Synthesis, Solution Behavior, Molecular and Supramolecular Structures of the Water-soluble Gold(I) Saccharinate Complexes M[Au(Sac)$_2$] (M = Na, K, NH$_4$)

Maria Agostina Cinellu[a], Laura Maiore[a], Annette Schier[b], Hubert Schmidbaur[b], and Davide Rossi[c]

[a] Dipartimento di Chimica, Università di Sassari, via Vienna 2, I-07100 Sassari, Italy
[b] Department Chemie, Technische Universität München, Lichtenbergstraße 4, D-85747 Garching, Germany
[c] Coventya S. p. A., Divisione Auromet®, Via Chiusa, I-51031 Agliana, Italy

Reprint requests to Prof. M. A. Cinellu. E-mail: cinellu@uniss.it, or
Prof. H. Schmidbaur. E-mail: H.Schmidbaur@lrz.tum.de

Three gold(I) saccharinate complexes of the type M[Au(Sac)$_2$] (M = Na, K and NH$_4$) have been prepared by treatment of Au(tht)Cl (tht = tetrahydrothiophene) with saccharine and MOH in MeOH-acetone. The compounds are very stable in the solid state but moderately soluble and of limited stability in water. Single crystal X-ray diffraction analysis of the three compounds revealed a linear coordination of the gold atom by the two *N*-bonded saccharinato ligands. For M = Na, the two hetero-bicyclic ligands are roughly coplanar with a *cis* orientation of the two carbonyl groups which allows for a chelation of the sodium cation. For M = K, NH$_4$, the ligands form large dihedral angles with a *trans* orientation of the donor sites out of which the potassium cations are coordinated in bridging positions between neighboring anions, and the ammonium ions are hydrogen-bonded, respectively.

Key words: Gold Complexes, Saccharinate Complexes, Gold Plating

Introduction

Solubility in water is a highly desirable property for metal complexes involved in industrially important processes, both from an economic and an environmental point of view. In gold chemistry recent successful applications of both gold(I) and gold(III) complexes in homogeneous catalysis [1], as well as in chrysotherapy [2], have spurred interest in water-soluble species. For any scale-up from laboratory to industrial processes in the former, and for optimum biocompatibility in the latter, solubility and long-term stability in water as a solvent at ambient or slightly elevated temperatures are almost indispensable. In addition, established processes such as gold electroplating and electroforming are currently on trial because they rely heavily on the usage of environmentally precarious gold sources, mainly cyanides [3]. Cyanides are also the prime reagents in the mining industry for the recovery of gold from ores, and for gold recycling [4]. Water-soluble gold complexes are preferred reagents for the deposition of gold-microbumps on silicon wafers using organic photoresists for pattern formation [5]. As a consequence, search for environmentally benign, non-toxic, water-soluble gold complexes is currently a matter of great concern in most of the gold-handling industries.

As part of a program aimed at the development of water-soluble non-cyanide gold(I) complexes for gold electroplating applications, a series of disaccharinate complexes was now synthesized and their solution and structural properties investigated.

Saccharin (SacH), itself, does not coordinate to metal ions, but its deprotonated form (saccharinate = Sac) readily forms a great variety of complexes with a large number of metal ions [6]. As far as we are aware, only two saccharinate gold(I) complexes, both heteroleptic, have been known, namely [Au(PEt$_3$)-(Sac)] [7] and [Au(IPr)(Sac)], [IPr = bis(2,6-diisopropylphenyl)-imidazol-2-ylidene] [8]. An X-ray structure determination of the latter compound showed *N*-coordination (η^1) of the saccharinate ligand to the gold atom.

Na[Ag(Sac)$_2$] was prepared in 2004, and its structure has been determined [9a]. The two ligands are *N*-η^1 bonded to the silver atom, which has a bent

N–Ag–N configuration [N–Ag–N 158.99(5)°] owing to an additional coordination of a sulfone oxygen atom of a neighboring anion. The sodium atom is chelated by the two carbonyl oxygen atoms of the saccharinato ligands. In polymeric [Ag(Sac)]$_n$ two saccharinate ligands bridge two silver atoms *via* their N and carbonyl O atoms to form eight-membered ring dimers. Sulfone O coordination makes the silver atoms three-coordinate and links the dimers to one-dimensional chains [9b]. In the mononuclear complex (Ph$_3$P)$_2$Ag-(Sac) the silver atom is also three-coordinate (N, P, P) [9c], but with other auxiliary ligands coordination numbers 3 and 4 at silver have been observed [9a].

Experimental Section

General information

All starting materials were used as received from commercial sources. (Tetrahydrothiophene)gold(I) chloride, Au(tht)Cl, was prepared according to a literature method [10]. Elemental analysis was performed with a Perkin-Elmer Elemental Analyzer 240B by Mr. A. Canu (Dipartimento di Chimica, Università di Sassari). Conductivity measurements were performed with a Philips PW 9505 conductometer. Infrared spectra were recorded with a Jasco FT-IR 480 Plus spectrophotometer using Nujol mulls. UV/Vis spectra were recorded on a Hitachi U-2010 spectrometer. ^{1}H NMR spectra were recorded on a Varian VXR 300 spectrometer operating at 299.9 MHz.

Preparation of Na[Au(Sac)$_2$], 1

A freshly prepared solution of saccharin (366.3 mg, 2 mmol) and NaOH (80 mg, 2 mmol) in 30 mL of CH$_3$OH was slowly added to a stirred suspension of Au(tht)Cl (320.6 mg, 1 mmol) in 30 mL of acetone. The resulting suspension was stirred for 30 min at r. t., until a colorless solution was obtained; this was evaporated to dryness under reduced pressure and the residue extracted with acetone and filtered over Celite. The colorless filtrate was concentred to a small volume and diethyl ether added to give a white precipitate of **1**: 479 mg (82 %). M. p.: > 283 °C. – Anal. for **1**·(CH$_3$)$_2$CO·H$_2$O (C$_{17}$H$_{16}$AuN$_2$NaO$_8$S$_2$): calcd. C 30.92, H 2.44, N 4.24; found C 30.88, H 2.40, N 4.28. – Λ_M (H$_2$O, 5×10^{-4} mol L^{-1}): 64 Ω^{-1} cm^2 mol^{-1}; (acetone, 5×10^{-4} mol L^{-1}): 78 Ω^{-1} cm^2 mol^{-1}. – IR: ν(C=O) 1690 (s), ν(SO$_2$, asym) 1288 (s), ν(SO$_2$, sym) 1158 (s) cm^{-1}. – ^{1}H NMR (CD$_3$COCD$_3$): δ = 7.80 – 7.90 m [8H].

Preparation of K[Au(Sac)$_2$], 2

Compound **2** was prepared similarly; K[Sac] was obtained by treatment of saccharine with an equimolar amount of

KOH. Yield: 86 %. M. p.: 281 – 283 °C. – Anal. for **2**·H$_2$O (C$_{14}$H$_{10}$AuKN$_2$O$_7$S$_2$): calcd. C 27.19, H 1.63, N 4.53; found C 26.95, H 1.55, N 4.60. – Λ_M (H$_2$O, 5×10^{-4} mol L^{-1}): 66 Ω^{-1} cm^2 mol^{-1}; (acetone, 5×10^{-4} mol L^{-1}): 72 Ω^{-1} cm^2 mol^{-1}. – IR: ν(C=O) 1673 (s), ν(SO$_2$, asym) 1297 (s), ν(SO$_2$, sym) 1158 (s) cm^{-1}. – ^{1}H NMR (CD$_3$-COCD$_3$): δ = 7.78 – 7.91 m [8H].

Preparation of NH$_4$[Au(Sac)$_2$], 3

Compound **3** was prepared similarly; [NH$_4$][Sac] was obtained by treatment of saccharine with an equimolar amount of aqueous NH$_4$OH. Yield 90 %. M. p.: 225 °C (decomp.). – Anal. for **3**·H$_2$O (C$_{14}$H$_{14}$AuN$_3$O$_7$S$_2$): calcd. C 28.15, H 2.36, N 7.03; found C 27.97, H 2.36, N 7.06. – Λ_M (H$_2$O, 5×10^{-4} mol L^{-1}): 64 Ω^{-1} cm^2 mol^{-1}; (acetone, 5×10^{-4} mol L^{-1}): 70 Ω^{-1} cm^2 mol^{-1}. – IR: ν(C=O) 1679 (s), ν(SO$_2$, asym) 1294 (s), ν(SO$_2$, sym) 1156 (s) cm^{-1}. – ^{1}H NMR (CD$_3$COCD$_3$): δ = 7.79 – 7.94 m [8H].

Structure determinations

Crystals suitable for X-ray diffraction of **1**, **2**, and **3** were obtained by slow diffusion of diethyl ether into an acetone solution of the complexes. The crystalline samples were placed in inert oil, mounted on a glass pin, and transferred to the cold gas stream of the diffractometer. Crystal data were collected using an Oxford Xcalibur^{TM} 3 system with monochromated MoK_α radiation (λ = 0.71073 Å) at 143 K. The structures were solved by Direct Methods (SHELXS-97) and refined by full-matrix least-squares calculations on F^2 (SHELXL-97). Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms in compounds **1** – **3** were located and refined isotropically, except for C–*H* atoms in compounds **2** and **3**, which were refined using a riding model with fixed isotropic contributions, and the O–*H* hydrogen atoms in compound **2**, which were found and hold constant in further refinement cycles. Further information on crystal data, data collection and structure refinement are summarized in Table 1. Important interatomic distances and angles are shown in Table 2.

CCDC 695216 (**1**), 695217 (**2**) and 695218 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Preparation

Complexes M[Au(Sac)$_2$] (M = Na, **1**; K, **2**; NH$_4$, **3**) were obtained as white microcrystalline, non-hygroscopic solids by the reaction of Au(tht)Cl with two equivalents of M[Sac] in MeOH-acetone, followed

Formula	$1 \cdot (CH_3)_2CO \cdot H_2O$	$2 \cdot H_2O$	$3 \cdot H_2O$
Formula	$C_{17}H_{16}AuN_2NaO_8S_2$	$C_{14}H_{10}AuK\,N_2O_7S_2$	$C_{14}H_{14}AuN_3O_7S_2$
M_r	660.39	618.43	597.37
Crystal system	triclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$	$Fdd2$	$P2_1/n$
a, Å	8.4217(1)	25.6605(6)	9.0071(1)
b, Å	11.5093(1)	30.8019(4)	12.8913(2)
c, Å	11.8915(2)	8.6643(2)	14.7949(2)
α, deg	65.461(1)	90	90
β, deg	87.671(1)	90	90.657(1)
γ, deg	88.058(1)	90	90
V, Å^3	1047.45(2)	6848.2(2)	1717.79(4)
ρ_{calc}, g cm^{-3}	2.094	2.399	2.310
Z	2	16	4
$F(000)$, e	636	648	1144
μ(MoK_α), mm^{-1}	7.29	9.12	8.853
T, K	143	143	143
hkl range	$\pm 11, -14 \rightarrow +15, \pm 15$	$+30, +36, \pm 10$	$\pm 10, -15, +17$
θ range, deg	$3.02 - 27.90$	$3.09 - 25.40$	$2.76 - 25.69$
Measured reflections	30506	39764	40724
Unique reflections	4994	3148	3151
R_{int}	0.026	0.000	0.039
Refls. used for refinement	4994	3148	3151
Absorption correction	semi-empirical	semi-empirical	semi-empirical
Refined parameters	344	244	268
Final $R1/wR2$ values^a [$I \geq 2\sigma(I)$]	0.019/0.048	0.045/0.118	0.022/0.052
(shift/error)$_{\text{max}}$ (last cycle)	< 0.001	< 0.001	< 0.001
x (Flack)	–	$-0.03(1)$	–
ρ_{fin} (max/min), e Å^{-3}	1.31/-1.65	3.20/-1.34	1.24/-0.81

Table 1. Crystal data, data collection and structure refinement parameters for compounds **1 – 3**.

^{a} $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1 / [\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0303$ (**1**), 0.0816 (**2**), 0.0262 (**3**); $b = 1.77$ (**1**), 241.61 (**2**), 8.54 (**3**).

	1		**2**		**3**
Au1–N1	1.994(2)	Au1–N1	2.013(8)	Au1–N1	2.001(3)
Au1–N2	1.998(2)	Au1–N2	2.010(9)	Au1–N2	2.000(3)
Na1–O5	2.435(2)	K1–O1A$^{\#2}$	2.691(8)		
Na1–O4A$^{\#1}$	2.370(2)	K1–O2B$^{\#3}$	2.855(8)		
Na1–O6	2.419(2)	K1–O3C$^{\#4}$	2.718(9)		
Na1–O7	2.353(2)	K1–O5	2.689(9)		
Na1–O8	2.320(2)	K1–O6D$^{\#5}$	2.920(9)		
		K1–O8	2.658(8)		
S1–O1	1.438(2)	S1–O1	2.1429(8)	S1–O1	1.435(3)
S1–O2	1.435(2)	S1–O2	1.440(8)	S1–O2	1.421(3)
S2–O3	1.441(2)	S2–O3	1.441(10)	S2–O3	1.434(3)
S2–O4	1.441(2)	S2–O4	1.430(9)	S2–O4	1.431(3)
C1–O5	1.223(3)	C1–O5	1.214(15)	C1–O5	1.228(5)
C8–O6	1.219(3)	C8–O6	1.224(14)	C8–O6	1.222(5)
C15–O7	1.214(4)				
N1–Au1–N2	176.28(8)	N1–Au1–N2	178.0(8)	N1–Au1–N2	176.59(15)
O5–Na1–O6	135.34(8)	O5–K1–O8	99.9(3)		
O7–Na1–O8	89.80(9)	O5–K1–O6D$^{\#5}$	170.7(2)		
S2–O4–Na1'	128.61(12)	O1'–K1–O3C$^{\#4}$	169.6(3)		

Table 2. Selected bond lengths [Å] and angles [deg] in compounds **1 – 3**^{a}.

^{a} Symmetry code: $^{\#1}$ $-x, 2-y, z$; $^{\#2}$ $x, y, 1+z$; $^{\#3}$ $x - 0.25, -y + 0.25, z + 0.75$; $^{\#4}$ $-x, -y, z$; $^{\#5}$ $-x, -y, z+1$.

by recrystallization from acetone-Et$_2$O. Slow diffusion of diethyl ether into concentrated acetone solutions of the compounds afforded, respectively, **1** $\cdot$ (CH$_3$)$_2$CO $\cdot$ H$_2$O, **2**$\cdot$H$_2$O, and **3**$\cdot$H$_2$O. Complexes **1 – 3** are stable in the solid state for months, provided that light is excluded.

Solution behavior

Molar conductivity (Λ_M) measurements were carried out at r. t. both in water and in acetone with concentrations of about 5×10^{-4} M; the Λ_M values of **1 – 3** are *ca.* 65 Ω^{-1} cm^2 mol^{-1} in water and 70 – 78
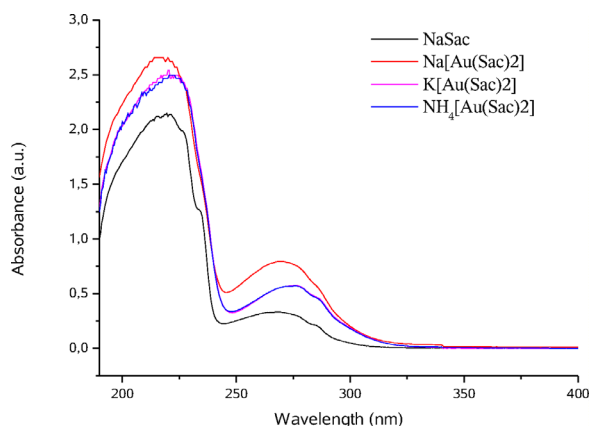
Fig. 1. Electronic spectra of Na[Sac] ($c = 2 \times 10^{-4}$ M in water) and M[Au(Sac)₂] ($c = 1 \times 10^{-4}$ M in water; color online).
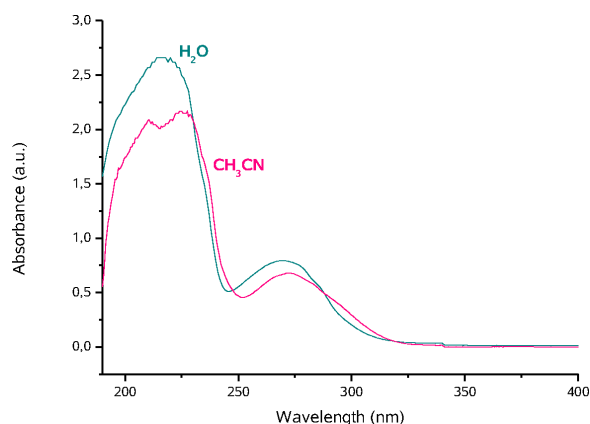

Fig. 2. Electronic spectra of Na[Au(Sac)₂] ($c = 1 \times 10^{-4}$ M) in water and CH₃CN (color online).

Ω^{-1} cm² mol⁻¹ in acetone, smaller than the $118 - 131$ Ω^{-1} cm² mol⁻¹ and $100 - 140$ Ω^{-1} cm² mol⁻¹ expected for 1 : 1 electrolytes in water and in acetone solution, respectively [11]. This is likely due to ion-pair formation promoted by hydrogen bond interactions between the NH_4 cation and the saccharinate anions in the case of complex **3**, or by coordination (or even chelation) of the metal cation M^+ by the oxygen atoms of the ligands coordinated to the gold atom [12] in the case of **1** and **2** (see below).

Complexes **1 – 3** are moderately soluble in water: at r. t. (21 °C) the solubility ranges from 0.67 mg mL⁻¹ for complex **3** to 1.25 mg mL⁻¹ for complex **1**, while at 70 °C it is *ca.* 9 mg mL⁻¹ for all complexes; the pH values of the aqueous solutions are 5.2 for **1**, 3.3 for **2**, and 2.7 for **3**. The solubility at r. t. is 6 – 7 times higher in acetone and MeCN than in water.

The solution behavior of **1 – 3** in different solvents was analyzed by absorption UV/Vis spectroscopy. Electronic spectra of the three complexes and of the Sac⁻ anion are shown in Fig. 1. In aqueous solution, the Sac⁻ anion exhibits two main absorption bands at $\lambda_{max} = 220$ nm ($\varepsilon = 10{,}166$ L mol⁻¹ cm⁻¹) and 268 nm ($\varepsilon = 1628$ L mol⁻¹ cm⁻¹) which are assigned to the intraligand $L \rightarrow L^*$ transitions; the first band is very slightly shifted upon coordination only in complex **1** (to 216 nm), while the second band is red-shifted to 273 nm in **1**, and to 276 nm in **2** and **3**; spectra of **2** and **3** are almost superimposable. The ε values of the two bands for complex **1** are higher than those of **2** and **3**, and significantly higher than those for the Sac⁻ anion (for **1**: $\varepsilon = 26{,}637$ and 6910 L mol⁻¹ cm⁻¹). There is little effect of the solvent on the λ_{max} value of the two
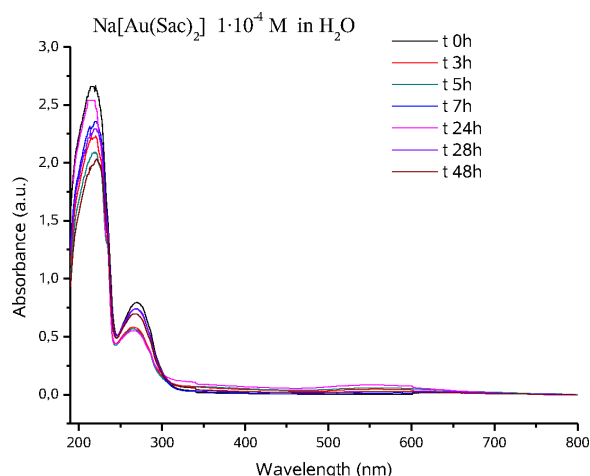

Fig. 3. Decomposition profiles of Na[Au(Sac)₂] (**1**) (initial concentration 1×10^{-4} M in water) at 21 °C. Spectra were recorded at various times over a period of 48 h (color online).

bands, as similar UV/Vis spectra were recorded *e. g.* for solutions of **1** in CH₃CN (Fig. 2).

The stability of the complexes towards disproportionation in water was evaluated by UV/Vis spectroscopy monitoring a solution of **1** (1×10^{-4} M) over a period of 48 h at 21 °C. A moderate, progressive decrease in intensity of the band at 273 nm was observed: after 24 h the concentration of the complex was reduced by 28 %, after 48 h by 35 %. A concomitant increase in intensity of the broad band around 550 nm due to the formation of metallic gold as a mirror at the walls of the vessel and as small deep-colored particles was observed. The resulting time-dependent spectral profiles for these degradation processes, mainly the
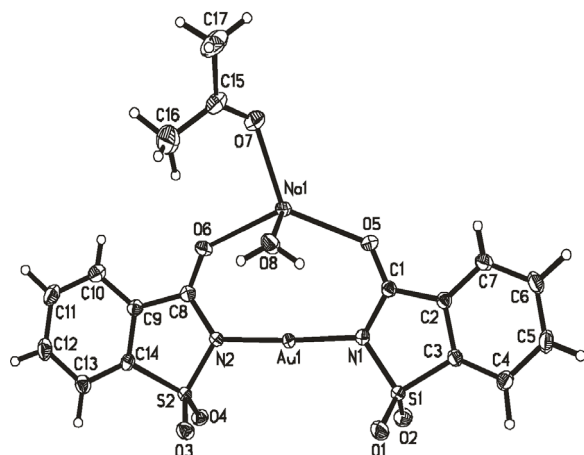
Fig. 4. Asymmetric unit of the crystals of Na[Au(Sac)₂]·H₂O·Me₂CO (**1**). The coordination of the sodium cation is incomplete.

Fig. 6. Asymmetric unit of the crystals of K[Au(Sac)₂]·H₂O (**2**). For the potassium cation, the complete coordination environment is shown.
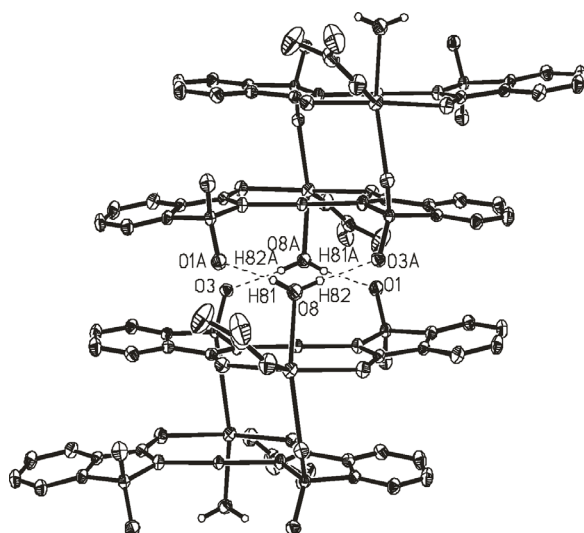

Fig. 5. Section of a string of stacked molecular units of complex **1**: Pairs of asymmetric units (Fig. 4) are aggregated to centrosymmetrical dimers (two of which are shown), which are connected *via* hydrogen bonds involving the water molecules. Note that the sodium cations are pentacoordinated.

disproportionation of gold(I) to gold(0) and gold(III), are shown in Fig. 3.

Structural characterization

The three compounds crystallized from aqueous acetone solutions upon slow diffusion of diethyl ether at ambient temperature, **1** as an acetone solvate monohydrate, and **2** and **3** as monohydrates. The crystals
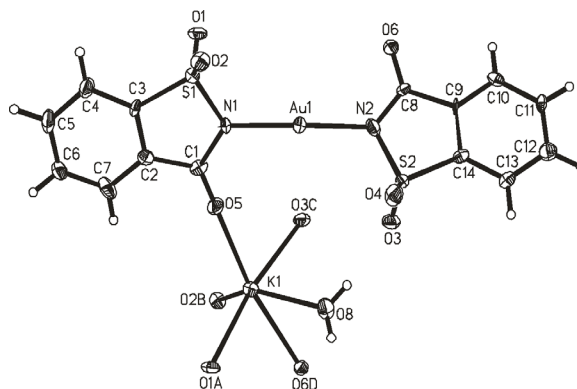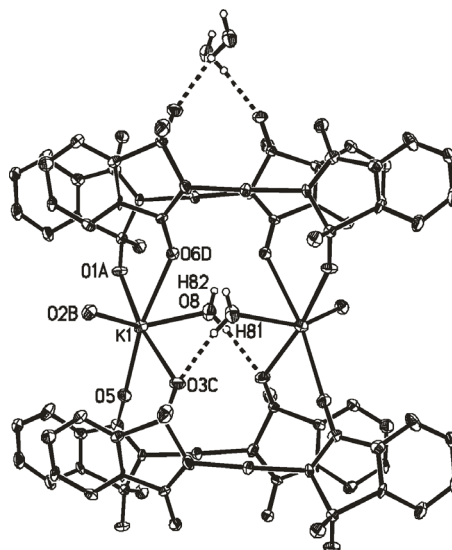

Fig. 7. Section of a string of stacked molecular units of complex **2**: Monomeric units are connected *via* the potassium cations and *via* hydrogen bonds involving the water molecules.

have different crystal systems and space groups (**1**: triclinic, $P\bar{1}$, $Z = 2$; **2**: orthorhombic, $Fdd2$, $Z = 16$; **3**: monoclinic, $P2_1/n$, $Z = 8$).

All three structures contain bis(saccharinato)aurate(I) anions with the saccharinato ligands N-η^1 bonded to the linearly two-coordinated gold atom (Figs. 4, 6 and 8). The bicyclic ring systems of the ligands are virtually planar, but the planes of the two ligands at each gold atom are roughly coplanar only in the crystals of complex **1**. The corresponding dihedral angles for **2** and **3** are as high as 43.3° and 31.0°, respectively. Moreover, the ligand pair in **1** has the *cis*
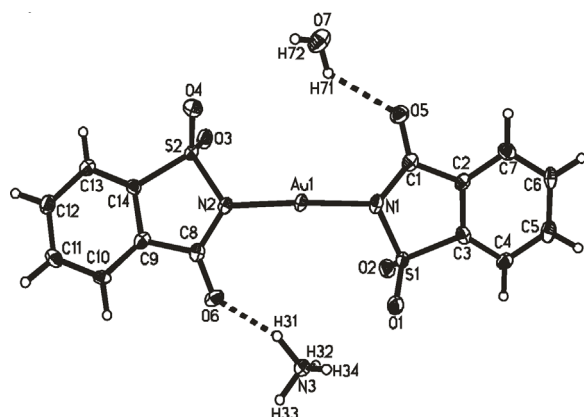
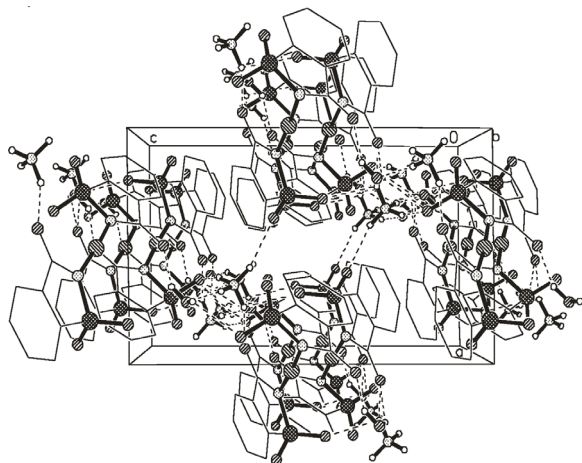Fig. 8. Asymmetric unit of the crystals of NH₄[Au(Sac)₂] · H₂O (**3**).

Fig. 9. Plot of the unit cell of crystals of complex **3** looking down the *b* axis. Monomeric units are arranged in stacks and connected *via* hydrogen bonds involving the ammonium cations and the water molecules.

orientation, while the ligand pairs in **2** and **3** have the *trans* orientation.

In the crystals of **1** the sodium cations are attached to the carbonyl oxygen atoms of the two saccharinate ligands of one anion to form a chelate ring (Fig. 4) in which the Na1···O5/O6 contacts are almost equal [2.419(2) and 2.435(2) Å, respectively]. By contrast, in the crystals of **2** the potassium cation is attached to two saccharinato ligand carbonyl oxygen atom of two different anions at significantly different distances [K1–O5 2.689(9), K1–O6D 2.920(9) Å] (Fig. 6, Table 2). The coordination sphere of the sodium cation in crystals of **1** further contains the oxygen atoms of the water (O8) and acetone molecules (O7) and of a sul-

Table 3. Selected hydrogen bonds (excluding C–H···E contacts) of compounds **1 – 3** (distances in [Å], angles in [deg]; for assignments of atoms to units in space, see text and Figs.).

	Donor–H···Acceptor	D–H	H···A	D···A	D–H···A
1	O8–H81···O1	0.84	2.03	2.864	172
	O8–H82···O3	0.92	2.03	2.944	170
2	O8–H8···O6	0.85	2.49	2.872	108
	O8–H8···O3	0.86	2.06	2.904	171
3	N3–H31···O6	1.00	1.90	2.845	156
	N3–H31···O4	1.00	2.49	2.975	109
	N3–H32···O7	0.90	1.96	2.849	172
	N3–H33···O2	0.96	2.08	2.968	154
	N3–H34···O1	0.93	2.59	2.893	100
	N3–H34···O3	0.93	2.07	2.973	162
	O7–H71···O5	0.81	2.12	2.760	136
	O7–H72···O2	0.89	2.39	2.971	124
	O7–H72···O6	0.89	2.51	3.273	144

fone group of another anion (O4A) to give coordination number 5 with the geometry of a distorted trigonal bipyramid.

The potassium atom in crystals of **2** is hexacoordinated with a distorted octahedral geometry generated by three sulfone oxygen atoms of two different ligands (O1A, O2B, O3C), and one water molecule (O8), in addition to the two carbonyl oxygen atoms (O5, O6D). These interionic contacts give rise to the formation of centrosymmetrical dimeric units of compound **1** which are further aggregated into strings of such dimers *via* hydrogen bonding between the coordinated water molecules (H₂O8) and sulfone oxygen atoms O1 and O3 (Fig. 5).

In crystals of compound **2** the connectivity pattern leads to one-dimensional stacks of ion pairs in which no smaller oligomers can be distinguished. Relevant metal-oxygen distances are listed in Table 2. The water molecules of the monohydrate are engaged in hydrogen bonding with the sulfone oxygen atoms O3 and the carbonyl oxygen atoms O6 of two different anions establishing additional connectivities between the cations and anions (Fig. 7).

In crystals of compound **3** the ammonium cation is entertaining hydrogen bonds *via* all four of its hydrogen atoms with one carbonyl oxygen atom and four sulfone oxygen atoms of different saccharinato ligands, and with one water molecule. The water molecule is further engaged in hydrogen bonds with two carbonyl and one sulfone oxygen atoms of saccharinato ligands. These N–H···O and O–H···O distances (D···A) are all in the range from 2.845 to 2.975 Å. The connectivity pattern can be described as a hydro-

gen bonding network along and between columns of hydrated pairs (Figs. 8, 9). Further details of hydrogen bonds in compounds **1** – **3** are listed in Table 3.

Conclusion

The present work has shown that a series of homoleptic di(saccharinato)gold(I) complexes M[Au-(Sac)$_2$] with different cations M can be prepared in high yields by conventional processes and from convenient precursors. The products can readily be crystallized from acetone or mixed solvents as hydrates (M = K, **2**; M = NH$_4$, **3**) or solvate hydrates (M = Na, **1**). The crystalline materials are stable in air at ambient temperature, but light-sensitive upon long-term storage. However, the solubility and stability of the salts in water is limited (a few grams per liter), and slow decomposition is observed, in particular if the pH of the solutions deviates significantly from neutrality, and at elevated temperatures. For any potential applications, *e. g.* for electrolytic or electroless deposition of gold, the stability would have to be improved through either suitable substitution of the ligands, introduction of other cations M, or the choice of a solvent systems which can rise further the solubility and lend improved stability to the solutions.

In the structural studies it has been shown that the saccharinato ligand becomes attached to the gold(I) center exclusively *via* the nitrogen atom. The dihedral angle between the two saccharinato ligands is obviously very variable, and *cis* coplanar (**1**) and almost perpendicular (**3**) conformations can be adopted depending on the nature of the counterion M. Chelation of M based on the coplanar *cis* conformation is possible for small cations (**1**), but bridging of anions

by metal coordination is probably more common for larger cations (**2**).

The structures of the compounds Na[E(Sac)$_2$] with E = Au (**1**, this work) and Ag [9a] are very similar in that both complexes are arranged in centrosymmetrical dimers in which for each anion the ligands are in a coplanar *cis* arrangement with the carbonyl oxygen atoms coordinated to the sodium atom. On the other hand, there is also a significant difference in that the gold atoms are in an almost ideal linearly two-coordinated state while the silver atoms are three-coordinate owing to a significant contact to a sulfone oxygen atom of the symmetry-related unit. It should be noted, however, that the crystals of the silver compound are anhydrous whereas crystals of the gold compound contain water and acetone solvate molecules.

In conductivity studies in aqueous and acetone solutions it has been demonstrated that the metal chelation/coordination is retained at least in part even at high dilution suggesting the presence of ion pairs. In the crystals of **1** (M = Na), dinuclear units with a crystallographically imposed center of inversion are present, while in **2** (M = K) the ionic components are assembled in columns. In the crystalline hydrates/solvates of **1** and **2**, and even more so of **3** (M = NH$_4$), hydrogen bonding between the water molecules and ammonium cations as donors and the carbonyl and sulfone oxygen atoms of the saccharinato ligands as acceptors lends further support to the stability of the crystal lattices.

[1] a) A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem.* **2006**, *118*, 8064; *Angew. Chem. Int. Ed.* **2006**, *45*, 7896; b) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180.

[2] a) L. Messori, G. Marcon, in *Metal ions and their complexes in medications*, (Eds.: A. Sigel and H. Sigel), *Metal Ions in Biological Systems*, Vol. 41, FontisMedia S. A. and Marcel Dekker, Inc., Lausanne, **2004**, pp. 279; b) L. Messori, G. Marcon, in *Metal complexes in tumor diagnosis and anticancer agents*, (Eds.: A. Sigel and H. Sigel), *Metal Ions in Biological Systems*, Vol. 42, FontisMedia S. A. and Marcel Dekker, Inc., Lausanne, **2004**, pp. 385.

[3] M. Grimwade, *Gold Technol.* **1996**, *18*, 4.

[4] M. D. Adams, M. W. Johns, D. W. Dew, in *Gold: Progress in Chemistry, Biochemistry and Technology*, (Ed.: H. Schmidbaur), Wiley, Chichester, **1999**, pp. 65.

[5] a) M. Kato, Y. Okinaka, *Gold Bull.* **2004**, *37*, 37; b) T. A. Green, *Gold Bull.* **2007**, *40*, 105.

[6] a) G. Jovanovski, *Croatica Chem. Acta* **2000**, *73*, 843; b) E. J. Baran, V. T. Yilmaz, *Coord. Chem. Rev.* **2006**, *250*, 1980.

[7] S. J. Berners-Price, M. J. DiMartino, D. T. Hill, R. Kuroda, M. A. Mazid, P. J. Sadler, *Inorg. Chem.* **1985**, *24*, 3425.

[8] P. de Frémont, E. D. Stevens, M. D. Eelman, D. E. Fogg, S. P. Nolan, *Organometallics* **2006**, *25*, 5824.

[9] a) V. T. Yilmaz, S. Hamamci, C. Thöne, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1641; b) R. Weber, M. Gilles, G. Bergerhoff, *Z. Kristallogr.* **1993**, *206*, 275; c) S. W. Ng, *Z. Kristallogr.* **1995**, *210*, 206.

[10] R. Usón, A. Laguna, M. Laguna, *Inorg. Synth.* **1989**, *26*, 85.

[11] W. J. Geary, *Coord. Chem. Rev.* **1971**, *7*, 81.

[12] N. S. Poonia, A. V. Bajaj, *Chem. Rev.* **1979**, *79*, 389.