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PREPARATION AND PROPERTIES OF GOLD(III)DITHIOCARBAMATO COMPLEXES

BY

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The preparations of a series of compounds containing the bis(N,N-di-alkyl-dithiocarbamato)gold(III)-ion of formula $[\text{Au}(\text{R}_2\text{dtc})_2]^+X^-$, with $\text{R} = \text{H}$, Me, Et, $n$-Pr, $n$-Bu and Ph, and with $X^- = \text{Br}^-$, $\text{ClO}_4^-$, $\text{PF}_6^-$, $\text{AgBr}_2^-$, $\text{AuBr}_2^-$, $\text{B(Ph)}_4^-$, $\text{Au(S}_2\text{C}_6\text{H}_3\text{CH}_3)_2^-$, and $\text{Au(S}_2\text{C}_6\text{H}_3\text{CN)}_2^-$ are reported.

The C—N stretching frequencies are measured in the crystalline state as well as in chloroform solutions. These data show that some negative ions have a distinct effect on the C—N stretching frequency in the solid state, but this effect is absent in chloroform solutions. Since X-ray studies have shown that these anions are situated near the nitrogen atom of the cation their effect on the C—N frequencies is due to a polarisation of the C—N bond.

Electric conductivity measurements reveal these complexes to be 1:1 electrolytes in nitrobenzene solutions. From the measurements in this solvent several limiting ionic conductances are determined.

Introduction

The recently reported complexes, all with the same cation, $[\text{Au(R}_2\text{dtc})_2]^+X^-$ where $X^- = \text{Br}^-$, $\text{AuBr}_2^-$ and $\text{AuBr}_4^-$ for $\text{R} = n$-butyl, show differences in the C—N stretching frequencies in the infrared spectra. This effect was considered to be due to an inductive effect on the nitrogen by the anions situated close beside it between the butyl chains$^2$.

Further investigations have been made to study this effect in the series $\text{Au(R}_2\text{dtc})_2X$, with $X = \text{ClO}_4^-$, $\text{PF}_6^-$, $\text{B(Ph)}_4^-$, $\text{Au(mnt)}_2^-$ and $\text{Au(tdt)}_2^-$ for $R = n$-butyl and with $X = \text{Br}^-$ and $\text{AuBr}_2^-$ for $R = \text{H}$, methyl, ethyl, $n$-propyl, and phenyl. The infrared spectra have been recorded in the crystalline state as well as in chloroform solutions. To demonstrate that this interaction exists only in the solid state and to show the ionic character of these complexes, conductivity measurements in nitrobenzene were carried out.

1 In this paper the following abbreviations are used: $R_2\text{dtc} = N,N$-di-alkyldithiocarbamate ion $= \text{S}_2\text{CNR}_2^-$, mnt = maleonitriledithiolate ion $= \text{S}_2\text{C}_6(\text{CN})_2^-$, tdt = toluene-3,4-dithiolate ion $= \text{S}_2\text{C}_6\text{H}_2\text{CH}_3^-$.


A scale of limiting ionic equivalent conductances in this solvent based indirectly on tetraisoamylammonium tetraisoamylborate as reference electrolyte is proposed by Coetzee and Cunningham\(^4\). Because these values were obtained by a conversion from their measurements in acetonitrile, we measured the single ion conductivities of several ions of some of the reported complexes in nitrobenzene and compared these with the parameters proposed.

Results and Discussion

The C—N stretching frequencies for several of the newly prepared and related complexes are given in Table I. From these data it can be concluded that the perchlorate and the hexafluorophosphate ions also have a distinct effect on the charge on the nitrogen, resulting in an increased value for the C—N stretching frequency compared with the other complexes. Further information concerning this influence can be obtained from the resolution of the crystal structures of three other compounds \(\text{Au(n-Bu}_{2}\text{dtc)}_{2}\text{CuBr}_{2}\), \(\text{Au(n-Bu}_{2}\text{dtc)}_{2}\text{AgBr}_{2}\), and \(\text{Au(n-Bu}_{2}\text{dtc)}_{2}\text{AuBr}_{2}\).

<table>
<thead>
<tr>
<th>(X^{-})</th>
<th>(\text{Au(n-Bu}<em>{2}\text{dtc)}</em>{2}X) solid</th>
<th>(\text{Au(n-Bu}<em>{2}\text{dtc)}</em>{2}X) soln.</th>
<th>(\text{Au(R}<em>{2}\text{dtc)}</em>{2}\text{Br}) solid</th>
<th>(\text{Au(R}<em>{2}\text{dtc)}</em>{2}\text{Br}) soln.</th>
<th>(\text{Au(R}<em>{2}\text{dtc)}</em>{2}\text{AuBr}_{2}) solid</th>
<th>(\text{Au(R}<em>{2}\text{dtc)}</em>{2}\text{AuBr}_{2}) soln.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Br}^{-})</td>
<td>1575</td>
<td>1547</td>
<td>1475</td>
<td>1455</td>
<td>insol.</td>
<td></td>
</tr>
<tr>
<td>(\text{ClO}_{4}^{-})</td>
<td>1565</td>
<td>1548</td>
<td>1600</td>
<td>1550</td>
<td>1580</td>
<td>Me</td>
</tr>
<tr>
<td>(\text{PF}_{6}^{-})</td>
<td>1565</td>
<td>1548</td>
<td>1550</td>
<td>1550</td>
<td>1570</td>
<td>Et</td>
</tr>
<tr>
<td>(\text{AuBr}_{3}^{-})</td>
<td>1565</td>
<td>1545</td>
<td>1575</td>
<td>1547</td>
<td>1550</td>
<td>n-Pr</td>
</tr>
<tr>
<td>(\text{CuBr}_{3}^{-})</td>
<td>1550</td>
<td>1543</td>
<td>1540</td>
<td>1545</td>
<td>n-Pr</td>
<td>n-Pr</td>
</tr>
<tr>
<td>(\text{AgBr}_{3}^{-})</td>
<td>1550</td>
<td>1543</td>
<td>1442</td>
<td>1430</td>
<td>Ph</td>
<td>Ph</td>
</tr>
<tr>
<td>(\text{AuCl}_{4}^{-})</td>
<td>1550(^a)</td>
<td>1545</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{AuBr}_{5}^{-})</td>
<td>1550(^a)</td>
<td>1545</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{AuI}_{3}^{-})</td>
<td>1550(^a)</td>
<td>1542</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Au(mnt)}_{2}^{-})</td>
<td>1550</td>
<td>1547</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Au(tdt)}_{2}^{-})</td>
<td>1550</td>
<td>1541</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) Ref. 3


Since the AgBr$_2^-$ ion is located close to the sulphur atoms of the dithiocarbamate this ion cannot influence the charge of the nitrogen. Moreover, in the Au(n-Bu$_2$dtc)$_2$Au(mnt)$_2$ compound the cations and the anions alternate in rows with a mutual distance of approximately 5 Å and since the same value for the C—N frequency is found (1550 cm$^{-1}$) for all the complexes Au(n-Bu$_2$dtc)$_2$X with $X =$ CuBr$_2^-$, AgBr$_2^-$, AuCl$_2^-$, AuBr$_2^-$, AuI$_2^-$ and Au(mnt)$_2^-$, we conclude that there is no interaction between these anions and the nitrogen atom in the crystalline state.

For the ethyl and $n$-propyl dithiocarbamates there is, surprisingly, a reversed effect; the C—N frequency for the Br$^-$ complexes is even lower compared with the AuBr$_2^-$ compounds. The differences in frequencies for these anions may also be due to electrostatic effects in the crystalline state and therefore the C—N frequencies for the Au(R$_2$dtc)$_2^+$ compounds were measured in chloroform solutions (Table I). From the values obtained it can be concluded that these interactions are absent in solution. For the ethyl, $n$-propyl and $n$-butyl compounds a constant value is found (1545 cm$^{-1}$). Such a less marked change in frequency ascending the homologous series is found also for the cupric $N,N$-di-alkyldithiocarbamates $[^8]$ [Cu(R$_2$dtc)$_2$; $R =$ Et, $n$-Pr, $n$-Bu]. When $R =$ H and phenyl the C—N frequency is found at lower energy in the solid state and in solution (Table I), as could be expected especially for an electron-withdrawing group $[^9]$. A comparison of the spectra recorded in chloroform and in the solid state shows no significant shifts for other absorption bands in the range 700–1700 cm$^{-1}$.

**Conductance study.** The concentration-dependence of the equivalent conductivities ($\Lambda_e$) is expressed by the Onsager limiting law $\Lambda_e = \Lambda_0 - A\sqrt{C}$, where $C$ is the equivalent concentration. $\Lambda_0$ can be determined by plotting $\Lambda_e$ as a function of $\sqrt{C}$.

For several of the reported complexes $\Lambda_e$ was measured in nitrobenzene in the concentration range $10^{-3}$–$10^{-4}$ molar. $\Lambda_0$ and $A_{\exp}$ were determined using the method of least squares (Table II). These values of $A$ can also be calculated assuming a 1:1 electrolyte to be present, using data for dielectric constant and viscosity given for nitrobenzene (25.0°)$^{10}$: $A_{\text{calc}} = \alpha \Lambda_0 + \beta = 0.780 \Lambda_0 + 44.12$. These values of $A_{\text{calc}}$ are in good agreement with those observed ($A_{\exp}$).

The observed limiting conductivities are also comparable with the data given for $n$-Bu$_4$NB(Ph)$_4$ $^{11}$ and for $n$-Bu$_4$NBF(Ph)$_3$ $^{10}$.

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$^7$ J. H. Noordik and P. T. Beurskens, to be published. We thank Drs. Noordik and Dr. Beurskens for communication prior to publication.


$^{11}$ E. G. Taylor and C. A. Kraus, ibid. 69, 1731 (1947).


With the single ion conductivities given$^4$ for the Br$^-$ ion (21.9) and the B(Ph)$_4^-$ ion (10.8) and with the measured values of $\Lambda_0$, the single ion conductivity for the Au($n$-Bu$_2$dtc)$_2^+$ ion was determined: $\lambda_0^+ = 9.1$. With this value for Au($n$-Bu$_2$dtc)$_2^+$ single ion conductivities for several negative ions could be derived (Table III).

Table III

<table>
<thead>
<tr>
<th>Ion</th>
<th>cm$^2$ohm$^{-1}$eq.$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClO$_4^-$</td>
<td>21.4$^a$</td>
</tr>
<tr>
<td>AuBr$_2^-$</td>
<td>21.0</td>
</tr>
<tr>
<td>PF$_6^-$</td>
<td>20.5</td>
</tr>
<tr>
<td>AuI$_3^-$</td>
<td>19.8</td>
</tr>
<tr>
<td>AuBr$_4^-$</td>
<td>17.9</td>
</tr>
<tr>
<td>Au(tdt)$_2^-$</td>
<td>12.7$^b$</td>
</tr>
<tr>
<td></td>
<td>12.6$^c$</td>
</tr>
<tr>
<td>Co(tdt)$_3^-$</td>
<td>15.0$^a$</td>
</tr>
<tr>
<td>Ni(tdt)$_3^-$</td>
<td>15.5$^a$</td>
</tr>
</tbody>
</table>

$^a$ Ref. 4.
$^b$ From Au($n$-Bu$_2$dtc)$_2$Au(tdt)$_2$.
$^c$ From (n-Bu)$_4$NAu(tdt)$_2$.
$^d$ Calculated from ref. 12.
The single ion conductivities given by Coetzee and Cunningham in acetonitrile and nitrobenzene show the following relationship (Table IV):

\[
\frac{\lambda_0 \text{ in acetonitrile}}{\lambda_0 \text{ in nitrobenzene}} = 5.35
\]

Using this ratio the single ion conductivities for Ni(tdt)²⁻ and Co(tdt)²⁻ in nitrobenzene could be calculated from the conductance data in acetonitrile giving 15.5 and 15.0, respectively, comparable with the measured value for Au(tdt)²⁻ (12.6).

Table IV

<table>
<thead>
<tr>
<th>Ion</th>
<th>acetonitrile</th>
<th>nitrobenzene</th>
<th>(\frac{\lambda_0 \text{acetonitrile}}{\lambda_0 \text{nitrobenzene}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₄N⁺</td>
<td>94.55</td>
<td>17.0</td>
<td>5.56</td>
</tr>
<tr>
<td>Et₄N⁺</td>
<td>85.05</td>
<td>16.1</td>
<td>5.34</td>
</tr>
<tr>
<td>(n-Pr)₄N⁺</td>
<td>70.65</td>
<td>13.2</td>
<td>5.35</td>
</tr>
<tr>
<td>(n-Bu)₄N⁺</td>
<td>61.93</td>
<td>11.55</td>
<td>5.36</td>
</tr>
<tr>
<td>(i-Am)₄N⁺</td>
<td>57.24</td>
<td>10.70</td>
<td>5.35</td>
</tr>
<tr>
<td>(i-Am)₄B⁻</td>
<td>57.24</td>
<td>10.70</td>
<td>5.35</td>
</tr>
<tr>
<td>(Ph)₄B⁻</td>
<td>57.72</td>
<td>10.79</td>
<td>5.35</td>
</tr>
<tr>
<td>Br⁻</td>
<td>100.05</td>
<td>21.93</td>
<td>4.56</td>
</tr>
<tr>
<td>I⁻</td>
<td>100.03</td>
<td>21.25</td>
<td>4.80</td>
</tr>
</tbody>
</table>

Experimental

Materials. Au(n-Bu₂dtc)Br₂, Au(n-Bu₂dtc)₂AuBr₄, Au(n-Bu₂dtc)₂AuBr₅, Au(n-Bu₂dtc)₂AuI₃, Au(n-Bu₂dtc)₂CuBr₂, n-Bu₄NaAu(tdt), n-Bu₄NaAu(mnt), Na₂mnt, n-Bu₄ClO₄, n-Bu₄NBPh₄, were prepared as described.

Toluene-3,4-dithiol was obtained commercially (Merck, Darmstadt). AgBr was prepared from aqueous solutions of silver nitrate and sodium bromide and was used immediately after several washings with distilled water and acetonitrile.

\(N,N,N',N'\)-Tetra-alkylthiuram disulfides were prepared as described by Åkerström.\(^{17}\)

Analyses. Metals were analyzed by atomic absorption spectrophotometric methods.


\(^{14}\) J. Locke and J. A. McCleverty, ibid. 5, 1157 (1966).


\(^{16}\) a. F. Accascina, S. Petrucci and R. M. Fuoss, ibid., 81, 1301 (1959);


\(^{17}\) S. Åkerström, Arkiv Kemi 14, 387 (1959).
The other elemental analyses were carried out in the Micro-analytical Department of this University. All melting points are uncorrected.

**Preparations.**

\(\text{Au}(n\text{-Bu}_2\text{dtc})_2\text{PF}_6\). 10 g of anion exchange resin (Amberlite IR A 400) were converted to the \(\text{PF}_6^-\) form by passing a solution of 5 g \(n\text{-Bu}_2\text{NPF}_6\) in water through the exchange column. Water was removed with ethanol and the ethanol with dimethyl sulfoxide (DMSO). A solution of 1.1 g of \(\text{Au}(n\text{-Bu}_2\text{dtc})_2\text{AuBr}_2\) in DMSO was passed through the column and the resin was washed with DMSO. The solution and washings were collected and the solvent was removed in vacuo. After several crystallizations from acetonitrile and carbon tetrachloride solutions, 0.35 g of yellow crystals was obtained, m.p. 156.8-157.5°.

Found : C, 28.9; H, 4.8; N, 3.6; S, 17.4; Au, 26.2.
Calcd. for \(C_{18}H_{36}AuF_6N_2PS_4\) (M = 750.7): C, 28.80; H, 4.80; N, 3.73; S, 17.08; Au, 26.24.

\(\text{Au}(n\text{-Bu}_2\text{dtc})_2\text{ClO}_4\) was prepared following the procedure described for the \(\text{PF}_6^-\) complex, except that sodium perchlorate was used and nitrobenzene was taken as solvent. Recrystallizations from mixtures of chloroform and diethyl ether gave yellow crystals, m.p. 138.0-138.5°.

Found : N, 3.8; S, 18.0; Au, 28.7.
Calcd. for \(C_{18}H_{36}AuClO_4S_4\) (M = 705.2): N, 3.79; S, 18.19; Au, 27.93.

\(\text{Au}(n\text{-Bu}_2\text{dtc})_2\text{B}(\text{Ph})_4\). This complex was prepared by adding an equimolar amount of \(\text{NaB}(\text{Ph})_4\) in 5 ml of ethanol to 0.68 g of \(\text{Au}(n\text{-Bu}_2\text{dtc})_2\text{Br}\) in 15 ml of methylene chloride. The resulting solution was filtered and the solvent evaporated in vacuo. The residue was dissolved in methylene chloride. To this solution diethyl ether was slowly added giving 0.8 g of orange red needles, m.p. 160-161°.

Found : C, 54.7; H, 6.6; Au, 21.2.
Calcd. for \(C_{42}H_{56}AuBN_2S_4\) (M = 924.96): C, 54.54; H, 6.10; Au, 21.29.

\(\text{Au}(n\text{-Bu}_2\text{dtc})_2\text{Au}(t\text{dt})_2\). This compound was prepared by adding to a solution of 0.68 g of \(\text{Au}(n\text{-Bu}_2\text{dtc})_2\text{Br}\) in methylene chloride an equimolar amount (0.75 g) of \(n\text{-Bu}_4\text{NAu}(t\text{dt})_2\) in 15 ml of methylene chloride at 0°. To promote crystallization 200 ml of methanol were added. The dark green product was filtered and washed with methanol and diethyl ether.

Recrystallization from acetone or methylene chloride/diethyl ether mixtures gave a green product in 90% yield, m.p. 134-135°.

Found : C, 33.4; H, 4.3; N, 2.4.
Calcd. for \(C_{18}H_{24}AuNS_4\) (M = 1111.2): C, 34.59; H, 4.35; N, 2.52.

\(\text{Au}(n\text{-Bu}_2\text{dtc})_2\text{Au}(\text{mnt})_2\). This complex was prepared similarly to the procedure given for \(n\text{-Bu}_2\text{NAu}(\text{mnt})_2\)\(^{18}\), only an equivalent amount of \(\text{Au}(n\text{-Bu}_2\text{dtc})_2\text{Br}\) in 5 ml of ethanol was added to precipitate the \(\text{Au}(\text{mnt})_2^-\) ion. The precipitate was filtered and recrystallized from acetone giving brown yellow needles, m.p. 169-170°.

Found : C, 28.9; H, 3.3; N, 8.1; S, 23.3; Au, 36.0.
Calcd. for \((C_{13}H_{18}AuN_2S_4)_2\) (M = 1083.1): C, 28.83; H, 3.35; N, 7.76; S, 23.68; Au, 36.38.
To a solution of 2.0 g of Au(n-Bu₄dtc)₂Br in 200 ml of acetonitrile an excess of freshly prepared AgBr (0.9 g) was added. The mixture was stirred at 45° for several hours. The solution was filtered and the solvent evaporated slowly. Orange needles were obtained in 50% yield, m.p. 168.5-170.0°.

Found : C, 24.8; H, 4.3; N, 3.2; S, 14.8; Au, 23.0; Br, 17.4
Calcd. for C₁₁H₃₆AgAuBr₂N₂S₄ (M = 873.4) : C, 24.75; H, 4.15; N, 3.21; S, 14.68; Au, 22.55; Br, 18.30.

Au(R₂dtc)₂Br with R = H, Me, Et, n-Pr, and phenyl were prepared as described for the analogous n-butyl compound². An equivalent amount of the appropriate thiuram disulfide (dissolved in chloroform or methanol) was added to aqueous AuBr₂-containing solutions.

Au(H₂dtc)₂Br, m.p. > 360°; anal. found: C, 5.5; H, 0.87; N, 5.8; Au, 42.7.
Calcd. for C₅H₁₀AuBrN₂S₄ (M = 461.2): C, 5.21; H, 0.87; N, 6.07; Au, 42.71.
Au(Me₂dtc)₂Br, m.p. 248° dec.; anal. found: C, 14.0; H, 2.3; N, 5.3; Au, 37.5.
Calcd. for C₁₀H₂₂AuBrN₂S₄ (M = 517.3): C, 13.93; H, 2.34; N, 5.41; Au, 38.08.
Au(Et₂dtc)₂Br, m.p. 186°; anal. found: C, 21.0; H, 3.4; N, 5.0; S, 22.2; Au, 34.2.
Calcd. for C₁₅H₃₀AuBrN₂S₄ (M = 573.4): C, 20.95; H, 3.52; N, 4.89; S, 22.37; Au, 34.33.
Au(n-Pr₂dtc)₂Br, m.p. 157°; anal. found: C, 26.7; H, 4.5; N, 4.6; S, 20.3; Au, 32.8.
Calcd. for C₂₀H₄₀AuBrN₂S₄ (M = 629.5): C, 26.71; H, 4.45; S, 20.37; Au, 31.29.
Au(Ph₂dtc)₂Br, m.p. 264°; anal. found: C, 40.4; H, 2.7; N, 3.7; Au, 25.5.
Calcd. for C₂₅H₅₀AuBrN₂S₄ (M = 765.6): C, 40.79; H, 2.63; N, 3.66; Au, 25.73.

Au(R₂dtc)₂AuBr₂ with R = Me, Et, n-Pr, and phenyl were prepared by the procedure described above for the bromide complexes. Only half an equivalent amount of the corresponding thiuram disulfide was used.

Au(Me₂dtc)₂AuBr₂, m.p. 266° dec.; anal. found: C, 9.1; H, 1.6; N, 3.4; S, 16.0; Au, 51.2.
Calcd. for C₉H₁₈Au₂Br₂N₂S₄ (M = 794.1): C, 9.08; H, 1.52; N, 3.53; S, 16.15; Au, 49.60.
Au(Et₂dtc)₂AuBr₂, m.p. 149°; anal. found: C, 14.2; H, 2.4; N, 3.2; Au, 46.2.
Calcd. for C₁₅H₃₀Au₂Br₂N₂S₄ (M = 850.3): C, 14.13; H, 2.37; N, 3.29; Au, 46.33.
Au(n-Pr₂dtc)₂AuBr₂, m.p. 120°; anal. found: C, 18.6; H, 3.1; N, 3.0; S, 14.2; Au, 43.5.
Calcd. for C₂₀H₄₀Au₂Br₂N₂S₄ (M = 906.4): C, 18.55; H, 3.11; N, 3.09; S, 14.15; Au, 43.46.
Au(Ph₂dtc)₂AuBr₂, m.p. 268°; anal. found: C, 29.9; H, 2.0; N, 2.6; S, 12.3; Au, 37.4.
Calcd. for C₂₅H₅₀Au₂Br₂N₂S₄ (M = 1042.5): C, 29.96; H, 1.93; N, 2.69; S, 12.30; Au, 37.79.

Physical measurements

Infrared spectra were recorded with a Perkin Elmer 157 or a Hitachi EP1-G3 spectrophotometer, using the KBr disc technique, checked against Nujoll mulls. Electric conductivities in nitrobenzene were measured as described previously³.

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