

[$(N, N', N''$ -Tricyclohexyl)- N'' -cyclohexylcarbamoylguanidinium] Tetrachloroaurate(III) as a Product of the Reaction of Dicyclohexylcarbodiimide with $\text{HAuCl}_4 \cdot \text{aq}$

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Tetrachloroauric(III) Acid Hydrate,
Dicyclohexylcarbodiimide, Guanidinium Salt, X-
Ray

Reaction of tetrachloroauric(III) acid hydrate with dicyclohexylcarbodiimide (dcc) in dichloromethane in the presence of equimolar amounts of triethylamine leads to a complex reaction mixture. One of the components was shown by X-ray crystallography to be [$(N, N', N''$ -tricyclohexyl)- N'' -cyclohexylcarbamoylguanidinium] tetrachloroaurate(III) (**1**) which contains as a cation the addition product of dcc with the corresponding urea.

Introduction

In the course of our studies on gold(I) complexes of ketimines and carbodiimines a series of simple (imine)gold(I) complexes [1–3] were obtained starting from simple gold(I) compounds. We have now also investigated reactions of gold(III) compounds with carbodiimines. These experiments gave mixtures of unexpected products, which have not been completely identified. The reaction of tetrachloroauric(III) acid hydrate with dicyclohexylcarbodiimide leads to the title compound, which was characterized by X-ray crystallography.

Results and Discussion

The reaction of tetrachloroauric(III) acid hydrate with dicyclohexylcarbodiimide in the presence of triethylamine in dichloromethane leads to a complex reaction mixture from which orange crystals can be grown by layering the solution with

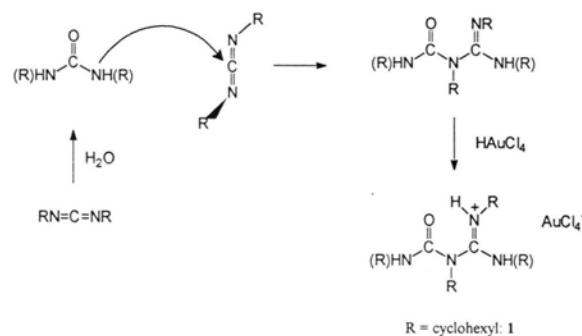
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pentane. The colour of the crystals turns black after several weeks if samples are stored under nitrogen at room temperature. Rapid decomposition of the solid occurs on heating above 140 °C.

The proton NMR spectra of solutions of the compound in CDCl_3 indicate the presence of cyclohexyl rings and N-H groups but no detailed analysis was carried out. Investigation of the crystals by X-ray crystallography showed that the product is composed of [$(N, N', N''$ -tricyclohexyl)- N'' -cyclohexylcarbamoylguanidinium] cations and tetrachloroaurate(III) anions.

The formation of **1** can be accounted for by the following mechanistic pathway: One equivalent of dcc reacts with one molecule of crystal water contained in the tetrachloroauric(III) acid to give the N,N' -dicyclohexylurea.

This urea molecule can act as a nucleophile for a second carbodiimide unit. Subsequent protonation of the imine nitrogen atom leads to the corresponding tetrachloroaurate(III) salt **1**.



Crystal Structure

The compound crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$ formula units in the unit cell. The lattice consists of independent [$(N, N', N''$ -tricyclohexyl)- N'' -cyclohexylcarbamoylguanidinium] cations, tetrachloroaurate(III) anions, and one equivalent of water per formula unit.

The tetrachloroaurate(III) anion has a square planar geometry with an average Au-Cl bond length of 2.27 Å and average Cl-Au-Cl angles of 90° and 178.6°, respectively.

The core of the cation is defined by a planar guanidinium unit and a planar carbamoyl unit, connected at the nitrogen atom N2, which enclose an angle very close to 90°. The C2-N3 and C2-N4 bond distances [1.321(5) and 1.296(5) Å] in the



guanidinium part are clearly shorter than the C2-N2 bond length [1.411(4) Å] indicating a delocalization of the positive charge mainly over N3 and N4.

The dimensions of the O1-H01-O group are indicative of hydrogen bonding between one of the hydrogen atoms of the water molecule and the carbonyl oxygen atom of the carbamoyl unit [O1-O 2.763, O1-H01 0.842 and O-H01 1.959 Å and O-H01-O1 159.4°].

The dimensions of the cation in **1** are similar to those found in the tetramethyl analogue [4]. The intramolecular hydrogen bond between the carbonyl group and a NH proton, which occurs in the unsubstituted carbamoyl guanidinium chloride [5] is prevented in **1** by the trans conformation of the carbamoyl group, which is probably due to steric effects.

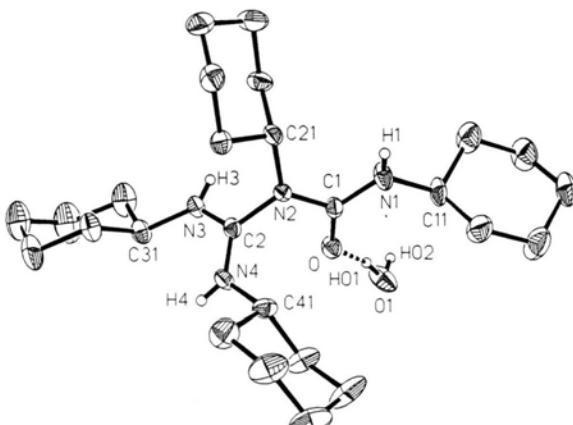


Fig. 1. Molecular structure of the cation in **1**. ORTEP, 50% probability ellipsoids, cyclohexyl ring hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°):
 O-C1 1.234(4), N1-C1 1.335(5), N1-C11 1.465(5), N1-H1 0.79(4), N2-C1 1.386(4), N2-C2 1.411(4), N2-C21 1.498(4), N3-C2 1.321(5), N3-C31 1.468(4), N3-H3 0.79(5), N4-C2 1.296(5), N4-H4 0.75(4), N4-C41 1.476(4), C1-N1-C11 121.5(3), C1-N1-H1 119(3), C11-N1-H1 117(3), C1-N2-C2 114.9(3), C1-N2-C21 125.7(3), C2-N2-C21 118.6(3), C2-N3-C31 126.6(3), C2-N3-H3 110(4), C31-N3-H3 123(4), C2-N4-C41 125.9(3), C2-N4-H4 119(3), C41-N4-H4 115(3), O-C1-N1 124.2(3), O-C1-N2 118.8(3), N1-C1-N2 117.0(3), N4-C2-N3 123.7(3), N4-C2-N2 119.7(3), N3-C2-N2 116.6(3).

Experimental Section

The experiments were carried out under an atmosphere of dry, purified nitrogen. Glassware was dried and filled with nitrogen, solvents were distilled and kept under nitrogen. NMR: Jeol GX 400, TMS as internal standard. IR: Perkin-Elmer

(type 1600 series FT-IR). Starting materials were commercially available.

*[(N, N', N''-Tricyclohexyl)-N''-cyclohexylcarbamoyl-guanidinium] tetrachloroaurate(III) (**1**)*

To a solution of HAuCl₄·3H₂O (312 mg, 0.8 mmol) and NEt₃ (0.11 ml, 0.8 mmol) in dichloromethane (20 ml) was added dicyclohexylcarbodiimide (82 mg, 0.4 mmol) at room temperature. After 3 h the solution was layered with pentane to precipitate orange crystals (ca. 100 mg), decomposition 140 °C.

¹H-NMR (d₆-acetone, room temperature): 5.75 [broad s, NH], 1.15–1.90 [m, cyclohexyl-H]. – IR(KBr): 1652 [st, ν(C=O)]; 3290, 3306 and 3376 [st, ν(N-H)], 3520 [w, broad, ν(OH)].

Crystal Structure Determination

A suitable crystal of compound **1** was sealed into a glass capillary and used for measurement of precise cell constant and intensity data collection.

Table I. Crystallographic data of compound **1**.

Compound	1
empirical formula	C ₂₆ H ₄₉ AuCl ₄ N ₄ O ₂
formula weight	788.46
crystal system	monoclinic
space group (No.)	P2 ₁ /n (14)
a [Å]	12.700(1)
b [Å]	19.358(2)
c [Å]	13.580(1)
α [°]	90
β [°]	100.04(1)
γ [°]	90
V [Å ³]	3287.5(5)
ρ _{calc} [gcm ⁻³]	1.593
Z	4
F(000) [e]	1584
μ(Mo-K _α) [Å]	0.71073
T [°]	-74
diffractometer	Enraf Nonius CAD4
scan	ω-θ
hkl Range	0 ≤ h ≤ 15, -23 ≤ k ≤ 0, -16 ≤ l ≤ 16
Measured reflections	5826
Unique reflections	5826
Observed reflections	5820
[with I ≥ 2σ(I)]	
R _{int}	0.0000
Refined parameters	354
H Atoms (found/calc.)	5 / 44
Absorption corr.:	semi empirical
T _{min} / T _{max}	0.999 / 0.604
R based on (OMIT 4) ^[a]	0.0270
wR2 ^[a]	0.0596
Weighting scheme (1/k) ^[a]	0.0302 / 4.7191
ρ _{fin} (max/min) ^[b] [eÅ ⁻³]	+ 1.787 / - 1.009

[a] R = Σ(||F_o|-|F_c|)/Σ|F_o|. –

wR2 = {[Σw(F_o²-F_c²)]²/[Σ[w(F_o²)²]]}^{1/2}. –

w = 1/2σ²(F_o²) + (lp)² + kp, p = (F_o² + 2F_c²)/3;

[b] residual electron densities located at gold atoms.

During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for the compound. Diffraction intensities were corrected for Lp and absorption effects. The structure was solved by direct methods and refined by full matrix least squares calculations against F^2 [6]. The thermal motion of all non-hydrogen atoms was treated anisotropically. All C-H hydrogen atoms were calculated in idealized positions and allowed to ride on their corresponding carbon atoms. Their isotropic thermal parameters were tied to that of the adjacent atom by a factor of 1.5 (Table I). Important interatomic distances and angles are given in the figure caption. Crystal and structure solution data are

summarized in Table 1. Further information may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-407351 (**1**), the names of the authors, and the journal citation.

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- [1] W. Schneider, A. Bauer, H. Schmidbaur, *J. Chem. Soc., Dalton Trans.* **1997**, 415.
 - [2] W. Schneider, A. Bauer, A. Schier, H. Schmidbaur, *Chem. Ber.*, in press.
 - [3] W. Schneider, K. Angermaier, H. Schmidbaur, *Z. Naturforsch.* **51b**, 801 (1996).
 - [4] E. Allenstein, W. Schwarz, W. Schimpf, J. Weidlein, *Z. Anorg. Allg. Chem.* **554**, 181 (1987).
 - [5] M. J. Begley, P. Hubberstey, C. H. M. Moore, *J. Chem. Res. (S)* **1985**, 380.
 - [6] G. M. Sheldrick, *SHELXL-93*, Göttingen (1993).