeBr]_n$ which must be synthesized *via* different routes. With the strongly basic *p*-dimethylaminopyridine a complex other than the common trinuclear six-membered ring compounds has been discovered.

Preparative studies

For the preparation of the ternary compound $[GaSBr]_n$, freshly synthesized $Ga[GaBr_4]$ is dissolved in anhydrous toluene as its bis-arene complex[11–15] and treated with elemental sulfur. A colourless precipitate is formed which can be isolated by filtration (79% yield). The reaction can be formulated as shown in eqn. (1). The $GaBr_3$ by-product was not traced in the S/Br system, but $GaBr_3$ was isolated as the 1 : 2 tetrahydrofuran complex in the corresponding Se/Br system (below).

$$n\ Ga[GaBr_4] + S_n \longrightarrow n\ GaBr_3 + [GaSBr]_n \quad (1)$$

This $[GaSBr]_n$ product is readily dissolved in acetonitrile upon addition of an excess of pyridine[7,8] or a substituted pyridine to give clear solutions. The $[GaSBr]_n$ also dissolves quickly in neat pyridines even at room temperature. From the solutions the corresponding complexes $[GaSBr(pyr)]_3$ can be precipitated on cooling or by the addition of diethyl ether or *n*-hexane [eqn. (2)]. In the present study the complexes with 3,5-dimethylpyridine, 4-*tert*-butylpyridine and 4-dimethylaminopyridine were isolated and crystallized:

$$3/n\ [GaSBr]_n + 3\ pyr \longrightarrow [GaSBr(pyr)]_3$$

pyr = 3,5-$Me_2C_5H_3N$ **1**; 4-$^tBuC_5H_4N$ **2**; 4-$Me_2NC_5H_4N$ **3** (2)

The yields of the reactions are generally high (typically 60–70%), but a significant amount of material may be lost in the crystal growth. Single crystals of compound **1** were obtained from acetonitrile as the solvate $\mathbf{1}\cdot CH_3CN$, **1a**.

The reaction of $[GaSBr]_n$ with 4-dimethylaminopyridine takes a different course if the components are heated in acetonitrile to reflux temperature, or if compound **3** is reacted further with the pyridine in boiling acetonitrile. Upon cooling the reaction mixture to −30 °C colourless crystals of a product different from **3** are obtained. This compound was identified (by X-ray crystallography) as an ionic material composed of a bicyclic dication and bromide anions (**4**). The process may thus be formulated as follows [eqn. (3)]:

$$5[GaSBr(pyr)]_3 + 6\ pyr \longrightarrow 3\ (pyrGaBr_3) + 3[Ga_4S_5(pyr)_6]Br_2$$

pyr = 4-$Me_2NC_5H_4N$ **4** (3)

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Elemental *selenium* does not react with $Ga[GaBr_4]$ in a similar way to sulfur in toluene, but in tetrahydrofuran (thf) the reaction was found to be successful. From the resulting solution the $[GaSeBr]_n$ product as well as the 2 : 1 adduct $[GaBr_3(OC_4H_8)_2]$ could be isolated [eqn. (4)].

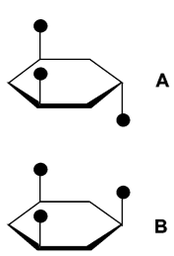
$$n\ Ga[GaBr_4] + Se_n \xrightarrow{thf} [GaSeBr]_n + n\ [GaBr_3(OC_4H_8)_2] \quad (4)$$

A suspension of $[GaSeBr]_n$ in thf becomes clear upon addition of an excess of 3,5-dimethylpyridine and crystals of complex **5**·thf, **5a**, can be precipitated by layering the solution with *n*-hexane [eqn. (5)]. Recrystallization from hot acetonitrile results in the solvate **5**·CH_3CN, **5b**, as also obtained with the sulfur analogue. The yield of the solvate **5a** is low (13.5%) owing to the high solubility of the compound.

$$3/n\ [GaSeBr]_n + 3\ pyr \longrightarrow [GaSeBr(pyr)]_3 \quad (5)$$
$$pyr = 3,5\text{-}Me_2C_5H_3N \quad \mathbf{5}$$

Since the bromine compound **1** was found to have an interesting structure possibly influenced by the specific requirements of the 3,5-dimethylpyridine ligand, the corresponding chlorine compound **6** was also synthesized and structurally characterized in the present study. The preparation followed the established procedure.[7,8] The product was crystallized free of solvent from 3,5-dimethylpyridine/hexane, but crystals obtained from tetrahydrofuran were found to be a solvate **6a**. Surprisingly, the two crystalline forms feature the trinuclear, six-membered ring compound in two different conformations (in chair and tub forms, but with the pyridine ligands consistently in a *cis*,*trans*,*trans* orientation).

Compounds **1**–**5** and the chloro-analogue **6** have been characterized by elemental analyes and by variable-temperature ^{1}H NMR spectroscopy. Room-temperature spectra (in acetonitrile and in dichloromethane) have shown consistently that there is rapid exchange of the pyridine ligands leading to time-averaged spectra exhibiting only one set of resonances for virtually equivalent ligands. Upon cooling the solutions in CD_2Cl_2 to −70 °C these resonances are split into two sets which can be assigned to a dominant component with the *cis*,*trans*,*trans* configuration and a minor component with the all-*cis* configuration. Assuming ring flexibility (chair–tub) in solution even at the low-temperature limit, these two configurations imply two types of ligands in the *cis*,*trans*,*trans* case, **A**, but only one type for the all-*cis* case, **B** (Scheme 1). The dominance of the *cis*,*trans*,*trans* arrangement is in agreement with the findings in the crystal structure analyses of all compounds investigated by X-ray diffraction (below).



Scheme 1 Schematic illustration of the two possible configurations for the compounds **1**–**3**, **5** and **6**: *cis*,*trans*,*trans*, **A**, and all-*cis*, **B**, with planarized six-membered rings.

The temperature-dependent NMR phenomena can easily be illustrated by the examples of the ^{t}BuC_5H_4N complex **2** and one of the 2,5-$Me_2C_5H_3N$ complexes, **1**. The ^{1}H NMR spectrum of the former (**2**, in CD_2Cl_2) has three resonances of the ligand at 1.37 (^{t}Bu) and 7.68/8.82 ppm (C_6H_4). At −70 °C, these signals are split into three sets of resonances. Three signals [at 1.34 (^{t}Bu), 7.88 and 8.66 ppm (d, *J* 6.5 Hz, C_6H_4)] are readily assigned to the all-*cis* form **B**. For the *cis*,*trans*,*trans* form two sets of resonances are observed in the intensity ratio 2 : 1 [1.26 and 1.34 for ^{t}Bu, 7.54/7.69 and 8.68/8.91 ppm (all d, *J* 6.4 Hz, C_6H_4)]. From the intensity ratio of the signals of the two isomers a molar ratio of 6 : 1 can be calculated (at −70 °C in CD_2Cl_2). The coalescence temperature for the ^{t}Bu singlet resonance is −10 °C. Since more than one ligand exchange mechanism (dissociative, associative, inter- and intramolecular) may be operative, no attempts have been made to calculate activation energies for any of these processes.

Compound **1** (in CD_2Cl_2) also has three resonances in its ^{1}H NMR spectrum at room temperature [2.40 (Me), 7.71 and 8.62 ppm (C_5H_3)]. At −70 °C the corresponding signals for the all-*cis* isomer appear at 2.47, 8.04 and 8.44 ppm (all s, intensity ratio 6 : 1 : 2). The *cis*,*trans*,*trans* isomer has its resonances at 2.23, 2.43 (12 : 6, Me), 7.60/7.78 and 8.31/8.72 ppm (2 : 1 : 4 : 2, C_5H_3). The molar ratio of all-*cis* and *cis*,*trans*,*trans* isomers is 1 : 7 (at −70 °C in CD_2Cl_2). The coalescence temperature for the methyl resonances of compound **1** is −5 °C. The chemical shift data and intensity ratios are similar for the selenium analogue **5**, but its coalescence temperature is higher at +15 °C.

It follows from the spectra of the compounds with the 3,5-dimethylpyridine ligand that both the ring inversion and the rotation of the ligands about the Ga–N axis is rapid on the NMR time scale at the low temperature limit of the experiments (−70 °C). All temperature-dependent phenomena observed in the range between +25 and −70 °C are due to intra- or inter-molecular exchange of pyridine ligands between trinuclear isomers (**A** and **B**) with highly flexible chair/tub conformations and free ligand rotation.

The ^{1}H NMR spectrum of the borax-type compound **4** (in CD_2Cl_2 at 25 °C) exhibits only one signal for the Me_2N groups of all ligands (at 3.09 ppm). Only the C_6H_4 resonances show some poorly resolved splitting which may indicate inequivalent ligands in the dianion as well as some isomerization or ligand redistribution in solution. Owing to the limitations of solubility this problem was not investigated any further.

Structural investigations

The crystal structures of compounds **1**, **2** and **5** were all shown to be based on trinuclear molecules with a six-membered ring unit, in agreement with the results obtained previously for the parent pyridine complexes $[GaYX(pyr)]_3$ with Y = S, Se, X = Cl, Br, and pyr = pyridine.[7,8] The conformations of the six-membered rings and the distribution of the substituents/ligands over the axial and equatorial positions are all different and differ significantly from those of the corresponding alkylgallium sulfide complexes[16,17] and of the symmetrical trianion $[(GaCl_2S)_3]^{3-}$.[18]

Of the compounds with L = 3,5-dimethylpyridine (lutidine), **1** and **5** crystallize as 1 : 1 solvates with acetonitrile (**1a**, **5b**) in the monoclinic space group $P2_1/c$ with $Z = 4$ formula units (trimers) in the unit cell. The asymmetric unit holds one of these trimers without any crystallographically imposed symmetry, and one solvent molecule (Fig. 1). The six-membered ring is in a tub conformation. The three bromine atoms reside in the equatorial positions which puts the three lutidine molecules in the axial positions, two below and one above the ring unit, representing a *cis*,*trans*,*trans*-arrangement. This ligand distribution approaches mirror symmetry (point group C_s). The two pyridine rings on the same side of the rings (N2 and N3) face each other, but the inter-arene distance [*ca*. 3.732 Å] is too long to suggest significant π–π-stacking effects. The third lutidine molecule is bisected roughly at right angle by that virtual mirror plane. The structure of **1** in **1a** thus resembles that of the *chloride* complex $[GaSCl(pyr)]_3$, but is different from that of the *bromide* $[GaSBr(pyr)]_3$.[7,8]

From tetrahydrofuran (instead of acetonitrile), the selenium compound **5** crystallizes as a tetrahydrofuran solvate **5a** in the

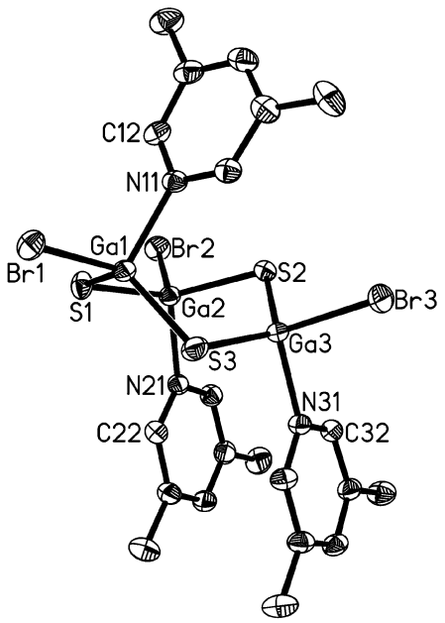


Fig. 1 Molecular structure of compound **1** in the acetonitrile solvate crystal (**1a**). The conformation approaches mirror symmetry (point group C_s) with the virtual mirror plane passing through Ga1, Br1, N11 and S2. Selected bond lengths [Å] and angles [°]: Ga1–S1 2.2187(8), Ga1–S3 2.2214(8), Ga2–S1 2.2207(7), Ga2–S2 2.2328(7), Ga3–S2 2.2198(7), Ga3–S3 2.2288(8), Ga1–Br1 2.3581(4), Ga2–Br2 2.3340(4), Ga3–Br3 2.3578(4), Ga1–N11 2.027(2), Ga2–N21 2.021(2), Ga3–N31 2.031(2); Ga1–S1–Ga2 99.66(3), Ga2–S2–Ga3 103.47(3), Ga3–S3–Ga1 98.00(3).

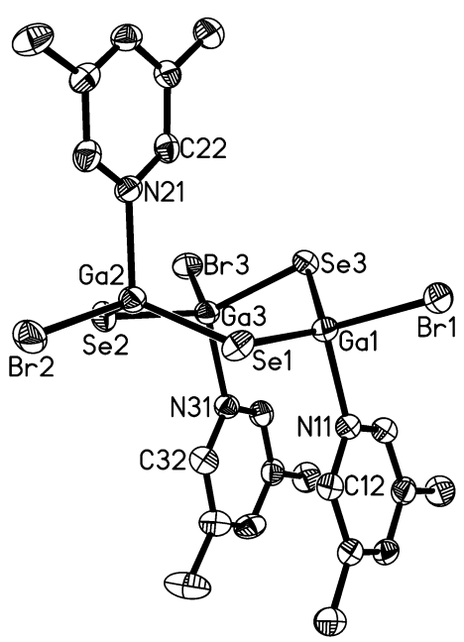


Fig. 2 Molecular structure of compound **5** in the tetrahydrofuran solvate crystal (**5a**). The conformation is very similar to that of compound **1** shown in Fig. 1. Selected bond lengths [Å] and angles [°]: Ga1–Se1 2.3452(6), Ga1–Se3 2.3464(6), Ga2–Se1 2.3372(6), Ga2–Se2 2.3389(6), Ga3–Se2 2.3449(6), Ga3–Se3 2.3453(6); Ga1–Se1–Ga2 104.16(2), Ga2–Se2–Ga3 104.07(2), Ga3–Se3–Ga1 99.22(2). Ga–Br and Ga–N distances are similar to those in compound **1**.

monoclinic space group $C2/c$ with $Z = 8$ formula units (trimers) in the unit cell. The individual molecules (Fig. 2) are very similar to those of the sulfur analogue **1** in **1a**, but the unique lutidine molecule has a different orientation: It is approximately parallel to the virtual mirror plane [dihedral angle Br2–Ga2–N21–C22 −167.2(3)°] instead of perpendicular [dihedral angle Br1–Ga1–N1–C12 −87.0(2)° in **1a**]. A superposition of the two molecules (in **1a** and **5a**, Fig. 3) shows that this rotatory variation is the only major difference of the two structures. This result corroborates the observation that the nature of the halogen (in this pair of compounds the bromine) is determining the structure, while the substitution S/Se has no effect other than a lengthening of the Ga–S/Se bonds in the ring.

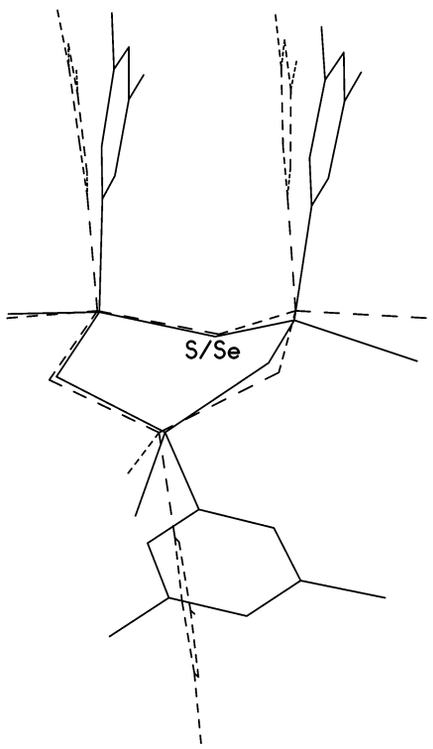


Fig. 3 Superposition of the molecular structures of **1** and **5** (in **1a** and **5a**) showing the rotatory variation of one ligand molecule as the major difference of the two structures.

Compound **2**, $[(4\text{-}^{t}BuC_5H_4N)GaSBr]_3$, crystallizes in the orthorhombic system, space group $P2_12_12_1$ ($Z = 4$), with one complete trinuclear molecule in the asymmetric unit (Fig. 4). The six-membered ring is strongly distorted and shows no approach to any symmetrical conformation. To a first approx-

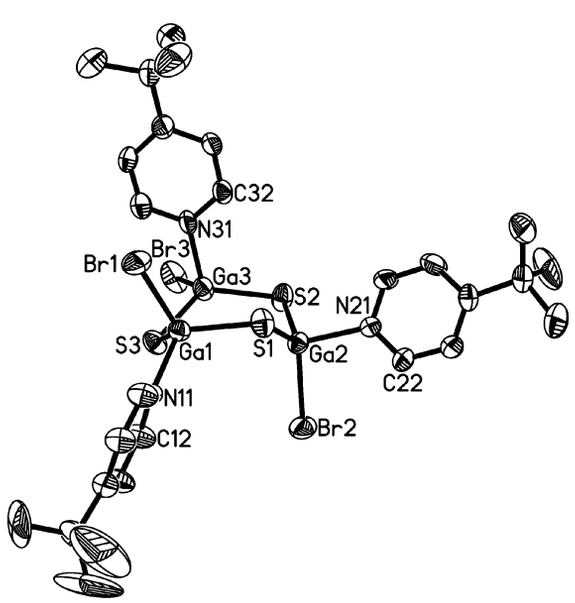


Fig. 4 Molecular structure of compound **2**. The bond lengths and angles are similar to those in compound **1** (Fig. 1), but the ligand distribution is not approaching any symmetry (point group C_1).

imation, the pyridine ligands can be assigned to one axial (N31) and two equatorial positions (N11 and N21), referring to a (distorted) tub conformation with point group C_1. Similar conformations were found[8] for $[(pyr)GaSBr]_3$ and $[(pyr)GaSeBr]_3$. It therefore appears that the more symmetrical structures of the bromide compounds **1** and **5** (approaching point group C_s) are the exception, while the unsymmetrical structure of compound **2** follows the example of the simple pyridine analogues. Since 4-*tert*-butylpyridine (with its *tert*-butyl group far away from the nitrogen donor center) can be assumed to have a steric effect similar to that of pyridine, the structural variation found for **1** and **5** can be ascribed to the steric requirements of the lutidine ligands.

Crystals of the *chloro*-analogue of compound **1** with the formula $[GaSCl(3,5\text{-}Me_2C_5H_3N)]_3$, **6**, are not isomorphous with **1**, but are found to be triclinic, space group $P\bar{1}$ with $Z = 2$ trinuclear molecules in the unit cell. The asymmetric unit thus contains one molecule with no crystallographically imposed symmetry. At variance with all previous results[7,8,16–18] on related compounds, this molecule has a *chair* conformation with the pyridine ligands in a *cis*,*trans*,*trans* arrangement (Fig. 5). The structure approaches the requirements of mirror symmetry, but the rotation of the pyridine ring at Ga3 away from the perpendicular orientation is still large as shown by the dihedral angles Cl3–Ga3–N31–C32 and Cl3–Ga3–N31–C36 of −80.1(2) and 105.7(2)°, respectively. Two of the ligands (at Ga1 and Ga2) are face-to-face to each other, but the distance between the rings its too long to suggest efficient π-stacking (3.851 Å).

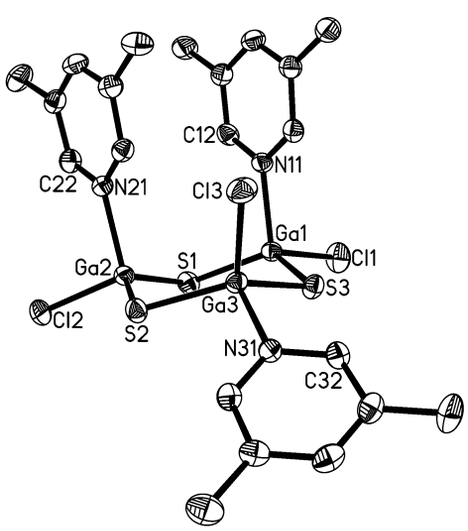


Fig. 5 Molecular structure of compound **6**. The conformation approaches mirror symmetry (point group C_s) with the virtual mirror plane passing through Ga3, Cl3, N31 and S1. Selected bond lengths [Å] and angles [°]: Ga1–S1 2.2178(9), Ga1–S3 2.2138(9), Ga2–S1 2.2175(9), Ga2–S2 2.2204(9), Ga3–S2 2.2203(9), Ga3–S3 2.2173(9), Ga1–Cl1 2.1932(9), Ga2–Cl2 2.2098(9), Ga3–Cl3 2.2197(9), Ga1–N11 2.024(3), Ga2–N21 2.038(3), Ga3–N31 2.028(3); Ga1–S1–Ga2 101.54(3), Ga2–S2–Ga3 105.46(4), Ga3–S3–Ga1 105.68(4).

Crystals of the tetrahydrofuran solvate **6a** are also triclinic (space group $P\bar{1}$, $Z = 4$) with two independent trinuclear molecules in the asymmetric unit. These two molecules have both the conventional *tub* conformation and the *cis*,*trans*,*trans* ligand distribution (Fig. 6). However, there are large deviations from mirror symmetry in both cases owing to a rotation of the pyridine ring planes of the ligands at Ga3 and Ga4 away from the idealized mirror plane or a plane perpendicular to it (the dihedral angles Cl3–Ga3–N31–C36 and Cl4–Ga4–N41–C42 are 155.0(3) and 138.6(3)°, respectively). There is no need for a more detailed discussion of the conformation because of the similarity with the structure of complex **1**. The tetrahydrofuran

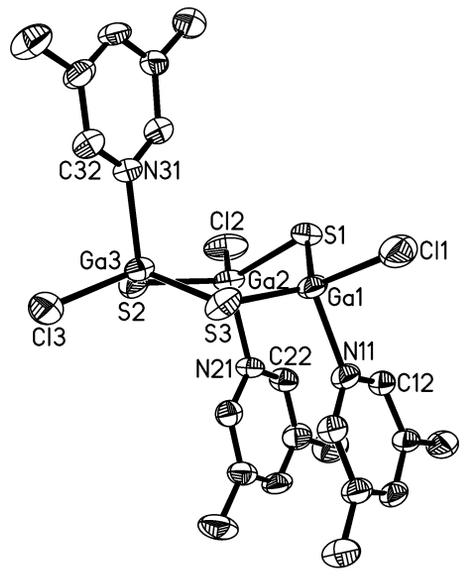
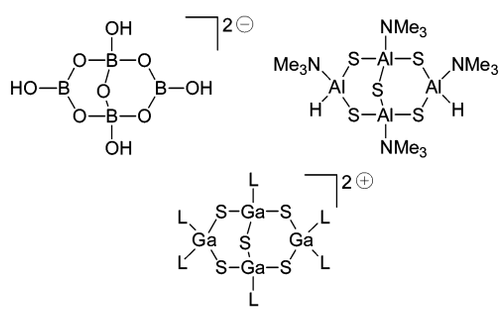


Fig. 6 Molecular structure of one of the independent molecules in the solvate **6a**. The conformation approaches mirror symmetry (point group C_s) with the virtual mirror plane passing through N31, Ga3, Cl3 and S1. Selected bond lengths [Å] and angles [°]: Ga1–S1 2.218(2), Ga1–S3 2.217(2), Ga2–S1 2.217(1), Ga2–S2 2.211(2), Ga3–S2 2.211(2), Ga3–S3 2.219(2), Ga1–Cl1 2.202(2), Ga2–Cl2 2.195(2), Ga3–Cl3 2.198(2), Ga1–N11 2.029(4), Ga2–N21 2.030(4), Ga3–N31 2.043(4); Ga1–S1–Ga2 101.67(5), Ga2–S2–Ga3 105.17(6), Ga3–S3–Ga1 106.38(6).

molecules in **6a** were all found to be disordered (Experimental section).

The trinuclear 4-dimethylaminopyridine complex **3** obtained from the reactants at room temperature could not be crystallized due to its insolubility in organic solvents, but the product generated upon heating of complex **3** to reflux temperature (in acetonitrile) in the presence of excess 4-dimethylaminopyridine has been obtained as single crystals (**4**). The specimens investigated were shown to be merohedral twins and to contain disordered solvent (acetonitrile), but the structure refinement resulted in a satisfactory solution. The crystals are tetragonal, space group $I4_1/a$, with $Z = 8$ formula units in the unit cell. The lattice is built of tetranuclear dications $[Ga_4S_5(L)_6]^{2+}$ associated with two Br^- anions. The dication has crystallographically imposed C_2 symmetry with the two-fold axis passing through the sulfur atom S2 (Fig. 7). Deviations from the maximum attainable symmetry C_{2v}, caused by the orientation of the pyridine rings, are very small. Two six-membered rings share the atom triple Ga2–S2–Ga2′. The bridgehead gallium atoms (Ga2, Ga2′) bear only one pyridine ligand, while the other two (Ga1, Ga1′) bear two pyridine ligands and should be considered the two centers of the positive charge.

The structure of the *dication* in compound **4** is an analogue of the well-known *dianion* in the mineral borax $Na_2[B_4O_5(OH)_4]$[19] and of the *neutral* molecule $[Al_4S_5H_2L_2]$ (L = NMe_3)[20] shown in Scheme 2. In all three species the bicyclic framework



Scheme 2 Examples of compounds with borax-type structures.[19,20]

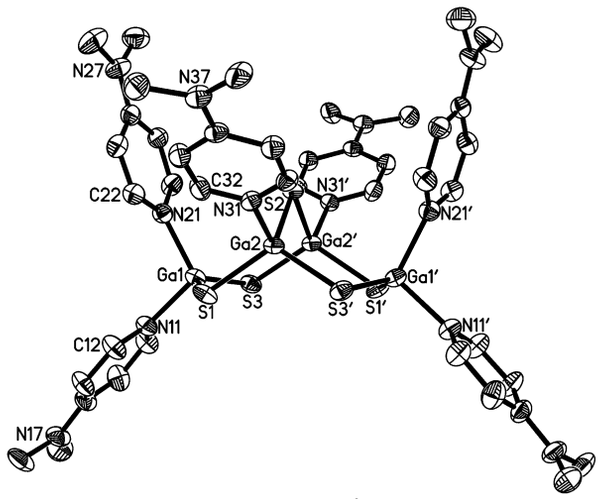


Fig. 7 Structure of the dication $[Ga_4S_5(L)_6]^{2+}$ in crystals of the dibromide salt **4** (containing disordered solvent). The dication has crystallographically imposed twofold symmetry with the axis passing through the sulfur atom S2 and bisecting the angle Ga2–S2–Ga2′. Selected bond lengths [Å] and angles [°]: Ga1–S1 2.221(2), Ga1–S3 2.211(2), Ga2–S2 2.240(1), Ga2–S1 2.244(2), Ga2–S3′ 2.246(2), Ga1–N11 1.991(5), Ga1–N21 1.991(5), Ga2–N31 2.022(4); Ga1–S1–Ga2 101.10(6), Ga2–S2–Ga2′ 100.20(7), Ga1–S3–Ga2′ 113.35(6).

consists of the 4 : 5 combination of Group 3 (B, Al, Ga) and Group 6 elements (O, S). It is very probable that similar units will be found in many other systems based on these components. Preparative studies will therefore be continued in this Laboratory.

The 1 : 2 complex $[GaBr_3(OC_4H_8)_2]$ (**7**) crystallizes in the orthorhombic space group *Pbcn* ($Z = 4$). The discrete molecule features the gallium atom in a trigonal-bipyramidal (*TBPY*) environment with the two tetrahydrofuran molecules and two of the bromine atoms (Br1, Br1′) related by a two-fold axis passing through Ga1 and Br2 (Fig. 8). The Br–Ga–Br angles [Br1–Ga1–Br1′ 117.82(2)°, Br1–Ga1–Br2 121.09(1)°] differ very little from the 120° expected for a regular *TBPY* geometry, and the O–Ga–O [179.1(1)°] angle is very close to 180°. The tetrahydrofuran ligands have a standard envelope conformation. Compound **7** is isotypical to the corresponding Group 13 complexes of the type $[MCl_3(OC_4H_8)_2]$ with M = Al, Ga, In.[21] In $[InBr_3(OC_4H_8)_2]$ the metal is in the same *TBPY* environment, but the compounds are not isotypical.[22]

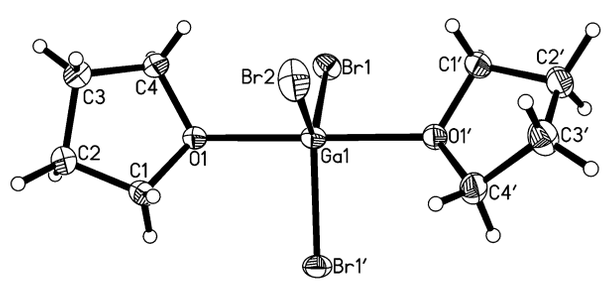


Fig. 8 Molecular structure of $[GaBr_3(OC_4H_8)_2]$, **7**. The molecule has a crystallographically imposed two-fold axis passing through Ga1 and Br2. Selected bond lengths [Å] and angles [°]: Ga1–Br1 2.3174(4), Ba1–Br2 2.3303(6), Ga1–O1 2.141(2); O1–Ga1–O1′ 179.1(1), Br1–Ga1–Br1′ 117.82(2), Br1–Ga1–Br2 121.09(1). All angles O–Ga–Br are close to 90°.

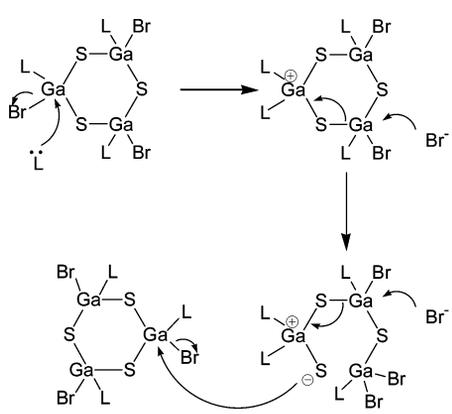
Discussion

In the present study it has been demonstrated that pure molecular pyridine complexes soluble in organic solvents are readily synthesized *in situ* from insoluble and impure ternary compounds $[GaSBr]_n$ and $[GaSeBr]_n$ [eqns. (2) and (5)]. The two starting materials can be prepared from $Ga[GaBr_4]$ and elemental sulfur or selenium. The $GaBr_3$ liberated in this process [eqns. (1) and (4)] has been isolated and identified as its tetrahydrofuran complex. The pyridine complexes have been shown to be cyclic molecules with the sulfur- or selenium-bridged gallium atoms each bearing one bromine atom and one pyridine ligand. The six-membered rings are in distorted tub conformations with the ligand atoms distributed over different positions (equatorial or axial) depending largely on the steric requirements of the pyridine molecules. With small pyridine ligands (pyridine,[7,8] 4-*tert*-butylpyridine) an asymmetric structure (point group C_1) is observed (**2**), while for more bulky ligands (3,5-lutidine) a geometry which approaches mirror symmetry (**1**, **5**) is obtained.

For comparison, the sulfide *chloride* complex with 3,5-lutidine was prepared in two crystalline forms. The solvent-free compound $[GaSCl(3,5\text{-}Me_2C_5H_3N)]_3$ features the trinuclear molecule in the *chair* conformation, not previously observed for all other compounds of this series. The tetrahydrofuran solvate has a structure similar to that of the selenium analogue **1**, but with different torsional angles regarding the orientation of the pyridine plane of the unique ligand.

According to temperature-dependent ^1H NMR results, the complexes dissolved in CD_2Cl_2 or CD_3CN do not fully retain the structures found in the crystal. The *cis*,*trans*,*trans* isomers are in equilibria with all-*cis* isomers with a molar ratio of *ca.* 6 : 1 at −70 °C in dichloromethane (**A**, **B**). Ring inversion movements (chair/tub/skew) are rapid even at this low-temperature limit of the experiments.

With a more strongly nucleophilic pyridine, 4-dimethylaminopyridine, a molecular 1 : 1 complex (**3**) is also obtained if the reaction is carried out at room temperature. However, in refluxing acetonitrile this primary adduct is degraded and reorganized to give a bicyclic, dicationic species as the bromide salt (**4**), with the pyridine complex of $GaBr_3$ as the by-product [eqn. (3)]. Regarding the mechanism of this multistep process it seems plausible to assume that the strongly basic pyridine attacks a gallium atom of a six-membered ring with substitution of a bromine atom generating a cationic center $S_2Ga(L)_2$. The bromide anion is able to attack the neighbouring gallium atom and induce a ring opening generating a sulfide nucleophile which is essential for an attack of a second trimer. A series of substitutions of this type will finally lead to the transfer of an $S_2Ga(L)_2$ unit which is the cornerstone for closure of the second, fused ring (Scheme 3).



Scheme 3 Possible mechanism for the degradation and reorganization of the complex **3** to the bromide salt **4**.

The structural investigations in the present work and of preceding studies have shown that the trinuclear complexes have cyclic structures with delicate conformations sensitive to even minor changes in the nature of the substituents and the nature of the solvent. While the exchange of sulfur by selenium has no

significant effects (sulfur and selenium analogues with the same set of ligands are generally isostructural[7,8]), the changes from chloride to bromide or from pyridine to a substituted pyridine lead to major reorganization of the substitution pattern.

Reactions with the related gallium hydrides, fluorides and iodides proved to take a very different course and are presently under further investigations.

Experimental

All experiments were carried out in an inert atmosphere either in a glovebox or using Schlenck techniques. Glassware was oven-dried and filled with nitrogen, and solvents were dried and kept under dry nitrogen. Standard equipment was used throughout. Gallium sulfide chloride was prepared *via* established routes.[7]

Gallium sulfide bromide

In a typical reaction, $Ga[GaBr_4]$ (4.17 g, 9.08 mmol) was dissolved in toluene (100 ml) and sulfur (0.291 g, 9.08 mmol) was added. Subsequently the reaction mixture was stirred at 60 °C for 4 h. A colourless precipitate formed which was filtered off, washed with two 20 ml portions of toluene and dried in a vacuum (1.30 g, 79% yield). The product is insoluble in all common organic solvents except pyridines. GaSBr, calc.: S 17.65, Br 43.98; found: S 16.51, Br 44.78%.

Trimeric pyridine complexes of gallium sulfide bromide

Compound 1. GaSBr (1.53 g, 8.42 mmol) was dispersed in acetonitrile (20 ml) and 3,5-lutidine (1.35 g, 12.63 mmol) added with stirring at 20 °C. A colourless solution formed first from which a colourless solid precipitated while the mixture was stirred for 12 h. The product was filtered off, washed twice with diethyl ether, dried in a vacuum, and recrystallized from hot acetonitrile (1.63 g, 67% yield): mp 215 °C with decomposition; ^{1}H NMR (CD_3CN, 20 °C): δ 2.38 (s, 6H, Me), 7.86 (s, 1H, *p*-H), 8.50 (br s, 2H, *o*-H). $C_{21}H_{27}Br_3Ga_3N_3S_3{\cdot}CH_3CN$ (907.56), calc.: C 30.44, H 3.33, Br 26.41, N 6.17, S 10.06; found: C 30.90, H 3.37, Br 25.50, N 6.58, S 10.16%.

Compound 2. GaSBr (0.50 g, 2.75 mmol) was dissolved in 4-*tert*-butylpyridine (20 ml) to give a clear solution. Upon addition of 40 ml of *n*-hexane a colourless precipitate formed which was filtered off, washed twice with *n*-hexane (10 ml) and dried in a vacuum (0.55 g, 63% yield): mp 217 °C with decomposition; ^{1}H NMR (CD_3CN): δ 1.35 (s, 9H, Me), 7.71 and 8.73 (br m, 2 × 2H, *o*/*m*-H). $C_{27}H_{39}Br_3Ga_3N_3S_3$ (950.71) calc.: C 34.11, H 4.14, Br 25.21, N 4.42; found: C 35.97, H 4.22, Br 25.42, N 4.63%.

Compound 3. GaSBr (1.72 g, 9.47 mmol) was dispersed in acetonitrile (20 ml) and a solution of 4-dimethylaminopyridine (1.73 g, 14.20 mmol) in 10 ml of acetonitrile was added with stirring at 20 °C. A colourless solution was formed first, but in the course of 2 h a colourless precipitate appeared, which was filtered off, washed twice with 20 ml of diethyl ether and dried in a vacuum (1.63 g, 67% yield): $C_7H_{10}N_2GaSBr$ (303.67), calc.: C 27.67, H 3.32, Br 26.30, N 9.22, S 10.55; found: C 27.90, H 3.47, Br 25.97, N 9.20, S 9.56%.

Compound 4. (a) 0.224 g (0.736 mmol) of compound **3** was dissolved in 10 ml of acetonitrile, 0.300 g (2.45 mmol) of 4-$Me_2NC_5H_4N$ was added and the reaction mixture heated to reflux until a clear solution resulted. This solution was cooled to −30 °C overnight to precipitate colourless crystals of compound **4** (0.072 g, 37% yield). (b) Similar results were obtained when the reaction described for the preparation of compound **3** was carried out in acetonitrile under reflux conditions: mp 134 °C with decomposition; ^{1}H NMR (CD_2Cl_2, 20 °C): δ 3.09 (s, 18H, Me_2N), 6.62 (br m, 6H, *m*-H), 8.14–8.52 (m, 6H, *o*-H). $C_{42}H_{60}Br_2Ga_4N_{12}S_5$ (1332.05), calc.: C 37.87, H 4.54, Br 12.00, N 12.62, S 12.04; found: C 38.46, H 4.97, Br 11.18, N 12.98, S 10.80%.

Gallium selenide bromide

Tetrahydrofuran (25 ml) was condensed onto $Ga[GaBr_4]$ (2.66 g, 5.79 mmol) kept in a trap at liquid-nitrogen temperature. After slow warming to room temperature a clear solution was obtained. Grey selenium (0.434 g, 5.50 mmol) was added and the black suspension stirred for 10 h at 20 °C, followed by heating to reflux for 48 h. The reaction mixture was then filtered and the filtrate cooled to −78 °C. Large colourless crystals formed which were separated and subjected to X-ray analysis. Addition of *n*-hexane to the mother-liquor led to the precipitation of GaSeBr, which was filtered, washed with *n*-hexane (2 × 10 ml) and dried in a vacuum. The product contained tetrahydrofuran and therefore the yield could only be estimated (*ca*. 55%).

Compound 5. A sample of the GaSeBr still containing some tetrahydrofuran (above, 0.25 g, 0.98 mmol) was treated with 3,5-dimethylpyridine (0.21 g, 1.95 mmol) in 10 ml of tetrahydrofuran at 20 °C. A clear solution was formed immediately. Layering this solution with *n*-hexane afforded colourless crystals of the product **5a** (0.12 g, 13.5% yield). A 1 : 1 solvate **5b** crystallizes from acetonitrile solutions: mp 204 °C with decomposition; ^{1}H NMR (CD_3CN, 20 °C): δ 2.4 (br s, 6H, Me), 7.87 (m, 1H) and 9.0 (m, 2H) (*p*-/*o*-H). $C_{21}H_{27}Br_3Ga_3N_3Se_3{\cdot}CH_3CN$ (1048.28), calc.: C 26.35, H 3.06, Br 22.87, N 5.43; found: C 26.99, H 2.88, Br 22.11, N 5.87%.

Compound 6. GaSCl (1.37 g, 10.0 mmol) was dispersed in acetonitrile (20 ml) and 3,5-lutidine (1.45 g, 13.53 mmol) added with stirring at 20 °C. A colourless solution formed first from which a colourless solid precipitated while the mixture was stirred for 12 h. The product was filtered off, washed twice with diethyl ether and dried in a vacuum (1.56 g, 64% yield). The product can be crystallized from warm thf or from 3,5-lutidine–hexane: mp 198 °C with decomposition; ^{1}H NMR (CD_2Cl_2, 20 °C): δ 2.38 (s, 6H, Me), 7.69 (s, 1H, *p*-H), 8.57 (br s, 2H, *o*-H). $C_{21}H_{27}Br_3Ga_3N_3S_3{\cdot}CH_3CN$ (907.56), calc.: C 34.40, H 3.71, Cl 14.51, N 5.73, S 13.12; found: C 34.57, H 3.79, Cl 14.83, N 5.80, S 12.84%.

Determination of the crystal structures

Specimens of suitable quality and size of **1a**, **2**, **4**, **5a**, **5b**, **7** and of $[GaSCl(3,5\text{-}Me_2C_5H_3N)]_3$ and its thf-solvate (**6**, **6a**) were mounted on the ends of quartz fibers in inert perfluoropolyalkylether and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo-Kα radiation. The structures were solved by a combination of direct methods (SHELXS-97) and difference-Fourier syntheses and refined by full matrix least-squares calculations on F^2 (SHELXL-97).[23] The thermal motion was treated anisotropically for all non-hydrogen atoms. The hydrogen atoms were calculated in ideal positions and allowed to ride on their parent atoms with fixed isotropic contributions except for those of **5a** and the solvent-free **6** which were located and refined with isotropic displacement parameters. The Flack parameter for compound **2** is −0.004(13). The structure of **4** was refined as a merohedral twin. The refined BASF parameter for the merohedral twinning is 0.3373(16). Further informations on crystal data, data collection and structure refinement are summarized in Tables 1 and 2. All manipulations concerning the crystals of **7** had to be carried out at temperatures below −20 °C to avoid thermal decomposition of the compound. Two solvent molecules of the tetrahydrofuran solvate **6a** were found disordered and anisotropic refinement of these solvent molecules was therefore not possible. The contributions of two

Table 1 Crystal data, data collection and structure refinement of **1a**, **2**, **4** and **5a**

	1a	**2**	**4**	**5a**
Empirical formula	$C_{21}H_{27}Br_3Ga_3N_3S_3 \cdot CH_3CN$	$C_{27}H_{39}Br_3Ga_3N_3S_3$	$C_{42}H_{60}Br_2Ga_4N_{12}S_5$	$C_{21}H_{27}Br_3Ga_3N_3Se_3 \cdot C_4H_8O$
M	907.58	950.68	1332.02	1079.33
Crystal system	Monoclinic	Orthorhombic	Tetragonal	Monoclinic
Space group	$P2_1/c$	$P2_12_12_1$	$I4_1/a$	$C2/c$
a/Å	11.2953(1)	12.1740(2)	18.8111(1)	34.8960(6)
b/Å	20.4052(2)	14.5494(3)	18.8111	10.8132(2)
c/Å	14.5137(1)	21.0291(5)	38.3540(4)	18.5066(3)
β/°	107.0775(5)	90	90	100.2085(6)
V/Å^3	3197.66(5)	3724.77(13)	13571.85(17)	6872.7(2)
D_c/g cm^{-3}	1.885	1.695	1.304	2.086
Z	4	4	8	8
F(000)	1758	1872	5360	4112
μ(Mo-Kα)/cm^{-1}	64.74	55.62	29.36	90.25
T/K	143	143	143	143
Refls. measured	87942	97033	159925	85104
Refls. unique (R_{int})	7114 (0.042)	8278 (0.120)	6171 (0.065)	7085 (0.053)
Refined parameters/restraints	332/0	352/1	301/0	349/0
$R1$ [$I \geq 2\sigma(I)$]	0.0292	0.0561	0.0503	0.0322
$wR2$[a]	0.0642	0.0988	0.1480	0.0733
Weighting scheme parameters	a = 0.0231	a = 0.0000	a = 0.0944	a = 0.0247
	b = 3.2884	b = 4.5776	b = 50.3199	b = 22.7121
σ_{fin}(max./min.)/e Å^{-3}	0.548/ −0.363	0.840/ −0.841	1.638/ −0.446	0.907/ −0.799

[a] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$.

Table 2 Crystal data, data collection and structure refinement of **5b**, **6**, **6a** and **7**

	5b	**6**	**6a**	**7**
Empirical formula	$C_{21}H_{27}Br_3Ga_3N_3Se_3 \cdot CH_3CN$	$C_{21}H_{27}Cl_3Ga_3N_3S_3$	$C_{21}H_{27}Cl_3Ga_3N_3S_3 \cdot 2C_4H_8O$[b]	$C_8H_{16}Br_3GaO_2$
M	1048.28	733.15	805.25[b]	453.66
Crystal system	Monoclinic	Triclinic	Triclinic	Orthorhombic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$Pbcn$
a/Å	11.4470(1)	9.3211(2)	10.6251(2)	10.5892(2)
b/Å	20.5176(2)	12.2126(3)	17.5283(3)	10.1503(2)
c/Å	14.5765(2)	13.7055(4)	19.6150(4)	12.6862(2)
α/°	90	108.3148(10)	88.2030(6)	90
β/°	107.3034(4)	91.3859(12)	88.3145(6)	90
γ/°	90	102.7276(16)	89.7267(15)	90
V/Å^3	3268.57(6)	1437.37(6)	3648.86(12)	1363.56(4)
D_c/g cm^{-3}	2.130	1.694	1.466[b]	2.210
Z	4	2	4	4
F(000)	1984	732	1624[b]	864
μ(Mo-Kα)/cm^{-1}	94.83	33.04	26.12[b]	107.86
T/K	143	143	223	143
Refls. measured	87910	35769	87816	37512
Refls. unique (R_{int})	6950 (0.051)	4952 (0.044)	12728 (0.063)	1453 (0.087)
Refined parameters/restraints	332/0	406/0	689/60	97/0
$R1$ [$I \geq 2\sigma(I)$]	0.0252	0.0304	0.0483	0.0254
$wR2$[a]	0.0566	0.0655	0.1139	0.0597
Weighting scheme parameters	a = 0.0153	a = 0.0000	a = 0.0289	a = 0.0152
	b = 3.3085	b = 1.6041	b = 7.0295	b = 2.5611
σ_{fin}(max./min.)/e Å^{-3}	0.581/ −0.383	0.307/ −0.311	0.493/ −0.510	0.633/ −0.494

[a] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$. [b] Without contributions of disordered solvent.

further disordered thf molecules lying on centers of inversion were taken into account by the SQUEEZE method.[24] The total potential solvent accessible volume is 342.5 Å^3. Absorption corrections for all structures except **4** were carried out using DELABS, as part of the PLATON suite of programs.[24]

CCDC reference numbers 208324–208331

See http://www.rsc.org/suppdata/dt/b3/b302815a/ for crystallographic data in CIF or other electronic format.

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