# Group 13 Complexes of 5-Methyl-1,3,5-dithiazinane[‡]

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The synthesis of mono-N adducts of 5-methyl-1,3,5-dithiazinane (**1**) with $Al(CH_3)_3$, $Al(CH_3)_2Cl$, $AlCl_3$, $AlBr_3$ (**5**–**8**), a bis-N adduct with $InCl_3$ (**9**), and the corresponding dithiazinanium salts with the anions $AlBr_4^-$, $AlCl_4^-$, $GaCl_4^-$ and $BCl_4^-$ (**10**–**14**) are reported. Compounds **5**–**7** adopt a preferred conformation in solution at room temperature and **8** at –10 °C. $\Delta G^{\neq}$ values for the ring inversion were calculated for **5**–**8**. Compounds **6**–**14** were studied by single-crystal X-ray diffraction. The solution and solid-state analyses showed that the rings are present in all cases in a chair conformation. In compounds **5**–**8** the tetrahedral aluminum atom is found in an equatorial position. In the indium compound **9** the metal atom has a tbp geometry. For dithiazinanium rings **10**–**14** dipolar intra- and intermolecular interactions between halogen atoms and C–H and N–H are reported. Two different conformations for the $N–CH_3$ were found in compound **14**.
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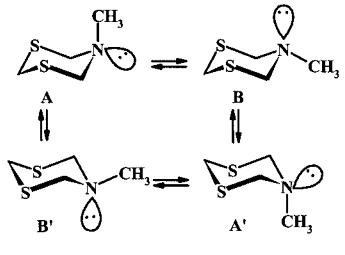
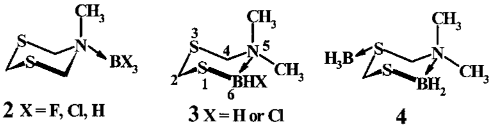
## Introduction

We are currently investigating the coordinating and conformational behavior of 5-methyl-1,3,5-dithiazinane (**1**).[1,2] This compound is in conformational equilibrium with the methyl group in an unexpected axial position and has five lone pairs available for coordination (Scheme 1). The geminal position of the heteroelements makes the CH protons relatively acidic,[2b] meaning that they could coordinate molecules bearing lone pairs through hydrogen bonding. Dithiazinane rings are fragile in the presence of metals and moisture and, as a consequence, their coordination chemistry is practically unknown except for the results from our group.[1,2,3a]



Scheme 1. A and A′ are the preferred conformers in the conformational equilibrium of 5-methyldithiazinane **1**; the processes from A to B and A′ to B′ involve nitrogen inversion and from A to B′ and A′ to B ring inversion

Boron Lewis acids have been used as a probe for the basic sites of compound **1**, giving the $N \rightarrow BX_3$ adducts **2**.[2] An excess of borane ($BH_3$ or $BHCl_2$) produces 6-borata-5-aza-1,3-dithiocyclohexanes **3**[1b,2d,2f] (Scheme 2). Nitrogen is always the preferred coordination site, and the $S \rightarrow B$ coordinative bond in **4** has been only observed when the borata heterocycle bearing a $BH_2$ group is treated with an excess of $BH_3$·THF; its weak $S \rightarrow BH_3$ bond is readily broken upon removal of the solvent.[1c][2f]



Scheme 2

An important discovery has been the fact that the conformational equilibrium of **1** is abruptly stopped by N-coordination to $BH_3$ or boron halides. This unexpected result was explained by significant proton-hydride and proton-halide intramolecular stabilizing interactions.[2a,3]

These findings stimulated us to continue the exploration of the coordinating properties of compound **1** with other group 13 compounds. Here, the synthesis of N adducts of dithiazinane **1** with $Al(CH_3)_3$, $Al(CH_3)_2Cl$, $AlCl_3$, $AlBr_3$

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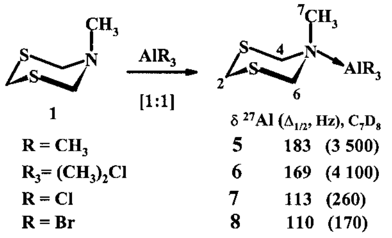
and $InCl_3$ is reported, as well as variable-temperature NMR experiments in order to obtain the $\Delta G^{\neq}$ of the ring inversion and to understand the coordination effect in the conformational equilibrium. The study of the molecules **5−8** in solution is complemented by X-ray diffraction analysis of **6−9**. The corresponding dithiazinanium salts **10−14** bearing the anions $AlBr_4^-$, $AlCl_4^-$ $GaCl_4^-$ and $BCl_4^-$ and $Cl^-$, respectively, are formed in the presence of traces of moisture. Their X-ray diffraction data disclosed interesting intermolecular interactions in the solid state.

## Results and Discussion

### 5-Methyl-1,3,5-dithiazinane Complexes

The reaction of compound **1** with equimolar amounts of $Al(CH_3)_3$, $Al(CH_3)_2Cl$, $AlCl_3$ or $AlBr_3$ in toluene (or $CHCl_3$) at 4 °C gave exclusively the N→Al mono adducts **5−8**, as established by NMR spectroscopy, especially by $^{27}Al$ NMR studies, which showed the characteristic resonances (δ = 110−183 ppm) for tetracoordinate aluminum atoms at room temperature (reported range between 100 and 200 ppm)[4] (Scheme 3). In the $^{13}C$ NMR spectra, the coordination effect is readily noted at room or at low temperature for C-2, C-4 and C-6, which are shifted to lower frequencies by up to 3 ppm, while $N-CH_3$ presents only a modest effect (Δδ = 1 ppm), indicating that it remains in an axial position. At room temperature, the $^1H$ NMR spectra of compounds **5−7** (at −10 °C for **8**) in $C_7D_8$ present separated and coupled signals for all the ring protons, showing that the rings are present in a fixed conformation due to the N-coordination. By comparison with the $^1H$ NMR spectra of N-boron adducts of dithiazinane,[1b,1c,2e] it was also deduced that the aluminum is placed in an equatorial position (Table 1). Opening of the dithiazinane ring in the presence of an excess of $AlMe_3$ proceeds by the breaking of two C−S bonds and the formation of an $MeEt_2N$-$AlMe_3$ adduct ($^{27}Al$ δ = 139 ppm, $\Delta_{1/2}$ = 866 Hz). The $^{13}C$ NMR spectrum for this adduct shows signals for N−Et at δ = 49.66 and 9.27 ppm and for N−Me at δ = 40.79 ppm.



| | | δ $^{27}Al$ | ($\Delta_{1/2}$, Hz) |
|---|---|---|---|
| R = $CH_3$ | **5** | 183 | (3 500) |
| $R_3$= $(CH_3)_2Cl$ | **6** | 169 | (4 100) |
| R = Cl | **7** | 113 | (260) |
| R = Br | **8** | 110 | (170) |

Scheme 3. Preferred conformation of compounds **5−8** and their $^{27}Al$ NMR data (in $C_7D_8$)

Variable temperature $^1H$ NMR experiments in $C_7D_8$ were performed in order to estimate the energies for ring inversion. The solutions were heated up to 75 °C without either a breaking of the Al−N bond or an opening of the ring, contrary to the situation observed for borane adducts.[1b,1c,2d] The ring-inversion energy is related to the size of the substituents at the nitrogen atom. A group with a big steric effect will be in an equatorial position, with a high ring-inversion energy.[5] On the other hand, a second effect — that the ring inversion energy is augmented by hydride-proton and halide-proton stabilizing interactions[2a,3a] — could be added to the anchorage of the ring conformation, as we have established for other boron adducts. The $\Delta G^{\neq}$ values for the ring inversion of compounds **5−8** are summarized in Table 1. All the aluminum groups

Table 1. $^1H$ NMR (400 MHz) data [δ ($^nJ$)] of anchored compounds **5−8** and their $\Delta G^{\neq}$ values (kJ/mol)

| | Solvent | H-2eq | H-2ax | H-4eq and H-6eq | H-4ax and H-6ax | H-7 | $\Delta G^{\neq}$ |
|---|---|---|---|---|---|---|---|
| **1** (25 °C) | [$D_8$]toluene | 3.58 (s) | 3.58 (s) | 3.89 (s) | 3.89 (s) | 2.39(s) | − |
| **1** (−90 °C) | [$D_8$]THF<br>$T_c$, −41 °C | 3.60<br>(dt, $^2J$ = 13.3,<br>$^4J$ = 2.6 Hz) | 4.60<br>(d, $^2J$ = 13.3 Hz) | 3.93<br>(dd, $^2J$ = 13.3,<br>$^4J$ = 2.6 Hz) | 4.95<br>(d, $^2J$ = 12.7 Hz) | 2.60(s) | 46.0[a] |
| **5** (−10 °C) | [$D_8$]toluene<br>$T_c$, 59 °C | 2.30<br>(dt, $^2J$ = 13.9,<br>$^4J$ = 2.6 Hz) | 3.12<br>(d, $^2J$ = 13.9 Hz) | 3.25<br>(dd, $^2J$ = 13.6,<br>$^4J$ = 2.6 Hz) | 4.03<br>(d, $^2J$ = 13.6 Hz) | 2.28 (s) | 62.6 ± 0.5 |
| **6** (−15 °C) | [$D_8$]toluene<br>$T_c$, 75 °C | 2.24<br>(d, $^2J$ = 13.9 Hz) | 3.12<br>(d, $^2J$ = 13.9 Hz) | 3.30<br>(d, $^2J$ = 13.9 Hz) | 4.23<br>(d, $^2J$ = 13.9 Hz) | 2.30 (s) | 66.0 ± 0.5 |
| **7** (10 °C) | [$D_8$]toluene<br>$T_c$, 75 °C | 1.93<br>(dt, $^2J$ = 13.3,<br>$^4J$ = 2.2 Hz) | 2.73<br>(d, $^2J$ = 13.3 Hz) | 3.45<br>(dd, $^2J$ = 13.5,<br>$^4J$ = 2.2 Hz) | 4.24<br>(d, $^2J$ = 13.5 Hz) | 2.44 (s) | 68.5 ± 0.5 |
| **8** (−60 °C) | [$D_8$]toluene<br>$T_c$, −5 °C | 1.65<br>(d, $^2J$ = 13.9 Hz) | 2.50<br>(d, $^2J$ = 13.9 Hz) | 3.45<br>(d, $^2J$ = 12.4 Hz) | 4.24<br>(d, $^2J$ = 12.4 Hz) | 2.37 (s) | 51.7 ± 0.5 |
| **5** (−10 °C) | $CDCl_3$ | 3.48<br>(dt, $^2J$ = 13.9,<br>$^4J$ = 2.2 Hz) | 4.26<br>(d, $^2J$ = 13.9 Hz) | 3.88<br>(dd, $^2J$ = 13.0.<br>$^4J$ = 2.2 Hz) | 4.62<br>(d, $^2J$ = 13.9 Hz) | 2.83 (s) | − |
| **6** (27 °C) | $CDCl_3$ | 3.47 (s br) | 4.26 (s br) | 3.99 (s br) | 4.79 (s br) | 2.96 (s) | − |
| **7** (−10 °C) | $CDCl_3$ | 3.49<br>(d, $^2J$ = 14.3 Hz) | 4.31<br>(d, $^2J$ = 14.3 Hz) | 4.20<br>(d, $^2J$ = 13.8 Hz) | 4.95<br>(d, $^2J$ = 13.8 Hz) | 3.18 (s) | − |
| **8** (−55 °C) | $CDCl_3$ | 3.48<br>(d, $^2J$ = 14.3 Hz) | 4.32<br>(d, $^2J$ = 14.3 Hz) | 4.29<br>(d, $^2J$ = 13.6 Hz) | 5.03<br>(d, $^2J$ = 13.6 Hz) | 3.19 (s) | − |

[a] Same value was found in $CDCl_3/CFCl_3$.[7] δ (ppm) of $AlCH_3$: for **5**, −0.69 (s) in [$D_8$]toluene and −0.89 (s) in $CDCl_3$; for **6**, −0.47(s) in [$D_8$]toluene and −0.63(s) in $CDCl_3$.

fix the dithiazinane conformation as is seen from their $\Delta G^{\neq}$ values when compared with data of the free dithiazinane ($\Delta G^{\neq}$ = 46.0 kJ/mol in [D$_8$]THF and in CDCl$_3$/CFCl$_3$ [6]). In compounds **5−8** the size of the coordinating group determines the inversion of the ring, as in the case of AlMe$_3$ and AlClMe$_2$ adducts. A second effect stabilizing the inversion could be the interactions between the halogen atoms and the acidic C−H protons. Therefore, it is expected that AlClMe$_2$, AlCl$_3$ and AlBr$_3$ need a higher energy for the ring inversion due to possible cooperative, weak H···X interactions. Analyses of the results shows that the highest ring-inversion energy was found for the AlCl$_3$ adduct **7**. The lowest energy corresponds to the AlBr$_3$ adduct **8** but there is no clear explanation for this behavior, because the low energy is observed despite the fact that AlBr$_3$ is a big group and the Al−N bond length in **8** (1.982 Å) is the shortest in the series (**5−8**) indicating a strong bond {the same trend was found in the dissociation energy of pyridine·AlCl$_3$ (77.3 kJ/mol) and pyridine·AlBr$_3$ (73.6 kJ/mol)[7]}. Therefore, we have carefully analyzed the halide-proton contacts in the solid state in order to find the reason for the conformational behavior of this adduct. An explanation could be that bromine atoms present a weaker interaction than chlorine with the hydrogen atoms as a consequence of their lower electronegativity and their larger size.[8]

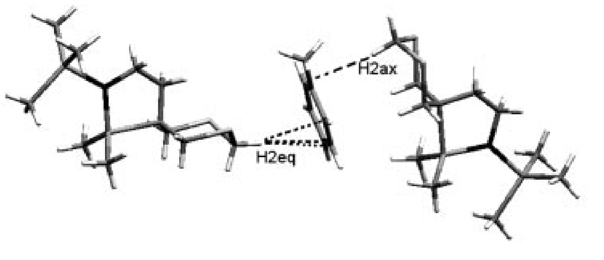


Figure 1. View of *O*-dimethylaluminum-*O*-trimethylaluminum-2(1,3,5)-dithiazinan-5-yl-ethanolate showing a polymeric array produced by π-interactions of toluene with SCH$_2$S protons (distances are: H2$_{eq}$−C$_{ortho}$ 2.79 Å, H2$_{eq}$−C$_{meta}$ 2.74 Å and H2$_{eq}$−C$_{para}$ 2.80 Å, and H2$_{ax}$−C$_{ipso}$ 2.75 Å)[9]

An interesting fact concerning the $^1$H NMR chemical shifts of the C-2 protons in compounds **4−8** in toluene is that they are well shielded. This can be explained by an arrangement of the toluene aromatic ring density in front of the C-2 protons, as was observed in the solid state in the X-ray molecular structure of another derivative of dithiazinane[9] (Figure 1).

We were unable to obtain single crystals of compound **5,** in contrast to compounds **6** (obtained from C$_6$H$_5$CH$_3$ at −20 °C), **7** (from CH$_2$Cl$_2$ at 25 °C) and **8** (from C$_6$H$_5$CH$_3$ at 25 °C). In all cases the aluminum atoms are tetracoordinate and are found in equatorial positions. The angles at the nitrogen atoms deviate little from the ideal tetrahedral angles. The N−Al bond [**6**: 2.044(2) Å; **7**: 1.993(5) Å; **8**: 1.982(5) Å] is, in all cases, slightly shorter than the ideal covalent bond length (2.05 Å)[10] indicating a strong coordinative bond. The dithiazinane ring has a chair conformation. In all compounds one of the hydrogen atoms of the N-methyl group is pointing towards the space in the middle of the sulfur atoms where the sulfur orbitals (50% p character)[11] are also pointing. The C−H···S distances range from 2.76 to 2.85 Å. This is significantly shorter than the sum of the van der Waals radii (3.0 Å). The bond lengths and angles are given in Tables 2 and 3 and the crystallographic data and selected data collection in Table 4.

In compound **6** the chlorine atom is arranged in a staggered position between the methyl and a methylene group of the ligand (Figure 2a). Two short, weak contacts were found between Cl···H4eq (2.860 Å) and Cl···H7 (3.080 Å) ($\Sigma r_{VDW}$ = 3.1 Å). The Cl···H4eq interaction can be also

Table 2. Selected bond lengths [Å]

| **6** | | **7** | | **8** | | **9** | | **10** | | **12** | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cl1−Al1 | 2.176(1) | S1−C6 | 1.797(6) | Cl1−Al1 | 2.136(1) | Al6−N5 | 1.982(5) | In1−Cl1A | 2.376(1) | Ga1−Cl3 | 2.160(2) |
| S1−C6 | 1.807(3) | S3−C4 | 1.793(7) | Cl2−Al1 | 2.147(1) | Br1−Al6 | 2.272(2) | In1−Cl2 | 2.383(1) | Ga1−Cl4 | 2.174(2) |
| S2−C4 | 1.804(3) | Cl2−Al1 | 2.101(3) | Cl3−Al1 | 2.122(1) | Br3−Al6 | 2.272(2) | In1−N1A | 2.413(3) | S1−C6 | 1.772(9) |
| Al1−C9 | 1.974(3) | Cl1−Al1 | 2.110(3) | Cl4−Al1 | 2.134(1) | Br2−Al6 | 2.270(2) | In1−Cl1 | 2.376(1) | S3−C2 | 1.777(7) |
| N5−C6 | 1.474(4) | N5−C4 | 1.492(8) | S1−C2 | 1.783(5) | S1−C2 | 1.813(7) | In1−N1 | 2.413(3) | N5−C4 | 1.499(9) |
| N5−C7 | 1.497(3) | N5−C6 | 1.495(7) | S3−C4 | 1.788(4) | S3−C2 | 1.808(7) | S3−C2 | 1.817(4) | N5−C7 | 1.514(10) |
| S1−C2 | 1.806(4) | S1−C2 | 1.806(7) | N5−C4 | 1.490(5) | S1−C6 | 1.793(7) | S3−C4 | 1.820(4) | Ga1−Cl2 | 2.174(1) |
| S2−C2 | 1.799(5) | S3−C2 | 1.806(7) | N5−C7 | 1.508(4) | S3−C4 | 1.799(6) | S5−C4 | 1.808(4) | Ga1−Cl1 | 2.185(2) |
| Al1−C8 | 1.955(3) | Cl3−Al1 | 2.112(3) | S1−C6 | 1.789(4) | N5−C4 | 1.509(7) | S5−C6 | 1.824(4) | S1−C2 | 1.812(8) |
| Al1−N5 | 2.044(2) | Al1−N5 | 1.993(5) | S3−C2 | 1.791(4) | N5−C6 | 1.506(7) | N1−C2 | 1.486(5) | S3−C4 | 1.792(8) |
| N5−C4 | 1.495(3) | N5−C7 | 1.493(7) | N5−C6 | 1.497(5) | N5−C7 | 1.512(8) | N1−C6 | 1.486(4) | N5−C6 | 1.509(8) |

| **11** | | **13** | | | | **14** | | | |
|---|---|---|---|---|---|---|---|---|---|
| S1−C6 | 1.791(5) | S1A−C6A | 1.79(2) | Br2−Al1 | 2.309(5) | Cl2−B1 | 1.875(10) | S32−C22 | 1.807(8) |
| S3−C2 | 1.792(6) | S1A−C2A | 1.82(1) | Br3−Al1 | 2.275(5) | Cl3−B1 | 1.858(9) | S32−C42 | 1.786(6) |
| F1−B1 | 1.368(7) | S3A−C2A | 1.76(2) | Br4−Al1 | 2.275(5) | Cl4−B1 | 1.792(9) | N5−C4 | 1.496(7) |
| F3−B1 | 1.349(7) | S3A−C4A | 1.77(1) | S1−C2 | 1.79(1) | Cl5−B1 | 1.781(9) | N5−C6 | 1.521(8) |
| N5−C7 | 1.495(6) | N5A−C6A | 1.48(2) | S1−C6 | 1.81(2) | S1−C2 | 1.784(7) | N5−C7 | 1.474(9) |
| N5−C4 | 1.501(6) | N5A−C7A | 1.49(2) | S3−C4 | 1.79(2) | S1−C6 | 1.776(7) | N52−C42 | 1.481(7) |
| | | N5A−C4A | 1.50(2) | S3−C2 | 1.82(2) | S3−C2 | 1.796(7) | N52−C62 | 1.482(8) |

Table 3. Selected bond angles [°]

| **6** | | **7** | | **8** | | **9** | | **13** | |
|---|---|---|---|---|---|---|---|---|---|
| C2−S1−C6 | 96.83(15) | C6−S1−C2 | 98.4(3) | N5−Al6−Br3 | 107.10(15) | Cl1A−In1−Cl1 | 119.65(5) | C6AS1AC2A | 99.3(8) |
| C2−S2−C4 | 97.77(16) | C4−S3−C2 | 98.5(3) | N5−Al6−Br1 | 106.46(16) | Cl1A−In1−N5A | 91.80(8) | C2A−S3A−C4A | 99.1(8) |
| C8−Al1−C9 | 117.77(15) | N5−Al1−Cl1 | 106.28(17) | N5−Al6−Br2 | 106.35(15) | Cl1A−In1−N5 | 90.33(8) | C6A−N5A−C7A | 109.6(11) |
| C9−Al1−N5 | 107.22(11) | N5−Al1−Cl2 | 105.91(18) | Br2−Al6−Br1 | 114.72(7) | Cl1A−In1−Cl2 | 120.17(3) | C6A−N5A−C4A | 112.7(12) |
| C9−Al1−Cl1 | 110.17(12) | N5−Al1−Cl3 | 106.52(19) | Br2−Al6−Br3 | 110.53(8) | Cl1−In1−Cl2 | 120.17(3) | C7A−N5A−C4A | 111.9(11) |
| C8−Al1−N5 | 107.24(11) | Cl1−Al1−Cl3 | 112.43(13) | Br3−Al6−Br1 | 111.20(8) | Cl1−In1−N5A | 90.33(8) | S3A−C2A−S1A | 113.1(8) |
| C8−Al1−Cl1 | 111.63(12) | Cl2−Al1−Cl1 | 112.84(13) | C6−S1−C2 | 97.5(3) | Cl1−In1−N5 | 91.80(8) | N5A−C4A−S3A | 113.1(9) |
| N5−Al1−Cl1 | 101.35(8) | Cl2−Al1−Cl3 | 112.23(12) | C4−S3−C2 | 97.4(3) | Cl2−In1−N5 | 87.88(7) | N5A−C6A−S1A | 113.9(11) |
| C4−N5−C7 | 110.8(2) | C4−N5−Al1 | 107.9(4) | C4−N5−Al6 | 108.5(4) | Cl2−In1−N5A | 87.88(7) | C2−S1−C6 | 96.3(7) |
| C4−N5−Al1 | 109.02(16) | C4−N5−C6 | 110.5(5) | C6−N5−Al6 | 108.8(4) | N1−In1−N5A | 175.8(1) | C4−S3−C2 | 96.3(7) |
| C6−N5−C7 | 112.0(2) | C4−N5−C7 | 110.9(5) | C7−N5−Al6 | 108.6(4) | C2−S3−C4 | 97.69(18) | Br1−Al1−Br3 | 111.8(2) |
| C6−N5−Al1 | 104.69(14) | C6−N5−Al1 | 108.6(4) | C4−N5−C7 | 110.9(5) | C4−S5−C6 | 98.34(18) | Br1−Al1−Br4 | 110.0(2) |
| C6−N5−C4 | 110.6(2) | C7−N5−Al1 | 108.0(4) | C6−N5−C4 | 109.1(4) | C2−N5−In1 | 106.8(2) | Br3−Al1−Br4 | 110.3(2) |
| C7−N5−Al1 | 109.54(17) | C7−N5−C6 | 110.7(5) | C6−N5−C7 | 110.9(5) | C6−N5−In1 | 108.0(2) | Br1−Al1−Br2 | 108.0(2) |
| S2−C2−S1 | 112.19(19) | S1−C2−S3 | 111.6(4) | S3−C2−S1 | 111.7(3) | C7−N5−In1 | 107.3(2) | Br3−Al1−Br2 | 106.1(2) |
| N5−C4−S2 | 115.79(19) | N5−C4−S3 | 116.9(5) | N5−C4−S3 | 116.9(4) | C2−N5−C6 | 111.0(3) | Br4−Al1−Br2 | 110.6(2) |
| N5−C6−S1 | 117.59(17) | N5−C6−S1 | 117.0(5) | N5−C6−S1 | 117.1(4) | C7−N5−C2 | 111.8(3) | C7−N5−C4 | 112.4(13) |
| | | | | | | C7−N5−C6 | 111.7(3) | C7−N5−C6 | 114.6(13) |
| | | | | | | N5−C2−S3 | 116.6(2) | C4−N5−C6 | 108.5(12) |
| | | | | | | S5−C4−S3 | 112.7(2) | S1−C2−S3 | 112.5(8) |
| | | | | | | N5−C6−S5 | 116.2(3) | N5−C4−S3 | 118.2(11) |
| | | | | | | | | N5−C6−S1 | 117.6(10) |

| **10** | | **11** | | **12** | | **14** | | | |
|---|---|---|---|---|---|---|---|---|---|
| Cl1−Al1−Cl2 | 106.98(5) | C6−S1−C2 | 98.5(2) | Cl3−Ga1−Cl2 | 111.28(9) | C6−S1−C2 | 98.8(3) | Cl3−B1−Cl2 | 102.7(5) |
| Cl3−Al1−Cl1 | 110.91(6) | C2−S3−C4 | 98.5(2) | Cl2−Ga1−Cl1 | 106.81(7) | C4−S3−C2 | 97.3(3) | Cl4−B1−Cl3 | 111.6(5) |
| Cl3−Al1−Cl2 | 110.83(6) | C6−N5−C4 | 111.7(4) | Cl2−Ga1−Cl4 | 109.46(7) | C62−S12−C22 | 98.0(3) | Cl5−B1−Cl2 | 110.5(5) |
| Cl3−Al1−Cl4 | 109.73(5) | C6−N5−H5 | 110.6(41) | Cl3−Ga1−Cl1 | 110.75(8) | C42−S32−C22 | 97.0(3) | Cl5−B1−Cl3 | 112.3(5) |
| Cl4−Al1−Cl1 | 109.69(6) | C7−N5−C4 | 110.8(4) | Cl3−Ga1−Cl4 | 110.02(8) | C4−N5−C6 | 110.9(5) | Cl5−B1−Cl4 | 114.0(5) |
| Cl4−Al1−Cl2 | 108.62(5) | C7−N5−C6 | 109.7(4) | Cl4−Ga1−Cl1 | 108.42(8) | C7−N5−C4 | 114.5(5) | S1−C2−S3 | 111.9(4) |
| C2−S1−C6 | 98.52(19) | F2−B1−F3 | 111.3(5) | C6−S1−C2 | 98.4(4) | C7−N5−C6 | 114.0(5) | N5−C4−S3 | 114.4(4) |
| C4−S3−C2 | 98.2(2) | F2−B1−F1 | 105.6(5) | C2−S3−C4 | 99.0(4) | C42−N52−C62 | 111.9(5) | N5−C6−S1 | 114.1(4) |
| C4−N5−C6 | 111.9(3) | F3−B1−F1 | 110.4(5) | C4−N5−C6 | 111.2(5) | C42−N52−C72 | 109.9(5) | S12−C22−S32 | 111.8(4) |
| C4−N5−C7 | 110.1(3) | F4−B1−F1 | 108.8(6) | C4−N5−C7 | 110.0(5) | C62−N52−C72 | 110.7(5) | N52−C42−S32 | 113.8(4) |
| C6−N5−C7 | 110.6(3) | F4−B1−F3 | 107.6(5) | C6−N5−C7 | 110.8(6) | Cl4−B1−Cl2 | 105.0(4) | N52−C62−S12 | 114.1(4) |
| S1−C2−S3 | 113.4(2) | F4−B1−F2 | 113.0(7) | S3−C2-S | 112.9(4) | | | | |
| N5−C4−S3 | 114.2(2) | S3−C2−S1 | 111.7(3) | N5−C4−S3 | 113.0(5) | | | | |
| N5−C6−S1 | 113.2(3) | N5−C4−S3 | 113.2(3) | N5−C6−S1 | 114.0(5) | | | | |
| | | N5−C6−S1 | 112.7(3) | | | | | | |

deduced from the sharp Cl−Al−N angle (101.25°), which means that Cl approaches H4eq. Intermolecular interactions are confined to a Cl1′···H2eq distance of 2.774 Å (Figure 2b).

In the $N\rightarrow AlCl_3$ adduct **7**, the $N\rightarrow Al$ bond length is 1.993(5) Å. There are six weak cooperative intramolecular van der Waals contacts of the Cl atoms with the hydrogen atoms of neighboring CH units (range 2.92−3.00 Å) leading to a rather symmetrical orientation of the $AlCl_3$ molecule to the $H_3CN(CH_2)_2$ group. The Cl−Al−N angles are slightly sharper [105.9(2), 106.3(2) and 106.5(2)°] than those of a regular tetrahedron and cause the CH and Cl atoms to approach each other (Figure 3). A weak intermolecular S···Cl interaction of 3.467 Å is also observed[8a,8b,12] ($\Sigma r_{VDW}$ = 3.70 Å).

In the solid state, compound **8** has an $N\rightarrow Al$ bond length of 1.982(5) Å, with Br−Al−N bond angles of 107.1(2)°, 106.5(2)° and 106.4(2)°. Six short, weak intramolecular contacts between bromine and the neighboring hydrogen atoms are found, with H···Br distances ranging from 2.97 to 3.12 Å [$\Sigma r_{VDW}$ H···Br = 3.2 Å] (Figure 4b).

In the crystal, each molecule has three intermolecular interactions with three neighboring molecules, through H···Br van der Waals contacts [2.89, 2.90 and 3.04 Å]. The interaction of two sulfur atoms of one molecule with two bromine atoms,[13] each from a different molecule, is shown in Figure 5, including a short Br···H contact (2.887 Å).

The equimolecular reaction of compound **1** with $InCl_3$ in toluene at room temperature gives a white solid that crystallized from $CHCl_3$. It proved to be the 2:1 adduct **9** (Scheme 4).

The structure of **9** in the solid state reveals a pentacoordinate indium atom bound to two molecules of dithiazinane **1** through its N atoms, which are placed at the apical positions of a trigonal bipyramidal arrangement about the indium center. The molecule has $C_2$ symmetry, the two-fold axis running through the In−Cl2 bond (Figure 6). The N−In bond lengths are 2.413(3) Å. The N atoms of both

Table 4. Crystal data and data collection

| | **6** | **7** | **8** | **9** | **10** | **11** | **12** | **13** | **14** |
|---|---|---|---|---|---|---|---|---|---|
| Formula | $C_6H_{15}AlClNS_2$ | $C_4H_9AlCl_3NS_2$ | $C_4H_9AlBr_3NS_2$ | $C_8H_{18}Cl_3InN_2S_4$ | $C_4H_{10}AlCl_4NS_2$ | $C_4H_{10}BF_4NS_2$ | $C_4H_{10}Cl_4GaNS_2$ | $C_8H_{19}S_4N_2AlBr_4$ | $C_8H_{20}BClN_2S_4$ |
| Mol. wt. | 227.74 | 268.57 | 401.95 | 491.65 | 305.05 | 223.06 | 347.77 | 618.11 | 460.59 |
| Cryst. size (mm) | 0.45 × 0.5 × 0.8 | 0.1 × 0.2 × 0.3 | 0.22 × 0.25 × 0.32 | 0.1 × 0.1 × 0.1 | 0.1 × 0.2 × 0.45 | 0.2 × 0.2 × 0.3 | 0.29 × 0.33 × 0.42 | 0.2 × 0.2 × 0.1 | 0.15 × 0.2 × 0.3 |
| Cryst. system | Triclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Triclinic |
| Space group | $P\bar{1}$ | $P2_1/n$ | $C2/c$ | $C2/c$ | $P2_1$ | $P2_1/n$ | $P2_1$ | $P2_1/n$ | $P\bar{1}$ |
| a (Å) | 6.629(2) | 6.9685(11) | 24.4453(19) | 9.412(1) | 6.3285(5) | 6.3380(10) | 6.3195(10) | 8.1153(11) | 9.240(2) |
| b (Å) | 8.884(2) | 15.507(3) | 7.0171(6) | 11.203(1) | 11.4100(9) | 11.709(2) | 11.4084(16) | 13.3781(16) | 11.180(2) |
| c (Å) | 10.371(2) | 10.1903(14) | 16.4329(13) | 16.819(2) | 8.7702(7) | 12.742(3) | 8.7657(14) | 18.211(2) | 11.560(2) |
| α (°) | 99.655(2) | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 100.85(3) |
| β (°) | 91.893(3) | 91.132(3) | 121.465(2) | 90.162(2) | 101.626(2) | 96.17(3) | 101.455(2) | 95.448(2) | 112.48(3) |
| γ (°) | 109.986(3) | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 105.98(3) |
| V (Å$^3$) | 563.2(2) | 1101.0(3) | 2404.3(3) | 1773.5(3) | 620.29(9) | 940.1(3) | 619.38(16) | 1968.2(4) | 1001.2(3) |
| *Z* | 2 | 4 | 8 | 4 | 2 | 4 | 2 | 4 | 4 |
| ρ(calcd.) (Mg/m$^3$) | 1.343 | 1.620 | 2.221 | 1.841 | 1.438 | 1.576 | 1.865 | 2.086 | 1.528 |
| μ (mm$^{-1}$) | 0.735 | 1.235 | 10.436 | 2.241 | 1.096 | 0.574 | 3.374 | 8.637 | 1.132 |
| *F*(000) | 240 | 544 | 1520 | 976 | 272 | 456 | 344 | 1192 | 472 |
| Index range | $-5 \le h \le 8$ | $-8 \le h \le 8$ | $-22 \le h \le 31$ | $-11 \le h \le 12$ | $-7 \le h \le 6$ | $-8 \le h \le 8$ | $-7 \le h \le 7$ | $-10 \le h \le 10$ | $-11 \le h \le 11$ |
| | $-11 \le k \le 11$ | $-19 \le k \le 19$ | $-8 \le k \le 8$ | $-14 \le k \le 14$ | $-13 \le k \le 13$ | $-15 \le k \le 15$ | $-15 \le k \le 8$ | $-15 \le k \le 16$ | $-14 \le k \le 14$ |
| | $-12 \le l \le 12$ | $-8 \le l \le 13$ | $-19 \le l \le 19$ | $-21 \le l \le 21$ | $-10 \le l \le 10$ | $-16 \le l \le 16$ | $-10 \le l \le 10$ | $-23 \le l \le 23$ | $-15 \le l \le 14$ |
| 2θ (°) | 58.32 | 58.42 | 58.06 | 57.70 | 58.12 | 55.00 | 57.78 | 3.78 to 59.48 | 55.08 |
| Temp (K) | 193(2) | 193(2) | 193(2) | 193(2) | 193(2) | 293(2) | 193(2) | 193(2) | 293(2) |
| Refl. collected | 3226 | 6234 | 6790 | 4990 | 3603 | 4072 | 3686 | 11462 | 7734 |
| Refl. unique | 1693 | 1791 | 2186 | 1773 | 1892 | 2152 | 2103 | 3912 | 4458 |
| Refl. observed 4σ | 1532 | 783 | 1632 | 1455 | 1820 | 1463 | 1802 | 2037 | 3048 |
| *R* (int.) | 0.0262 | 0.1946 | 0.0596 | 0.0447 | 0.0269 | 0.0330 | 0.0550 | 0.1701 | 0.0335 |
| No. variables | 160 | 101 | 101 | 83 | 149 | 123 | 114 | 178 | 186 |
| GOOF | 1.087 | 0.905 | 0.998 | 0.9770 | 1.070 | 1.065 | 1.007 | 1.066 | 1.022 |
| Final *R* (4σ) | 0.0464 | 0.0610 | 0.0431 | 0.0320 | 0.0264 | 0.0845 | 0.0413 | 0.0909 | 0.0923 |
| Final *wR*2 | 0.1228 | 0.0894 | 0.0972 | 0.0741 | 0.0694 | 0.2424 | 0.0923 | 0.2133 | 0.2476 |
| Larg res peak e/Å$^3$ | 0.327 | 0.341 | 0.713 | 1.279 | 0.389 | 0.925 | 0.594 | 1.200 | 1.168 |

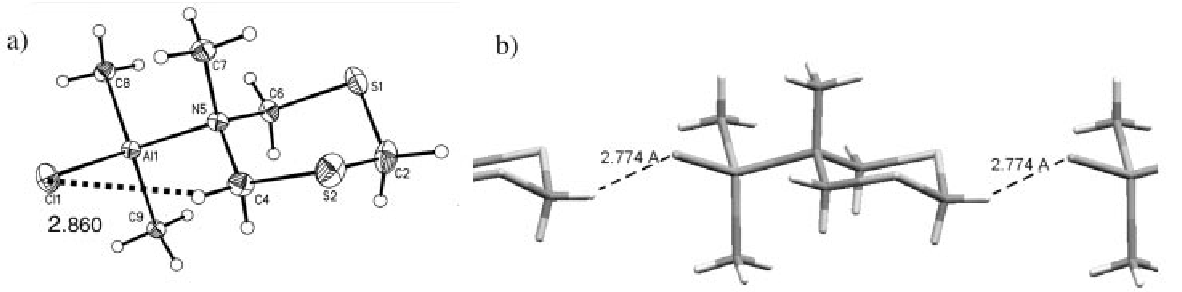


Figure 2. a) ORTEP representation of compound **6**; b) intermolecular Cl···H distances (Å)

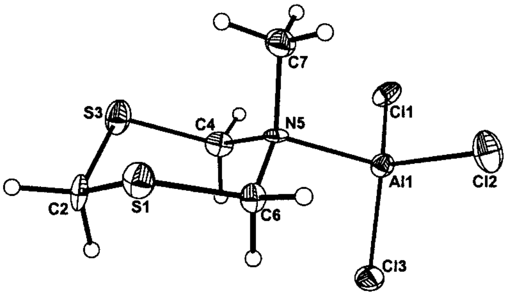


Figure 3. ORTEP representation of compound **7**

dithiazinane rings stand almost in orthogonal planes. The equatorial In−Cl bond lengths are 2.376(1) Å [Cl1 and Cl1A] and 2.383(3) Å [Cl2], the angles Cl−In−Cl are close to 120° and the N5−In1−N5A angle is 175.8(1)°. To the best of our knowledge, only two other similar structures corresponding to bis-adducts are reported in the Cambridge Crystallographic Database — bis(dibenzylamine)indium trichloride[14a] and bis(trimethylamine)indium trichloride.[14b] Similar structures have been found for ether adducts $[InCl_3(OR_2)_2]$.[14c] In the database, only one monoamine adduct $(Me_3Sn)_3N \rightarrow InCl_3$ is reported.[14d]

In compound **9**, the dithiazinane rings retain the chair conformation, with the methyl group in an axial position (Figure 6). Twelve H···Cl distances [three each of 2.630, 2.744, 2.800 and 2.885 Å] are shorter than the van der Waals contacts (Figure 7).

The orientation of the molecule **9** in the lattice is characterised by intermolecular interactions between sulfur atoms in a tail-to-tail arrangement (Figure 8). The S···S distances [3.429 and 3.433 Å; $\Sigma r_{VDW}$ = 3.60 Å] are similar to those found in elemental sulfur (3.502, 3.376 for monoclinic $S_8$).[15] Cl2 has two intermolecular hydrogen bonds (H···Cl = 2.684 Å)[16] with two axial C-2 hydrogen atoms of two different molecules.

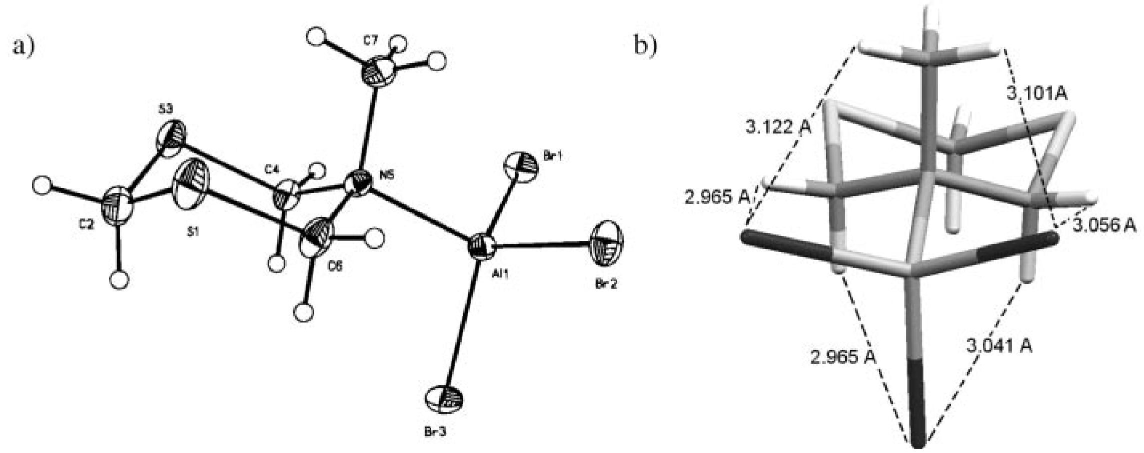


Figure 4. a) ORTEP representation of compound **8**; b) the six weak intramolecular dipolar van der Waals interactions found in **8** (Å)

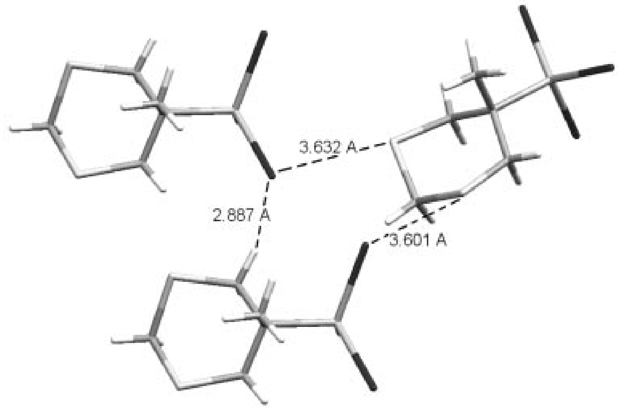
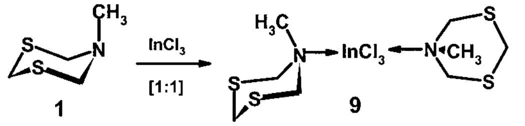


Figure 5. Arrangement of the unit cell of compound **8** showing the intermolecular contacts (Å) between three molecules



Scheme 4

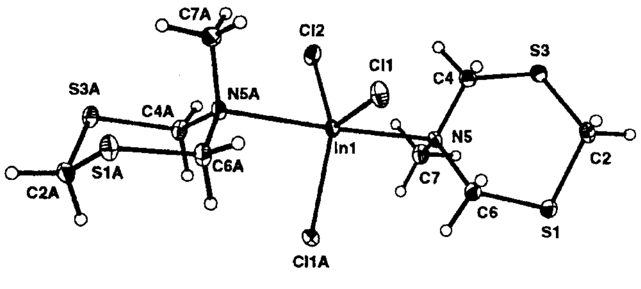


Figure 6. a) ORTEP representation of compound **9**

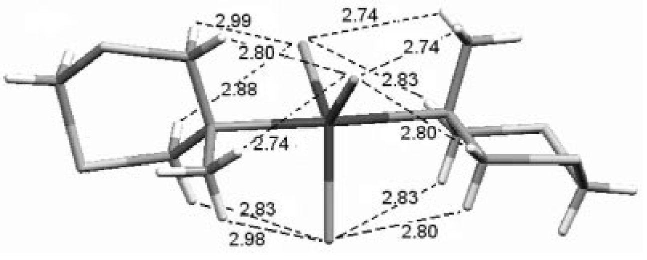


Figure 7. Short intramolecular H···Cl contacts (Å) in compound **9**

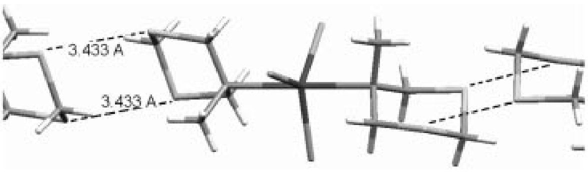


Figure 8. Intermolecular sulfur-sulfur interactions (Å) in the crystal of compound **9**

## 5-Methyl-1,3,5-dithiazinan-5-ium Cations with $AlCl_4^-$, $AlBr_4^-$, $GaCl_4^-$ $BCl_4^-$ and $Cl^-$ Anions (10−14)

The 5-methyl-1,3,5-dithiazinanium salts with $MX_4^-$ anions [$AlCl_4^-$ **10**, $BF_4^-$ **11**, $GaCl_4^-$ **12**, $AlBr_4^-$ **13**, $BCl_4^-$ and $Cl^-$ **14**] are formed by hydrolysis of the corresponding $N \rightarrow MX_3$ adducts. They are crystalline solids that are insoluble in organic solvents ($CH_2Cl_2$, $CHCl_3$, $C_7H_8$); their structures were established by X-ray diffraction analysis. The molecular structure of the free dithiazinane ligand in the solid state shows that the methyl group adopts an axial position.[1d] Here it is very interesting to note that the dithiazinane rings present two conformations in the solid state, one with the methyl group in an equatorial position (**10**−**12**) and the other of a dithiazinanium salt with the methyl in an equatorial position and connected to one molecule of free dithiazinane with the N−Me group in an axial position (**13**); the actual structure is $L(LH^+)AlBr_4^-$. In another extraordinary case, conformations with methyl groups in equatorial or in axial positions were found in the same crystal (**14**). To the best of our knowledge this is the first solid-state structure of a dithiazinanium ring with the methyl group in an axial position.

In compounds **10**−**12** the dithiazinane is protonated, the methyl group is present in the equatorial position and the anion is placed on top of the heterocycle. The distances

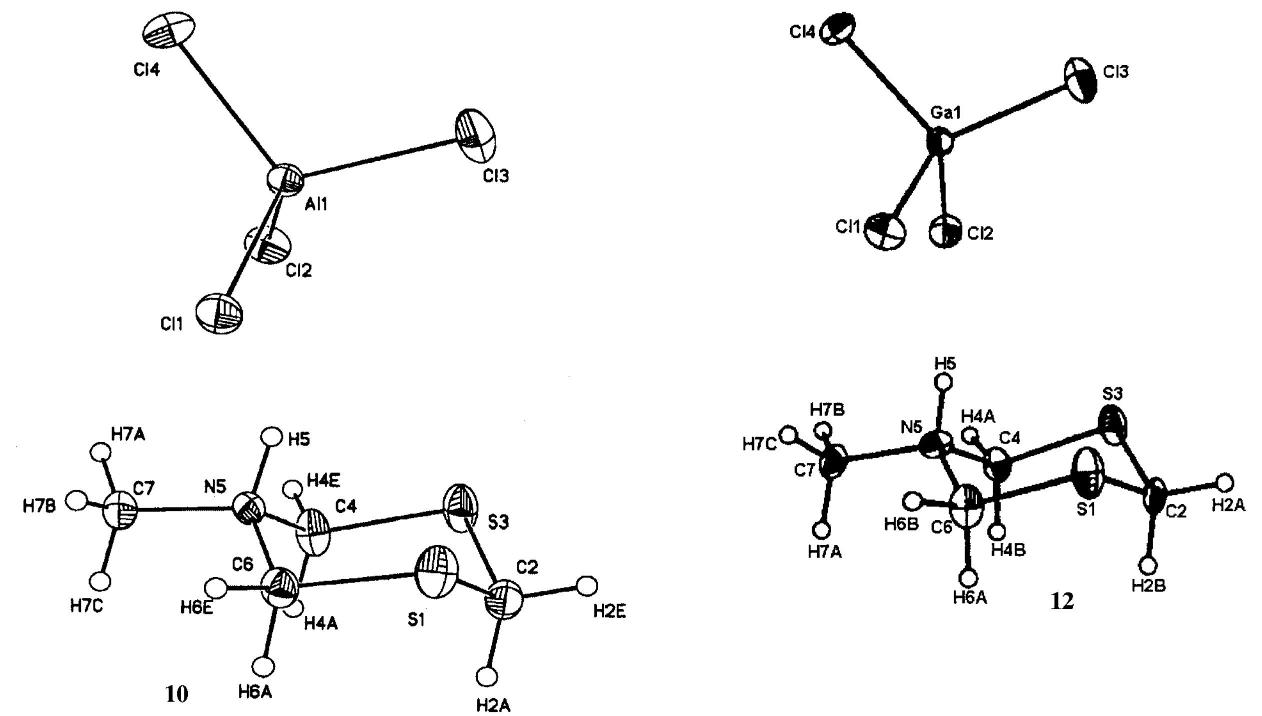


Figure 9. ORTEP representation of the crystal structures of **10** and **12**

between N−H5 and the halogen atoms of the anion are: for compound **10** 2.470 and 3.100 Å, for **11** 2.280 and 2.502 Å and for **12** 2.216 and 2.958 Å. Hydrogen bonding closes the X−M−X angle of the atoms near N−H5 [in **10**, 106.98(5)° in **11**, 105.6(5)° and in **12**, 106.81(7)°]. The angle C7−N5−H5 is sharp [101.03(1)° in **12**, 104.4(4)° in **11** and 108(3)° in **10**]. The tetrahedral geometry of the nitrogen atoms is distorted in **10** and **12** due to the hydrogen bonds between the N−H and the halogen atoms; the angles for **10** are C4−N5−H5 99(3)° and C6−N5−H5 116(3)° and for **12** 105.09(1)° and 118.36(1)° (Figures 9 and 10).

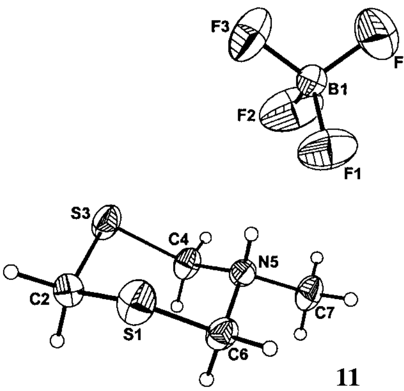


Figure 10. ORTEP representation of the crystal structure of **11**

In compounds **10**−**12** up to five dithiazinane hydrogen atoms participate in intermolecular interactions by hydrogen−halogen contacts. In Figure 11, the intermolecular interactions of anions and the heterocyclic cation in the lattice of **10** are shown. Around each anion five cycles are organized with five different interactions.

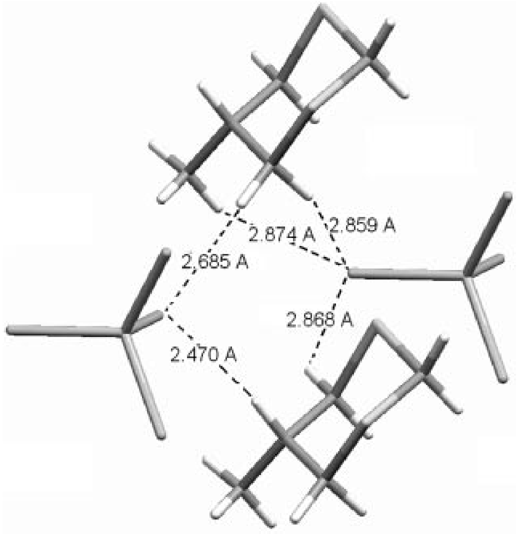


Figure 11. Arrangement (distances in Å) of anion and heterocyclic cations in compound **10**

Compound **11** presents six intermolecular hydrogen bonds with six short distances (Figure 12). Compound **12** also has many intermolecular contacts in the unit cell, with seven intermolecular hydrogen halogen bonds for each molecular unit (Figure 13).

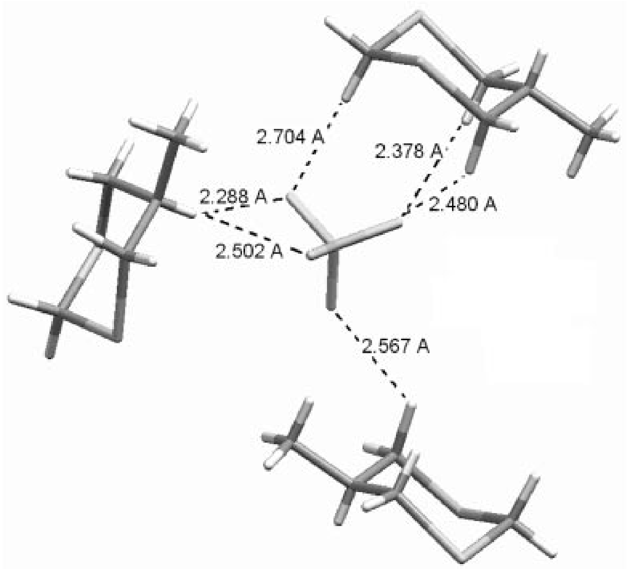


Figure 12. Arrangement of anions and heterocyclic cations in the cell of compound **11**

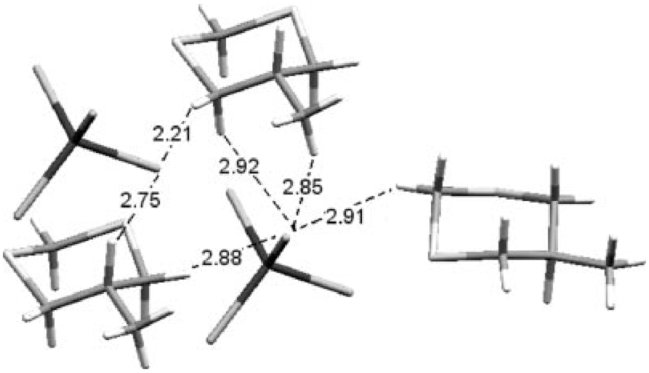


Figure 13. Arrangement of anions and heterocyclic cations in the unit cell of compound **12** (Å)

Compound **13** presents a very interesting molecular arrangement in the solid state because it co-crystallizes with a free dithiazinane molecule. In the asymmetric unit the free ligand has the methyl group in an axial position and the protonated ligand has the methyl group in an equatorial position (Figure 14). The heterocycles interact through a strong nitrogen-hydrogen bond N5H5A···N12 [2.068 Å] and one C−H···S hydrogen bond [2.974 Å].[6,17]

The unit cell of compound **14** is quite interesting because it shows a mixture of two different conformers of the protonated dithiazinane, one with the methyl group in an equatorial position and the other in an axial position. The cell also contains two different anions: $BCl_4^-$ and $Cl^-$. The chloride ion is strongly bound to two N−H units (one axial and other equatorial) each one belonging to different conformers of the protonated dithiazinane. The corresponding H···Cl distances are H5···Cl1 (2.180 Å) and H5A···Cl1 (2.257 Å; Figure 15b). The interaction between the N−H and the chloride contributes to a significant distortion around the nitrogen atom. For the dithiazinanium with the axial methyl group, the C4−N5−H5 angle is 104(1)° and the C6−N5−H5 angle is 94(1)°. In the dithiazinanium with the equatorial methyl group the corresponding angles are 104(1)° and 103(2)°.

The position of the $BCl_4^-$ group merits some comments: there are two face-to-face $BCl_4^-$ anions, and the distance between the two Cl atoms of two $BCl_4^-$ units (2.480 Å) is much shorter than the sum of the van der Waals radii (3.4−3.6 Å). This short distance, which, in principle, should produce a strong repulsive interaction between the chlorides, has no simple explanation, however, there are eight CH···Cl contacts altogether, and these may be responsible for stabilizing this molecular arrangement (Figure 16). Reports of Cl···Cl interactions in the solid state can be found in the literature.[18]

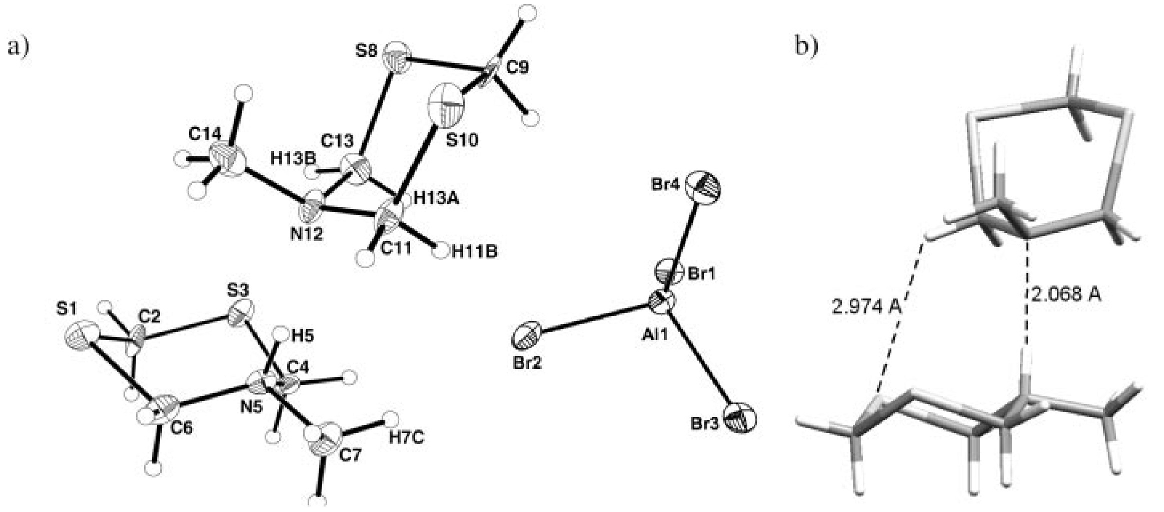


Figure 14. Crystal structure of compound **13**: a) ORTEP representation; b) interactions (Å) between dithiazinanium and dithiazinane molecules

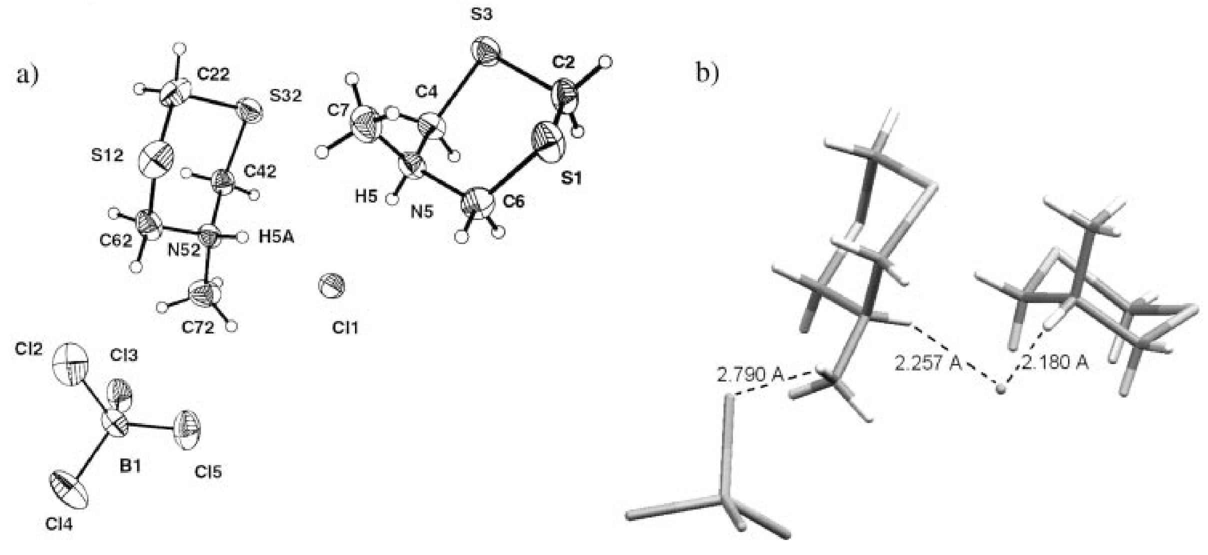


Figure 15. Crystal structure of compound **14**: a) ORTEP representation; b) distances (Å) between H5 and H5A with $Cl^-$ and $BCl_4^-$.

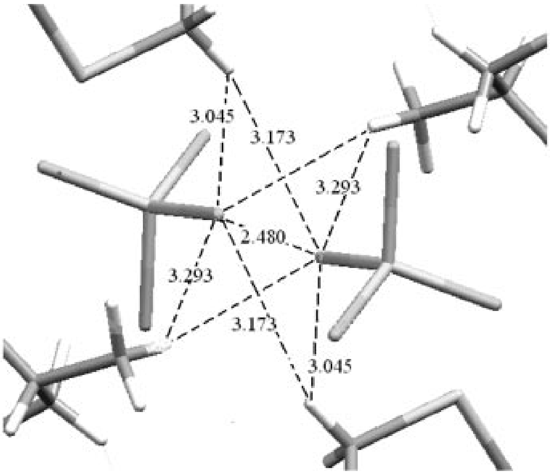


Figure 16. A projection showing the arrangement of anion and heterocycle fragments in the unit cell of **14**

## Conclusion

Dithiazinane is an interesting ligand which forms coordination compounds with dimethylaluminum chloride, aluminum trihalides and indium trichloride. The coordination occurs only through the nitrogen atom. It was found by NMR spectroscopy in solution that coordination leads to preferred conformations for the dithiazinane cycle. The ring-inversion energies were calculated from NMR experiments in solution. Opening of the cycle by $AlMe_3$ was found to occur by C−S bond breaking. In the solid state these compounds show many intramolecular and intermolecular interactions, most of them of van der Waals type, but others appear to be weak intermolecular polar interactions, which determine the preferred conformations. CH···Hal and NH···Hal intermolecular interactions were observed in many cases. The sulfur atoms are also involved in short intermolecular S···S contacts in compound **9** and S···Br contacts in **8**. In solution and in the solid state, C2H···π interactions were detected.

The dithiazinanium ion interacts with anions rich in lone pairs, such as $MX_4^-$ or $X^-$, through its acidic NH hydrogen atoms, in very versatile ways, and through different conformers.

## Experimental Section

All anhydrous solvents were freshly distilled prior to use. $^{1}H$, $^{13}C$ and $^{27}Al$ NMR spectra were recorded with 270 or 400 MHz $^{1}H$ Jeol instruments and are referenced to TMS ($^{1}H$ and $^{13}C$) and $Al(OH)_6^{3+}$ for $^{27}Al$. Melting points were measured on a Gallenkamp apparatus and are uncorrected.

Crystal data and data collection are reported in Table 4. Enraf−Nonius Kappa and Siemens−P4 diffractometers with CCD detectors were used. Absorption correction was performed using the program SADABS. Computations for all compounds were done by using SHELXS-97 (Sheldrick 1990) and SHELXL-97 (Sheldrick 1997).[19] Atomic scattering factors for neutral C, N, O and H atoms were taken from ref.[20] Hydrogen atoms were found in difference electron density maps. The NH hydrogen atoms were freely refined isotopically.

CCDC-217486 to -217494 (for **6−14**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

**General Procedure for the Preparation of N→AlR$_{3-n}$X$_n$ (*n* = 3, 2, 0) Adducts:** Two solutions in dry toluene and under an $N_2$ atmosphere containing equivalent stoichiometric amounts of the aluminum reagent $AlR_{3-n}X_n$ ($n$ = 3,2,0) and compound **1** were slowly mixed at 4 °C and stirred for 20 min. A precipitate formed which was removed by filtration and recrystallized from toluene.

**5-Methyl-1,3,5-dithiazinane(N-Al)trimethylalane (5):** Compound **1** (225 mg, 1.66 mmol) in toluene (20 mL) and a solution of $AlMe_3$ in hexane (2 M, 1.66 mmol, 0.83 mL) were mixed. The white solid formed was isolated and crystallized from toluene (yield: 310 mg, 90%). The crystals were not adequate for X-ray diffraction studies, m.p. 76−78 °C. $^{13}$C NMR ($CDCl_3$, −10 °C): δ = 56.9 (C4 and C6), 36.6 (*C*7), 31.7 (C2), −9.8 (Al*C*$H_3$) ppm. $^{13}$C NMR ($C_6D_5CD_3$ at −10 °C): δ = 56.5 (C4 and C6), 35.6 (C7), 30.6 (C2), −6.9 (Al*C*$H_3$) ppm. $C_7H_{18}AlNS_2$ (215.29): calcd. C 40.55, H 8.75, N 6.76; found C 40.43, H 8.73, N 6.57.

**5-Methyl-1,3,5-dithiazinane(N-Al)dimethylaluminum Chloride (6):** A 1 M solution of $AlMe_2Cl$ in hexane (1.33 mmol, 1.33 mL) was slowly added at room temp. to a solution of compound **1** (180 mg, 1.33 mmol) in toluene (20 mL). A yellow solid separated which was isolated and crystallized from toluene at −20 °C (yield: 270 mg, 90%), m.p. 91−93 °C. $^{13}$C NMR ($CDCl_3$, 27 °C): δ = 56.9 (C4 and C6), 36.2 (C7), 31.5 (C2), −10.0 (Al*C*$H_3$) ppm. $^{13}$C NMR ($C_6D_5CD_3$ at −15 °C): δ = 56.2 (C4 and C6), 35.1 (C7), 30.4 (C2), −7.7 (Al*C*$H_3$) ppm. $C_6H_{15}AlClNS_2$ (235.72): calcd. C 31.64, H 6.64, N 6.15; found C 30.88, H 6.21, N 5.60.

**5-Methyl-1,3,5-dithiazinane(N-Al)aluminum Trichloride (7):** A solution of $AlCl_3$ (165 mg, 1.23 mmol) in $CH_2Cl_2$ (20 mL) and a solution of compound **1** (167 mg, 1.23 mmol) in $CH_2Cl_2$ (20 mL) were mixed. Compound **7** precipitated as a white solid which was isolated and crystallized from toluene at room temp. (260 mg, 80%), m.p. 104−106 °C. $^{13}$C NMR ($CDCl_3$, −10 °C): δ = 57.0 (C4 and C6), 36.1 (C7), 31.1 (C2) ppm. $^{13}$C NMR ($C_6D_5CD_3$, 10 °C): δ = 56.8 (C4 and C6), 35.3 (C7), 30.1 (C2) ppm. $C_4H_9AlCl_3NS_2{\cdot}C_7H_8$ (286.98): calcd. C 25.42, H 3.93, N 4.68; found C 25.64, H 4.60, N 4.80.

**5-Methyl-1,3,5-dithiazinane(N-Al)aluminium Tribromide (8):** $AlBr_3$ (210 mg, 0.78 mmol) in toluene (20 mL) and compound **1** (106 mg, 0.78 mmol) dissolved in toluene (20 mL) were mixed. Adduct **8** was obtained as a yellow solid which was crystallized from toluene at room temp. (yield: 230 mg, 75%) and m.p. 110−112 °C. $^{13}$C NMR ($CDCl_3$, −55 °C): δ = 57.1 (C4 and C6), 36.3 (C7), 31.5 (C2) ppm. $^{13}$C NMR ($CDCl_3$, −55 °C): δ = 56.5 (C4 and C6), 35.2 (C7), 29.7 (C2) ppm. $C_4H_9AlBr_3NS_2$ (401.94): calcd. C 11.95, H 2.26, N 3.48; found C 11.75, H 2.56, N 3.41.

**Bis[5-Methyl-1,3,5-dithiazinane(N-Al)]indium Trichloride (9):** A solution of **1** (100 mg, 0.74 mmol) in $CHCl_3$ (20 mL) was added to a suspension of $InCl_3$ (164 mg, 0.74 mmol) in $CHCl_3$ at room temp. The mixture was stirred for 30 min and the solid was isolated by filtration. Crystallization of the white solid from $CHCl_3$ at room temp. gave 160 mg (90%) of **9**. $C_8H_{18}Cl_3InN_2S_4{\cdot}2CHCl_3$ (657.14): calcd. C 15.84, H 2.91, N 4.26; found C 16.19, H 2.94, N 3.89.

**General Procedure for the Preparation of 5-Methyl-1,3,5-dithiazinan-5-ium Salts 10−14:** Two solutions under a $N_2$ atmosphere, one of the aluminum or borane reagent ($AlR_{3-n}X_n$, $BX_3$) and the other of compound **1** in the same solvent, were slowly mixed (in a 1:1 ratio) at 4 °C, and stirred for 20 min. The precipitate was removed by filtration and the filtrate was stirred for 20 min in an open system. The salts were obtained as crystalline solids.

**5-Methyl-1,3,5-dithiazinan-5-ium Tetrachloroaluminate (10):** Compound **10** was obtained as crystals (m.p. 84−86 °C) in 90% yield. $C_8H_{20}AlCl_5N_2S_4$ (476.47): calcd. C 15.43, H 2.54, N 3.33; found C 15.65, H 2.66, N 3.41.

**5-Methyl-1,3,5-dithiazinan-5-ium Tetrafluoroborate (11):** A solution of $BF_3{\cdot}OEt_2$ (11.6 M, 0.032 mL, 0.37 mmol) was added at −78 °C to compound **1** (50 mg, 0.37 mmol) in $CDCl_3$ (1 mL) under an $N_2$ atmosphere. After two weeks of storing at room temp., some white crystals were obtained (m.p. 79−80 °C). $C_4H_{10}AlBF_4NS_2$ (223.06): calcd. C 21.54, H 4.52, N 6.28; found C 21.15, H 4.66, N 6.13.

**5-Methyl-1,3,5-dithiazinan-5-ium Tetrachlorogallate (12):** $GaCl_3$ (240 mg, 1.36 mmol) in toluene and compound **1** (184 mg, 1.36 mmol) dissolved in toluene (20 mL) were mixed at 4 °C. Compound **12** was obtained as a white solid. It was crystallized from toluene at room temp. and proved to have the composition $(\mathbf{1}{\cdot}H^+)GaCl_4{\cdot}C_7H_8$ (420 mg, 90%); m.p. 54−56 °C. $^{1}$H NMR ($CDCl_3$): δ = 4.5 (s, 4 H), 4.0 (s, 2 H), 3.0 (s, 3 H) ppm. $^{13}$C NMR: δ = 58.4 (C4 and C6), 36.9 (C7), 32.4 (C2) ppm. $C_4H_{10}Cl_4GaNS_2{\cdot}C_7H_8$ (439.84): calcd. C 15.43, H 2.54, N 3.33; found C 15.65, H 2.66, N 3.41.

**5-Methyl-1,3,5-dithiazinan-5-ium Tetrabromoaluminate (13):** The white solid was recrystallized from toluene at room temp. (m.p. 83−85 °C). $C_8H_{19}AlBr_4N_2S_4$ (618.11): calcd. C 15.43, H 2.54, N 3.33; found C 15.65, H 2.66, N 3.41.

**Bis(5-Methyl-1,3,5-dithiazinan-5-ium) Tetrachloroborate Chloride (14):** A solution of $BCl_3{\cdot}DMS$ (4 M, 0.09 mL, (0.37 mmol) was added to a solution of compound **1** (50 mg, 0.37 mmol) in $CDCl_3$. The mixture was stored for one week at room temp., after which time some white crystals had separated; m.p. 109−111 °C. $C_8H_{19}BCl_4N_2S_4$ (424.13): calcd. C 22.66, H 4.52, N 6.60; found C 22.43, H 4.50, N 6.00.

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