Gold Diselenocarbamato Complexes

By J. G. M. VAN DER LINDEN and W. P. M. NIJSSEN

With 1 Figure

Abstract. The preparation, u. v. and i. r. spectra and electrical conductivity of some gold diselenocarbamato complexes Au(et₂dsc), [Au(et₂dsc)₂]Br, [Au(bu₂dsc)₂][AuBr₂] and Br₂Au(et₂dsc) are reported. [Au(et₂dsc)₂]Br undergoes a reversible one-electron reduction with E₁/₂ = −0.43 V vs. SCE, in contrast with the irreversible reduction observed for the analogous sulfur complex.

Gold-diselenocarbamato-Komplexe

Inhaltsübersicht. Darstellung, UV- und IR-Spektren und die elektrische Leitfähigkeit der Golddiselenocarbamato-Komplexe Au(et₂dsc), [Au(et₂dsc)₂]Br, [Au(bu₂dsc)₂][AuBr₂] und Br₂Au(et₂dsc) werden beschrieben. Die Reduktion durch Übertragung eines Elektrons des [Au(et₂dsc)₂]Br bei E₁/₂ = −0.43 V (gegen SCE) ist reversibel, im Gegensatz zu der irreversiblen Reduktion des analogen Schwefelkomplexes.

The existence of gold(II)diselenocarbamate has recently been detected with esr techniques1). However, no pure sample of a gold diselenocarbamato complex could be obtained by these investigators.

We succeeded to prepare in low yields crystalline samples of Au(et₂dsc), [Au(et₂dsc)₂]Br and Br₂Au(et₂dsc). (R₂dsc = N,N-di-alkyldiselenocarbamate; R₂dsc = N,N-di-alkyldithiocarbamate). The gold(I) complex was obtained from the reaction of dibromoaurato(I)-containing solutions with Zn(et₂dsc)₂ and the rapid extraction and purification of the formed precipitate. The gold(I) complex is unstable in solution and disproportionates easily. Thus, [Au(et₂dsc)₂]Br was prepared from the reaction of AuBr₂ with Zn(et₂dsc)₂, when the reaction mixture was left standing overnight. From excess AuBr₂ with Zn(bu₂dsc)₂ the [Au(bu₂dsc)₂][AuBr₂] complex was prepared. Treatment of [Au(et₂dsc)₂]Br with bromine resulted in the formation of Br₂Au(et₂dsc).

The ultraviolet spectrum of $\text{Au(et}_2\text{dsc)}$ in DMF is nearly equal to that found for $[\text{Au(bu}_2\text{dte)}]_2$ (Fig. 1). For the $[\text{Au(et}_2\text{dsc)}]_2\text{Br}$ complex in dichloromethane solution the absorption maxima are shifted to a lower frequency as compared with the $[\text{Au(bu}_2\text{dte)}]_2\text{Br}$ complex. The intense band found at 34.3 kK ($\varepsilon \approx 46.000$) may be compared with the band at 36.1 kK found for the sulfur analog. The absorption maxima found at 30.9 kK ($\varepsilon \approx 24.000$) and 28.9 kK ($\varepsilon \approx 23.000$) for the selenocomplex may be compared with the intense band at 31.6 kK found for $[\text{Au(bu}_2\text{dte)}]_2\text{Br}$ (Fig. 1).

The results of the recorded infrared spectra are given in Table 1. The C–N stretching frequency for the gold(III)diselenocarbamates is found approximately 10 cm$^{-1}$ lower as compared with the sulfur complexes. The $\nu$ (Au–Se) is calculated at 264 cm$^{-1}$ (found: 253 cm$^{-1}$ and 259 cm$^{-1}$) from the gold-sulfur stretching frequency at 378 cm$^{-1}$ and with only the mass effect taken in consideration.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu$ (C–N)</th>
<th>$\nu$ (Au–S) or $\nu$ (Au–Se)</th>
<th>$\nu$ (Au–Br)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Au(et}_2\text{dte)}]_2$</td>
<td>1493</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Au(et}_2\text{dsc)}$</td>
<td>1494</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Au(et}_2\text{dte)}]_2\text{Br}$</td>
<td>1545</td>
<td>378</td>
<td></td>
</tr>
<tr>
<td>$[\text{Au(et}_2\text{dsc)}]_2\text{Br}$</td>
<td>1533</td>
<td>253</td>
<td></td>
</tr>
<tr>
<td>$[\text{Au(bu}_2\text{dte)}]_2[\text{AuBr}_4]$</td>
<td>1550</td>
<td>380</td>
<td>255</td>
</tr>
<tr>
<td>$[\text{Au(bu}_2\text{dsc)}]_2[\text{AuBr}_4]$</td>
<td>1539</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>$\text{Br}_2\text{Au(et}_2\text{dte)}$</td>
<td>1573</td>
<td>378</td>
<td>243, 216</td>
</tr>
<tr>
<td>$\text{Br}_2\text{Au(et}_2\text{dsc)}$</td>
<td>1562</td>
<td>259</td>
<td>247, 222</td>
</tr>
</tbody>
</table>


Conductivity measurements of [Au(et₂dsc)₂]Br in nitrobenzene in the concentration range (2—9) · 10⁻⁴ molar revealed this complex to be a 1:1 electrolyte with \( \Lambda_0 = 33.3 \text{ cm}^2 \text{ ohm}^{-1} \text{ mole}^{-1} \). With this value and the single ion conductivity of the bromide ion (21.9) the single ion conductivity \( \lambda_{\text{sel}}[\text{Au(et₂dsc)}_2] = 11.4 \) could be calculated. This value is about the same as was found for Au(bu₂dtc)⁺ and Cu(bu₂dtc)⁺ being 9.1⁴ and 9.2⁵, respectively.

Like the sulfur containing complexes the Au(et₂dsc)⁺ ion could be reduced at \(-0.43 \text{ V vs SCE}\) in CH₂Cl₂ solution using a rotating platinum electrode. The redox reaction was reversible \( (E_{3/4} - E_{1/4} = 63 \text{ mV}) \) in contrast with the irreversible reduction found at \(-0.26 \text{ V}\) for the analogous [Au(et₂dtc)₂]Br compound⁶).

In view of the similar behaviour of the Au(et₂dsc)⁺ and Au(et₂dsc)⁺ complexes it is reasonable to assume that they have the same planar geometry.

Experimental

Physical measurements. Infrared spectra were recorded with a Perkin Elmer 257 and a Hitachi EPI-L spectrophotometer, using the KBr disc technique. Ultraviolet spectra were recorded with a Unicam SP 800 spectrophotometer. Voltammetric⁷) and electrical conductivity measurements⁴) were carried out as described.

Preparations. \( \text{Au(et₂dtc)}^\text{4} \), \( [\text{Au(et₂dtc)}_2]\text{Br}^\text{4} \), \( [\text{Au(bu₂dtc)}_2][\text{AuBr}_3]^\text{2} \), \( \text{Br}_2\text{Au} (\text{et₂dtc})^{10} \) and Zn(et₂dsc) were prepared as described.

\text{Au(et₂dsc)}. A saturated aqueous salt solution of 0.30 g KAuBr₄ was reduced at \(-5^\circ \text{C}\) with an equivalent amount of sodium sulphite as described⁸). This solution was immediately added to 0.15 g Zn(et₂dsc)₂ dissolved in 10 ml of DMF. A red precipitate was obtained which was extracted with three 100 ml portions of chloroform. The yellow chloroform solution was filtered and to the filtrate diethyl ether was added until the first cloudiness. After cooling at 0°C for three hours the formed red precipitate was filtered and thoroughly washed with methanol to remove the gold(III)diselenocarbamates. In this way 0.05 g of a crystalline product was obtained mp. 174°C dec.

Anal. found: C 14.5; H 2.4; N 3.1; Au 45.9; calc. for C₄H₁₀NSe₂Au: C 13.68; H 2.30; N 3.19; Au 44.86.

⁴) J. G. M. VAN DER LINDEN, Recueil Trav. chim. Pays-Bas 90, 1027 (1971).
⁵) A. W. GAL, personal communication.
[Au(et$_2$dsc)$_2$]Br. A solution of 0.61 g KAuBr$_4$ in 750 ml of a methanol-water mixture (2:1) saturated with potassium bromide was reduced as described above. This solution was added to 0.30 g Zn(et$_2$dsc)$_2$ dissolved in 15 ml of chloroform. The solution turned red and was stirred for five hours. After standing overnight a dark brown precipitate was formed, which was removed by filtration. The filtrate was extracted twice with 100 ml of chloroform. The chloroform was removed in vacuo and the orange red product was recrystallized twice from ethanol giving 0.05 g orange red needles mp. 265°C dec. Another 0.05 g crystalline product was obtained by adding diethyl ether to the ethanol filtrates.

**Anal. found:** C 16.0; H 2.5; N 3.9; Br 10.4; Au 26.3;
calc. for C$_{15}$H$_{36}$N$_2$Se$_4$AuBr: C 15.78; H 2.65; N 3.68; Br 10.50; Au 25.89.

[Au(bu$_2$dsc)$_2$][AuBr$_4$]. 1.1 g KAuBr$_4$ in 700 ml of a saturated salt solution was reduced as described above. This solution was immediately added to 0.32 g Zn(bu$_2$dsc)$_2$ dissolved in 25 ml of DMF. The resulted solution was extracted with CH$_2$Cl$_2$ during which extraction an appreciable amount of the complex decomposed in gold and selenium. A red product result after filtration and evaporation of the solvent. This product was washed with methanol and recrystallized from dichloromethane and diethyl ether. 0.05 g of a yellow crystalline product was obtained obtained mp. 149—152°C.

**Anal. found:** C 19.1; H 3.2; N 2.5; Au 35.2;
calc. for C$_{18}$H$_{36}$N$_2$Se$_4$Au$_2$Br$_2$: C 18.8; H 3.16; N 2.44; Au 34.18.

Br$_2$Au(et$_2$dsc$-)$. To a solution of 0.04 g of [Au(et$_2$dsc)$_2$]Br in 10 ml of CH$_2$Cl$_2$ was added 0.01 g Br$_2$ in 10 ml of the same solvent. Diethyl ether was added till the first cloudiness appeared. On cooling 0.02 g brown needles were obtained mp. 286°C dec. This product showed no conductivity in nitrobenzene solutions. The recrystallization of 0.01 g of this product in acetonitrile yielded 0.005 g red needles.

**Anal. found:** C 10.9; H 2.1; N 2.7;
calc. for C$_6$H$_{14}$NSe$_2$AuBr$_2$: C 10.03; H 1.68; N 2.34.

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