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 $\text{Au}(\text{et}_2\text{dsc})$, $[\text{Au}(\text{et}_2\text{dsc})_2]\text{Br}$, $[\text{Au}(\text{bu}_2\text{dsc})_2][\text{AuBr}_2]$ and $\text{Br}_2\text{Au}(\text{et}_2\text{dsc})$ are reported. $[\text{Au}(\text{et}_2\text{dsc})_2]\text{Br}$ undergoes a reversible one-electron reduction with $E_{1/2} = -0.43$ 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 $\text{Au}(\text{et}_2\text{dsc})$, $[\text{Au}(\text{et}_2\text{dsc})_2]\text{Br}$, $[\text{Au}(\text{bu}_2\text{dsc})_2][\text{AuBr}_2]$ und $\text{Br}_2\text{Au}(\text{et}_2\text{dsc})$ werden beschrieben. Die Reduktion durch Übertragung eines Elektrons des $[\text{Au}(\text{et}_2\text{dsc})_2]\text{Br}$ bei $E_{1/2} = -0,43$ 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 $\text{Au}(\text{et}_2\text{dsc})$, $[\text{Au}(\text{et}_2\text{dsc})_2]\text{Br}$ and $\text{Br}_2\text{Au}(\text{et}_2\text{dsc})$. ($\text{R}_2\text{dsc} = \text{N,N-di-alkyldiselenocarbamate}$; $\text{R}_2\text{dtc} = \text{N,N-di-alkyldithiocarbamate}$). The gold(I) complex was obtained from the reaction of dibromoaurate(I)-containing solutions with $\text{Zn}(\text{et}_2\text{dsc})_2$ and the rapid extraction and purification of the formed precipitate. The gold(I) complex is unstable in solution and disproportionates easily. Thus, $[\text{Au}(\text{et}_2\text{dsc})_2]\text{Br}$ was prepared from the reaction of AuBr_2^- with $\text{Zn}(\text{et}_2\text{dsc})_2$, when the reaction mixture was left standing overnight. From excess AuBr_2^- with $\text{Zn}(\text{bu}_2\text{dsc})_2$ the $[\text{Au}(\text{bu}_2\text{dsc})_2][\text{AuBr}_2]$ complex was prepared. Treatment of $[\text{Au}(\text{et}_2\text{dsc})_2]\text{Br}$ with bromine resulted in the formation of $\text{Br}_2\text{Au}(\text{et}_2\text{dsc})$.

¹⁾ R. KIRMSE, B. LORENZ, W. WINDSCH and E. HOYER, Z. anorg. allg. Chem. **384**, 160 (1971).

The ultra violet spectrum of $\text{Au}(\text{et}_2\text{dsc})$ in DMF is nearly equal to that found for $[\text{Au}(\text{bu}_2\text{dte})_2]_2^{2+}$ (Fig. 1). For the $[\text{Au}(\text{et}_2\text{dsc})_2]\text{Br}$ complex in dichloromethane solution the absorption maxima are shifted to a lower frequency as compared with the $[\text{Au}(\text{bu}_2\text{dte})_2]\text{Br}$ complex³). The intense band found at 34.3 kK ($\epsilon \simeq 46.000$) may be compared with the band at

Fig. 1. Ultraviolet spectra of gold diselenocarbamate complexes

36.1 kK found for the sulfur analog. The absorption maxima found at 30.9 kK ($\epsilon \simeq 24.000$) and 28.9 kK ($\epsilon \simeq 23.000$) for the selenocomplex may be compared with the intense band at 31.6 kK found for $[\text{Au}(\text{bu}_2\text{dte})_2]\text{Br}$ (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 $\nu(\text{Au—Se})$ 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 1
Infrared Absorption Bands of Gold diselenocarbamate Complexes (cm^{-1})

Complex	$\nu(\text{C—N})$	$\nu(\text{Au—S})$ or $\nu(\text{Au—Se})$	$\nu(\text{Au—Br})$
$[\text{Au}(\text{et}_2\text{dte})_2]$	1493		
$\text{Au}(\text{et}_2\text{dsc})$	1494		
$[\text{Au}(\text{et}_2\text{dte})_2]\text{Br}$	1545	378	
$[\text{Au}(\text{et}_2\text{dsc})]\text{Br}$	1533	253	
$[\text{Au}(\text{bu}_2\text{dte})_2][\text{AuBr}_2]$	1550	380	255
$[\text{Au}(\text{bu}_2\text{dsc})_2][\text{AuBr}_2]$	1539	250	250
$\text{Br}_2\text{Au}(\text{et}_2\text{dte})$	1573	378	243, 216
$\text{Br}_2\text{Au}(\text{et}_2\text{dsc})$	1562	259	247, 222

²) H. J. A. BLAAUW, Ph. D. Thesis, Nijmegen 1965.

³) P. T. BEURSKENS, J. A. CRAS and J. G. M. VAN DER LINDEN, Inorg. Chem. [Washington] **9**, 475 (1970).

Conductivity measurements of $[\text{Au}(\text{et}_2\text{dsc})_2]\text{Br}$ in nitrobenzene in the concentration range $(2-9) \cdot 10^{-4}$ 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 $\lambda_0[\text{Au}(\text{et}_2\text{dsc})_2^+] = 11.4$ could be calculated. This value is about the same as was found for $\text{Au}(\text{bu}_2\text{dte})_2^+$ and $\text{Cu}(\text{bu}_2\text{dte})_2^+$ being 9.1⁴) and 9.2⁵), respectively.

Like the sulfur containing complexes the $\text{Au}(\text{et}_2\text{dsc})_2^+$ ion could be reduced at -0.43 V vs SCE in CH_2Cl_2 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 V for the analogous $[\text{Au}(\text{et}_2\text{dte})_2]\text{Br}$ compound⁶).

In view of the similar behaviour of the $\text{Au}(\text{et}_2\text{dsc})_2^+$ and $\text{Au}(\text{et}_2\text{dte})_2^+$ 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. Voltametric⁷) and electrical conductivity measurements⁴) were carried out as described.

Preparations. $\text{Au}(\text{et}_2\text{dte})_2^8$), $[\text{Au}(\text{et}_2\text{dte})_2]\text{Br}^4$), $[\text{Au}(\text{bu}_2\text{dte})_2][\text{AuBr}_2]^9$), $\text{Br}_2\text{Au}(\text{et}_2\text{dte})^{10}$) and $\text{Zn}(\text{et}_2\text{dsc})_2^{11}$) were prepared as described.

$\text{Au}(\text{et}_2\text{dsc})$. A saturated aqueous salt solution of 0.30 g KAuBr_4 was reduced at -5°C with an equivalent amount of sodium sulphite as described⁸). This solution was immediately added to $0.15 \text{ g Zn}(\text{et}_2\text{dsc})_2$ 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 $\text{C}_5\text{H}_{10}\text{NSe}_2\text{Au}$: 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.

⁶) J. G. M. VAN DER LINDEN, *J. inorg. nuclear Chem.* **34**, 1645 (1972).

⁷) J. G. M. VAN DER LINDEN and H. G. J. VAN DE ROER, *Inorg. Chim. Acta* **5**, 254 (1971).

⁸) S. ÅKERSTROM, *Ark. Kemi* **14**, 387 (1959).

⁹) P. T. BEURSKENS, H. J. A. BLAAUW, J. A. CRAS and J. J. STEGGERDA, *Inorg. Chem. [Washington]* **7**, 805 (1968).

¹⁰) P. T. BEURSKENS, J. A. CRAS and J. J. STEGGERDA, *Inorg. Chem. [Washington]* **7**, 810 (1968).

¹¹) D. BARNARD and D. T. WOODBRIDGE, *J. chem. Soc. [London]* **1961**, 2922.

[Au(et₂dsc)₂]Br. A solution of 0.61 g KAuBr₄ 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(et₂dsc)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 C₁₀H₂₀N₂Se₄AuBr: C 15.78; H 2.65; N 3.68; Br 10.50; Au 25.89.

[Au(bu₂dsc)₂] [AuBr₂]. 1.1 g KAuBr₄ in 700 ml of a saturated salt solution was reduced as described above. This solution was immediately added to 0.32 g Zn(bu₂dsc)₂ dissolved in 25 ml of DMF. The resulted solution was extracted with CH₂Cl₂ 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 mp. 149–152°C.

Anal. found: C 19.1; H 3.2; N 2.5; Au 35.2;
calc. for C₁₈H₃₆N₂Se₄Au₂Br₂: C 18.8; H 3.16; N 2.44; Au 34.18.

Br₂Au(et₂dsc). To a solution of 0.04 g of [Au(et₂dsc)₂]Br in 10 ml of CH₂Cl₂ was added 0.01 g Br₂ 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 C₅H₁₀NSe₂AuBr₂: C 10.03; H 1.68; N 2.34.

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Nijmegen, Department of Inorganic Chemistry, University of Nijmegen, The Netherlands.

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Anschr. d. Verf.: J. G. M. VAN DER LINDEN and W. P. M. NIJSSEN
Department of Inorganic Chemistry, Toernooiveld
Nijmegen (The Netherlands)