Preparation and Crystal Structure of Bis(isocyanide)gold(I) Bis(phenylene-1,2-dithiolato)aurates(III)

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The reaction of (isocyanide)gold(I) chlorides [(RNC)AuCl, R = ^{*t*}Bu, ^{*c*}Hex] with phenylene-1,2-dithiol and sodium methoxide (molar ratio 2:1:2) in methanol / dichloromethane leads to the formation of deep green mixed-valent salts [(RNC)₂Au]⁺[Au(S₂C₆H₄)₂]⁻ in *ca.* 35% yield. As determined by single crystal X-ray diffraction methods, the two compounds have entirely different supramolecular structures. For R = ^{*t*}Bu stacked planar anions and rod-like cations form alternating layers, while for R = ^{*c*}Hex alternating cations and anions are arranged in chains with long S--Au contacts [3.422 Å].

Introduction

The reaction of (phosphine)gold(I) or (isocyanide)gold(I) halides $[(R_3P)AuX / (RNC)AuX;$ X = Cl, Br, I; R = alkyl, aryl] with simple thiols RSH in the presence of an auxiliary base affords high yields of the corresponding thiolates LAuSR. Many of these compounds have interesting structural properties and are key substrates for many applications ranging from "liquid golds" for gilding to preparations for chemotherapy [1]. Difunctional thiols HS-Q-SH with the -SH groups well separated by an organic spacer -Q- (an alkanediyl, alkenediyl, alkynediyl, or arenediyl) give the same type of dinuclear thiolates LAu-S-Q-S-AuL [2 - 5].

By contrast, related reactions with phenylene-1,2-dithiol (dithiocatechol) with (phosphine)gold(I) halides are reported to lead to an unexpected redox process in which gold(III) complexes of a deep green colour are produced [6, 7]. In a typical example, (Et₃P)AuCl and 1,2-C₆-H₄(SH)₂ are converted to a significant extent (together with several by-products, not all of which have been identified) into a salt with the colourless bis(triethylphosphine)gold(I) cation [(Et₃P)₂Au]⁺ and the green bis(phenylene-1,2-dithiolato)gold(III) anion [Au(S₂C₆H₄)₂]⁻ [6]. With ⁱPro₃P similar results were obtained, but smaller amounts of the green by-product were observed [8]. In an attempt to probe this unusual reaction with complexes in which the tertiary phosphine is replaced by an isocyanide ligand, very similar results have now been obtained [8]. The products have very interesting supramolecular structures as illustrated in the present report.

Reaction Products

^tButyl- and ^chexyl-isocyanide were chosen as the ligands RNC because they were expected to exert similar electronic, but different steric effects. Their gold(I) complexes are readily prepared from (dimethylsulfide)- or (tetrahydrothiophene)gold(I) chloride and the free isocyanide, and the products can be dissolved in dichloromethane [9, 10]. These solutions are then treated at room temperature with a methanol solution of disodium phenylene-1,2-dithiolate, prepared in situ from $1,2-C_6H_4$ (SH)₂ and two equivalents of MeONa. After evaporation of the solvents the products can be extracted from the residue with dichloromethane. Crystallization from dichloromethane / pentane gives deep green needles in yields of ca. 35%. There is a mixture of byproducts in the mother liquors ($\mathbf{R} = {}^{t}\mathbf{B}\mathbf{u}, {}^{c}\mathbf{H}\mathbf{e}\mathbf{x}$) of which two can be separated ($R = {}^{c}Hex$). They have been identified as a co-crystallisate of a tetranuclear cluster $[(^{c}HexNC)Au_{2}(S_{2}C_{6}H_{4})]_{2}$ and a carbene complexe { $(^{c}HexNC)Au[C(NH^{c}Hex)_{2}]$ }Cl [8].

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Fig. 1. Cation and anion of the cyclohexylisocyanide complex **2**. [ORTEP drawing with 50% probability ellipsoids]. Selected distances [Å] and angles [°]: Au1-S1 2.308(1), Au1-S2 2.305(1), Au2-C1 1.968(6), C1-N1 1.146(8), N1-C223 1.443(7); S1-Au1-S2 89.78(5), S1-Au1-S2'90.22(5), S1-Au1-S1'180.0, S2-Au1-S2'180.0, C1-Au2-C1'180.0, Au2-C1-N1 175.2(6), C1-N1-C223 177.1(6).

2 (RNC)AuCl + 1,2-C₆H₄(SNa)₂
$$\rightarrow$$

[(RNC)₂Au]⁺[Au(1,2-S₂C₆H₄)₂]⁻ + by-products
1: R = ^{*t*}Bu, 2: R = ^{*c*}Hex

Compounds 1 and 2 have been identified by their elemental analyses, and FAB mass spectra have confirmed both the cation and the anion of compound 2. The NMR spectra (in CDCl₃ solution at 20°C) gave the expected signals for the ¹H and ¹³C nuclei (Experimental Part). The chemical shifts of the anion resonances are almost identical for both compounds. The compounds are stable in air and not sensitive to light. The crystals can be dissolved in dichloromethane, trichloromethane and tetrahydrofuran, but they are insoluble in pentane and diethyl ether.

Crystal Structures

Crystals of the *cyclohexyl* isocyanide complex **2** are triclinic, space group $P\overline{1}$, with one formula unit in the unit cell. The asymmetric unit contains one half of the cation and one half of the anion, the remainder of the two ions being generated by inversion symmetry (Fig. 1).

The cation is a rod-like entity with a quasi-linear array of no less than seven atoms. The cyclohexyl rings are in a chair conformation. In the anion, the atoms of each dithiolate ligand are planar with the two planes parallel to each other, but slightly tilted



Fig. 2. Stacking of cations and anions of compound 2 in the unit cell. View parallel to the *b* axis.

against the AuS_4 unit, which is planar by symmetry. The geometry of this anion is known from previous investigations on salts containing different cations [11, 12].

The cations and anions of compound 2 are stacked alternatingly in columns parallel to the b axis of the crystal (Fig. 2). The main axis of the cation is



Fig. 3. Cation and anion of the ¹butylisocyanide complex **1**. [ORTEP drawing with 50% probability ellipsoids]. Selected distances [Å] and angles [°]: Au1-S1 2.307(1), Au1-S2 2.305(1), Au2-C1 1.966(5), C1-N1 1.143(6), N1-C2 1.461(6); S1-Au1-S2 89.75(4), S1-Au1-S2' 90.25(4), S1-Au1-S1' 180.0, S2-Au1-S2' 180.0, C1-Au2-C1' 169.9 (3), Au2-C1-N1 176.7 (4), C1-N1-C2 175.2(5).



Fig. 4. Orientation of the anions of complex 1 in the unit cell.

roughly parallel to one of the two S-Au-S axes of the anion. The gold atoms of a given column are on a common straight line with an Au- -Au distance of as much as 3.881 Å. Because of the tilt of the ions against this metal axis, the closest contact between the ions is between a sulfur and a gold atom at 3.422 Å. Therefore, the stacking of the columns is not based on aurophilic interactions, which are known to be most significant for contacts between gold atoms in the oxidation state (+I).

Crystals of compound 1 are monoclinic, space group C2/c, with Z = 4 formula units in the unit cell. The asymmetric unit contains one half of both



Fig. 5. Orientation of the cations of complex 1 in the unit cell.



Fig. 6. Complete population of the unit cell of complex 1.

the cation and the anion. The remainder of the ions is generated by twofold axes passing through the gold atoms (Fig. 3). The structure of the anion resembles that of compound **1** and of other salts recorded in the literature. The cations have a quasi-linear chain of seven atoms terminated at both ends by branching methyl groups, but surprisingly there is a significant bending at the gold atom: C1-Au2-C1' 169.9(3)°. The cations thus may be referred to as slightly bent long-bar dumb-bells (a weight-lifting gear).

The packing of cations and anions in the structure is rather complex and shows no close contacts

	1	2
Crystal data		
Formula	$C_{22}H_{26}Au_2N_2S_4$	$C_{26}H_{30}Au_2N_2S_4$
Mr	840.62	892.69
Crystal system	monoclinic	triclinic
Space group	C2/c	ΡĪ
a (Å)	16.8619(2)	6.8936(3)
b(A)	13.1972(2)	7.7610(3)
c (Å)	13.6019(2)	13.1656(7)
α (°)	90	76.949(2)
β (°)	122.517(1)	86.711(2)
γ (°)	90	83.584(2)
$V(A^3)$	2552.3(1)	681.5(1)
$\rho_{\rm calc} ({\rm g}{\rm cm}^{-3})$	2.188	2.175
Z	4	1
F(000)	1576	422
μ (Mo-K α) (cm ⁻¹)	118.22	110.08
Data collection		
$T(^{\circ}C)$	-130	-130
Measured reflections	44955	21114
Unique reflections	$2808 [R_{int} = 0.047]$	$2874 [R_{int} = 0.068]$
Absorption correction	DELABS	DELABS
$T_{\rm min}/T_{\rm max}$	0.304/0.742	0.082/0.536
Refinement		
Refined parameters	190	157
Final <i>R</i> values $[I > 2\sigma(I)]$		
R1	0.0267	0.0332
$wR2^{[a]}$	0.0583	0.0845
(shift/error) _{max}	< 0.001	< 0.001
$\rho_{\text{fin}} (\text{max/min}) (\text{e}\text{\AA}^{-3})$	1.107/-3.452	1.878/-1.609

Table 1. Crystal data, data collection, and structure refinement.

^[a] $wR2 = \{ [\Sigma w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2};$ $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]; p = (F_o^2 + 2F_c^2)/3;$ a = 0.0149 (1), 0.0000 (2); b = 25.01 (1), 0.000 (2).

between the components. It is obvious that the platelike anions and the long-bar dumb-bell cations are difficult to accommodate together to give an efficient space-filling arrangement. There is neither an alternating stacking of cations and anions nor a separate close stacking of the anion platelets. Neighbouring anion platelets are strongly tilted against each other (roof-like) and the large space between these scales is filled with the long-bar dumb-bell cations. Figs. 4 and 5 show the orientation of anions and cations separately, while Fig. 6 gives a superposition representing the complete population.

Experimental Part

All experiments were routinely carried out in an atmosphere of dry nitrogen. Glassware was oven-dried and filled with nitrogen and solvents were distilled, degassed and saturated with nitrogen. Standard equipment was used throughout. The dithiol and isocyanides were commercially available, the gold complexes were prepared following published procedures [9, 10]. General procedure for the preparation

The dithiol 1,2-C₆H₄(SH)₂ is treated with two equivalents of MeONa in 2 ml of anhydrous methanol. This solution is added to a solution of two equivalents of the complex (RNC)AuCl in 2 ml of dichloromethane with stirring at r. t. After 1 h the solvents are removed in a vacuum and the residue is extracted with 4 ml of dichloromethane. Careful layering of the green solution with pentane and cooling to -20 °C (or diffusion of pentane vapour into the solution in a closed system kept at this temperature) induces the crystallization of the products. Green crystals, stable in air and light.

Compound 1: ^{*i*}BuNCAuCl (100 mg, 0.317 mmol); MeONa (17 mg, 0.317 mmol); C₆H₄(SH)₂ (23 mg, 0.159 mmol); yield 45 mg (34%). C₂₂H₂₆Au₂N₂S₄ (840.65) calcd. C 31.43, H 3.12, N 3.33; found C 30.07, H 3.10, N 3.30. NMR (CDCl₃, 20 °C) ¹H: 1.52 (s, 18H, Me); 6.86 and 7.19 (AA'BB', 8H, C₆H₄). ¹³C{¹H}: 29.5 (s, Me); 59.6 (s, CC₃); 133.6 (br. s, CAu); 123.5, 128.3 and 142.4 (all s, C₆H₄).

Compound 2: ^{*c*}HexNCAuCl (100 mg, 0.293 mmol), MeONa (16 mg, 0.293 mmol), C₆H₄(SH)₂ (21 mg, 0.147 mmol); yield 41 mg (31%). $C_{26}H_{30}Au_2N_2S_4$ (892.73) calcd. C 34.98, H 3.39, N 3.14; found C 33.10, H 3.46, N 3.63. MS (FAB+/-): m/z = 415.6(100%) [(RNC)₂Au]⁺; 477.2 (4.4%) [Au(S₂C₆H₄)₂]⁻. NMR (CDCl₃, 20 °C) ¹H. 1.38, 1.68, 1.91, and 3.84 (all m, 22H, ^cHex); 6.81 and 7.16 (AA'BB', 8H, C₆H₄). ¹³C{¹H}: 23.1, 24.9, 31.90, and 55.2 (all s, ^cHex); 140.0 (br. s, CAu); 124.4, 128.4 and 142.5 (all s, C₆H₄).

Crystal structure determination

Specimens of suitable quality and size were mounted on the ends of quartz fibers in F06206R oil and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo-K_{α} radiation. The structures were solved by a combination of direct methods (SHELXS-97) and difference-Fourier syntheses and refined by full matrix least-squares calculations on F^2 (SHELXL-97). The thermal motion was treated anisotropically for all non-hydrogen atoms. All hydrogen atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions. Further information on crystal data, data collection and structure refinement are summarized in Table 1. Important interatomic distances and angles are shown in the corresponding Figure Captions. Displacement parameters and tables of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDS 186714, 186715.

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