Synthesis of chlorodiphenylgermanium dithiocarbamates

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Thirteen chlorodiphenylgermanium dithiocarbamates of the general formula, Ph₂Ge(Cl)S₂CNRR', [where NRR' = NMe₂, NEt₂, N(n-Pr)₂, N(n-Bu)₂, N(CH₂)₄, N(CH₂)₅, N(CH₂CH₂)₂O, N(CH₂CH₂OH)₂, N(CH₃)Ph, NPh₂, N(CH₃)COPh, N(COCH₂)₂, N(CH=CH)₂] have been prepared by the reaction of dithiocarbamates with the appropriate diphenylgermanium dichloride in 1:1 stoichiometry. Their structures have been characterized by elemental analyses, IR, ¹H NMR and mass spectra. These results reveal that the dithiocarbamate ligands are coordinated to Ge in an anisobidentate fashion.

In recent years, the chemistry of organogermain compounds was extensively studied because of their biological activity. In our earlier work, the triphenylgermanium heterocyclic carboxylates, dithiocarbamates, alkynyl or alkenyl phosphate were synthesized and their structure and biological activities were also studied. So far, the diphenylgermanium derivatives of dithiocarbamate have not been reported. Herein we report the synthesis of chlorodiphenylgermanium dithiocarbamates by the reaction of diphenylgermanium dichloride with dithiocarbamates in 1:1 stoichiometry and their IR, ¹H NMR and mass spectra are discussed.

Experimental Section

Melting points were determined using a kofler instrument, but the temperature was not calibrated. ¹H NMR spectra were recorded on a Jeol-FX-90Q spectrometer in CDCl₃ using TMS as internal reference (chemical shifts in δ, ppm); IR spectra on a Nicolet-460 spectrophotometer using KBr pellets in the 4000-400cm⁻¹ range. The carbon, hydrogen and nitrogen contents of the compounds were determined by a PE-2400II 11 06-element al analyses instrument. The mass spectra were recorded on a HP-5988A mass spectrometer operating at 70 eV.

Dithiocarbamates were prepared according to the reported method. Carbon disulfide was dried over phosphorus(V) oxide and distilled prior to use.

The compounds 1-13 were synthesized according to the following equation.

Ph₂GeCl₂ + R'R'NC₂S₂Na → Ph₂Ge(Cl)S₂CNRR'

(1-13)

NRR'=N(CH₃)₂ (1), N(C₂H₅)₂ (2), N(n-C₃H₇)₂ (3), N(n-C₄H₉)₂ (4), N(CH₂)₄ (5), N(CH₂)₅ (6), N(CH₂CH₂O)₂ (7), N(CH₂CH₂OH)₂ (8), N(CH₃)Ph (9), N-Pb₂ (10), HN(CH₃)COPh (11), N(OCH₂)₂ (12), N(CH=CH)₂ (13)

Ph₂GeCl₂ (1.0 mmole) and anhydrous sodium dithiocarbamate (1.0 mmole) were added to 10 mL of dry carbon disulfide and stirred for 8 hr at 30°C under N₂ atmosphere. The precipitated salts were removed by filtration and the filtrate was slowly evaporated in vacuo. The white solid thus obtained, were recrystallized from dichloromethane-hexane and dried to give colourless crystals.

Results and Discussion

The elemental analyses and physical properties of compounds 1-13 are shown in Table I. They are soluble in organic solvents such as benzene, methylene chloride, chloroform, carbon disulfide and tetrahydrofuran. They were prepared under scrupulously water-free conditions. Otherwise, no germanium containing dithiocarbamate derivatives were formed but diphenylgermanium oxides could be detected.

The IR spectra of compounds 1-13 are shown in Table II. The phenyl group in all compounds showed absorption at 3049-3073 cm⁻¹. The characteristic stretching vibration of germanium carbon (Ge-Ph) is identified by a very strong absorption at 1091-1100 cm⁻¹. The O-H stretching vibration in compound 8 exhibits a strong absorption at 3424 cm⁻¹ and that of C=O in compounds 11 and 12 at 1664 and 1694 cm⁻¹. A new absorption band appears at 453-463 cm⁻¹ which is the characteristic vibrations of Ge-S bond formed. One obvious feature of the IR spectra is the similarity of the stretching bands arising from the dithiocarbamate group. The relatively high value for 𝜏(C=S=N) is similar to that reported for analogous tin compounds. This suggests that the dithiocarbamate group of these compounds are linked to Ge in a bidentate fashion.
Table I — Physical and analytical data of the compounds 1-13

<table>
<thead>
<tr>
<th>Compd</th>
<th>Mol. formula</th>
<th>Yield (%)</th>
<th>m.p. °C</th>
<th>Found % (Calcd)</th>
<th>C</th>
<th>H</th>
<th>N</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>C21H18CIN5S2Ge</td>
<td>65.0</td>
<td>115-17</td>
<td>47.38 4.36 3.73</td>
<td>47.10</td>
<td>4.21</td>
<td>3.66</td>
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<td>2</td>
<td>C21H18CIN5S2Ge</td>
<td>70.2</td>
<td>134-35</td>
<td>49.46 4.81 3.55</td>
<td>49.74</td>
<td>4.91</td>
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<td>3</td>
<td>C21H18CIN5S2Ge</td>
<td>58.8</td>
<td>160-62</td>
<td>52.31 5.68 3.30</td>
<td>52.03</td>
<td>5.52</td>
<td>3.19</td>
</tr>
<tr>
<td>4</td>
<td>C21H18CIN5S2Ge</td>
<td>57.7</td>
<td>174-76</td>
<td>54.89 6.23 3.03</td>
<td>54.50</td>
<td>6.05</td>
<td>3.00</td>
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<tr>
<td>5</td>
<td>C21H18CIN5S2Ge</td>
<td>72.5</td>
<td>135-37</td>
<td>49.75 4.52 3.49</td>
<td>49.98</td>
<td>4.44</td>
<td>3.43</td>
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<td>C21H18CIN5S2Ge</td>
<td>80.2</td>
<td>147-49</td>
<td>50.84 4.71 3.25</td>
<td>51.17</td>
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<td>156-58</td>
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<td>3.30</td>
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<td>4.56</td>
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<td>9</td>
<td>C21H18CIN5S2Ge</td>
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<td>100-01</td>
<td>53.88 4.03 3.21</td>
<td>54.08</td>
<td>4.08</td>
<td>3.15</td>
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<td>140-41</td>
<td>59.60 4.05 2.73</td>
<td>59.27</td>
<td>3.98</td>
<td>2.76</td>
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<tr>
<td>11</td>
<td>C21H18CIN5S2Ge</td>
<td>52.8</td>
<td>110-12</td>
<td>53.06 3.65 3.30</td>
<td>53.38</td>
<td>3.84</td>
<td>2.96</td>
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<td>12</td>
<td>C21H18CIN5S2Ge</td>
<td>61.5</td>
<td>119-21</td>
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<td>46.78</td>
<td>3.23</td>
<td>3.21</td>
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<tr>
<td>13</td>
<td>C21H18CIN5S2Ge</td>
<td>58.7</td>
<td>48-50</td>
<td>50.16 3.23 3.31</td>
<td>50.48</td>
<td>3.49</td>
<td>3.46</td>
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Table II — IR spectra of compounds 1-13

<table>
<thead>
<tr>
<th>Compd (Ph-H)</th>
<th>C≡N</th>
<th>(CS)2</th>
<th>(Ge-Ph)</th>
<th>(Ge-S)</th>
<th>Other</th>
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<tr>
<td>1 3055m 1487m</td>
<td>1182s 992s 1098s</td>
<td>456s</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>2 3068n 1495s</td>
<td>1151s 997s 1091s</td>
<td>463s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 3049m 1487s</td>
<td>1150s 995s 1095s</td>
<td>475s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 3059m 1489m</td>
<td>1146s 993s 1100s</td>
<td>460m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 3045m 1482s</td>
<td>1140s 998s 1099s</td>
<td>455s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 3054m 1484m</td>
<td>1157s 997s 1100s</td>
<td>459s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7 308m 1480s</td>
<td>1151s 991s 1096s</td>
<td>453s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8 3069m 1481s</td>
<td>1176s 917s 1092s</td>
<td>462s 3424s (OH)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9 3050s 1484s</td>
<td>1149s 998s 1099s</td>
<td>462s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 3053m 1483s</td>
<td>1147m 997m 1100s</td>
<td>459s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11 3052m 1484m</td>
<td>1182m 997m 1100s</td>
<td>459s 1664s (C=O)</td>
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<tr>
<td>12 3073m 1485s</td>
<td>1192s 1002s 1100s</td>
<td>459s 1694s (C=O)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13 3052m 1480s</td>
<td>1138s 992s 1094s</td>
<td>454s</td>
<td></td>
<td></td>
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</table>

In IR spectra, the important bands that arise from v(CS)2asym and v(CS)2sym appear at 1138-1182 and 992-1002cm⁻¹, respectively. The Δv value v(CS)2asym - v(CS)2sym is 146-190cm⁻¹, which is much smaller than the Δν* for the R2NCS2R'⁹ but it is larger than the Δν' for analogous tin compounds¹⁰. This shows the dithiocarbamate group of compounds 1-13 are coordinated to germanium atom in an anisobidentate fashion⁴.

The ¹H NMR spectra of compounds 1-13 are given in Table III. It is observed that the chemical shifts of the proton of the phenyl group(Ge-Ph) of compounds 1-13 exhibit signals at δ 7.29-7.65 ppm as multiplet, and shift upfield as compared to that of the diphenylgermanium dichloride. The proton signals of methylene or methyl connected directly with nitrogen appear at δ 3.67-4.02 ppm. They shift downfield at δ 0.5-0.8 ppm as compared to that of the salts of appropriate acid. It is possible that the coordinated dithiocarbamyl group is more electronegative than without any coordination¹⁰.

The important mass spectra are listed in Table IV. Parent molecular ions in low abundance are detected for the title compounds. No ions of mass higher than the parent are detected, nor are there fragments containing more than one germanium atom. So these compounds have monomeric structure. The most

Table III — ¹H NMR spectra of the compounds 1-13

<table>
<thead>
<tr>
<th>Compd</th>
<th>¹H NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.68(6Hs, NCH3), 7.36-7.62(10Hm,GeC6H5)</td>
</tr>
<tr>
<td>2</td>
<td>1.30(6Ht, J=6.23Hz, CH3), 3.82 (4Hs, J=6.23Hz, NCH3), 7.40-7.67(10Hm,GeC6H5)</td>
</tr>
<tr>
<td>3</td>
<td>0.98(6Ht, J=7.18Hz, CH3), 1.71 (4Hm,CH2), 3.79(4Ht, J=6.42Hz,NCH3), 7.35-7.60(10Hm,GeC6H5)</td>
</tr>
<tr>
<td>4</td>
<td>0.95 (6Ht, J=6.96Hz, CH3), 1.24-1.67(8Hm,CH2CH2), 3.88(4Ht, J=6.32Hz, NCH3), 7.30-7.57(10Hm,GeC6H5)</td>
</tr>
<tr>
<td>5</td>
<td>1.87(4Ht, J=7.00Hz, CH2CH3), 3.86(4Ht, J=6.40Hz,NCH3), 7.33-7.65 (10Hm,GeC6H5)</td>
</tr>
<tr>
<td>6</td>
<td>1.72 (6Hm,CH2CH2CH2), 3.72(4Hs, J=6.25Hz,NCH3), 7.36-7.57(10Hm,GeC6H5)</td>
</tr>
<tr>
<td>7</td>
<td>3.87(4Ht, J=7.12Hz,NCH3), 4.10(4Hs, J=7.12Hz,OCH2), 7.29-7.62(10Hm,GeC6H5)</td>
</tr>
<tr>
<td>8</td>
<td>4.02(4Ht, J=6.85Hz,NCH3), 4.16(4Hs, J=6.85Hz,OCH2), 7.30-7.50(10Hm,GeC6H5)</td>
</tr>
<tr>
<td>9</td>
<td>3.67(3Hs,NCH3), 7.42-7.57(10Hm,GeC6H5), 7.63-7.85(5Hm,NC6H5)</td>
</tr>
<tr>
<td>10</td>
<td>3.76-7.50(10Hm,GeC6H5), 7.57-7.85 (10Hm,NC6H5)</td>
</tr>
<tr>
<td>11</td>
<td>2.38 (3Hs,COCH3), 7.37-7.51 (10Hm,GeC6H5), 7.69-7.81 (5Hm,NC6H5)</td>
</tr>
<tr>
<td>12</td>
<td>2.77(4Hs,COCH2), 7.34-7.52(10Hm,GeC6H5)</td>
</tr>
<tr>
<td>13</td>
<td>2.77(4Hm,NCH=NCH3), 7.35-7.56(10Hm,GeC6H5)</td>
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Table IV — Mass spectra for compounds 1, 6, 7, 9 and 13

<table>
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<tr>
<th>Fragment Ions</th>
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<th>6</th>
<th>7</th>
<th>9</th>
<th>13</th>
</tr>
</thead>
<tbody>
<tr>
<td>M⁺</td>
<td>386(4.6)</td>
<td>423(5.5)</td>
<td>425(5.2)</td>
<td>445(4.1)</td>
<td>405(5.1)</td>
</tr>
<tr>
<td>M⁺-Cl</td>
<td>348(6.4)</td>
<td>388(8.0)</td>
<td>390(10.5)</td>
<td>410(5.8)</td>
<td>370(8.0)</td>
</tr>
<tr>
<td>M⁺-S₂CNRR’</td>
<td>263(13.5)</td>
<td>263(10.2)</td>
<td>263(20.1)</td>
<td>263(23.4)</td>
<td>263(357)</td>
</tr>
<tr>
<td>Ph₂Ge⁺</td>
<td>228(100)</td>
<td>228(100)</td>
<td>228(100)</td>
<td>228(100)</td>
<td>228(100)</td>
</tr>
<tr>
<td>RR’NCS₂H⁺</td>
<td>161(1.2)</td>
<td>183(42.2)</td>
<td>130(42.2)</td>
<td>150(22.4)</td>
<td>110(18.2)</td>
</tr>
<tr>
<td>RR’NCS⁺</td>
<td>88(60.4)</td>
<td>128(54.8)</td>
<td>161(1.2)</td>
<td>183(42.2)</td>
<td>130(42.2)</td>
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abundant ions in these spectra is germanium containing fragment at m/z 228 which could be assigned to Ph₂Ge⁺.

Acknowledgements

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References