Variations in the Chain Structure of Cationic (Phosphine)gold(I) Dialkylthiophosphate Complexes
Max Preisenberger, Annette Schier, Hubert Schmidbaur*
Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany
Z. Naturforsch. 53 b, 781–787 (1998); received May 18, 1998

Gold Complexes, Phosphinates, Thiophosphinates, Dithiophosphinates

Treatment of dithiophosphoric acid diesters (RO)2P(S)SH with appropriate quantities of tris[(phosphine)gold(I)]oxonium tetrafluoroborates ([R3P(Au)2(O)2]BF4−) in dichloromethane gives di- or trinuclear complexes of the types ([RO2P(S)Au(PR3)2]2+)2+ (2) BF4− as colourless, crystalline salts. As determined by single crystal X-ray diffraction studies, in the 1:2 complexes (with R = R' = Me and R' = Et, R = Ph and o-Tol), each gold atom is attached to a different sulfur atom, but with short intracationic Au–Au contacts. These cations are associated to form strings through intermolecular Au–Au contacts in the first case (R = Et), but through additional Au–S contacts in the second (R = Ph). For R = o-Tol, the cations are not associated at all owing to steric hindrance. This result is indicative of very small energy differences between the two modes of association. The 1:3 complexes are fluxional in solution and show virtually equivalent R3PAu groups in the NMR spectra at 20°C, but at low temperature non-equivalent ligands can be distinguished as shown previously for analogous dithiophosphinate derivatives.

Introduction

Gold(I) complexes with phosphine and sulfur donors are known to show association phenomena in the solid state, and in favourable cases also in solution, featuring sub-van der Waals Au–Au contacts of the linearly two-coordinate metal atoms [1 - 8]. These interactions are strong enough to determine the organisation of the molecular or ionic units in a lattice, because they are associated with bond energies comparable to those of hydrogen bonds [9 - 13]. Theoretical studies have shown that the energy terms of this “aurophilic bonding” vary with the nature of the ligands L and X in molecules of the type L-Au-X [14 - 17]. For a set of soft donor ligands (L = phosphine; X = thiolate, iodide etc.) the Au–Au interactions are particularly strong and may reach values of up to 10 kcal/mole.

This prediction was confirmed by a large number of experimental findings for various combinations of L and X, but cases have also been found where non-classical Au–Au bonding was overruled by conventional Au–X coordination [18 - 20]. These observations should be taken as caveats, because they suggest a delicate balance of several factors that may contribute to the overall situation.

During a study of multinuclear gold complexes of thiophosphinates, thiophosphinates and related compounds we have now encountered another group of compounds, where minor variations in the composition have a marked influence on the supramolecular structure. These results are presented here as a supplement to our previous pertinent communications [21, 22].

Preparation and Characterization of the Complexes

The compounds described in this contribution have all been prepared using tris[(phosphine)gold(I)]oxonium salts {([R3P(Au)2(O)2]BF4−) as auurating agents for dithiophosphoric acid diester substrates, (RO)2P(S)SH, in dichloromethane as solvent, and in the presence of excess NaBF4. With two equivalents of the oxonium salt the 2:1 complexes were obtained in high yields (85-95%), and with three equivalents the corresponding trinuclear compounds were generated (60-75% yield) (Scheme 1). Similar results were obtained previously with diorganophosphinic and organophosphonic acids [22].

The products were isolated by crystallization as colourless, air-stable solids, soluble in di- and trichloromethane. Their composition was confirmed by elemental analysis and by FAB mass spectro-
Scheme 1

The $^{1}{H}$, $^{13}C$ and $^{31}P$ NMR spectra were instrumental in showing that in dichloromethane or chloroform solution the AuPR$_3$ units of the 1:2 complexes are structurally equivalent. The 1:3 complexes also show virtual equivalence of the three AuPR$_3$ groups at room temperature, but previous studies of related compounds have already shown that this observation is due to rapid site exchange in solution. At low temperature (-75°C) the signals are split into two components indicating a ground state structure with reduced symmetry. This result is in agreement with previous findings for analogous dithiophosphinate complexes [22].

Structural Results

Three compounds of the present series could be obtained as single crystals by layering dichloromethane solutions of the complexes with pentane or diethyl ether.

{(EtO)$_2$P[SAu(Ph)$_3$)$_2$}$_2$+ BF$_4^-$ 5 forms triclinic crystals, space group $P1$, with four formula units in the unit cell. The asymmetric unit comprises two crystallographically independent cations and anions, which both have no element of symmetry (Fig. 1). The cations are associated to form chains along the $x$ axis (Fig. 2), the geometry of which is clearly governed by intra- and intermolecular Au–Au interactions. The meandering string of gold atoms is a repeating sequence of -Au1-Au2-Au3-Au4- units with four different Au–Au contacts and four different Au–Au–Au angles:

\[
\begin{align*}
Au1 - Au2 & = 3.2754(6) \text{ Å} \\
Au2 - Au3 & = 3.1389(5) \text{ Å} \\
Au3 - Au4 & = 3.5070(6) \text{ Å} \\
Au4 - Au1 & = 3.0258(5) \text{ Å}
\end{align*}
\]

All of these distances and angles fall in the range commonly observed in the supramolecular chemistry of L-Au-X molecules, and the overall structure of this complex is therefore "as expected". The remainder geometrical details of the cations, the geometry of the anions, and the crystal packing show no anomalies.

{(MeO)$_2$P[SAu(PMe$_3$)$_2$]}$_2$+ BF$_4^-$ 6 crystallizes (with two equivalents of CH$_2$Cl$_2$) in the monoclinic space group $I2/a$ with 8 formula units in the unit cell. The lattice is built from chains of cations along the crystallographic $y$ axis (Fig. 3) which are surrounded by the anions and the solvent molecules.
Fig. 2. View of the supramolecular structure of 5. Formation of a chain (along the x axis) through intermolecular Au–Au contacts (Å): Au(1)-Au(2) 3.2754(6), Au(2)-Au(3') 3.1389(5), Au(3)-Au(4) 3.5070(6), Au(4)-Au(1) 3.0258(5).

Fig. 3. View of the supramolecular structure of 6. Formation of a chain through intermolecular Au–Au and Au–S contacts.

The individual cationic units have no crystallographically imposed symmetry, but approach quite closely the geometry with a twofold axis bisecting the O-P-O and S-P-S angles (Fig. 4). The internal distances and angles are similar to those in the above analogue, but the Au1–Au2 contact (3.451 Å) is about 0.3 Å longer probably owing to steric effects.

Very surprisingly, however, the intermolecular contacts between the cations within the chains are quite different: Instead of clear-cut Au–Au interactions (the metal–metal distances being by far the shortest intercationic contacts), the Au–S groups of neighbouring cations are shifted parallel to form a rhombic Au2S2 unit. In this unit the diagonal Au1–Au2' contact [3.387 Å] is just as long as the edges Au1–S2 and Au2–S1 [3.358 and 3.439 Å, respectively], and therefore the bonding between the cations appears to be determined not only by gold-gold contacts, but also by two weak gold-sulfur contacts. It should be noted that the sum of the van der Waals radii for Au–Au is much larger than for Au–S, which suggests that the Au–Au contacts represent stronger bonding than Au–S contacts of a similar length.

An inspection of the environment of the cation chains does not reveal any conspicuous congestion which could induce the distortions responsible for the slipped disposition of the components. It rather appears that the energy loss associated with the slippage of the Au–S units is small, such that even minor packing forces can lead to an interconversion.

\{(EtO)2P[S(Au(P(o-Tol)3))2]+ BF4−\} crystallizes (with one equivalent of CHCl3) in the trigonal space group P3 with Z = 6. The cations are stacked in chains along the z axis, but there are no short contacts between Au and Au or Au and S atoms. Clearly the bulk of the P(o-Tol)3 ligand prevents any short intra- and intercationic bonding interaction (Fig. 5).

Conclusion

The present work has shown that minor changes in the steric requirements of the substituents of the title compounds can modify and finally prevent intra- and intermolecular second-order bonding which otherwise is co-determining the supra-
molecular structures. The energy associated with Au-Au bonding is larger than the energies of other Au-X contacts (e.g., X = S), but the former can be overruled and replaced by Au-X coordination if energy terms associated with packing forces required a shift or slippage of the components of the lattice.

**Experimental Part**

**General:** All experiments were carried out under an atmosphere of dry, purified nitrogen. Glassware was dried and filled with nitrogen, solvents were distilled and kept under nitrogen. NMR: JEOL-GX 270 (109.4 MHz), TMS as internal standard, phosphoric acid as external standard. MS: Finnigan MAT 90. Microanalyses: In-house analyzers (by combustion techniques). Starting materials were either commercially available or were prepared following literature procedures:

\[
\text{[(Ph}_3\text{P})\text{Au}]_3\text{O} \cdot \text{BF}_4^- + \text{BF}_4^- \quad \text{(1)}
\]

To a solution of \{[(Ph3P)Au]3O} + BF4~ (212 mg, 0.14 mmol) in dichloromethane (20 ml) were added NaBF4 (100 mg, 0.91 mmol) and (EtO)2 P(S)SH (36 µl, 40 mg, 0.21 mmol). After stirring for 1 h the solvent was removed in vacuo and the white precipitate was extracted with 10 ml of dichloromethane. Addition of pentane to the filtrate led to the precipitation of 220 mg (88 %) of 1 as a white solid. The compound is airstable and soluble in dichloromethane and chloroform, but insoluble in pentane and diethylether. M.p. 184°C (decomp.). C40H40Au2BF402P3S2 (1190.53); C 40.12 (calcd. 40.35), H 3.35 (3.39), S 5.47 (5.39). 1H NMR (CDCl3): δ = 7.37 - 7.74 (m, 30 H, Ph), 4.30 (dq, 4 H, 3J_H = 7, 2J_C_P = 10 Hz, OCH2CH3), 1.36 (t, 6 H, 3J_H = 7 Hz, OCH2CH3); 13C{1H} NMR (CDCl3): δ = 134.0 (d, 2J_C_P = 14 Hz), 132.4 (s), 129.5 (d, 3J_C_P = 12 Hz), 127.8 (d, 1J_C_P = 60 Hz) (ortho-, para-, meta-, ipso-C of AuPPh3), 65.1 (d, 2J_C_P = 7 Hz, OCH2CH3), 16.0 (d, 3J_C_P = 8 Hz, OCH2CH3); 31P{1H} NMR (CDCl3): δ = 102.2 (s, 1 P, (EtO)2PS2), 37.5 (s, 2 P, AuPPh3). FAB-MS (NBA), m/z (%): 1103 (100) [M]+, 841 (30) [M - PPh3]+, 644 (18) [M - AuPPh3]+.

\[
\text{[(EtO)}_2\text{P}[\text{SAu(PPh}_3\text{h}])_2 \cdot \text{BF}_4^- \quad \text{(2)}
\]

To a solution of \{[(Ph3P)Au]3O} + BF4~ (212 mg, 0.14 mmol) in dichloromethane (20 ml) were added (EtO)2 P(S)SH (23 µl, 26 mg, 0.14 mmol) dissolved in dichloromethane (10 ml) and NaBF4 (100 mg, 0.91 mmol) at 0°C. After stirring for 2 h the solution was filtered. Evaporation of the solvent from the filtrate in vacuo gave 182 mg (75 %) of complex 4 as a white solid. The compound is stable in solution at 0°C for several hours. 1H NMR (CDCl3): δ = 7.41 - 7.59 (m, 45 H, Ph), 4.36 (dq, 4 H, 3J_H = 7, 2J_C_P = 10 Hz, OCH2CH3), 1.36 (t, 6 H, 3J_H = 7 Hz, OCH2CH3); 13C{1H} NMR (CDCl3): δ = 133.9 (d, 2J_C_P = 14 Hz), 132.5 (s), 129.5 (d, 3J_C_P = 12 Hz), 128.0 (d, 1J_C_P = 61 Hz) (ortho-, para-, meta-, ipso-C of AuPPh3), 66.5 (d, 2J_C_P = 8 Hz), 16.0 (d, 3J_C_P = 8 Hz); 31P{1H} NMR (CDCl3, RT): δ = 101.2 (s, 1 P, (EtO)2PS2), 35.5 (s, 3 P, AuPPh3); (CD2Cl2, -75°C): δ = 101.9 (s, 1 P, (EtO)2PS2), 36.1 (s, 1 P, AuPPh3), 35.4 (s, 2 P, AuPPh3).

\[
\text{(EtO)}_2\text{P}[\text{SAu(oTol}h]_2 \cdot \text{BF}_4^- \quad \text{(3)}
\]

The synthesis was analogous to that of 1 with (EtO)2P(S)SH (32 µl, 35 mg, 0.19 mmol), NaBF4 (100 mg, 0.91 mmol) and \{[(oTol)3PAu]3O} + BF4~ (201 mg, 0.19 mmol) to give 232 mg (96 %) of 3. The compound is airstable as a solid and soluble in dichloromethane and chloroform, but insoluble in pentane and diethylether. Colourless crystals could be obtained from chloroform solution by layering with pentane. M. p. 187°C (decomp.). C46H52Au2BF402P3S2 * 2 CH2Cl2 (1442.10); C 40.05 (calcd. 39.94), H 3.92 (3.91). 1H NMR (CDCl3): δ = 7.51 (m, 6 H, H3-oTol), 7.39 (m, 6 H, H4-oTol), 7.21 (m, 6 H, H5-oTol), 7.21 (m, 6 H, H6-oTol), 4.18 (dq, 4 H, 3J_H = 7, 2J_C_P = 10 Hz, OCH2CH3), 2.62 (s, 18 H, CH3-oTol), 1.23 (t, 6 H, 3J_H = 7 Hz, OCH2CH3); 13C{1H} NMR (CDCl3): δ = 142.6 (d, 2J_C_P = 12 Hz, C2-oTol), 133.6 (d,
The synthesis was analogous to that of 2 with \((\text{EtO})_2\text{P} \cdot \text{S} \cdot \text{SH}\) (26 µl, 29 mg, 0.16 mmol) and \{[(\text{oTol})_3\text{PAu}]_3\}^+ \cdot \text{BF}_4^- (220 mg, 0.15 mmol) to give 149 mg (91 %) of 6. The compound is airstable and soluble in dichloromethane and chloroform, but insoluble in pentane and diethylether. Colourless crystals could be obtained from dichloromethane solution by layering with diethylether at -30°C. M.p. 187°C (decomp.). \(\text{CsH}_{36}\text{Au}_2\text{BF}_4\cdot \text{O}_2\text{P}\cdot \text{S}_2\) (1162.49); C 38.86 (calcd. 39.20), H 3.30 (3.12), S 5.14 (5.51). \(^1\text{H} \text{NMR} \) (CDCl3): \(\delta = 7.44 - 7.69\) (m, 30 H, Ph), 3.80 (d, 6 H, \(2J_{\text{H},\text{P}} = 15\) Hz, OCH3); \(^1\text{C} \{'\text{H}\} \text{NMR} \) (CDCl3): \(\delta = 133.8\) (d, 39 Hz) (ortho-, para-, meta-, ipso-C of AuPPh3), 5.46 (d, \(2J_{\text{C},\text{P}} = 8\) Hz, OCH3); \(^3\text{P} \{'\text{H}\} \text{NMR} \) (CDCl3): \(\delta = 108.3\) (s, 1 P, \((\text{MeO})_2\text{P}\cdot \text{S}\)_2); 37.8 (s, 2 P, AuPPh3). FAB-MS (NBA), \(m/z \%\): 1075 (100) [M\(^+\)].

\[\{\text{MeO}_2\text{P}[\text{SAu(PMe_3)_2}]\}^+ \cdot \text{BF}_4^- \ (7)\]

The synthesis was analogous to that of 1 with \((\text{MeO})_2\text{P} \cdot \text{S} \cdot \text{SH}\) (34 µl, 37 mg, 0.20 mmol), NaBF4 (100 mg, 0.91 mmol) and \{[(\text{MeP})\text{Au}]_3\}^+ \cdot \text{BF}_4^- (125 mg, 0.14 mmol) to give 149 mg (91 %) of 5. The compound is airstable and soluble in dichloromethane and chloroform, but insoluble in pentane and diethylether. Colourless crystals could be obtained from dichloromethane solution by layering with diethylether. M.p. 167°C (decomp.). \(\text{C}_{8}\text{H}_{24}\text{Au}_2\text{BF}_4\cdot \text{O}_2\text{P}\cdot \text{S}_2\) (789.98); C 42.28 (calcd. 42.37), H 3.30 (3.12), S 8.20 (8.09). \(^1\text{H} \text{NMR} \) (CDCl3): \(\delta = 7.51\) (m, 6 H, H3-oTol), 7.39 (m, 6 H, H4-oTol), 7.23 (m, 6 H, H5-oTol), 6.91 (m, 6 H, H6-oTol), 3.80 (d, 6 H, \(2J_{\text{H},\text{P}} = 15\) Hz, OCH3); 2.64 (s, 18 H, CH3-oTol); \(^1\text{C} \{'\text{H}\} \text{NMR} \) (CDCl3): \(\delta = 108.3\) (s, 1 P, \((\text{MeO})_2\text{P}\cdot \text{S}\)_2); 34.5 (s, 2 P, Au(PPh3)). FAB-MS (NBA), \(m/z \%\): 1159 (100) [M\(^+\)].

\[\{\text{MeO}_2\text{P}[\text{SAu(PMe_3)_2}]\}^+ \cdot \text{BF}_4^- \ (8)\]

The synthesis was analogous to that of 1 with \((\text{MeO})_2\text{P} \cdot \text{S} \cdot \text{SH}\) (30 µl, 39 mg, 0.24 mmol), NaBF4 (100 mg, 0.91 mmol) and \{[(\text{MeP})\text{Au}]_3\}^+ \cdot \text{BF}_4^- (150 mg, 0.16 mmol) to give 161 mg (85 %) of 8. M.p. 174°C (decomp.). \(\text{CsH}_{34}\text{Au}_2\text{BF}_4\cdot \text{O}_2\text{P}\cdot \text{S}_2\) (789.98); C 32.13 (calcd. 12.45), H 3.00 (3.06), S 8.20 (8.09). \(^1\text{H} \text{NMR} \) (CDCl3): \(\delta = 3.86\) (d, 6 H, \(2J_{\text{H},\text{P}} = 15\) Hz, OCH3), 1.68 (d, 18 H, \(2J_{\text{H},\text{P}} = 11\) Hz, AuPMe3); \(^1\text{C} \{'\text{H}\} \text{NMR} \) (CDCl3): \(\delta = 54.4\) (d, \(2J_{\text{C},\text{P}} = 7\) Hz, OCH3), 15.9 (d, \(2J_{\text{C},\text{P}} = 38\) Hz, AuPMe3); \(^3\text{P} \{'\text{H}\} \text{NMR} \) (CDCl3): \(\delta = 109.4\) (s, 1 P, \((\text{MeO})_2\text{P}\cdot \text{S}\)_2); -3.5 (s, 2 P, Au(PMe3)). FAB-MS (NBA), \(m/z \%\): 703 (100) [M\(^+\)].

Crystal Structure Determination

Suitable single crystals of 3, 5, and 6 were sealed into glass capillaries and used for measurement of precise cell constants and intensity data collection. During data
Table I. Crystal data, data collection, and structure refinement for compounds 5, 6, and 3.

<table>
<thead>
<tr>
<th></th>
<th>5</th>
<th>6</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Crystal data</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formula</td>
<td>C_{10}H_{28}Au_{2}BF_{4}O_{2}P_{3}S_{2}</td>
<td>C_{47}H_{53}Au_{5}BCl_{3}F_{4}O_{2}P_{3}S_{2}</td>
<td>C_{47}H_{53}Au_{5}BCl_{3}F_{4}O_{2}P_{3}S_{2}</td>
</tr>
<tr>
<td>M_r</td>
<td>818.10</td>
<td>1332.29</td>
<td>1332.29</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
<td>monoclinic</td>
<td>trigonal</td>
</tr>
<tr>
<td>Space group</td>
<td>P1</td>
<td>P2/a</td>
<td>P3</td>
</tr>
<tr>
<td>a (Å)</td>
<td>10.141(1)</td>
<td>26.769(2)</td>
<td>24.271(2)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>10.517(1)</td>
<td>12.236(1)</td>
<td>24.271(2)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>22.729(1)</td>
<td>29.293(2)</td>
<td>15.410(2)</td>
</tr>
<tr>
<td>α (°)</td>
<td>96.15(1)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
<td>97.51(1)</td>
<td>103.12(1)</td>
<td>90</td>
</tr>
<tr>
<td>γ (°)</td>
<td>95.23(1)</td>
<td>90</td>
<td>120</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>2380.0(4)</td>
<td>9344.3(12)</td>
<td>7861.6(14)</td>
</tr>
<tr>
<td>ρ_{calc} (g cm⁻³)</td>
<td>2.283</td>
<td>2.894</td>
<td>1.767</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>F(000)</td>
<td>1520</td>
<td>5120</td>
<td>4068</td>
</tr>
<tr>
<td>μ(MoKα) (cm⁻¹)</td>
<td>127.23</td>
<td>67.44</td>
<td>59.67</td>
</tr>
<tr>
<td><strong>Data collection</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T (°C)</td>
<td>-78</td>
<td>-78</td>
<td>-70</td>
</tr>
<tr>
<td>Scan mode</td>
<td>ω/θ</td>
<td>ω/θ</td>
<td>ω</td>
</tr>
<tr>
<td>hkl Range</td>
<td>-12→12, -12→12, 0→27</td>
<td>0→32, 0→15, -36→35</td>
<td>-29→0, 0→29, -18→0</td>
</tr>
<tr>
<td>sin(θ/λ) max (Å⁻¹)</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
</tr>
<tr>
<td>Measured reflections</td>
<td>9288</td>
<td>9332</td>
<td>10998</td>
</tr>
<tr>
<td>Unique reflections</td>
<td>9288</td>
<td>9138 [R_{int} = 0.0331]</td>
<td>10222 [R_{int} = 0.0360]</td>
</tr>
<tr>
<td>Refls. used for refinement</td>
<td>8687</td>
<td>8332</td>
<td>8546</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Difabs</td>
<td>Difabs</td>
<td>Difabs</td>
</tr>
<tr>
<td><strong>Refinement</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Refined parameters</td>
<td>433</td>
<td>528</td>
<td>514</td>
</tr>
<tr>
<td>Final R values [I &gt;2σ(I)]</td>
<td>0.0336</td>
<td>0.0296</td>
<td>0.0535</td>
</tr>
<tr>
<td>wR2</td>
<td>0.0778</td>
<td>0.0630</td>
<td>0.1372</td>
</tr>
<tr>
<td>(shift/error)max</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>ρ_{fin}(max/min) (eÅ⁻³)</td>
<td>1.425/-1.233</td>
<td>1.281/-0.811</td>
<td>2.683/-1.895</td>
</tr>
</tbody>
</table>

[a] R = Σ||F_{o}|-|F_{c}||/Σ|F_{o}|; [b] wR2 = \{(Σ[w(F_{o}^2-F_{c}^2)^2]/Σ[w(F_{o}^2)^2])\}^{1/2}; w = 1/[σ^2(F_{o}^2)+(ap^2+bp)]; a = 0.0295 (5), 0.0305 (6), 0.0900 (3); b = 21.22 (5), 39.78 (6), 0.00 (3).

Collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for either compound. Diffraction intensities were corrected for Lorentz, polarization and absorption effects. The structures were solved by direct methods and refined by full matrix least-squares calculations against F². The thermal motion of all non-hydrogen atoms was treated anisotropically except for those of the highly disordered BF₄⁻ anion and of the CHCl₃ solvent molecule of compound 3. All hydrogen atoms were calculated in idealized positions and their isotropic thermal parameters were tied to that of the adjacent carbon atom by a factor of 1.5. Details on crystal data, data collection and structure refinement are summarized in Table I. Important interatomic distances and angles are given in the corresponding figure captions. Further information may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, quoting the depository numbers CSD-408715 (3), -408714 (5) and -408716 (6), the names of the authors, and the full journal citation.

Acknowledgements

This work was supported by Deutsche Forschungsgemeinschaft, by Fonds der Chemischen Industrie, and, through the donation of chemicals, by Degussa AG and Heraeus GmbH. The authors are grateful to Mr. Riede for establishing the X-ray data sets.