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Gold(I) Complexes of Thio- and Dithiocarbamate Esters. The Structure of Bis(*N*-methyl-*O*-ethyl-thiocarbamate)gold(I) Chloride

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Abstract

The complexes Au(TMDT)Br, Au(TMDT)Cl, [Au(PPh$_3$)(TMDT)]NO$_3$ and Au(MTC)$_2$Cl (TMDT = *N,N*-dimethyl-*S*-methyl-dithiocarbamate, MTC = *N*-methyl-*O*-ethyl-thiocarbamate) have been prepared and characterized. The crystal structure of Au(MTC)$_2$Cl was determined by X-ray crystallography and refined to $R = 0.035$ based on 2654 observed reflections. The compound is triclinic, space group $P\bar{1}$, with $a = 6.937(6)$, $b = 9.439(5)$, $c = 12.286(4)$ Å, $\alpha = 74.16(3)$, $\beta = 99.54(3)$, $\gamma = 108.06(3)°$. The structure consists of Au(MTC)$_2^+$ cations significantly distorted from the linear coordination, with a S–Au–S angle of 155.3(1)° and Au–S bond distances of 2.286(2) and 2.284(2) Å, and uncoordinated Cl$^-$ anions hydrogen bonded to the two MTC ligands in each cation, with N–H···Cl distances of 3.04(1) Å. ^{1}H NMR spectra of the dithiocarbamate complexes are consistent with coordination of the ligand through its thiocarbonyl sulfur atom.

Introduction

We reported previously on various platinum(II) and palladium(II) complexes of thio- and dithiocarbamate esters [1–3]. The interesting cytostatic properties displayed by some of these complexes *in vitro* [1, 2] prompted us to extend our research to gold(I) complexes. The antineoplastic activity of gold(I) complexes has been demonstrated recently [4]. This paper describes the gold(I) complexes Au(TMDT)Br, Au(TMDT)Cl, [Au(PPh$_3$)(TMDT)]NO$_3$ and Au(MTC)$_2$Cl (TMDT = *N,N*-dimethyl-*S*-methyl-dithiocarbamate, MTC = *N*-methyl-*O*-ethyl-thiocarbamate). The structure of the complex Au(MTC)$_2$Cl has been determined by X-ray crystallography.

Experimental

KAuBr$_4$, Au(PPh$_3$)NO$_3$, TMDT and MTC were prepared according to literature methods. All other chemicals were reagent grade.

Au(TMDT)Br

In a typical preparation a solution of TMDT (0.027 g, 0.2 mmol) in ethanol (5 ml) was added dropwise with continuous stirring to a solution of KAuBr$_4$ (0.055 g, 0.1 mmol) in ethanol (5 ml). The color of the solution changed from red to yellow. After a few minutes the product began to separate as yellow needles. The compound was filtered, washed with ethanol and dried.

Anal. Found: C, 11.7; H, 2.2; N, 3.3. Calc. for C$_4$H$_9$AuBrNS$_2$: C, 11.7; H, 2.2; N, 3.4%.

Au(TMDT)Cl

The compound was prepared as a white solid from (Et$_4$N)AuCl$_4$ with a method similar to that of the corresponding bromide.

Anal. Found: C, 13.0; H, 2.6; N, 3.6. Calc. for C$_4$H$_9$AuClNS$_2$: C, 13.1; H, 2.5; N, 3.8%.

[Au(PPh$_3$)(TMDT)]NO$_3$

To a solution of Au(PPh$_3$)NO$_3$ (0.128 g, 0.24 mmol) in CH$_2$Cl$_2$ (4 ml) a solution of TMDT

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(0.070 g, 0.52 mmol) in CH_2Cl_2 (2 ml) was added. The solvent was evaporated and the oily residue crystallized by treatment with a mixture of n-hexane and ether. The white compound was filtered, washed with n-hexane and dried.

Anal. Found: C, 40.1; H, 3.7; N, 4.1. Calc. for $C_{22}H_{24}AuN_2O_3PS_2$: C, 40.3; H, 3.7; N, 4.3%.

Au(MTC)₂Cl

To a solution of $AuCl_3$ (0.29 g, 0.95 mmol) in ethanol (3.5 ml) MTC (1.27 g, 10.66 mmol) was added. The color of the solution turned from orange to pale yellow in a few seconds when a white solid was formed. Addition of diethyl ether (10 ml) to the filtered solution caused the immediate precipitation of a yellow solid which was filtered off. Upon standing colourless crystals of the product separated.

Anal. Found: C, 20.0; H, 3.8; N, 5.4. Calc. for $C_8H_{18}AuClN_2O_2S_2$: C, 20.4; H, 3.9; N, 6.0%.

Proton NMR Spectra

Measurements of spectra of solutions in $CDCl_3$ were performed on a JEOL FX-90 spectrometer, with chemical shifts relative to external $SiMe_4$.

X-ray Data

A regular prismatic crystal of maximum dimensions 0.2 mm was used for measurements. Data collection was made on a Philips diffractometer with Mo Kα radiation. Cell dimensions were determined by least-squares refinement of 25 medium-angle settings. Crystal data: $C_8H_{18}AuClN_2O_2S_2$, formula weight = 467, triclinic, $P\bar{1}$, $a = 6.937(6)$, $b = 9.439(5)$, $c = 12.286(4)$ Å, $\alpha = 74.16(3)$, $\beta = 99.54(3)$, $\gamma = 108.06(3)°$, $U = 733$ Å^3, $D_c = 2.13$ g cm^{-3} for $Z = 2$; $\mu = 101$ cm^{-1} (Mo Kα). The crystal is stable under irradiation and of a total of 3529 unique reflections recorded, whose intensities were corrected for Lp and for absorption [5], 2654 with $I > 3\sigma(I)$ were considered as observed and used in subsequent calculations.

Solution of the structure was achieved by Patterson and Fourier methods alternated with cycles of least-squares refinement of the atomic parameters. At convergence, the residual conventional R factor was 0.035, based on the observed reflections. The function minimized was $\Sigma w(\Delta F)^2$, with $w = 1$. The SHELX-76 programs package and its scattering factors were used in the calculations [6]. Scattering factors for Au were those of ref. 7. Final atomic parameters are listed in Table 1; selected bond lengths and angles are reported in Table 2.

Results and Discussion

The complexes Au(TMDT)X (X = Br or Cl) and $Au(MTC)_2Cl$ were obtained by reaction of the ligands with AuX_4^- and $AuCl_3$, respectively. These reactions involving reduction of gold(III) to gold(I) by the thio- or dithiocarbamate ester are similar to the reactions of gold(III) halogeno-complexes with dialkylsulfides [8].

TABLE 1. Final atomic parameters

Atom	x/a	y/b	z/c
Atomic coordinates			
Au1	0.13405(5)	0.49712(4)	0.20631(3)
Cl1	0.3979(3)	0.7967(2)	0.3053(2)
S1	−0.1304(3)	0.5786(2)	0.0987(2)
C1	0.1355(11)	0.7517(8)	0.1129(6)
N1	0.0006(9)	0.8374(7)	0.1722(6)
C2	0.0123(17)	0.9843(12)	0.1843(10)
O1	−0.2865(7)	0.8108(5)	0.0625(4)
C3	−0.4646(11)	0.7185(9)	0.0026(7)
C4	−0.6049(13)	0.8162(10)	−0.0442(9)
S2	0.3237(3)	0.3283(2)	0.2811(2)
C5	0.5549(10)	0.4070(8)	0.3495(6)
N2	0.6111(10)	0.5451(7)	0.3657(6)
C6	0.8048(12)	0.6043(10)	0.4317(8)
O2	0.6864(7)	0.3276(5)	0.3882(4)
C7	0.6362(13)	0.1691(9)	0.3780(8)
C8	0.8066(13)	0.1058(10)	0.4393(9)
Calculated hydrogen coordinates			
H1	0.1255	0.8140	0.1992
H21	−0.0764	0.9694	0.2258
H22	−0.0635	1.0495	0.1040
H23	0.1341	1.0500	0.2146
H31	−0.4163	0.6892	−0.0654
H32	−0.5390	0.6149	0.0611
H41	−0.6381	0.8478	0.0115
H42	−0.7436	0.7501	−0.0819
H43	−0.5334	0.9141	−0.1082
H2	0.5275	0.6303	0.3323
H61	0.8234	0.7281	0.4322
H62	0.9311	0.6021	0.3919
H63	0.8042	0.5331	0.5170
H71	0.4963	0.1026	0.4161
H72	0.6187	0.1665	0.2895
H81	0.7775	0.0115	0.4343
H82	0.8226	0.1108	0.5272
H83	0.9451	0.1748	0.4006

The ^1H NMR spectrum of Au(TMDT)Br in $CDCl_3$ displays resonances at $\delta = 3.90$ (N-CH_3), 3.54 (N-CH_3), 2.94 (S-CH_3). The spectrum of the free ligand displays resonances at $\delta = 3.54$ (N-CH_3), 3.37 (N-CH_3), 2.63 (S-CH_3). The downfield shifts of the methyl resonances observed upon complexation are similar to those found for the platinum(II) complex $[Pt(S_2CNEt_2)(TMDT)]$ [1], whose crystal structure was determined, and indicate metal coordination through the thiocarbonyl sulfur atom. The solutions of the complex are not stable. Formation of metallic gold and darkening of the solutions upon standing

TABLE 2. Bond and contact distances (Å) and angles (°) for $Au(MTC)_2Cl$ (e.s.d.s in parentheses refer to the last significant digit)

Au–S(1)	2.286(2)	Au–S(2)	2.284(2)
S(1)–C(1)	1.70(1)	S(2)–C(5)	1.73(1)
C(1)–N(1)	1.30(1)	C(5)–N(2)	1.30(1)
N(1)–C(2)	1.47(2)	N(2)–C(6)	1.48(1)
C(1)–O(1)	1.32(1)	C(5)–O(2)	1.31(1)
O(1)–C(3)	1.48(1)	O(2)–C(7)	1.46(1)
C(3)–C(4)	1.49(1)	C(7)–C(8)	1.49(1)
Au···Cl(1)	3.280(2)		
Cl(1)···H(1)	2.13	Cl(1)···H(2)	1.97
Cl(1)···N(1)	3.04(1)	Cl(1)···N(2)	3.04(1)
S(1)–Au–S(2)	155.3(1)		
Au–S(1)–C(1)	113.1(3)	Au–S(2)–C(5)	113.6(3)
S(1)–C(1)–N(1)	125.5(6)	S(2)–C(5)–N(2)	123.9(6)
S(1)–C(1)–O(1)	120.8(5)	S(2)–C(5)–O(2)	120.3(6)
N(1)–C(1)–O(1)	113.7(6)	N(2)–C(5)–O(2)	115.7(7)
C(1)–N(1)–C(2)	123.6(7)	C(5)–N(2)–C(6)	122.1(7)
C(1)–O(1)–C(3)	119.8(6)	C(5)–O(2)–C(7)	120.3(6)
O(1)–C(3)–C(4)	106.6(6)	O(2)–C(7)–C(8)	107.4(7)

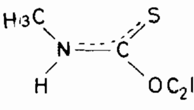
indicate that disproportion of gold(I) takes place according to the reaction

$$3Au(TMDT)Br = 2Au + Au(TMDT)Br_3 + 2TMDT$$

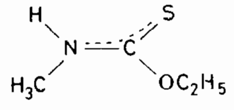
This is confirmed by the appearance of signals at $\delta = 3.86$, 3.65 and 2.94 identical with those displayed by a fresh solution of Au(TMDT)Br treated with bromine. Additional signals apparent from the aged solutions of Au(TMDT)Br are assigned as time averaged resonances of the residual gold(I) complex and the free ligand. The proton spectrum of Au(TMDT)Cl displays resonances at $\delta = 3.91$ (N-CH_3), 3.55 (N-CH_3) and 2.95 (S-CH_3), consistent with the same binding mode of TMDT as in the corresponding bromo complex.

The compound $[Au(PPh_3)(TMDT)]NO_3$ obtained by reaction of TMDT with $Au(PPh_3)NO_3$ can be formulated as a ionic species containing a two-coordinated gold(I) cationic complex. The proton spectrum displays resonances at $\delta = 3.93$ (N-CH_3), 3.70 (N-CH_3), 2.85 (S-CH_3) and *c.* 7.5 (C_6H_5). The downfield shift of the methyl resonances with respect to the free ligand is consistent with coordination of TMDT through the thiocarbonyl sulfur atom. The changes of chemical shifts of TMDT observed upon complexation in the phosphine complex are somewhat different from those observed in the other complexes, possibly due to the cationic nature of the complex and to effects of magnetic anisotropy of the phosphine ligand. It is noted that TMDT is not able to displace the chloride ligand from the complex $Au(PPh_3)Cl$. Thus, no changes of ^1H NMR resonances are observed upon mixing these species in $CDCl_3$. This result indicates a relatively low coordinating ability of the dithiocarbamate ester.

The ^1H NMR spectrum of a freshly prepared solution of 0.2 M $Au(MTC)_2Cl$ in $CDCl_3$ displays resonances at $\delta = 10.93$ (NH), 4.51 (CH_2), 2.93 (N-CH_3) and 1.38 (C-CH_3) ([$J(CH_2–CH_3)$] = 7 Hz, [J(NH–CH_3)] = 5 Hz), consistent with the presence of complexed MTC in the *anti* conformation, as found in the solid compound.



syn



anti

The spectrum of uncomplexed MTC in $CDCl_3$ displays two sets of resonances at $\delta = 4.50$ (CH_2), 3.08 (N-CH_3), 1.30 (C-CH_3) and at $\delta = 4.56$ (CH_2), 2.87 (N-CH_3), 1.37 (C-CH_3), ascribed to the *syn* and *anti* isomer, respectively, with intensities in the ratio 64:36 [9, 10].

The crystal structure of $Au(MTC)_2Cl$ is shown in Fig. 1 together with the atom-numbering scheme. The structure consists of $Au(MTC)_2^+$ cations significantly distorted from the linear coordination (the S–Au–S angle is 155.3(1)°), and uncoordinated Cl^- anions hydrogen bonded to the MTC ligands to

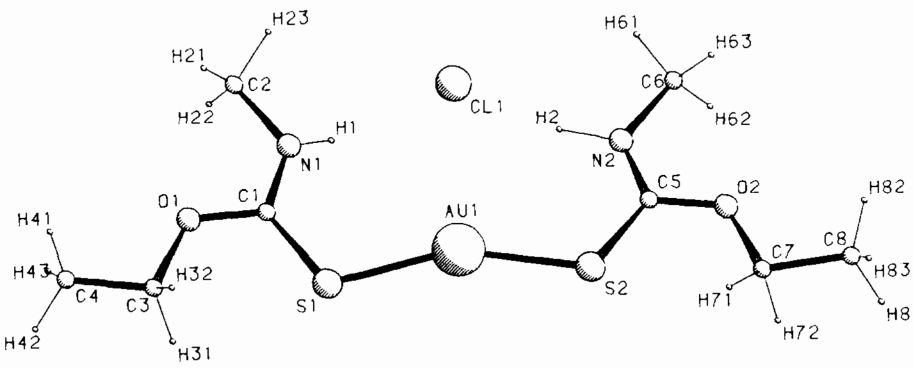


Fig. 1. The structure of $Au(MTC)_2Cl$.

form a ten-membered metallacycle. The ten atoms are approximately coplanar, the maximum deviation from the calculated mean plane being 0.2 Å. The conformation of each ligand with the methyl group in the *anti* position with respect to the sulfur atom can be accounted for by steric requirements. The *anti* conformation has been found also in the structure of a palladium(II) complex of this ligand, *trans*-Pd(MTC)$_2$(SCN)$_2$ [11], and of platinum(II) complexes of other thiocarbamic esters, *trans*-Pt(ETC)$_2$I$_2$ [12] and [Pt(PTC)$_3$Cl]Cl [13], (ETC = *N*-ethyl-*O*-ethyl-thiocarbamate, PTC = *N*-propyl-*O*-ethyl-thiocarbamate). The distortion from the linear coordination and the *cis* conformation of the MTC ligands about the gold atom, with the NH groups directed towards the Cl$^-$ anion, can be ascribed to the formation of two relatively strong N–H···Cl hydrogen bonds. A similar conformation has been found in the analogous gold(I) complex Au(imidazolidine-2-thione)$_2$Cl·H$_2$O [14], where the distortion from the linear coordination and the unexpected *cis* arrangement of the ligands are dictated by hydrogen bonding between the NH groups on the rings and the O atom of the crystallization water molecule. The Au–S bond lengths of 2.286(2) and 2.284(2) Å in Au(MTC)$_2$Cl are close to the corresponding values in the imidazolidine-2-thione complex (2.278(9) and 2.279(8) Å). The S–Au–S angle in the MTC complex, however, is noticeably smaller than the corresponding angle of 167.2(2)° in the other complex. The Au···Cl distance of 3.280(3) Å in Au(MTC)$_2$Cl is between the sum of the ionic radii (3.18 Å [15]) and that of the van der Waals radii (3.4–3.6 Å [16]) of Au and Cl, suggesting the presence of a relatively strong interaction between these ions. The observed distances for the C–S, C(sp^2)–N and C(sp^2)–O bonds in Au(MTC)$_2$Cl are close to the corresponding distances in *trans*-Pd(MTC)$_2$(SCN)$_2$ [11], and *trans*-Pt(ETC)$_2$I$_2$ [12]. The mean C–S bond length of 1.715 Å in Au(MTC)$_2$Cl corresponds to a π bond order of 0.4 according to a proposed relationship between bond order and length of carbon–sulfur bonds [17].

Supplementary Material

A Table of thermal parameters is available from the authors on request.

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