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

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The preparation, magnetic susceptibility, ultraviolet, infrared, and electron spin resonance spectra, electric conductivity, and X-ray diffraction of a series of compounds bis(N,N-di-*n*-butyldithiocarbamato)gold(III) dihaloaurate(I) of formula $[Au(S_2CN(n\text{-}C_4H_9)_2)_2][AuX_2]$, where X is Cl, Br, I, or CN, are reported. The chlorine, bromine, and iodine compounds are isomorphous and crystallize in the monoclinic space group C2/c. The crystal structure of the bromine compound has been determined by a three-dimensional X-ray analysis. The unit cell dimensions measured from photographs taken at $-150°$ are: $a = 22.38 \pm 0.03$, $b = 15.80 \pm 0.03$, $c = 8.11 \pm 0.04$ Å, $\beta = 98.2 \pm 0.3°$, $Z = 4$. The measured and calculated densities are $D_m = 2.18 \pm 0.01$ and $D_x = 2.18 \pm 0.01$ g cm^{-3}. About 1100 intensities were measured photometrically from equiinclination Weissenberg photographs taken at $-150°$. The structural parameters were refined by least-squares methods to a conventional R factor of 0.11. Although the stoichiometry of these compounds is appropriate for an oxidation state of 2, the diamagnetism and the dissociation as 1:1 electrolytes in nitrobenzene prove them to contain equivalent amounts of Au(I) and Au(III) in AuX_2^- and $[Au(S_2CN(n\text{-}C_4H_9)_2)_2]$, respectively. The Au(I) is linearly coordinated by two X in the AuX_2^- ion. The Au(I)–Br distance is 2.349 ± 0.005 Å. The Au(III) is in planar coordination with four S atoms in the $[Au(S_2CN(C_4H_9)_2)_2]^+$ ion. The two nonequivalent Au–S distances are 2.332 ± 0.009 and 2.333 ± 0.009 Å. Infrared data concerning C–N and Au–X stretching frequencies are in accord with the proposed structure. The halogen–gold stretching frequencies depend upon the nature of the ligand *trans* to the halogen and are little influenced by the oxidation state and the coordination symmetry of the gold.

Introduction

Compounds of composition AuX(dtc) (dtc = N,N-di-*n*-butyldithiocarbamate = $S_2CN(C_4H_9)_2$, X = Cl, Br, I, or CN) were prepared by Blaauw, *et al.*[1,2] They are readily obtained by the reaction of $[Au(dtc)]_2$ and the appropriate amount of halogen, dark intermediates with lifetimes of some seconds being observable. These complexes have a stoichiometry appropriate for divalent gold which, however, does not imply the actual presence of Au(II). Au(II) is only known in complexes with maleonitriledithiolate[3] and phthalocyanine.[4] Esr evidence is reported[5] for the existence of Au(II) in benzene solutions of Au(dtc) and tetraalkylthiuram disulfide. On the other hand $CsAuCl_3$,[6] $AuBr_2S(CH_2C_6H_5)_2$,[7] and some olefin–gold complexes[8] have been shown to consist of distinguishable Au(I) and Au(III).

As we were interested in the oxidation states of the gold atoms, we prepared the complexes AuX(dtc), with X = Cl, Br, or I, and $Au_2BrCN(dtc)_2$ and investigated these compounds by means of X-ray structure analyses, magnetic susceptibility measurements, ultraviolet, infrared, and electron spin resonance spectroscopy, and electric conductivity measurements in solution. All experimental results agree with the ionic configuration $Au(dtc)_2^+ \cdot AuX_2^-$ with clearly distinguishable Au(III) and Au(I) atoms, respectively. The coloring of the solution during the preparation of $Au(dtc)_2AuX_2$ is presumably due to an unstable Au(II) compound disproportionating to equimolar amounts of Au(I) and Au(III) species.

Experimental Section

Preparation of the Complexes.—The complexes $Au(dtc)_2AuX$ with X = Cl, Br, or I were prepared at room temperature by converting gold(I) N,N-di-*n*-butyldithiocarbamate[9] (0.01 mol) dissolved in chloroform (50 ml) with the halogen (0.005 mol) dissolved in carbon tetrachloride (15 ml). After the dark coloring had disappeared most of the solvent was evaporated and the complex was precipitated with carbon disulfide. Recrystallization from acetonitrile or glacial acetic acid gave yellow needles of the compound in 85% yield. These complexes can also be obtained in 75% yield by mixing equimolar amounts of AuX_2-(dtc)[1] and Au(dtc) in chloroform and treating the solution as described above.

The bromocyano compound $Au(dtc)_2AuBrCN$ was obtained from Au(dtc) (0.01 mol) in methylene chloride (50 ml) and cyanogen bromide (0.005 mol) in the same solvent (15 ml). The product was precipitated with ether in the form of yellow needles and recrystallized from ethanol.

Anal. Calcd for $Au(dtc)_2AuCl_2$ (mp 128.5–129°): Cl, 8.1; N, 3.2; S, 14.7. Found: Cl, 8.1; N, 3.2; S, 14.7. Calcd for $Au(dtc)_2AuBr_2$ (mp 143–144°): N, 2.9; S, 13.3. Found: N, 2.9; S, 13.2. Calcd for $Au(dtc)_2AuI_2$ (mp 134.5–135.5°): C, 20.5; H, 3.4; Au, 37.3; N, 2.6; S, 12.1. Found: C, 20.6; H, 3.4; Au, 37.3; N, 2.6; S, 12.7. Calcd for $Au(dtc)_2AuBrCN$ (mp 143.5–144°): C, 25.1; H, 4.0; Au, 43.4; N, 4.6; S, 14.1; Br, 8.8. Found: C, 25.1; H, 4.0; Au, 43.2; N, 4.7; S, 14.1; Br, 8.9.

Spectra.—Uv spectra were measured in methylene chloride and acetonitrile solutions in the range 200–1000 mμ using a Cary 14 instrument. Ir spectra in the region 5000–650 cm^{-1} were measured with a Beckman IR4 double-beam instrument. All specimens were examined in KBr pellets. Spectra of the compounds in Nujol mulls in the region 650–220 cm^{-1} were recorded on a Grubb-Parsons DM4 spectrophotometer. Esr spectra were measured on a Varian V-4502 instrument.

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Magnetic Susceptibility.—Magnetic susceptibility was measured with a standard Gouy-type balance at room temperature.

Electric Conductivity.—Electric conductivities[10] were measured with a Metrohm Konduktoskop E 365 and a Philips PR 9510/00 conductivity cell at 25°. A solution of 0.01 *M* KCl was used for calibration. Equivalent conductivities were measured for 10^{-5}–10^{-3} *M* solutions of $Au(dtc)_2AuBr_2$ in nitrobenzene. The nitrobenzene was purified by freezing out (twice) and vacuum distilling.

X-Ray Crystal Structure Analyses.—From Weissenberg photographs the structures of $Au(dtc)_2AuX_2$ with X = Cl, Br, or I appeared to be isomorphous. A three-dimensional analysis of the bromo compound is reported below. A three-dimensional investigation of the bromocyano compound is in progress; preliminary results indicate a different packing of similar structural units.

Crystal Structure Analysis[11] of $Au(dtc)_2AuBr_2$.—The compound $Au(dtc)_2AuBr_2$ crystallizes in the monoclinic system as prismatic needles along the *c* axis. A crystal of $0.05 \times 0.05 \times 2.0$ mm^3 was used for oscillation (around the *c*-axis), equiinclination Weissenberg (*hk*0 through *hk*6), and precession (*h*0*l* through *h*2*l*) photographs with nickel-filtered Cu Kα radiation (1.5418 Å). The cell dimensions at 20° and their root-mean-square errors (calculated from the experimental errors) are: $a = 22.46 \pm 0.06$, $b = 16.08 \pm 0.05$, $c = 8.19 \pm 0.03$ Å, $\beta = 98.2 \pm 0.3°$, $V = 2927 \pm 15$ Å^3, $Z = 4$. The calculated density was $D_x = 2.18 \pm 0.01$ g cm^{-3}; that measured in paraffin oil using a pycnometer was $D_m = 2.18 \pm 0.01$ g cm^{-3}. On a Nonius Weissenberg camera[12] the crystal was cooled by a cold nitrogen stream, maintaining its temperature at $-150 \pm 10°$. For measurement of the cell parameters, the oscillation and Weissenberg diagrams were now superimposed by KCl diffraction lines for calibration; the cell dimensions at −150°, assuming β to be $98.2 \pm 0.3°$, are: $a = 22.38 \pm 0.03$, $b = 15.80 \pm 0.03$, $c = 8.11 \pm 0.04$ Å. The systematic extinctions are: for *hkl*, $h + k = 2n + 1$; for *h*0*l*, $l = 2n + 1$ ($h = 2n + 1$), which are compatible with the space groups Cc and C2/c. The structure was solved assuming the crystal to be centrosymmetric, confirming the space group to be C2/c. Three-dimensional intensity data were obtained from seven layers of multiple-film Weissenberg photographs at −150°. Of the 2180 attainable symmetry-independent reflections, about 1100 reflections were measured with an optical densitometer and another 600 reflections were estimated visually (slightly above film background). The intensities were corrected for Lorentz, polarization, and Philips factors. No absorption correction was applied ($\mu R = 0.6$; maximum effect on the intensities, 15%). The seven layers were scaled by Wilson's statistical method.

The positions of the gold atoms (centers of symmetry) were deduced from the intensity distribution, and all remaining atoms except hydrogen atoms were located by Fourier methods.[13] The structure was refined by full-matrix least-squares methods.[14] The function that was minimized is: $\Sigma w(|F_o| - |F_c|)^2$. The weight *w* for each reflection was calculated as $w = n/(100 + |F_o| + 0.02|F_o|^2)$, with $n = 1$ for the 1100 measured reflections, $n = 0.25$ for the 600 visually estimated reflections, and $n = 0$ for the zero-observed reflections and for some unreliable 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 1100 measured reflections; values given in parentheses include the 600 visually estimated reflections.

After refinement of the seven scale factors and the positional and individual isotropic temperature factor parameters of all atoms, the *R* factor was 0.13 (0.16). Further refinement with anisotropic temperature factor parameters for the gold, bromine, and sulfur atoms and with fixed scale factors gave $R = 0.11$ (0.15). Finally the scale factors were included again causing only negligible changes in the positional and vibrational parameters (up to 0.5 times the estimated standard deviations) with the same *R* values. The vibrational parameters along *c* (β_{33}) will have little physical significance because of the high correlation coefficients (up to 0.98) between these parameters and the scale factors. The physical significance of the remaining anisotropic temperature factor parameters is reduced by the lack of an absorption correction. The final difference Fourier synthesis[15] showed some peaks of 3 electrons/Å^3 (50% of a carbon atom peak height) in the environment of the gold(III) position probably due to the uncertainty in the scattering power of the chelated atomic system.

Results and Discussion

Crystal Structure of $Au(dtc)_2AuBr_2$.—The atomic parameters are given in Table I. The structure is illustrated in Figures 1 and 2. Bond distances and angles[16] are given in Figure 3. The observed and calculated structure amplitudes are given in Table II.

The crystal structure analysis revealed the compound to be composed of two distinct units $Au(dtc)_2$ and $AuBr_2$. Considering magnetic and conductivity data these units must be positively and negatively charged, $Au(dtc)_2^+$ containing Au(III) and $AuBr_2^-$ Au(I).

In the direction of the needle axis *c* the ions $Au(dtc)_2^+$ are piled on top of each other, adjacent ions being related by a twofold axis. The cation, apart from the butyl chains, is planar within the accuracy of the structure determination; the gold–sulfur coordination is planar by symmetry. The geometry of the dtc group as compared with other dithiocarbamates[17] is normal. The gold–sulfur coordination is similar to the nickel–sulfur coordination in bis(diethyldithiocarbamato)nickel(II).[18] Owing to the greater Au–S distance, the S–Au–S angle (75°) is somewhat smaller than the S–Ni–S angle (79°) in the nickel compound. The gold(III) atoms are $0.5c = 4.095$ Å apart. The shortest van der Waals contact between adjacent cations is a sulfur–sulfur distance of 3.70 Å. The cages formed by the butyl chains of the cations are occupied by the $AuBr_2^-$ anions which are linear by symmetry. The shortest van der Waals contact between cation and anion is a bromine–nitrogen distance of 3.63 Å.

Magnetic Data.—Esr spectra of the bromo compound were measured at room temperature and at −190°, both in the solid state and in chloroform solution. No resonance signal could be obtained. The molar magnetic susceptibility of crystalline $Au(dtc)_2AuBr_2$ was measured at room temperature and found to be -480×10^{-6} cgsu mol^{-1}. This value is very close to the sum of the diamagnetic susceptibilities of the constituent

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(10) Thanks are due to Mr. J. G. M. van der Linden for conductivity measurements.

(11) Thanks are due to Mr. W. P. J. H. Bosman for technical assistance.

(12) A. Kreuger, *Acta Cryst.*, **8**, 348 (1955).

(13) We thank Mrs. E. Rutten-Keulemans for assistance in executing her Fourier program on an ELX1 computer in the initial stage of the analysis.

(14) The program ORFLS by Busing, Martin, and Levy (1962) was modified for simultaneous refinement of isotropic and anisotropic vibrating atoms and used on an IBM 360/40 computer.

(15) A Fourier program and some data handling programs for the IBM 360/40 computer were specially written for this research.

(16) Using "An Interatomic Distances and Angles Program" by R. Shiono and S. S. C. Chu.

(17) H. P. Klug, *Acta Cryst.*, **21**, 536 (1966).

(18) M. Bonamico, G. Dessy, C. Mariani, A. Vaciago, and L. Zambonelli, *ibid.*, **19**, 619 (1965).

TABLE I

ATOMIC PARAMETERS FOR $Au(dtc)_2AuBr_2$ WITH STANDARD DEVIATIONS[a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Au(III)	.0000	.0000	.5000	.0006(1)	.0026(1)	.0070(35)	.0000(1)	.0003(1)	.0005(1)
Au(I)	.2500	.2500	1.0000	.0010(1)	.0028(1)	.0127(35)	-.0005(1)	.0005(1)	.0004(2)
Br	.1986(2)	.1808(3)	.7654(6)	.0018(1)	.0045(2)	.0153(36)	-.0011(1)	.0002(2)	-.0004(4)
S(1)	.0423(4)	.1339(7)	.4813(13)	.0013(2)	.0043(5)	.0089(39)	-.0002(2)	.0003(4)	.0016(7)
S(2)	.0916(4)	-.0235(6)	.4015(13)	.0006(1)	.0024(4)	.0155(41)	.0002(2)	.0004(4)	-.0002(6)
N	.1437(13)	.1249(18)	.3359(39)	B = 2.33(.58) Å^2					
C(1)	.1023(13)	.0827(19)	.3985(40)	1.19(.52)					
C(2)	.1433(14)	.2195(21)	.3163(44)	1.60(.57)					
C(3)	.1016(21)	.2390(29)	.1569(64)	4.42(.98)					
C(4)	.0977(22)	.3373(32)	.1240(64)	5.06(1.06)					
C(5)	.0516(21)	.3599(31)	-.0237(61)	4.24(1.03)					
C(6)	.1926(17)	.0802(25)	.2581(52)	2.65(.75)					
C(7)	.2553(17)	.0946(25)	.3747(53)	2.87(.79)					
C(8)	.3022(16)	.0494(23)	.2859(48)	2.60(.67)					
C(9)	.3646(22)	.0669(33)	.3977(65)	4.77(1.06)					

[a] The key to 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 gold, bromine, and sulfur is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$, the components of the mean-square displacements of the atoms being $24.86\beta_{11}$, $12.65\beta_{22}$, and $3.264\beta_{33}$ Å^2.

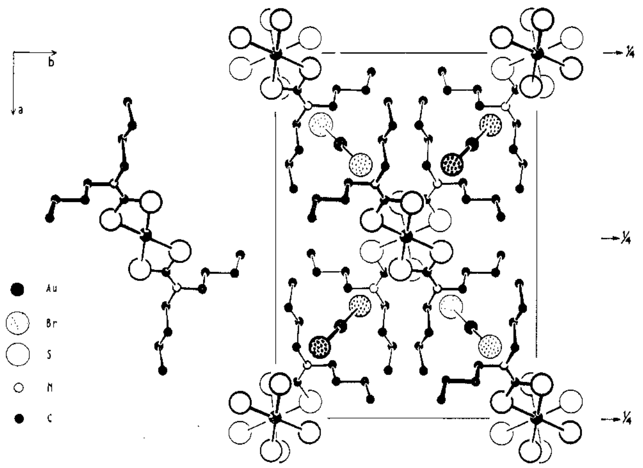

Figure 1.—Projection of $Au(dtc)_2AuBr_2$ along c. Arrows indicate a twofold axis at $z = \pm{}^1/_4$. The gold atoms are situated on a center of symmetry.

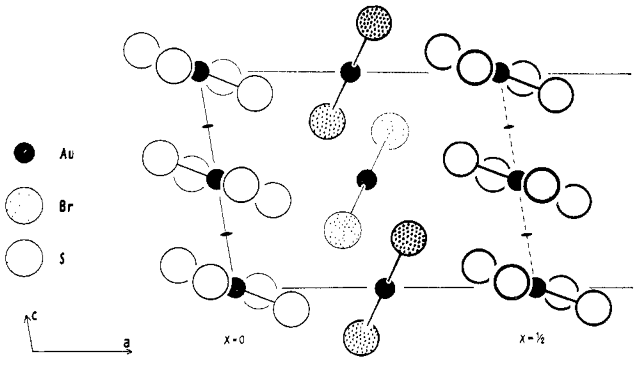

Figure 2.—Projection of $Au(dtc)_2AuBr_2$ along b. Nitrogen and carbon atoms omitted.

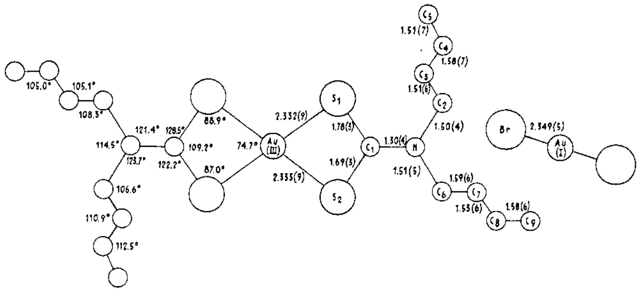

Figure 3.—Bond angles and distances in $Au(dtc)_2AuBr_2$ at −150°. Projection on the plane through the flat part of the cation. The gold atoms are situated on a center of symmetry. Standard deviations of the bond distances (Å) are given in parentheses. The accuracy of the bond angles is limited to 0.3° because of the inaccuracy of the monoclinic angle.

atoms (-420×10^{-6}). The results of esr and susceptibility measurements agree with the structure in which Au(III) is present in a square-planar low-spin d^8 configuration and Au(I) in a linearly coordinated d^{10} configuration.

Molecular Weight.—Cryoscopic molecular weight determination of the bromo compound in nitrobenzene yields 484, which agrees with a complete ionization into $Au(dtc)_2^+$ and $AuBr_2^-$ ions (calcd 481).

Conductance Study.—Equivalent conductivities of $Au(dtc)_2AuBr_2$ in nitrobenzene solutions were measured. In contrast to previously reported[1] results the following values were obtained: $\Lambda = 25.62$ (5.30), 27.82 (1.77), 28.65 (0.884), 29.24 (0.231), and 30.51 (0.042) ohm^{-1} cm^2 mol^{-1} (numbers in parentheses are concentrations in mmol/l.). These results are in the range 25–35 ohm^{-1} cm^2 mol^{-1}, which is normal for 1:1 type electrolytes

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $Au(dtc)_2AuBr_2$[a]

H,	K=0	L=0
2	42	-29
4	107	112
6	23	-12
8	72	73
10	50	46
12	68	65
14	8*	-7
16	74	73
18	33	-31
20	87	107
22	37R	16
24	47	53
28	23	28
H,	K=1	L=0
1	77R	126
3	52	51
5	68	64
7	38	33
9	66	62
11	74	72
13	37	33
15	38	38
17	19*	14
19	42	41
21	43	50
23	33	36
25	29	27
27	16*	18
H,	K=2	L=0
0	15	-11
2	107R	163
4	17	-14
6	67	54
8	26	20
10	99	103
12	35	31
14	81	81
18	64	73
22	62	68
26	32	33
H,	K=3	L=0
1	54	51
3	90	114
5	28	-22
7	68	70
9	67	65
11	74	70
13	87	88
17	50	52
19	30	29
21	26*	29
23	40	40
H,	K=4	L=0
0	51	54
2	4*	-2
4	87	51
6	17	-12
8	109	119
10	38	31
12	106	122
16	65	67
20	53	53
24	38	41
H,	K=5	L=0
1	69	74
3	26	21
5	72	76
7	33	27
9	59	63
11	67	71
13	35	33
15	58	59
17	19*	16
19	45	31
21	35	37
23	15*	23
25	25	25
27	7*	12
H,	K=6	L=0
0	39	34
2	89R	105
4	19	12
6	96	104
8	35	-35
10	109	119
12	14*	-14
14	74	80
18	60	45
20	14*	17
22	51	49
24	11*	13
26	31	38
H,	K=7	L=0
1	58	63
3	62	62
5	57	49
7	48	44
9	46	44
11	25	23
13	41	43
15	22*	24
17	28	26
19	35	28
21	40	32
23	36	33
25	7*	30
27	2*	12
H,	K=8	L=0
0	74	80
2	52	48
4	75	84
6	10*	-16
8	57	106
10	36	-38
12	71	69
16	42	41
18	20*	18
20	44	43
22	15*	19
24	47	44
H,	K=9	L=0
1	59	56
3	51	50
5	17*	11
7	67	63
9	27	29
11	43	33
13	23*	40
15	31	22
17	37	26
19	40	27
21	49R	27
23	38	31
25	7*	8
H,	K=10	L=0
2	60	63
6	79	79
10	79	76
14	51	56
16	22*	10
18	56	41
20	29R	5
22	51	37
H,	K=11	L=0
1	35	35
3	9*	9
5	61	63
9	44	46
11	46	47
13	30R	16
15	37	42
17	35	23
19	33	21
21	37	25
H,	K=12	L=0
0	62	69
2	14*	-14
4	67	66
8	53	56
12	63	51
10	26*	22
16	45	46
20	38	40
H,	K=13	L=0
1	22*	23
3	38	36
5	25*	21
7	35	35
9	37	27
11	29	24
13	58R	23
15	28	20
17	22	20
19	23	27
H,	K=14	L=0
2	65	67
6	50	51
8	12*	10
10	23	24
14	43	36
18	41	42
H,	K=15	L=0
1	22*	23
3	31	27
5	26*	28
7	26*	25
9	24*	15
11	21*	11
13	22*	17
15	23	11
17	26	26
H,	K=16	L=0
0	44	45
4	40	45
6	11*	12
8	32	28
12	34	22
16	31	27
H,	K=17	L=0
1	10*	14
3	13*	15
5	13*	29
7	26R	18
9	15*	13
11	13*	13
13	11*	8
15	19R	26
H,	K=18	L=0
2	20*	25
6	36	36
10	21	23
H,	K=19	L=0
3	14*	20
5	9*	14
7	22	21
9	6*	11
H,	K=20	L=0
4	15R	29
6	3*	3
H,	K=1	L=1
-27	24	-25
-25	28	33
-23	28	-31
-21	28	34
-19	22*	-25
-17	21*	30
-13	17*	25
-11	23	-31
-9	26R	35
-7	88R	-116
-5	58R	126
-3	40R	-98
-1	24R	56
1	62	-69
3	45	43
5	6*	4
7	37	28
9	29	-21
11	67	60
13	84	-74
15	47	59
17	54	-48
19	25	23
21	31	-27
H,	K=2	L=1
-10	28	31
-8	43R	-56
-6	18	-20
-4	15	-21
-2	30R	-41
2	5*	6
4	56	50
6	26	21
8	7*	-9
10	56	48
12	19	-16
16	12*	-13
18	24	-19
H,	K=3	L=1
-27	10*	14
-25	19	-19
-23	23	30
-21	22*	-29
-19	25	35
-17	20*	-31
-15	29	42
-13	18	-27
-11	30	37
-9	49R	-62
-7	52	62
-5	70	-90
-3	53	67
-1	69R	-83
1	77	89
3	51	-50
5	34	42
7	51	-45
9	83	71
11	57	-46
13	55	52
15	65	-54
17	35	28
19	40	-33
21	30	25
23	23	-17
25	9*	14
27	9*	-19
H,	K=4	L=1
-20	25	-29
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8	72	72
10	28*	-22
12	62	61
16	43	37
20	24	25
22	4*	10
H,	K=9	L=4
-23	30	29
-21	7*	13
-19	30	27
-17	40	33
-15	27*	27
-13	31	29
-11	19*	19
-9	34	33
-7	41	40
-5	20*	17
-3	57	56
-1	25*	20
1	37	32
3	52	45
5	37	33
7	51	44
11	36	32
13	30	29
15	21*	15
17	31	27
19	7*	17
H,	K=10	L=4
-22	36	36
-18	39	37
-14	53	47
-10	66	65
-6	67	71
-2	59	56
2	50	48
6	59	57
10	61	60
14	54	48
18	30	32
H,	K=11	L=4
-21	23	24
-17	19*	20
-15	38	32
-13	26*	24
-11	41	38
-9	35	31
-7	23*	20
-5	53	55
-1	36	33
1	29*	27
5	35	35
9	40	37
11	28*	26
13	24*	19
15	39	36
17	7*	15
19	15	14
H,	K=12	L=4
-20	29	31
-16	47	40
-12	55	45
-10	5*	10
-8	40	42
-6	22*	20
-4	49	51
0	54	50
4	51	49
6	11*	-2
8	78	42
12	40	34
16	32	33
H,	K=13	L=4
-19	17*	20
-15	25	23
-13	27	23
-11	23*	19
-9	20*	22
-7	25*	29
-5	15*	20
-3	30*	31
-1	23*	19
1	27*	27
3	26*	24
7	28*	26
9	19*	17
11	21*	21
13	26	23
H,	K=14	L=4
-18	28	33
-14	31	33
-10	31	27
-6	31	27
-2	55	54
2	62	51
6	45	39
10	29	25
14	21	20
H,	K=15	L=4
-13	21*	21
-3	32	23
-1	25*	26
1	22*	24
3	24*	19
5	17*	17
7	21*	20
9	26	17
11	17*	18
H,	K=16	L=4
-12	32	32
-8	23	21
-4	31	33
0	43	44
4	29	33
8	23	26
H,	K=17	L=4
-11	5*	24
-9	5*	12
-1	6*	23
1	4*	15
5	12*	14
9	13*	20
H,	K=1	L=5
-25	12*	15
-23	32	-29
-21	30	33
-19	14*	-17
-17	21	22
-15	9*	-14
-13	18	21
-11	10*	-15
-9	32	29
-7	48	-50
-5	46	50
-3	60	-81
-1	39	56
1	38	-34
3	29	24
5	23	-16
7	25	22
9	7*	-8
11	32	29
13	34	-32
15	33	36
17	28	-35
19	11*	17
21	10*	-17
23	2*	8
H,	K=2	L=5
-20	13*	16
-16	10*	15
-8	23	-20
-6	7*	5
-4	17	-20
-2	32	-29
0	20	13
2	27	-21
4	25	19
6	6*	7
8	10*	15
10	22	19
12	7*	-13
14	5*	12
H,	K=3	L=5
-23	22	20
-21	28	-21
-19	28	30
-17	19*	-21
-15	31	28
-13	16*	-19
-11	23	24
-9	23	-22
-7	33	32
-5	49	-51
-3	41	40
-1	49	-47
1	36	31
3	27	-27
5	38	22
7	16*	-13
9	25	21
11	22	-23
13	35	33
15	16*	-22
17	13*	19
19	16	-21
H,	K=4	L=5
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-16	19*	-18
-10	18	-16
-8	35	33
-6	22	-16
-2	15	15
0	23	-24
2	38	32
4	13*	-12
8	5*	9
10	25	-24
12	19*	20
H,	K=5	L=5
-25	9*	11
-23	7*	-11
-21	8*	15
-19	14*	-17
17	20	20
-15	53	-45
-13	31	29
-11	45	-36
-9	50	47
-7	24	-22
-5	27	26
-3	11*	-10
-1	26	26
1	25	-24
3	46	39
5	50	-46
7	38	34
9	50	-48
11	28	24
13	19*	-18
15	11*	18
19	6*	12
H,	K=6	L=5
-14	23	-23
-10	5*	8
-6	26	22
0	22	18
2	4*	0
4	7*	9
6	15*	-15
8	21	-21
12	5*	-9
14	6*	10
H,	K=7	L=5
-23	5*	7
-21	8*	-8
-19	24	23
-17	26	-22
15	30	29
13	55	-54
-11	42	38
-9	25	-20
-7	36	29
-5	5*	-9
-3	6*	7
-1	22	-19
1	37	36
3	30	-29
5	52	53
7	61	-59
9	22	24
11	20	-21
13	19*	20
15	9*	-13
H,	K=8	L=5
-16	9*	9
-12	8*	-13
-10	19	17
-6	10*	9
-4	18*	-16
-2	7*	-9
4	26	21
8	13*	-7
14	6*	11
H,	K=9	L=5
-23	5*	-16
-21	15	16
-17	35	27
-15	27	-23
-13	30	26
-11	27	-30
-9	39	39
-7	14*	-16
-3	35	-34
1	17*	-12
3	42	41
5	30	-27
7	28	30
9	21	-24
11	21	25
15	7*	13
17	6*	-15
H,	K=10	L=5
-20	13*	7
-18	8*	13
-12	9*	8
-8	24	24
-6	5*	-8
-4	11*	-13
-2	7*	-14
0	7*	-9
2	28	25
12	12*	16
H,	K=11	L=5
-21	4*	-8
-19	20	18
-17	7*	-11
-15	15*	14
-13	21	-19
-11	20	22
-9	15*	-18
-7	38	34
-5	22	-20
-3	8*	10
-1	31	-29
1	27	29
3	16*	-14
5	23	22
7	21	-20
9	7*	13
11	7*	-12
13	21	20
H,	K=12	L=5
-14	4*	-8
-12	6*	-11
-10	7*	16
-6	11*	14
0	11*	12
4	11*	12
10	14*	2
H,	K=13	L=5
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-17	6*	12
-15	19	-17
-11	8*	-10
-9	27	26
-7	10*	-14
-5	30	27
-3	24	-25
-1	32	29
1	10*	-18
3	20	23
5	7*	-11
9	11*	-16
11	7*	12
13	8*	-11
15	2*	19
H,	K=14	L=5
-6	5*	-4
H,	K=15	L=5
-11	15	9
-9	17	-11
-7	19	20
-5	19	-21
-3	20	22
-1	18	-19
1	16	18
H,	K=16	L=5
2	5*	9
H,	K=17	L=5
-9	10	12
-7	5*	-10
-5	3*	8
-3	4*	-15
-1	13	12
1	12	-12
3	11	12
H,	K=0	L=6
-20	36	41
-18	15*	22
-16	51	48
-14	15*	20
-12	60	59
-10	45	-38
-8	70	73
-6	23*	-9
-4	72	76
0	55	51
2	40	39
4	62	58
6	35	26
8	90	77
10	26*	-21
12	57	46
16	41	38
20	20	24
H,	K=1	L=6
-25	26	24
-23	33	29
-19	26*	27
-17	28*	32
-15	24	35
-13	49	44
-9	17*	26
-7	31	34
-5	33	36
-3	48	56
-1	41	31
1	41	35
3	42	37
5	46	36
7	75	63
9	15*	20
11	11*	18
13	11*	19
17	30	29
H,	K=2	L=6
-22	36	35
-18	30*	39
-16	19*	23
-14	63	57
-10	62	62
-8	24*	-12
-6	78	83
-4	13*	16
-2	81	66
2	50	38
4	32	22
6	80	65
10	66	58
14	51	48
18	36	42
20	8*	9
H,	K=3	L=6
-17	25*	30
-15	45	47
-13	19*	20
-11	48	46
-9	27*	33
-7	32	32
-5	65	64
-3	25	21
-1	48	41
3	30	19
5	60	52
7	15*	14
9	41	42
11	16*	25
13	15*	20
15	39	38
17	13*	24
19	26	29
H,	K=4	L=6
-24	31	31
-20	41	33
-16	63	52
-12	58	59
-8	62	64
-4	68	72
0	61	53
4	60	52
8	64	57
12	46	44
16	56	46
18	11*	13
20	29	33
H,	K=5	L=6
-23	17*	22
-19	31*	28
-17	15*	25
-15	27*	27
-13	42	36
-11	24*	29
-9	36	32
-7	47	45
-5	33	27
-3	71	54
1	35	34
3	32	30
5	15*	17
7	42	41
9	16*	24
11	16*	26
13	21*	27
15	11*	17
17	37	33
19	10*	19
H,	K=6	L=6
-22	42	35
-18	62	53
-14	58	52
-10	35	35
-6	55	48
-2	64	65
2	73	72
6	60	62
10	46	34
14	20*	27
18	35	35
H,	K=7	L=6
-21	57R	27
-17	44	33
-15	22*	24
-13	16*	20
-11	16*	22
-9	11*	18
-7	31*	24
-5	34	34
-3	34	31
-1	39	37
1	31*	32
3	32*	32
5	45	41
7	32*	26
9	32*	27
11	20*	21
15	9*	15
H,	K=8	L=6
-20	46	44
-16	50	53
-12	39	36
-8	34	31
-4	46	43
0	63	76
4	56	63
8	36	41
12	10*	22
16	13*	28
H,	K=9	L=6
-19	24*	23
-17	11*	17
-15	41	32
-11	32*	30
-9	11*	15
-7	25*	27
-5	33*	34
-1	32*	36
1	22*	25
3	23*	25
5	32*	32
9	26*	31
13	9*	16
15	9*	25
H,	K=10	L=6
-18	38	31
-14	56	47
-10	41	41
-6	36	42
-2	35	44
2	43	42
6	21*	42
10	24*	22
14	16*	34
H,	K=11	L=6
-17	30	24
-13	44	37
-9	30*	32
-7	11*	23
-5	11*	19
-3	27*	36
5	19*	9
7	14*	28
11	17*	21
13	12*	25
H,	K=12	L=6
-16	31	26
-12	44	40
-8	41	46
-4	30*	46
12	20*	37
H,	K=13	L=6
-15	11*	17
-11	15*	26
-9	9*	13
11	7*	15
H,	K=14	L=6
-14	17*	26
-10	19*	30
-6	15*	34
-2	13*	30
2	12*	30
6	11*	27
10	8*	27

[a] h, $^1/_4|F_o|$, and $^1/_4F_c$ are given for constant k and l. An asterisk indicates visually estimated reflection (slightly above film background). R signifies rejected reflection (bad spot on photograph). Zero-observed reflections are not given; they all have F_c below the minimum observable value.

in nitrobenzene.[19] Feltham and Hayter[20] have emphasized the need to carry out such measurements over a concentration range since molar conductances measured at only one concentration cannot give a definite conclusion about the type of electrolyte present. The concentration dependency is expressed by the Onsager limiting law: $\Lambda = \Lambda_0 - A\sqrt{c} = \Lambda_0 - (\alpha\Lambda_0 + \beta)\sqrt{c}$. By plotting Λ as a function of $\sqrt{c}$ we found for the compound under investigation $\Lambda_0 = 30.7$ ohm^{-1} cm^2 mol^{-1} and $A = 69.7$. This value of A can be compared with a value that can be calculated assuming a 1:1 electrolyte to be present.[21] Using data for dielectric constant and viscosity of nitrobenzene given by Fuoss,[22] $A = 0.780\Lambda_0 + 44.12$, which for $\Lambda_0 = 30.7$ gives $A = 68$. Observed and calculated values of A are in close agreement. It can therefore be concluded

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[19] C. M. Harris, *J. Chem. Soc.*, 682 (1959).

[20] R. D. Feltham and R. G. Hayter, *ibid.*, 4587 (1964).

[21] R. M. Fuoss, *J. Am. Chem. Soc.*, **81**, 2659 (1959).

[22] R. M. Fuoss and E. Hirsch, *ibid.*, **82**, 1013 (1960).

TABLE III

COMPARISON OF Au–Cl AND Au–Br STRETCHING FREQUENCIES AT 400–200 CM^{-1} [a]

Compound (X = Cl or Br)	Ref	Au–Cl, cm^{-1}		Au–Br, cm^{-1}		Oxidn no.
		Hard	Soft	Hard	Soft	
$Au(dtc)_2AuX_2$	This work	360–345		255		I
AuX_2 (dtc)	1, 2		335–320		240	III
AuXL						
L = $P(CH_3)_3$	23		311		226	I
L = $P(C_2H_5)_3$	23		312		210	I
L = $P(C_6H_5)_3$	23		329		233	I
L = $S(CH_3)_2$	23		324		228	I
L = $As(CH_3)_2$	23		317		210	I
$CsAuCl_4$	23	356				III
$KAuBr_4$	23			249		III
trans-$AuP(C_2H_5)_3ClBr_2$	23		311	263		III
AuX_3L						
L = pyridine	23	365		264, 261		III
L = $P(CH_3)_3$	23			260	213	III
L = $P(C_2H_5)_3$	23	371	302	263	215	III
$Cs_2Au_2Cl_6$ (with $AuCl_2^-$ and $AuCl_4^-$)	23	350, 340				I, III
Range		371–340	335–302	264–249	240–210	
Mean value		356	317	259	222	

[a] Hard and soft refer to the ligand in *trans* position to the Cl and Br atoms.

that $Au(dtc)_2AuBr_2$ is a 1:1 electrolyte in nitrobenzene solution.

Electronic Specta.—The ultraviolet spectra of the chloro, bromo, iodo, and bromocyano compounds are identical within the limits of experimental accuracy. In methylene chloride only two strong absorption bands at low frequency can be detected: 36,100 cm^{-1} (ϵ 48,000) and 31,400 cm^{-1} (ϵ 47,000) (see Figure 4). The absorption bands can be interpreted to be of the charge-transfer type of the $Au(dtc)_2^+$ species, no absorption of the anions being observed. There is a striking resemblance between the spectra of methylene chloride solutions of $Au(dtc)_2^+$ and the isostructural compound $Ni(dtc)_2$ (absorption bands at 40,800 cm^{-1} (ϵ 49,000) and 30,500 cm^{-1} (ϵ 50,000)).

Infrared Spectra.—Independent of X for all compounds $Au(dtc)_2AuX_2$, the dithiocarbamato ligand has a C–N stretch frequency at 1550 cm^{-1}. This value lies between the C–N stretch frequency of Au(dtc)[1] (1488 cm^{-1}) and those of dihalodithiocarbamatogold(III)[1] ($AuCl_2$(dtc), 1570 cm^{-1}; $AuBr_2$(dtc), 1565 cm^{-1}; and AuI_2(dtc), 1561 cm^{-1}) as is to be expected considering the structure of these compounds. In the infrared spectrum of $Au(dtc)_2AuBrCN$ the C≡N stretch frequency of the anion is observed at 2141 cm^{-1}, a value identical with the asymmetric C≡N stretch frequency in $KAu(CN)_2$.[23] In the region 650–220 cm^{-1} the following absorptions are found: for $Au(dtc)_2AuCl_2$: 615 w, 590 s, 505 w, 450 w, 410 m, 380 s, 360–345 br, s; for $Au(dtc)_2AuBr_2$: 615 w, 590 s, 505 w, 450 w, 410 m, 380 s, 255 s (w, weak; m, medium; s, strong; br, broad). The band at 380 cm^{-1} is assigned to the gold–sulfur stretching mode according to the normal coordinate analysis of the dithiocarbamato complexes, carried out by Nakamoto;[24] the bands at 255 and 360–345 cm^{-1} are attributed to the gold–bromine and gold–chlorine stretching frequencies, respectively. Unfortunately, however, the Au–^{35}Cl and Au–^{36}Cl frequencies were not clearly resolved. These data can be compared with those of Coates and Parkin[25] (see Table III). Obviously the gold–halogen stretching frequencies depend mainly on the ligand *trans* to the halogen in the complex. The same conclusion was recently reported[26] with regard to metal–halogen stretching frequencies in complexes of Rh and

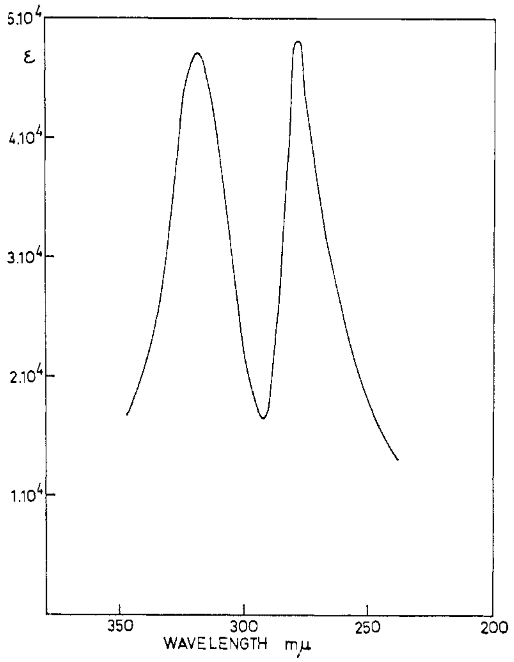

Figure 4.—Ultraviolet spectrum of $Au(dtc)_2AuBr_2$ in methylene chloride solution.

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[23] L. H. Jones cited by F. A. Cotton in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 334.

[24] K. Nakamoto, J. Fujita, R. A. Condrate, and Y. Morimoto, *J. Chem. Phys.*, **39**, 423 (1963).

[25] G. E. Coates and C. Parkin, *J. Chem. Soc.*, 421 (1963).

[26] M. A. Bennett, R. J. Clark, and D. L. Milner, *Inorg. Chem.*, **6**, 1647 (1967).

Ir. In Table III a (rather rough) separation is made between high and low frequencies, the corresponding ligands being classified as hard and soft, respectively. A further study of these infrared correlations may need a more subtle nomenclature. The oxidation number and the corresponding coordination symmetry of the gold seem to have (only) little influence on the gold–halogen stretching frequencies.

Contribution from the Department of Inorganic Chemistry,
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Structure and Properties of Dibromo-N,N-di-*n*-butyldithiocarbamato Complexes of Copper(III) and Gold(III)

By P. T. Beurskens, J. A. Cras, and J. J. Steggerda

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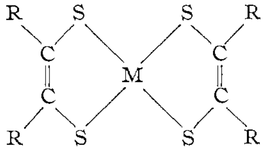
Preparation, crystal structure, and some magnetic and spectral properties of dibromo-N,N-di-*n*-butyldithiocarbamatocopper(III) and -gold(III), $CuBr_2S_2CN(n\text{-}C_4H_9)_2$ and $AuBr_2S_2CN(n\text{-}C_4H_9)_2$, are reported. These compounds form isomorphous crystals in the monoclinic space group C2/c. The cell dimensions measured from photographs are: $a = 13.85 \pm 0.03$, $b = 14.94 \pm 0.03$, $c = 7.28 \pm 0.02$ Å, $\beta = 98.8 \pm 0.3°$ for the copper compound and $a = 13.85 \pm 0.03$, $b = 14.94 \pm 0.03$, $c = 7.41 \pm 0.02$ Å, $\beta = 98.8 \pm 0.3°$ for the gold compound, with four molecules per unit cell. The crystal structure of the copper compound has been determined by a three-dimensional X-ray analysis. About 780 intensities were measured photometrically from equiinclination Weissenberg photographs. The structural parameters were refined by least-squares methods to a conventional R factor of 0.10. The ismorphous gold compound was refined in projection with 94 $hk0$ intensities until the R factor was 0.09. The compounds have Cu(III) and Au(III) in a planar fourfold coordination with two Br and two S. The Cu–S and the Cu–Br distances of 2.193 ± 0.006 and 2.311 ± 0.004 Å, respectively, are significantly smaller than those in Cu(II) compounds. This suggests an appreciable ionic contribution in the copper–ligand bonding. The diamagnetic behavior of these compounds is in accord with a low-spin d^8 configuration.

Introduction

During our work on the redox properties of dithiocarbamato complexes of transition metals we succeeded in synthesizing $CuBr_2(dtc)$ (dtc = N,N-di-*n*-butyldithiocarbamate = $S_2CN(C_4H_9)_2$) by a reaction analogous[1,2] to the preparation of $AuBr_2(dtc)$: $Cu(dtc) + Br_2 \rightarrow CuBr_2(dtc)$. This $CuBr_2(dtc)$ belongs to the very small group of Cu(III) compounds. Only potassium hexafluorocuprate(III), the alkaline earth and alkali cuprates(III), some periodato and tellurato complexes,[3] and the recently reported bisbiuretato complex[4] have been identified as Cu(III) compounds. In the series of planar complexes of the type



the significance of the oxidation number of the metal has been subject to discussion because the highest filled orbitals in these complexes have appreciable ligand character. We think the formal concept of oxidation number is however still appropriate for nomenclature purposes and for an easy counting of electrons. In this formal sense it can be said that Cu(III) complexes are known with bis(trifluoromethyl)-1,2-dithieten,[5] benzene-1,2-dithiolate,[6] and maleonitriledithiolate.[7] The compound $CuBr_2(dtc)$ having a lower coordination symmetry than the former compounds seems to be an interesting new member of the Cu(III) family. We report the crystal structure and some magnetic and spectral properties of it as well as of the isomorphous $AuBr_2(dtc)$.

Converting Cu(dtc) with 0.5 mol of Br_2 a compound of stoichiometric composition CuBr(dtc) is formed. On account of its paramagnetic character it seems to be a Cu(II) compound which is in contrast with the gold compound of similar composition, reported[8] to be $Au(dtc)_2^+AuBr_2^-$ with Au(III) and Au(I), respectively. Structural studies of this CuBr(dtc) are in progress.

Experimental Section[9]

Preparation of the Complexes.—Cu(dtc) was prepared from copper powder (Merck, electrolytically prepared) and tetra-*n*-butylthiuram disulfide (Fluka Praktikum) according to Åkerström.[10]

$CuBr_2$(dtc) was prepared from a solution of Cu(dtc) in carbon disulfide (25 mg/ml) which was converted at room temperature

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

[2] Cu(dtc) and Au(dtc) are polymeric in solution (see ref 3). Monomeric formulas are used for the sake of simplicity.

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