the neutral nickel dithiete species found in the perylene donor–acceptor molecular solid.[3] The neutral species has an Ni–S distance of 2.122 Å, 0.013 Å shorter than the 2.135 Å for the presently reported monoanion. While expansion of the Ni–S bond upon a one-electron reduction of the nickel complex is consistent both with theoretical predictions[19] and with the existing structural data,[20] it is only on the borderline of being statistically significant.

The perfluoromethyl carbons are very much bent out of the plane of the inorganic anion, seemingly as a consequence of either intramolecular or packing forces, but the large fluorine vibrational amplitudes shown in Figure 1 (mean amplitudes of 0.2–0.8 Å) imply that the CF_3 groups are nearly free rotors. Fluorine amplitudes of about the same size are extant in the structure of the cobalt dithiete dimer[21] but are small in the closely packed perylene–nickel dithiete molecular solid.[3]

The interaction between the organic cation and thiete ligands is illustrated in Figure 2 in which the view is normal to the nickel dithiete anion. The closest contacts (ranging between 3.4 and 4.3 Å, Table V) are between the tropylium ion and the thiete ligands, with the tropylium ion being in effect sandwiched between alternate thiete ligands to form a chainlike structure (Figure 3). The tropylium cations are inclined by 17° to the plane of the nickel dithiete monoanion.

Summary and Conclusions

The ability of nickel dithiete to behave as a strong organic oxidizing agent has been demonstrated by its reaction with cycloheptatriene to form the tropylium salt of nickel dithiete monoanion.

The packing in this ionic compound is loose compared to the neutral donor–acceptor complexes previously studied.[3] This implies that, for the nickel dithiete aromatic complexes, the covalent ground state may be more strongly binding than the excited ionic state.

Acknowledgments.—We wish to thank Professor A. H. Maki for stimulating discussions of nickel dithiete chemistry. Professor Phillip Radlick of this department generously donated samples of cycloheptatriene and tropylium tetrafluoroborate.

The computation center at Riverside, Calif., made available the IBM 360–50 for which we are grateful.

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CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC CHEMISTRY,
UNIVERSITY OF NIJMEGEN, NIJMEGEN, THE NETHERLANDS

Preparation, Structure, and Properties of Bis(N,N-di-*n*-butyldithiocarbamato)gold(III) Bromide and Bis(N,N-di-*n*-butyldithiocarbamato)gold(III) Tetrabromoaurate(III)

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Received April 11, 1969

The preparation, electric conductivity, and ultraviolet and infrared spectra of the compounds bis(N,N-di-*n*-butyldithiocarbamato)gold(III) bromide and tetrabromoaurate(III), $[Au(S_2CN(n\text{-}C_4H_9)_2)_2]Br$ and $[Au(S_2CN(n\text{-}C_4H_9)_2)_2][AuBr_4]$, are reported. The crystal structure of the bromide has been determined by a three-dimensional X-ray analysis. This compound crystallizes in the monoclinic space group P2/c. The unit-cell dimensions, measured from photographs, are $a = 11.45 \pm 0.02$ Å, $b = 4.97 \pm 0.01$ Å, $c = 22.62 \pm 0.03$ Å, and $\beta = 97.45 \pm 0.10°$, with two molecules per unit cell. Photometric measurement of equiinclination Weissenberg photographs yielded 1164 intensities. The structural parameters were refined by least-squares methods to a conventional R factor of 0.09. The structure analysis and all reported properties agree with the ionic structure $[Au(S_2CN(n\text{-}C_4H_9)_2)_2]^+Br^-$. The Au(III) is coordinated in planar fashion by four S atoms, the two nonequivalent Au-S distances being 2.309 ± 0.006 and 2.334 ± 0.006 Å. Preparation and properties of the tetrabromoaurate agree with a similar ionic structure $[Au(S_2CN(n\text{-}C_4H_9)_2)_2]^+[AuBr_4]^-$. This complex easily rearranges into the nonionic complex dibromo-N,N-di-*n*-butyldithiocarbamatogold(III). Other reactions and interconversions among $[AuS_2CN(n\text{-}C_4H_9)_2]_2$, $Au(S_2CN(n\text{-}C_4H_9)_2)_3$, $[Au(S_2CN(n\text{-}C_4H_9)_2)_2][AuBr_2]$, $AuBr_2S_2CN(n\text{-}C_4H_9)_2$, $[Au(S_2CN(n\text{-}C_4H_9)_2)_2]Br$, and $[Au(S_2CN(n\text{-}C_4H_9)_2)_2][AuBr_4]$ are described and discussed. Remarkable shifts of the C–N stretching frequency in the infrared spectra of the bromide and the tetrabromoaurate as compared with that of the analogous dibromoaurate[1] are explained in terms of the crystallographic positions of the anions near the nitrogen atom of the cation.

Introduction

Recently the structure and properties of the compounds $[Au(dtc)_2][AuBr_2]$[1] and $AuBr_2(dtc)$[2] (dtc = N,N-di-*n*-butyldithiocarbamate = $S_2CN(n\text{-}C_4H_9)_2$) were reported. The structure of the former was proved to be $[Au(dtc)_2]^+[AuBr_2]^-$ with Au(III)- and Au(I)-containing complex ions, respectively. We have now prepared the new complexes $[Au(dtc)_2]Br$ and $[Au(dtc)_2][AuBr_4]$. The preparations and electrical conductivity measurements reveal these structures to be ionic also, with the same cation, $Au(dtc)_2^+$. However,

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[1] P. T. Beurskens, H. J. A. Blaauw, J. A. Cras, and J. J. Steggerda, *Inorg. Chem.*, **7**, 805 (1968).

[2] P. T. Beurskens, J. A. Cras, and J. J. Steggerda, *ibid.*, **7**, 810 (1968).

Table I

Atomic Parameters for Au(dtc)$_2$Br with Standard Deviations[a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Au	.0000	.0000	.0000	.0060(1)	.0329(4)	.0014(0)	-.0059(2)	.0001(0)	-.0000(1)
Br	.5000	.8109(5)	.2500	.0107(2)	.0370(14)	.0039(1)	.0000	-.0026(1)	.0000
S(1)	.0534(3)	.0187(10)	.1019(1)	.0118(3)	.0488(20)	.0019(1)	-.0110(10)	-.0001(1)	.0009(5)
S(2)	.1629(3)	.2861(9)	.0128(2)	.0091(3)	.0507(22)	.0021(1)	-.0088(7)	.0000(1)	-.0004(4)
N	.2484(8)	.3122(21)	.1285(4)	.0073(9)	.0220(53)	.0019(2)	-.0005(19)	-.0005(4)	-.0027(10)
C(1)	.1671(11)	.2241(28)	.0875(5)	.0077(11)	.0277(68)	.0019(2)	-.0036(25)	.0000(4)	-.0008(12)
C(2)	.2491(11)	.2392(31)	.1923(6)	B = 4.0(3) Å^2					
C(3)	.1998(11)	.4734(36)	.2246(6)	4.6(3)					
C(4)	.1864(15)	.3871(37)	.2879(7)	5.9(4)					
C(5)	.1493(16)	.6312(41)	.3256(8)	6.7(4)					
C(6)	.3437(13)	.5007(40)	.1124(7)	5.9(3)					
C(7)	.4426(17)	.2569(44)	.1000(8)	7.6(5)					
C(8)	.5429(24)	.4147(54)	.0846(11)	10.3(7)					
C(9)	.6393(17)	.1964(45)	.0681(8)	7.6(5)					

[a] The key to the atomic numbering is given in Figure 3. The estimated standard deviations given in parentheses are the result of the least-squares refinement. The expression used for the temperature factors of the anisotropic refined atoms is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

they show remarkable shifts of the C–N stretching frequency in the infrared spectra as compared with that of the [Au(dtc)$_2$][AuBr$_2$] complex. Especially the increase of this frequency in the order [Au(dtc)$_2$][AuBr$_2$], [Au(dtc)$_2$][AuBr$_4$], AuBr$_2$(dtc), and [Au(dtc)$_2$]Br stimulated us to further investigations. Furthermore the observed[1] distortion of symmetry in the cation in [Au(dtc)$_2$][AuBr$_2$], *i.e.*, a difference between the two S–C bonds of borderline significance (3 esd's), made the determination of another crystal structure with the same cation of interest. Therefore the crystal structure of the bromide compound was solved.

Experimental Section[3]

Materials.—The compounds Au(dtc)$_2$AuBr$_2$,[1,4] AuBr$_2$(dtc),[4] and Na(dtc)[5] were prepared as described. N,N,N′,N′-Tetra-*n*-butylthiuram disulfide ((bu)$_4$ tds = $S_4C_2N_2(C_4H_9)_4$) was obtained commercially (Fluka, Praktikum).

Analyses.—Gold was analyzed by atomic absorption photometric methods, using diluted aqua regia solutions of gold as standards. The other elemental analyses were carried out by the microanalytical department of this university.

Preparations of Au(dtc)$_2$Br.—(A)[6] To a solution of 2.0 g of AuBr$_2$(dtc) in 50 ml of methylene chloride a freshly prepared equimolar amount of Na(dtc) in 50 ml of ethanol was slowly added, with stirring. An intermediate brownish black coloring disappeared rapidly. The solution was filtered, most of the solvent was evaporated, and a yellow product was precipitated with diethyl ether. Several recrystallizations from acetonitrile and diethyl ether gave orange-yellow needles, in 60% yield.

(B) An anion-exchange resin (30 g of Amberlite IRA-400 (Cl)) was converted to the Br$^-$ form with KBr in water. Water was removed with ethanol, and the ethanol was removed with dimethyl sulfoxide (DMSO). A solution of 1.5 g of Au(dtc)$_2$AuBr$_2$ in DMSO was passed through the column and the resin was washed with DMSO. The collected solutions and washings were treated as in (A); a yield of 70% was obtained.

(C) A 1.8-g sample of KAuBr$_4\cdot 2H_2O$ was dissolved in 350 ml of an aqueous saturated NaBr solution. The resulting solution was cooled to 0° and then carefully reduced with a 0.1 *M* Na_2SO_3 solution until the solution became colorless. Thereafter this solution was immediately added to a solution of 1.2 g of (bu)$_4$tds in 25 ml of ethanol. An orange-yellow precipitate was obtained, which was taken up in methylene chloride and treated as in (A); yield, 95%.

(D) To 1.6 g of Au(dtc)$_2$AuBr$_2$ in 20 ml of methylene chloride an equimolar amount of (bu)$_4$tds in 10 ml of methylene chloride was added. The solution turned from yellow to orange-red. The complex was precipitated with diethyl ether and recrystallized from acetonitrile and diethyl ether; yield, 60%.

(E) The anion-exchange resin, used in procedure B, being in the AuBr$_2^-$ form, was eluted with a solution of (bu)$_4$tds in DMSO. The solution was treated as in (A); yield, 35%.

In all cases the yellow crystalline products have been characterized and shown to be identical by their melting point (135.8–136.3°), ir spectra, and X-ray powder diagrams. *Anal.* Calcd for $C_{18}H_{36}N_2S_4AuBr$: C, 31.5; H, 5.3; N, 4.1; S, 18.7; Au, 28.7; Br, 11.7. Found: C, 31.5; H, 5.3; N, 4.2; S, 18.7; Au, 28.7; Br, 11.8.

Preparation of Au(dtc)$_2$AuBr$_4$.—To 1.0 g of Au(dtc)$_2$Br dissolved in 50 ml of methylene chloride an equimolar amount of KAuBr$_4$ in 10 ml of methylene chloride was added. After filtration the solution was treated with diethyl ether to precipitate the complex. The product was purified by dissolving it in methylene chloride, the solution was filtered if necessary, and an equal volume of diethyl ether was added; cooling to 0° gave red-violet crystals in 75% yield, mp 118–119°. *Anal.* Calcd for $C_{18}H_{36}N_2S_4Au_2Br_4$: C, 19.3; H, 3.2; S, 11.4; Au, 35.1. Found: C, 19.4; H, 3.2; S, 11.4; Au, 35.8.

Physical Measurements.—Electrical conductivities were measured in nitrobenzene solutions, as described before.[1] Uv spectra were measured in methylene chloride (Uvasol, Merck) solutions in the range 200–600 mμ, using a Zeiss PMQ II spectrophotometer. Ir spectra in the region 4000–650 cm^{-1} were measured with a Beckman IR4 double-beam instrument. All specimens were examined in KBr pellets. A Varian V-4502 instrument was used for esr measurements.

X-Ray Crystal Structure Analysis of Au(dtc)$_2$Br.—The compound Au(dtc)$_2$Br crystallizes in the monoclinic system as prismatic needles elongated on [010]. A crystal of size 0.065 ×

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(3) Thanks are due to Mr. P. J. J. Koonen and Mr. J. M. Smits for technical assistance.

(4) H. J. A. Blaauw, R. J. F. Nivard, and G. J. M. van der Kerk, *J. Organometal. Chem.* (Amsterdam), **2**, 236 (1964).

(5) S. Åkerström, *Arkiv Kemi*, **14**, 387 (1959).

(6) This method was suggested by H. J. A. Blaauw.

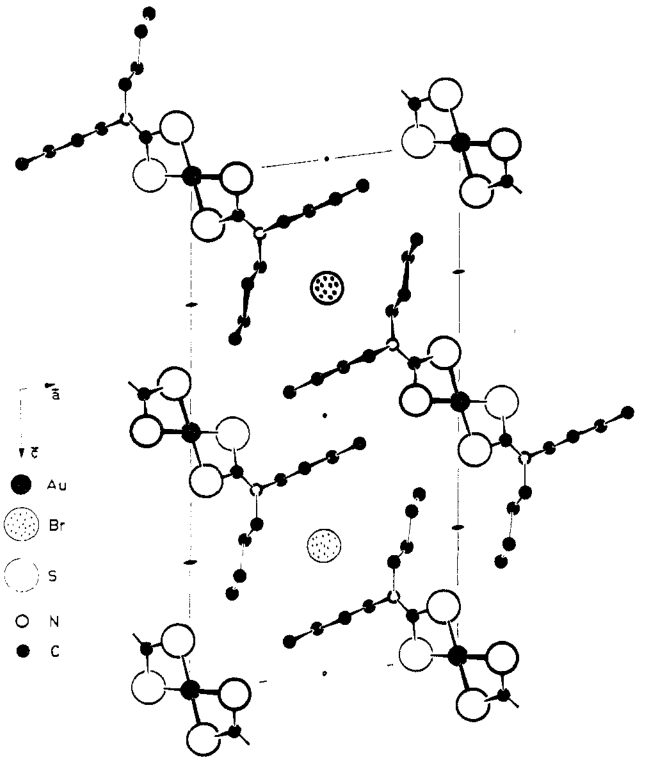

Figure 1.—Projection of Au(dtc)$_2$Br along *b*. The gold atoms are situated on centers of symmetry and the bromine atoms on twofold rotation axes; other centers and axes are indicated.

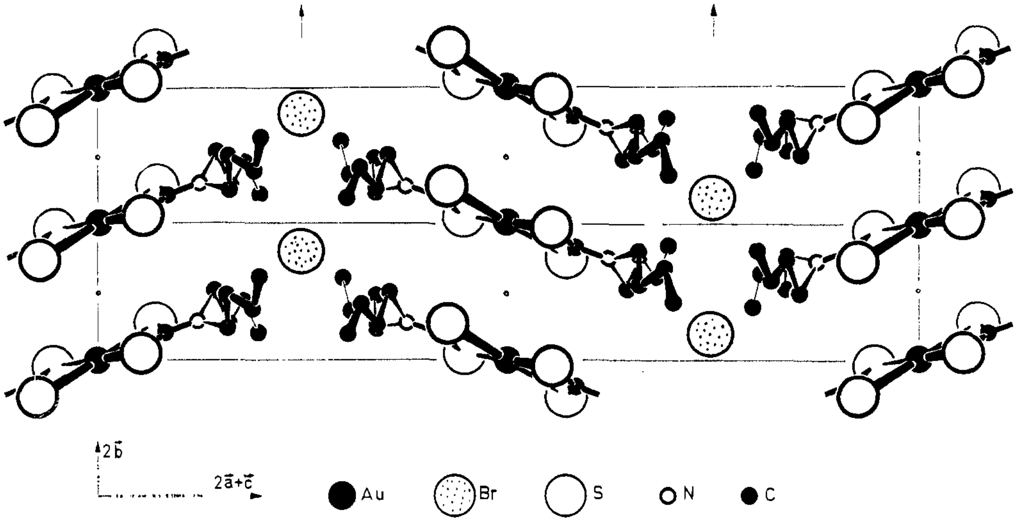

Figure 2.—Projection of Au(dtc)$_2$Br on the plane (102). Arrows indicate a twofold axis.

0.08 × 0.64 mm^3 was used for oscillation (around the *b* axis) and equiinclination Weissenberg (*h*0*l* through *h*4*l*) and precession (*hk*0, *hk*1, 0*kl*, and 1*kl*) photographs with nickel-filtered Cu Kα radiation (1.5418 Å). The unit-cell dimensions at 20°, measured from oscillation and Pt-calibrated Weissenberg photographs, and their root-mean-square errors were $a = 11.45 \pm 0.02$ Å, $b = 4.97 \pm 0.01$ Å, $c = 22.62 \pm 0.03$ Å, $\beta = 97.45 \pm 0.10°$, and $V = 1276 \pm 5$ Å^3. The calculated density is $D_x = 1.78 \pm 0.01$ g cm^{-3} for $Z = 2$, as compared to the density measured in paraffin oil using a pycnometer which is $D_m = 1.77 \pm 0.01$ g cm^{-3}. The systematic extinctions are *h*0*l* for *l* odd, which are compatible with the space groups Pc and P2/c. The structure was solved assuming the crystal to be centrosymmetric, confirming the space group to be P2/c. Three-dimensional intensity data were collected from five layers of integrated multiple-film Weissenberg photographs. Of about 2900 possible independent reflections, 1164 reflections were measured with an optical densitometer and another 632 reflections were estimated as zero or very weak reflections. The intensities were corrected for Lorentz and polarization factors. No absorption correction was applied (μ = 160 cm^{-1}; maximum effect on the intensities, 30%). The five layers were scaled by Wilson's statistical method.

The structure was solved by Patterson and Fourier[7] methods and refined by full-matrix least-squares[8] methods. The function that was minimized is $\Sigma w(|F_o| - |F_c|)^2$. The weight w for each reflection was calculated as $w = n/(50 + |F_o| + 0.01|F_o|^2)$ with $n = 1$ or 0.25 for the 1164 measured reflections ($n = 0.25$ for the 299 weakest of these) and $n = 0$ for the very weak or unobserved reflections. The atomic scattering factors were those of the neutral atoms, corrected for anomalous scattering ($\Delta f'$), using data from the "International Tables for X-Ray Crystallography." The conventional R factor is defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for the 1164 measured reflections; values given in parentheses include the very weak and zero observed reflections.

After refinement of the five scaling factors and the positional and individual isotropic temperature factor parameters of all atoms, except hydrogen atoms, the R factor was 0.08 (0.13). A difference Fourier synthesis showed some anisotropy of the gold, bromine, and sulfur atoms. The refinement was continued with fixed individual scaling factors. Three cycles of refinement of the overall scale factor, the positional parameters, anisotropic temperature factor parameters for Au, Br, S$_1$, S$_2$, N, and C$_1$, and isotropic temperature factors for C$_2$ through C$_9$ gave $R = 0.06$ (0.09). The physical significance of the anisotropic vibrational parameters is reduced by the uncertainty of the scale factors and the lack of an absorption correction. The final difference Fourier synthesis with the measured reflections up to sin θ = 0.5 showed a -1.0 e$^-$/Å^3 peak at the position of the gold atom, 0.5 e$^-$/Å^3 at S$_1$, and 1.5 e$^-$/Å^3 at the bromine atom position. At the calculated hydrogen atom positions 0.2–0.5 e$^-$/^{3}Å peaks were found.

Results and Discussion

Crystal Structure of Au(dtc)$_2$Br.—The atomic parameters are given in Table I. The structure is illustrated in Figures 1 and 2. Bond distances and angles[9] are given in Figure 3. The observed and calculated structure amplitudes are given in Table II.

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[7] A. Fourier program and some data-handling programs, written by P. T. B., were used on an IBM 360/50 computer.

[8] The program ORFLS by Busing, Martin, and Levy (1962) was modified and used for simultaneous refinement of isotropically and anisotropically vibrating atoms.

[9] Using "An Interatomic Distances and Angles Program," by R. Shiono and S. S. C. Chu.

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR Au(dtc)$_2$Br^a

```
  L, H=0 K=0
  2 121* 134
  4 134  144
  6  35   31
  8 171  197
 10 165  167
 12 137  137
 14  57   50
 16  82   77
 18  62   59
 20  69   67
 22  42   40
 24  30   29
 26  19   24

  L, H=1 K=0
-28  25   28
-26  30   30
-24  30   33
-22  69   64
-20  52   56
-18  96   92
-16  54   53
-14 108  104
-12 118  117
-10 216  225
 -8  41   47
 -6 156  173
 -4 127  124
  2 123  136
  6 215  224
  8 116  111
 10 133  127
 12  35   33
 14  75   72
 16  27   26
 18  79   67
 20  47   47
 22  42   37
 26  14   20
 28  12   14

  L, H=2 K=0
-28  27   33
-26  28   27
-24  41   41
-22  56   52
-20  86   80
-18  65   64
-16  83   74
-14  71   67
-12 150  144
-10  95   90
 -8 138  135
 -6  32   31
 -4 190  201
 -2 147  149
  0 144  146
  4  54   54
  8 161  157
 10  56   59
 12 112  111
 16  49   47
 18  45   44
 20  59   65

  L, H=3 K=0
-28  22   24
-26  28   25
-24  34   31
-22  55   51
-20  64   62
-18  51   49
-16  39   42
-14  85   65
-12  74   72
-10 104  107
 -8  39   36
 -6  76   78
 -4  43   39
 -2 176  173
  2 170  165
  4  45  -39
  6 148  139
  8  79   77
 10 104  104
 14  56   52
 16  62   59
 18  94   90
 20  33   37
 22  31   30
 24  18   21
 26  36   37

  L, H=4 K=0
-28  15   15
-26  16   19
-24  33   24
-22  39   40
-20  53   52
-18  24   19
-16  47   47
-14  36   37
-12  86   86
-10  49   52
 -8  93   93
 -6  22   23
 -4 118  115
 -2  65   62
  0 157  151
  4 140  132
  6  84   75
  8 162  161
 10  61   61
 12  77   72
 14  48   52
 16 104  100
 18  55   54
 20  51   56
 22  29   31
 24  36   39
 26  30   32
```

```
  L, H=5 K=0
-28  10   11
-24  28   26
-22  35   42
-20  34   28
-18  42   41
-16  25   23
-14  67   69
-12  65   65
-10  99   97
 -8  41   41
 -6 102  103
 -4  91   73
 -2 136  145
  0  99  101
  2 104   94
  4  97   97
  6 163  152
  8  94   93
 10 129  125
 12  43   41
 14 115  110
 16  54   56
 18  80   75
 20  36   34
 22  34   40
 24  22   25

  L, H=6 K=0
-26  14   17
-24  34   33
-22  36   34
-20  37   35
-18  38   40
-16  44   45
-14  72   73
-12 107  104
-10  71   70
 -8  85   88
 -6  65   63
 -4 160  158
 -2 113  111
  0 150  150
  2  62   57
  4 156  153
  6  92   81
  8 141  131
 10  47   48
 12  90   90
 14  41   41
 16  78   74
 18  43   40
 20  38   41
 24  27   29

  L, H=7 K=0
-26  13   21
-24  37   34
-22  45   43
-20  43   34
-18  41   38
-16  44   46
-14  91   90
-12  85   82
-10  87   86
 -8  47   49
 -6 114  116
 -4 105  103
 -2 136  127
  0  50   49
  2 113  109
  4  39   38
  6 123  127
  8  51   49
 10  75   75
 12  25   26
 14  55   49
 16  35   35
 18  44   44
 22  16   24

  L, H=8 K=0
-26  18   26
-24  32   32
-22  35   33
-20  31   32
-18  31   30
-16  70   74
-14  62   60
-12  62   64
-10  29   32
 -8  71   64
 -6  76   72
 -4 105  103
 -2  47   47
  0  69   69
  4  76   68
  6  51   49
  8  66   66
 12  44   43
 16  54   53
 20  22   25

  L, H=9 K=0
-24  22   22
-22  26   27
-20  22   23
-18  31   33
-16  41   42
-14  43   39
-12  39   36
-10  43   46
 -8  35   35
 -6  52   56
 -4  34   34
 -2  65   62
  0  20   14
  2  46   50
  4  26   34
  6  73   70
  8  20   20
 10  41   37
 14  56   56
 16  16   22
 18  28   33
 20  10   13
```

```
  L, H=10 K=0
-14  30   32
-12  25   29
 -8  32   40
 -6  34   36
 -4  67   65
  0  32   31
  2  19   22
  4  80   77
  6  24   30
  8  44   50
 12  47   50
 14  33   33
 16  37   38
 18  16   20

  L, H=11 K=0
-14  37   35
-10  31   32
 -8  37   32
 -6  48   49
 -4  31   34
 -2  31   38
  0  30   33
  2  61   65
  4  40   41
  6  43   48
  8  21   22
 10  46   47
 12  23   31
 14  39   43

  L, H=12 K=0
-12  30   28
-10  33   30
 -8  36   40
 -6  37   38
 -4  39   40
 -2  27   31
  0  46   51
  2  31   34
  4  45   48
  6  26   30
  8  35   40
 10  22   23
 12  31   36

  L, H=13 K=0
-10  24   27
 -6  36   38
 -4  30   27
 -2  34   39
  0  20   24
  2  29   36
  4  18   24
  6  26   34

  L, H=14 K=0
 -6  26   21
 -4  22   26
 -2  17   18

  L, H=0 K=1
  1  19  -23
  3 111 -125
  4  97  107
  5  66   70
  7  29  -28
  8 105  120
  9  42   38
 10  93   99
 11  70  -63
 12 106  106
 14  47   46
 15  44  -39
 16  61   60
 18  57   53
 20  70   70
 22  38   39
 24  24   27

  L, H=1 K=1
-24  31   26
-22  45   44
-20  58   57
-18  53   54
-16  48   45
-14  60   61
-13  37   28
-12  93   92
-11  34  -33
-10 110  119
 -9  22   21
 -8  99  103
 -7  72  -70
 -6  91   86
 -5  21   26
 -4  32   34
 -3  65  -64
 -1  30  -28
  2  80   69
  4  55   46
  5  78  -80
  6  77   80
  8 106  114
  9  77  -78
 10 141  161
 12  71   69
 13  32  -29
 14  57   57
 16  52   49
 18  80   77
 20  61   60
 22  41   40
 24  20   25
```

```
  L, H=2 K=1
-24  27   28
-22  40   44
-20  63   59
-18  54   53
-17  35  -32
-16  44   45
-14  59   53
-13  32  -28
-12 103  104
-11  31  -19
-10  98  105
 -9  40  -45
 -8 107  117
 -6  46   53
 -5  63  -61
 -4 122  128
 -3  24   21
 -2 136  145
 -1 135 -148
  0 196* 214
  1  18   16
  2  39   40
  3  92  -91
  4 109  110
  5  28   26
  6  99  100
  7  38  -35
  8 142  154
  9  43   41
 10 103  109
 11  35  -33
 12  65   66
 14  58   54
 16  76   73
 17  34   30
 18  74   72
 20  54   53
 22  33   34
 24  30   28

  L, H=3 K=1
-24  34   31
-22  48   49
-20  49   47
-18  55   54
-16  38   36
-15  30  -23
-14  86   88
-12  90   97
-11  52  -53
-10 112  122
 -8  58   55
 -7  31  -30
 -6  82   69
 -5  22   21
 -4 119  125
 -3  73  -68
 -2 149  174
 -1  46   46
  0 142  157
  1  24  -20
  2  85   85
  3  46   46
  4  87   86
  6 131  134
  7  48   45
  8 107  108
 10 106  110
 11  48   48
 12  59   59
 14  69   68
 15  64   58
 16  59   57
 18  74   70
 20  44   43
 22  37   35
 24  22   22

  L, H=4 K=1
-24  32   34
-22  55   46
-20  56   52
-18  45   46
-16  50   51
-14  69   67
-12  96  101
-11  46   46
-10  97  101
 -8  86   90
 -7  44   43
 -6  83   84
 -5  58  -50
 -4 121  129
 -3  59   57
 -2 103  111
 -1  40   35
  0 133  136
  1  73   67
  2  81   79
  4 100  101
  5  87   83
  6 100  100
  8 120  123
  9  58   54
 10  68   69
 12  69   70
 13  52   47
 14  37   36
 16  73   70
 18  56   54
 20  43   45
```

```
  L, H=5 K=1
-24  31   32
-22  47   46
-20  47   47
-18  35   38
-16  50   51
-14  73   74
-13  43   40
-12  93   94
-10  85   86
 -9  33   27
 -8  45   48
 -6  83   86
 -5  75   70
 -4 106  104
 -3  26   24
 -2 151  157
 -1  64   66
  0  72   66
  1  36  -30
  2  92   91
  3  73   71
  4  43   38
  6 119  119
  7  52   54
  8  91   86
 10  76   74
 11  42   38
 12  36   37
 14  51   51
 16  51   56
 18  53   53

  L, H=6 K=1
-24  30   33
-22  40   40
-20  39   34
-16  50   54
-15  38   34
-14  67   64
-12  84   84
-11  32   25
-10  57   53
 -8  65   57
 -7  31   27
 -6  65   62
 -4 101  105
 -3  45   42
 -2  83   86
 -1  27  -22
  0  76   72
  1  51   50
  2  63   60
  3  34  -32
  4  86   83
  6  91   79
  7  27  -29
  8  87   86
 10  39   39
 12  51   47
 14  51   45
 15  35  -29
 16  59   59
 18  39   38
 20  31   30

  L, H=7 K=1
-24  23   29
-22  35   32
-20  36   28
-18  35   34
-16  43   43
-14  65   62
-12  57   52
-10  54   54
 -8  50   46
 -6 [illegible] 69
 -5  29   26
 -4  82   81
 -3  39  -32
 -2  98   87
  0  53   52
  1  45  -34
  2  55   54
  4  67   61
  5  33  -26
  6  85   87
  8  65   62
  9  33  -31
 10  57   56
 12  35   29
 14  58   58
 16  44   42
 18  47   44
 20  25   22

  L, H=8 K=1
-16  30   35
-14  56   54
-12  58   52
-10  43   43
 -8  46   45
 -6  55   55
 -4  88   86
 -2  63   60
 -1  40  -35
  0  64   62
  2  37   35
  4  89   86
  6  64   62
  8  69   64
 10  37   33
 11  33  -22
 12  49   46
 14  48   45
 16  51   49
 18  28   30
```

```
  L, H=9 K=1
-16  39   36
-14  55   51
-12  39   39
-10  32   37
 -8  38   40
 -6  78   74
 -4  66   62
 -2  56   57
  0  32   37
  2  64   60
  3  36   35
  4  66   63
  6  67   68
  8  40   39
 10  40   43
 12  44   36
 14  44   45
 16  37   35

  L, H=10 K=1
-16  33   38
-14  37   35
-12  38   38
-10  33   33
 -8  52   50
 -6  56   54
 -4  54   52
 -2  43   43
  0  50   47
  1  37   32
  2  51   49
  4  51   54
  6  47   46
  8  41   42
 10  35   28
 12  40   39
 14  31   30

  L, H=0 K=2
  1  37   39
  2 104  104
  3  37  -37
  4  33   36
  5  37   37
  6  70   75
  7  32  -26
  8  72   69
  9  42   38
 10 103  104
 12  48   46
 14  53   53
 18  70   73
 20  46   47
 22  35   38

  L, H=1 K=2
-22  29   31
-20  61   57
-18  41   38
-16  33   28
-14  40   32
-13  24   22
-12  69   65
-10  69   71
 -8  78   88
 -6  28   22
 -5  17   24
 -4  91   98
 -3  16   -8
 -2  57   55
 -1  59   63
  0 168* 157
  1  20  -16
  2  69   72
  3  26   23
  4  95   94
  5  15  -10
  6  41   44
  7  67   60
  8 125  133
 10  77   79
 11  20   24
 12 100  100
 13  24  -15
 14  40   39
 15  25   24
 16  79   78
 18  61   62
 20  57   57
 22  31   36

  L, H=2 K=2
-22  39   39
-20  39   39
-18  31   32
-16  27   30
-14  59   61
-12  64   63
-11  43   41
-10 113  116
 -8  48   51
 -7  38   34
 -6 107  103
 -4  38   41
[illegible] 42 40
 -2 152* 158
  0 124  124
  1  35   32
  2 147  153
  3  20  -16
  4  63   60
  5  55   54
  6 134  139
  8  94   95
 10 121  129
 12  61   62
 13  33   26
 14  74   74
 16  67   66
 18  71   67
 20  46   49
 22  35   39
```

```
  L, H=3 K=2
-22  35   39
-20  48   50
-18  38   39
-16  54   54
-14  37   38
-12 111  113
-10  96   98
 -9  24   15
 -8 110  119
 -7  29  -24
 -6  60   59
 -5  66   63
 -4 109  114
 -2 145  146
 -1  43   40
  0 172  176
  1  39  -36
  2  77   73
  3  40   34
  4 114  109
  5  22  -17
  6  82   84
  7  28   32
  8 138  142
  9  22  -23
 10  85   85
 12  82   80
 14  40   43
 16  55   63
 18  43   43
 20  52   51

  L, H=4 K=2
-22  45   47
-20  40   44
-18  48   49
-16  41   41
-14  86   90
-12 102  109
-11  27   21
-10  95   94
 -8  48   46
 -6  81   79
 -4 125  121
 -3  24   21
 -2 179  184
 -1  40  -31
  0  70   73
  1  37   36
  2  90   90
  3  24  -17
  4  47   42
  5  22   19
  6 114  116
  7  32  -29
  8  76   73
 10  88   85
 14  57   53
 16  26   29
 18  55   56

  L, H=5 K=2
-22  35   40
-20  43   43
-18  33   37
-16  51   53
-14  74   75
-12  81   81
-10  53   53
 -8  77   75
 -6  57   57
 -4 116  122
 -2  46   43
  0  90   89
  1  32  -25
  2  34   33
  4  85   82
  5  24  -19
  6  48   48
  7  30   31
  8  85   87
 10  28   29
 12  44   43
 16  43   51
 18  37   37

  L, H=6 K=2
-22  33   35
-20  33   31
-18  32   33
-16  34   39
-14  61   60
-12  37   39
-10  56   60
 -8  25   23
 -6  71   71
 -5  29  -18
 -4  56   54
 -3  37   38
 -2  84   85
  0  40   39
  1  20   15
  2  44   37
  3  32  -17
  4  22   23
  5  37   33
  6  89   89
  8  51   54
  9  29   21
 10  56   54
 14  43   48
 16  43   45
 18  42   45
```

```
  L, H=7 K=2
-16  33   38
-14  35   31
-12  52   50
-10  31   28
 -8  41   39
 -6  44   46
 -5  30   29
 -4  72   70
 -2  53   53
  0  49   51
  1  27  -15
  2  30   25
  3  40   41
  4  90   91
  6  65   60
  7  33   32
  8  65   68
 11  27   25
 12  54   53
 14  47   48
 16  64   61

  L, H=8 K=2
-14  37   41
-12  39   42
-10  41   40
 -8  37   41
 -7  31   28
 -6  67   65
 -4  55   55
 -2  74   74
  0  30   30
  2  80   81
  4  56   58
  5  35   32
  6  82   82
  8  40   40
 10  56   57
 12  38   40
 14  58   58
 16  32   34
 18  37   39

  L, H=9 K=2
-16  31   35
-14  44   43
-12  47   46
-10  37   34
 -8  53   55
 -6  49   51
 -4  82   79
 -2  46   45
  0  66   64
  2  49   50
  4  68   69
  6  52   48
  8  55   56
 10  30   32
 12  47   48
 14  28   31
 16  38   40

  L, H=10 K=2
-16  29   36
-14  45   45
-12  35   35
-10  40   41
 -8  36   38
 -6  56   58
 -4  48   49
 -2  47   49
  0  39   41
  2  49   48
  4  41   39
  6  53   51
 10  36   36
 14  34   35

  L, H=11 K=2
-16  27   32
-14  29   30
-12  29   28
-10  25   26
 -8  36   36
 -6  39   40
 -4  43   39
  0  32   32
  4  43   44
  8  27   30
 12  22   27

  L, H=0 K=3
  2 138  125
  3  23   25
  4  37   38
  6  96  107
  7  33   28
  8  67   67
 10  99  102
 12  49   46
 14  53   55
 16  35   35
 18  49   49
 20  39   35
 22  29   32
```

```
  L, H=1 K=3
-22  25   29
-20  46   49
-18  47   45
-16  54   55
-14  33   31
-12  85   84
-11  23   22
-10  75   73
 -8  99  108
 -6  33   32
 -4  95  105
 -3  20   23
 -2  67   71
 -1  16   19
  0 159  143
  1  33   36
  2  53   56
  4  72   76
  5  30   31
  6  53   50
  8  87   91
  9  32   31
 10  57   54
 12  69   64
 14  24   27
 16  47   44
 18  34   32

  L, H=2 K=3
-22  38   41
-20  43   44
-18  49   48
-16  25   25
-14  56   56
-12  70   69
-10  97  102
 -8  50   42
 -6  60   59
 -5  25   26
 -4  58   53
 -3  29   27
 -2 106  112
 -1  43   43
  0  57   58
  2  90   93
  3  19   20
  4  23   24
  6  83   86
  8  45   40
 10  80   79
 12  23   24
 14  46   44
 18  51   49
 20  27   28

  L, H=3 K=3
-22  36   37
-20  42   42
-18  29   24
-16  31   35
-14  45   45
-13  31   26
-12  77   75
-10  49   43
 -8  62   60
 -6  27   31
 -4  89   90
 -3  50   45
 -2  51   47
  0  91   89
  2  27   23
  3  22  -14
  4  72   72
  6  26   19
  8  92   95
 10  40   39
 12  55   53
 16  47   47
 20  36   36

  L, H=4 K=3
-22  26   30
-20  25   25
-18  30   28
-16  32   27
-14  53   55
-12  38   37
-10  61   61
 -8  25   24
 -6  65   61
 -5  29   25
 -4  33   28
 -2 103  107
  0  52   47
  1  34  -29
  2  72   70
  4  23   17
  6  79   76
  8  63   62
 10  73   71
 14  46   49
 16  42   40
 18  49   51
 20  22   25
 22  25   27

  L, H=5 K=3
-16  28   32
-14  34   35
-12  61   61
-10  42   41
 -8  50   49
 -6  31   27
 -4  82   84
 -2  73   69
  0  81   78
  2  23   17
  4  79   80
  6  66   67
  8  92   91
 10  33   31
 12  51   51
 14  33   34
 16  63   60
 18  30   32
 20  32   35
```

```
  L, H=6 K=3
-16  29   29
-14  47   50
-12  48   49
-10  45   47
 -8  30   30
 -6  75   75
 -4  74   72
 -2  90   87
  0  33   32
  2  70   69
  3  31   29
  4  52   53
  6  97   98
  7  30   29
  8  39   36
 10  65   64
 12  28   26
 14  55   55
 15  25   25
 16  28   33
 18  38   41

  L, H=7 K=3
-16  31   34
-14  40   44
-12  54   56
-10  30   32
 -8  55   57
 -6  49   51
 -4  84   82
 -3  36   33
 -2  42   40
  0  74   71
  1  34   31
  2  42   40
  4  76   75
  6  46   42
  8  57   61
 10  27   27
 12  40   43
 13  22   26
 14  24   25
 16  40   43

  L, H=8 K=3
-16  30   33
-14  45   46
-12  35   36
-10  41   45
 -8  36   37
 -6  59   54
 -4  45   44
 -2  60   57
  0  34   30
  2  51   52
  4  33   32
  6  59   60
  9  26   28
 10  33   32
 14  35   34

  L, H=9 K=3
-16  27   33
-14  33   32
-12  31   31
 -8  32   34
 -6  34   34
 -4  45   49
 -2  26   29
  0  32   35
  4  38   48
  8  40   37
 12  26   36

  L, H=10 K=3
 -6  39   37
 -2  36   33
  2  38   38
  6  38   38
 10  26   30

  L, H=0 K=4
  1  24  -24
  2  57   67
  4  42   47
  6  42   41
  8  57   60
  9  29  -27
 10  63   64
 12  49   47

  L, H=1 K=4
-14  43 [illegible]
-12  58   55
-10  57   60
 -8  47   46
 -6  47   50
 -5  25  -18
 -4  42   47
 -3  26   26
 -2  82   82
 -1  34  -29
  0  67   67
  2  50   45
  3  32  -32
  4  46   49
  6  37   39
  7  28  -26
  8  59   59
 10  53   50
 12  35   35
```

```
  L, H=2 K=4
-14  37   38
-12  46   47
-10  43   41
 -8  43   44
 -7  29  -28
 -6  43   42
 -4  41   44
 -3  30  -24
 -2  59   54
  0  50   53
  1  29  -25
  2  30   40
  4  36   36
  5  33  -28
  6  35   34
  8  54   54
 10  43   44
 12  34   31

  L, H=3 K=4
-14  36   33
-12  33   41
-10  34   42
 -8  30   31
 -6  35   30
 -4  52   49
 -2  52   53
  0  49   49
  2  32   33
  6  55   55
  8  50   49
  9  31   30
 10  42   42

  L, H=4 K=4
-12  41   40
-10  33   36
 -8  35   31
 -6  34   34
 -5  31   28
 -4  51   53
 -2  44   44
 -1  37   34
  0  53   49
  2  40   36
  3  31   26
  4  43   43
  6  60   61
  7  46   44
  8  44   45
 10  41   40

  L, H=5 K=4
-12  43   42
-10  47   36
 -8  35   34
 -6  51   42
 -4  59   53
 -3  49   42
 -2  61   57
  0  51   49
  1  31   26
  2  40   44
  4  50   50
  5  43   47
  6  52   53
  8  53   50
 10  41   40

  L, H=6 K=4
-10  34   30
 -8  37   37
 -6  42   42
 -5  32   35
 -4  53   52
 -2  61   58
  0  42   43
  2  44   44
  3  32   32
  4  56   47
  6  43   43
  8  44   47

  L, H=7 K=4
 -6  44   40
 -4  54   50
 -2  54   47
  0  31   30
  2  23   31
  4  32   35
  6  44   40
  8  36   34
```

^{a} l, $|F_o|$, and F_c are given for constant h and k. Asterisks mark the four rejected reflections (bad spot on photograph or possible extinction). Zero observed reflections are not given; they all have $|F_c|$ below the minimum observable value.

The X-ray analysis confirmed the compound to be composed of the ionic units Au(dtc)$_2^+$ and Br$^-$. The cation, apart from the butyl chains, is planar. In the direction of the needle axis b the cations pack above one another. The gold atoms of adjacent cations are separated by the $\bar{b}$ translation, 4.97 (1) Å. Some interionic distances are: Au–S(2), 4.00 (1) Å; S(1)–S(2), 4.42 (1) Å; S(1)–C(1), 4.18 (2) Å; S(1)–N, 4.16 (2) Å. The cages formed by the butyl chains of the cations are occupied by the bromide ions. The shortest van der Waals distances are 3.67 (6) Å and 3.72 (6) Å for bromine–carbon contacts. The bromine–nitrogen distances are 4.46 (2) and 4.47 (2) Å.

The structural features of the present compound are similar to those of the compound Au(dtc)$_2$AuBr$_2$.[1] The cations Au(dtc)$_2^+$ have similar geometry in both compounds. However in the present compound a difference of 0.025 Å (4 esd's) between the two non-

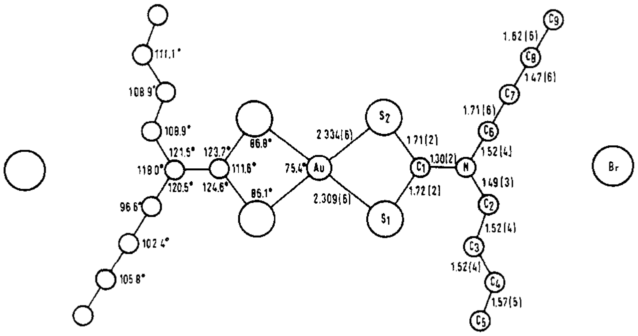
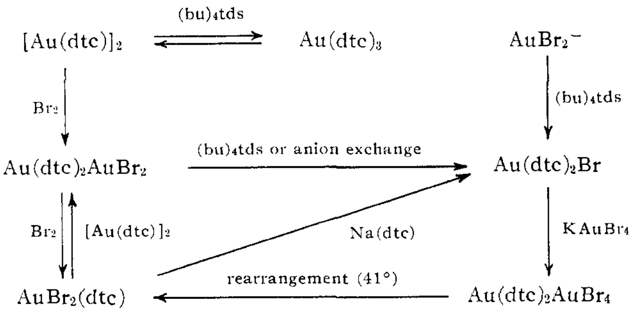


Figure 3.—Bond angles and distances in $Au(dtc)_2Br$ and atomic-numbering scheme. Projection on the coordination plane AuS_4. The gold atom is situated on a center of symmetry. Standard deviations of the bond distances (Å) are given in parentheses; the accuracy of the bond angles is in the range 0.25° for S–Au–S to 2.0° for C–C–C angles.

equivalent gold–sulfur bond distances is found. Because the estimations for the standard deviations, obtained by least-squares methods, are known to be too low and in view of the fact that absorption corrections were not made, this difference is not significant and we are convinced that the gold(III) coordination, in principle, is of D_{2h} symmetry.

The packing of the cations in the two structures, however, is different. In the present compound the orientation of adjacent cations is the same, whereas cations of two orientations alternate in $[Au(dtc)_2]^+[AuBr_2]^-$.

Synthesis and Reactions.—Preparations and chemical reactions of the present and some related complexes are presented in the scheme



Analogous to the reaction[10] of $[Au(dtc)]_2$ with $(bu)_4tds$ the dibromoaurate(I) ion was oxidized with $(bu)_4tds$ to obtain the complex $Au(dtc)_2Br$. This reaction was carried out in water (preparation method C), in a methylene chloride solution of $Au(dtc)_2AuBr_2$ (method D), and on an ion-exchange surface (method E; seealso method B). Another preparation (method A) of the same complex is given by the interesting reaction

$$AuBr_2(dtc) + Na(dtc) \longrightarrow Au(dtc)_2Br + NaBr$$

This reaction resembles a previously described[1] reaction

$$2AuBr_2(dtc) + [Au(dtc)]_2 \longrightarrow 2Au(dtc)_2AuBr_2$$

Both reactions show an intermediate dark coloring of the solution, similar to reactions in which Au(I) is oxidized. This phenomenon was studied by esr techniques at −60 to −40°, where the color remained for several minutes. No resonance signal could be obtained; thus the possibility of an unstable Au(II) intermediate was eliminated. By a metathetical reaction, $Au(dtc)_2AuBr_4$ was obtained. This ionic complex rearranged easily (boiling in methylene chloride, 41°) to the nonionic isomer $AuBr_2(dtc)$, identified by its lack of electrical conductivity and by its ir spectrum.

Conductivity.—Molar conductivities were measured in nitrobenzene solutions. The following results were obtained: for $Au(dtc)_2Br$, Λ (in $ohm^{-1}\ cm^2\ mol^{-1}$) = 24.65 (5.71), 25.75 (3.80), 26.61 (2.85), 26.90 (2.28), 27.36 (1.90), 27.73 (1.43), 28.06 (1.14), 28.66 (0.825); for $Au(dtc)_2AuBr_4$, Λ = 22.02 (3.75), 22.96 (25.01), 23.35 (1.88), 23.60 (1.50), 23.84 (1.25), 24.09 (0.94), 24.71 (0.75), 24.96 (0.63), 25.00 (0.54), 25.16 (0.47), 25.60 (0.34) (numbers in parentheses are millimolar concentrations). These results are consistent with the Onsager limiting law for 1:1 electrolytes in nitrobenzene.

Spectra.—The ultraviolet spectrum of $Au(dtc)_2Br$ was nearly identical with that reported[1] for the $AuBr_2^-$ compound. The two absorption bands, measured in methylene chloride, are 35,600 cm^{-1} (ϵ 37,600) and 31,600 cm^{-1} (ϵ 42,700). For the $Au(dtc)_2AuBr_4$ compound the values are 35,600 cm^{-1} (ϵ 46,000) and 31,600 cm^{-1} (ϵ 25,000).

In the infrared spectra of $Au(dtc)_2Br$ and $Au(dtc)_2AuBr_4$ the C–N stretching frequencies are at 1583 and 1560 cm^{-1}, respectively.

In the series[4] AuI_2dtc, $AuBr_2dtc$, and $AuCl_2dtc$ the C–N stretching frequencies are 1561, 1565, and 1570 cm^{-1}, respectively. The increase in this order is apparently due to the increasing electronegativity of the halogen, resulting in a higher positive charge on the nitrogen atom. In the ionic compounds $Au(dtc)_2AuBr_2$, $Au(dtc)_2AuBr_4$, and $Au(dtc)_2Br$ we have observed a similar increase of the C–N stretching frequencies: 1550, 1560, and 1583 cm^{-1}, respectively. This phenomenon can be explained by assuming an increasing positive charge on the nitrogen atom, induced by the anion, in that order. In view of the crystallographic position of the anion near the nitrogen atom, in this structure such a direct inductive effect is reasonable. The small bromide ion would certainly have the most pronounced inductive effect, followed by the larger $AuBr_4^-$ ion. The influence of $AuBr_2^-$ is small, apparently because of its orientation relative to the nitrogen atom (the N–Br distance is 3.69 (2) Å and the N–Au(I) distance is 4.39 (2) Å). Therefore the effect of the bromine will be partly compensated by the gold atom. The importance of the orientation of the anion is also shown by the isomorphic series[1] $Au(dtc)_2AuX_2$ where the C–N stretching frequencies are at 1550 cm^{-1}, independent of X for X = Cl, Br, and I.

Acknowledgment.—The authors wish to thank Professor J. J. Steggerda for his continued interest in this work.

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[10] S. Åkerström, *Arkiv Kemi*, **14**, 403 (1959).