Structural Investigation of Bis(isonitrile)gold(I) Complexes

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Dedicated to Professor Walter Siebert on the occasion of his 60th birthday

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The reaction of (MeNC)-, (PhNC)- and (MesNC)AuCl in tetrahydrofuran with an equimolar amount of the corresponding isonitrile ligand and one equivalent of Ag^+X^- ($X^- = BF_4^-$ or $CF_3SO_3^-$) leads to the formation of the bis(isonitrile)gold(I) complexes (MeNC)₂Au⁺ $CF_3SO_3^-$ (1), (PhNC)₂Au⁺ BF_4^- (2) and (MesNC)₂Au⁺ BF_4^- (3). The crystal structures of 1, 2 and 3 have been determined. In compound 1 there are rod-like cations with a parallel packing into meandering puckered layers, in which the gold atoms have alternating Au–Au contacts of 3.611 and 3.624 Å. In complex 2 the cations form long double-paddles, with the two paddles at an angle of 77.5°. The individual cations are well separated and have no sub-van-der-Waals Au–Au contacts. The crystal structure of 3 is similar, but with a smaller dihedral angle between the planes of the two mesityl rings (56.0°).

Introduction

The first bis(isonitrile)gold(I) complexes have been reported in 1973 [1, 2]. They were important sources for the preparation of bis(carbene) complexes of gold(I) [3,4], and in 1986 their use as starting materials and catalysts for the synthesis of chiral oxazolines was demonstrated [5]. The structure of the cations [RNCAuCNR]⁺ in these complexes was assumed to be linear, but no structure determination has been undertaken. Because presently there is not only an interest in the molecular structure of such species, but also in their supramolecular chemistry, we have now investigated three bis(isonitrile)gold(I) complexes containing the small methyl-, the flat phenyl- and the more extended mesitylisonitrile ligands, where different steric effects are expected to show a growing influence on the packing of the compounds.

Following our recent report on the investigation of simple (isonitrile)gold(I) halides [6], we present our results here on the synthesis and structure of $(MeNC)_2Au^+ CF_3SO_3^-(1)$, $(PhNC)_2Au^+ BF_4^-(2)$ and $(MesNC)_2Au^+ BF_4^-(3)$.

Results and Discussion

All three complexes were obtained in high yield (>80%) according to a general synthetic route:

$$(RNC)AuCl + RNC + AgX \rightarrow (RNC)_2AuX + AgCl (X = CF_3SO_3^- \text{ or } BF_4^-)$$

The products were identified and characterized by standard analytical and spectroscopic methods. The compounds are stable, colourless solids with melting points at 164°C (1), 159°C (2), and 228°C (3). The FAB mass spectra show the cations $[(RNC)_2Au]^+$ as the parent peaks in high abundance, accompanied by fragment ions generated by the loss of RNC or R. In the ¹³C{¹H} NMR spectra coupling of the ¹⁴N nucleus to the neighbouring carbon atoms is observed. The proton NMR spectrum of 1 shows only a broad singlet for the methyl groups, indicating poorly resolved second order splitting.

Single crystals of compound **1** suitable for Xray diffraction were obtained upon layering a dichloromethane solution with pentane. The compound crystallizes in the monoclinic space group $P2_1/m$ with four formula units in the unit cell. The lattice is built up by independent triflate anions and rod-like bis(methylisonitrile)gold(I) cations. The latter are arranged parallel to each other and form corrugated sheets, the gold atoms in meandering strings with two nearly equal gold-gold distances

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Fig. 1a. Structure of the rod-like cation $[(MeNC)_2Au]^+$ in **1** (ORTEP, 50% probability ellipsoids). Selected bond lengths (Å) and angles (°): Au-C11 1.96(1), Au-C21 1.98(1), N1-C11 1.13(2), N1-C12 1.46(2), N2-C21 1.11(2), N2-C22 1.40(2), C21-Au-C11 175.9(6), C12-N1-C11 179(2), C22-N2-C21 178(2), N1-C11-Au 178(1), N2-C21-Au 179.0(9).

(Au-Au' 3.624 and Au-Au" 3.611 Å). Disordered triflate anions are located in the cavities between the layers. The cations show a C-Au-C angle close to linearity (175.9(6)°) and Au-C distances Au-C11 1.96(1) and Au-C21 1.98(1) Å (Figures 1a,b). These distances are relatively long as compared to mono (isonitrile)gold(I) halides (average 1.94 Å [6]).

Crystals of compound **2** are monoclinic, space group $P2_1/n$, with four formula units in the unit cell (Table I). Unlike in **1** no close Au-Au contacts are observed. The geometry of the core atoms of the monomeric cation is very similar to that in the methyl analogue **1** (see the caption of Fig. 2). There are no sub-van-der-Waals contacts between the cations and the tetrafluoroborate anions. The planes defined by the phenyl paddles enclose an angle of 77.5°, and therefore the phenyl groups are nearly orthogonal to each other.

3 crystallizes in the monoclinic space group Cc with four formula units in the unit cell. The lattice features $[(MesNC)_2Au]^+$ cations, which show no aggregation. The individual cations have a quasilinear seven-atom rod between the two mesityl groups, the planes of which form an angle of only 56.0° (Fig. 3).

The present study has shown that bis(isonitrile)gold(I) salts with non-coordinating, non-



Fig. 1b. Supramolecular aggregation of the $[(MeNC)_2Au]^+$ cations in 1 via weak gold-gold interactions (Au-Au' = 3.611, Au-Au'' = 3.624 Å). For clarity, only the C-S cores of the triflate anions are shown. It should be noted, that the carbon atoms of neighbouring triflate anions face each other in the middle and the sulfur atoms are at the outside. The flourine and oxygen atoms are cylindrically disordered.

polarizable counterions (BF_4^- , $CF_3SO_3^-$) have ionic structures with strictly linear two-coordination of the gold centers. It is only with the smallest alkyl substituents (R = Me) that supramolecular aggregations are observed, which lead to puckered cation layers. The Au–Au contacts are long indicating rather weak interactions. With larger groups R no such aggregates are formed. The cations have the form of double paddles with the arene rings at interplanar angles of 77.5 and 56.0° for 2 and 3, respectively.

Experimental

General

All experiments were routinely carried out under dry and pure nitrogen. Solvents and glassware were dried and saturated / filled with nitrogen. NMR: Jeol GX 400, TMS as internal standard. MS: Finnigan MAT 90. Microanalysis: In-house analyzers (by combustion). Starting materials were either commercially available or were prepared following literature procedures: MeNC [7], PhNC [8], MesNC [9] (Mes = mesityl), (MeNC)AuCl [10, 11], (PhNC)AuCl and (MesNC)AuCl [6, 12].

Bis(methylisonitrile)gold(I) triflate, (1)

To a solution of (MeNC)AuCl (100 mg, 0.367 mmol) in 60 ml of dichloromethane a solution of MeNC (15 mg, 0.367 mmol) and AgCF₃SO₃ (94 mg, 0.367 mmol) in 10

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Compound	1	2	3
Empirical formula	$C_5H_6AuF_3N_2O_3S$	$C_{14}H_{10}AuBF_4N_2$	$C_{20}H_{22}AuBF_4N_2$
Formula weight	428.14	490.02	574.18
Crystal system	monoclinic	monoclinic	monoclinic
Space group (No.)	$P2_1/m$ (No.11)	$P2_1/n$ (No.14)	Cc (No.9)
a [Å]	7.649(1)	8.435(1)	12.538(1)
b [Å]	12.057(2)	12.922(1)	11.095(1)
c[Å]	12.425(1)	13.594(1)	14.864(2)
α [°]	90	90	90
β[°]	107.89(1)	94.79(1)	104.01(1)
γ [°]	90	90	90
$V[Å^3]$	1090.5(6)	1476.5(3)	2005.7(4)
$\rho_{\rm calc} [\rm g cm^{-3}]$	2.61	2.21	1.90
Z	4	4	4
F(000) [e]	784	912	1104
μ (Mo-K _{α}) [cm ⁻¹]	137.1	100.0	73.8
T [°C]	-68	-68	-68
Diffractometer	Enraf Nonius CAD4	Enraf Nonius CAD4	Enraf Nonius CAD4
scan	θ	ω	θ - θ
hkl Range	-9 < h < 9, -15 < k < 15,	0 < h < 10, 0 < k < 16,	0 < h < 14, 0 < k < 14
e	0 < l < 15	$-17 < \overline{l} < 17$	$-2\overline{3} < \overline{l} < 23$ — —
Measured/unique refl.	3360/2076	3568/2942	3816/3704
Observed reflections	1616	2505	3464
$F_o >$	$4\sigma(F_0)$	$4\sigma(F_0)$	$4\sigma(F_o)$
Refined parameters	143	199	251
H-Atoms (found/calc.)	-/6	-/10	-/22
Absorption corr.:	empirical	empirical	empirical
T_{min} / T_{max}	0.5720/0.9969	0.3925 / 0.9978	0.8062 / 0.9989
<i>R</i> *	0.0443	0.0383	0.0185
R_w **	0.0492	0.0498	0.0230
Weighting scheme ***	l = 1.0000/	l = 1.0000/	l = 1.0000/
	k = 0.000354	k = 0.000563	k = 0.00018
$\rho_{\rm fin}({\rm max/min}) [{\rm e}{\rm \AA}^{-3}]$	+ 1.40 / - 1.02	+ 1.25 / - 1.14	+ 0.63 / - 0.70

Table I. Crystallographic Data for $[(CH_3NC)_2Au]^+CF_3SO_3^-(1)$, $[(PhNC)_2Au]^+BF_4^-(2)$ and $[(MesNC)_2Au]^+BF_4^-(3)$.

* $R = \sum ||F_o| - |F_c|| / \sum |F_o| - |F_o| - |F_o| - |F_c| / \sum w F_o^2|^{1/2} - |F_o| - |F_o| / \sum w F_o^2|^{1/2} - |F_o| - |F_o| / \sum |F_o| - |F_o| / \sum |F_o| - |F_o| - |F_o| / \sum |F_o| - |F_o| - |F_o| / \sum |F_o| / \sum |F_o| - |F_o| / \sum |F_o| / \sum |F_o| - |F_o| / \sum |F_o| - |F_o| / \sum |F_o| - |F_o| / \sum |F_o| / \sum |F_o| - |F_o| / \sum |F_o| - |F_o| / \sum |F_o| / \sum$

ml of tetrahydrofuran is added during a period of 30 min at room temperature. After stirring for 1 h the solvents are removed in a vacuum. The off-white residue is taken up in dichloromethane and crystallized by adding pentane. 128 mg of colourless crystals of **1** are obtained (81%), m. p. 164°C.

¹H NMR (CDCl₃): δ = 3.6, br. s, CH₃. ¹³C{¹H} NMR (CDCl₃): δ = 139.5, t, ¹*J*(C,N) = 27.6 Hz, NCAu; 121.4, q, ¹*J*(C,F) = 321 Hz, CF₃; 30.5, br., CH₃N. MS (FAB): *m*/*z* = 278.9, [(MeNC)₂Au]⁺, 100%.

 $\begin{array}{c} C_5H_6AuF_3N_2O_3S~(428.14)\\ Calcd~C~14.03,~H~1.41,~N~6.54\%,\\ Found~C~14.03,~H~1.50,~N~6.43\%. \end{array}$

Bis(phenylisonitrile)gold(I) tetrafluoroborate, (2)

As described for compound **1**, from (PhNC)AuCl (130 mg, 0.387 mmol), PhNC (40 mg, 0.387 mmol) and AgBF₄

(75.7 mg, 0.387 mmol) in 15 ml of CH₂Cl₂ / 5 ml of thf. Yield 155 mg (82%), m. p. 159°C.

¹H NMR (CDCl₃): δ = 7.6 - 7.7, m, Ph-H; ¹³C{¹H} NMR (CDCl₃): δ = 147.0, t, ¹*J*(C,N) = 28 Hz, NCAu; 133.3, 130.6 and 128.0, all s, *ortho-, meta-, para-*C; 123.3, t, ¹*J*(C,N) = 14 Hz, *ipso-*C. MS (FAB): *m*/*z* = 403, [(PhNC)₂Au]⁺, 100%.

C₁₄H₁₀AuBF₄N₂ (490.02) Calcd C 34.29, H 2.04, N 5.71%, Found C 35.45, H 2.14, N 5.81%.

Bis(mesitylisonitrile)gold(I) tetrafluoroborate (3)

As described for compound 1, from (MesNC)AuCl (125 mg, 0.331 mmol), MesNC (48 mg, 0.331 mmol) and $AgBF_4$ (64.5 mg, 0.331 mmol) in 15 ml of CH_2Cl_2

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/ 5 ml of thf. Yield 162 mg (85%), m. p. 228°C with decomposition.

¹H NMR (CDCl₃): δ = 2.3, s, *para*-CH₃; 2.4, s, *ortho*-CH₃; 7.2, s, *meta*-H. ¹³C{¹H} NMR (CDCl₃): δ = 151.0, t, ¹J(C,N) = 23 Hz, NCAu; 143.0, 137.0 and 129.3, all s, *ortho-*, *meta-*, *para*-C; 120.2, br., *ipso*-C; 21.5, s, *para*-CH₃; 18.5, s, *ortho*-CH₃. MS (FAB): *m*/*z* = 487.3, [(MesNC)₂Au]⁺, 100%.

 $\begin{array}{c} C_{20}H_{22}AuBF_4N_2 \ (574.18) \\ Calcd \ C \ 41.84, \ H \ 3.86, \ N \ 4.88\%, \\ Found \ C \ 42.01, \ H \ 3.70, \ N \ 4.87\%. \end{array}$

Crystal structure determination:

Crystallographic and structure solution data of compounds 1, 2 and 3 are summarized in Table I, structural

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Fig. 2. Structure of the doublepaddle-like $[(PhNC)_2Au]^+$ cation in 2 (ORTEP, 50% probability ellipsoids). Selected bond lengths (Å) and angles (°): Au-Cl 1.987(9), Au-C8 1.992(9), N1-Cl 1.13(1), N1-C2 1.39(1), N2-C8 1.11(1), N2-C9 1.38(1), C8-Au-Cl 177.5(3), N1-Cl-Au 178.4(7), C2-N1-Cl 175.2(9), N2-C8-Au 179.0(7), C9-N2-C8 179.7(7).

Fig. 3. Structure of the cation $[(MesNC)_2Au]^+$ in **3** (ORTEP, 50% probability ellipsoids). Selected bond lenghts (Å) and angles (°). Au-C1 1.96(1), Au-C2 1.99(1), N1-C1 1.16(1), N1-C11 1.41(1), N2-C2 1.13(2), N2-C21 1.40(1), C2-Au-C1 173.6(4), C11-N1-C1 176(1), C21-N2-C2 174(1), N1-C1-Au 174.1(8), N2-C2-Au 173.6(9).

data in the captions of Fig. 1a, 2 and 3. Further information on the structure determinations may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information GmbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the names of the authors, the journal citation and the CSD number 59368.

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