ChemComm

Synthesis of the first complex with acetonine as ligand: the first crystal structure of an acetonine derivative

José Vicente,* María Teresa Chicote, Rita Guerrero and M. Carmen Ramírez de Arellano†

Grupo de Química Organometálica,‡ Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Apartado 4021, Murcia, 30071 Spain. E-mail: jvs@fcu.um.es

Received (in Cambridge, UK) 15th June 1999, Accepted 8th July 1999

The complex [Au(acetonine)$_2$]ClO$_4$ (3·ClO$_4$) (acetonine = 2,2,4,4,6-pentamethyl-2,3,4,5-tetrahydropyrimidine) is obtained by bubbling NH$_3$ through an acetone solution containing equimolar amounts of NaClO$_4$ and [AuCl(tht)] (tht = tetrahydrothiophene); the crystal structure of 3·ClO$_4$ was determined by X-ray crystallography.

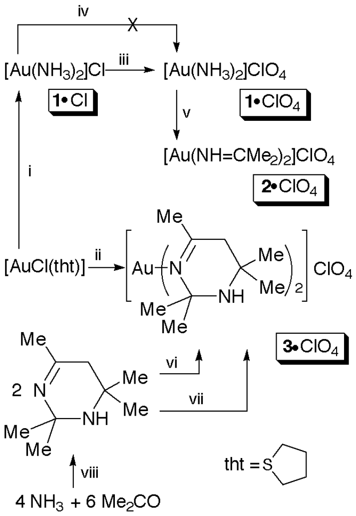
We have recently reported the synthesis of [Au(NH$_3$)$_2$]Cl (**1**·Cl) by reacting [AuCl(tht)][1] (tht = tetrahydrothiophene) with NH$_3$ in acetone (Scheme 1).[2] The reaction of **1**·Cl with TlCF$_3$SO$_3$ or AgClO$_4$ gives, respectively, **1**·CF$_3$SO$_3$ or **1**·ClO$_4$. The latter two complexes react with acetone to give the first acetiminogold(I) complexes [Au(NH=CMe$_2$)$_2$]X (**2**·CF$_3$SO$_3$,[3] **2**·ClO$_4$, Scheme 1) while **1**·Cl neither reacts with acetone nor with NaClO$_4$ in acetone, probably due to its low solubility in this solvent. In an attempt to prepare **1**·ClO$_4$ in a one-pot reaction, using NaClO$_4$ instead of AgClO$_4$, we bubbled NH$_3$ through an acetone solution containing equimolar amounts of [AuCl(tht)] and NaClO$_4$. However, a suspension formed from which a small amount of **1**·Cl was removed, and from the resulting solution the complex [Au(acetonine)$_2$]ClO$_4$ (**3**·ClO$_4$) (acetonine = 2,2,4,4,6-pentamethyl-2,3,4,5-tetrahydropyrimidine) was isolated in 88% yield (Scheme 1).

Acetonine was first characterized by Bradbury *et al.*[4] in 1947, based on its molecular refraction and its reduction and hydrolysis products. It has been reported to form among the decomposition products of acetimine NH=CMe$_2$,[5] but it is most frequently obtained from the reaction of acetone with ammonia; many attempts to improve its synthesis have recently been reported (most of them patents). Thermal or photochemical activation, as well as a wide variety of catalysts have been used.[6–13] Acetonine finds its main use in its reaction with acetone to give 2,2,6,6-tetramethyl-4-oxopiperidine (triacetonamine)[9,11,14–17] which is an attractive intermediate for the synthesis of pharmaceutical products, pesticides, photostabilizers for polymers *etc.*[18] With so much work devoted to acetonine and its derivatives we were rather surprised to find that neither a single acetonine complex of any element nor X-ray studies on acetonine itself or any substituted acetonine had been reported.

In the reaction of NH$_3$, [AuCl(tht)] and NaClO$_4$ leading to **3**·ClO$_4$, neither **1**·ClO$_4$ nor **2**·ClO$_4$ were detected. We have independently proved that these two complexes react with acetone solutions of NH$_3$ to give **3**·ClO$_4$ (Scheme 1) which could explain their absence among the reaction products, if they were formed. These results suggest that acetonine forms from the reaction of NH$_3$ with acetone and replaces tht in [AuCl(tht)]. The displacement of Cl$^-$ by ClO$_4^-$ (from [AuCl(tht)] or from the possible intermediate [AuCl(acetonine)], or even from the non-isolated **3**·Cl) is crucial in the formation of **3**·ClO$_4$ because, as mentioned above, in the absence of NaClO$_4$, [AuCl(tht)] and NH$_3$ react in acetone to give **1**·Cl. It is likely that in the latter reaction the insolubility of **1**·Cl prevents the substitution of NH$_3$ by acetonine to give **3**·Cl or [AuCl(acetonine)]. This and previous studies,[2,3] show the complexity of acetone solutions of NH$_3$ from which it is possible to isolate coordination compounds with NH$_3$, NH=CMe$_2$ and acetonine ligands.

The crystal structure of **3**·ClO$_4$ was determined by X-ray crystallography (Fig. 1).§ The structure consists of centrosymmetric [Au(acetonine)$_2$]$^+$ cations and perchlorate anions forming a chain through hydrogen bonds [N2···O2 3.26(1) Å, H2···O2 2.46(4) Å, N2–H2···O2 157(5)°]. In Fig. 1 the packing diagram along the *c* axis and the hydrogen bonds are shown. Although the gold atoms are in a chain there are no aurophilic interactions (Au···Au 5.921 Å). In the acetonine ring the C2–C1–N1–C4–N2 fragment is planar (mean deviation 0.0052 Å) and makes an angle of 44.7° with the C2–C3–N2 plane. The Au–N bond distance found in **3**·ClO$_4$ [2.040 (5) Å] is similar to those found in **2**·CF$_3$SO$_3$[3] [2.017(5), 2.018(2) Å] or other complexes containing Au–N(sp^2) bonds (range 1.985–2.07 Å).[19,20] The bond distances in the acetonine rings are similar to those found in compounds with the same hybridization and bond order.[21] ^{1}H and ^{13}C NMR spectra of **3**·ClO$_4$ show that the coordination of the gold center to the iminic nitrogen atom is maintained in solution, as no chiral centers seem to be present and one pair of Me groups show a change of chemical shift upon complexation [$\delta(\mathrm{Me})_{\mathrm{complex}} - \delta(\mathrm{Me})_{\mathrm{acetonine}}$] greater [0.57 ppm; asigned to methyls on C(6)] than the other one [0.09 ppm; asigned to methyls on C(4)].¶

This work was supported by DGES (PB-97/1047). R. G. and M. C. R. A. are grateful to Ministerio de Educación y Cultura (Spain) for Grants.



Scheme 1 *Reagents*: i, + 2 NH$_3$ − tht; ii, + 4 NH$_3$ + 6 Me$_2$CO + NaClO$_4$ − 6 H$_2$O − NaCl − tht; iii, + AgClO$_4$ − AgCl; iv, + NaClO$_4$; v, + 2 Me$_2$CO − 2 H$_2$O; vi, + [Au(NH$_2$)$_2$]ClO$_4$ − 2 NH$_3$; vii, + [Au(NH=CMe$_2$)$_2$]ClO$_4$ − HN=CMe$_2$; viii, − 6 H$_2$O.

---

† Present address: Departamento de Química Orgánica, Facultad de Química, Universidad de Valencia, 46100 Valencia, Spain. E-mail: mcra@fcu.um.es

‡ WWW: http://www.scc.um.es/gi/gqo/

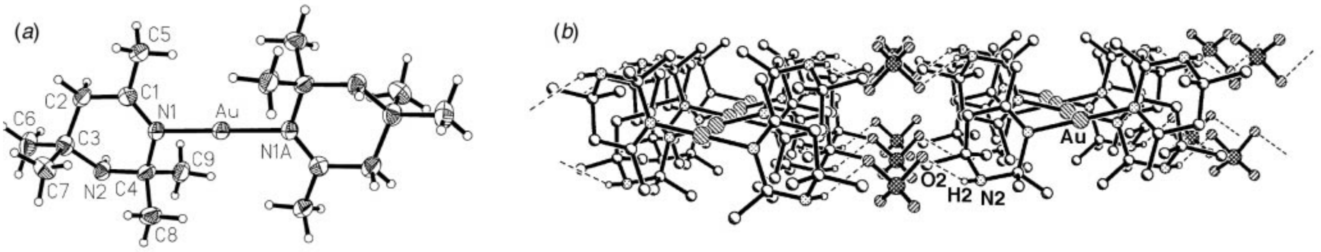


Fig. 1 (*a*) Crystal structure of the cation **3** showing the atom numbering scheme. Selected bond lengths (Å) and angles (°): Au–N1 2.040(5), N1–C1 1.297(8), C1–C2 1.502(8), C2–C3 1.528(7), C3–N2 1.469(7), N2–C4 1.474(7), C4–N1 1.510(7), N1–C1–C2 122.1(5), C1–C2–C3 112.6(5), C2–C3–N2 108.0(4), C3–N2–C4 118.3(4), N2–C4–N1 113.6(4), C4–N1–C1 122.6(5). (*b*) Packing diagram along the *c* axis of compound **3**·ClO_4 showing hydrogen bonds.

Notes and references

§ *Crystal data* for **3**·ClO_4: $C_{18}H_{36}AuClN_4O_4$, 0.48 × 0.40 × 0.02 mm, monoclinic, $C2/c$, a = 15.871 (2), b = 14.707 (2), c = 11.841 (2) Å, β = 123.910 (6)°, V = 2293.8 (5) Å^3, Z = 4, ρ_{calc} = 1.752 Mg m^{-3}, $2\theta_{max}$ = 50.0°, Mo-Kα radiation, λ = 0.71073 Å, ω-scans, T = 173(2) K, 3514 reflections measured, 1514 reflections observed [$I < 2\sigma(I)$], all 2009 independent reflections included in the refinement, R_{int} = 0.0383, absorption correction based on Ψ-scans (μ = 6.560 mm^{-1}, min./max. transmission = 0.140/0.732), the structure was solved by the heavy atom method and refined on F^2 using SHELXS86 and SHELXL93 (G. M. Sheldrick, University of Göttingen, Germany), 133 parameters, the N–H hydrogen was found on the difference Fourier synthesis and refined using an N–H distance restraint, other hydrogen atoms were refined as rigid methyl groups or using a riding model, the perchlorate anion is disordered over two sites, $R1$ [$I > 2\sigma(I)$] = 0.0287, $wR2$ (all reflections) = 0.0811, $\Delta\rho_{max}$ = 1.405 e Å^{-3} (at *ca.* 1 Å from the Au atom). CCDC 182/1322. See http://www.rsc.org/suppdata/cc/1999/1541 for crystallographic data in .cif format.

¶ Acetonine was isolated from an acetone solution of NH_3 by removing the solvent at room temperature. δ_H(300 MHz, $CDCl_3$) 1.12 [s, 6H, C(4)*Me*], 1.38 [s, 6H, C(2)*Me*], 1.87 (s, 2 H, CH_2), 1.96 [s, 3H, C(6)*Me*].

1 R. Usón, J. Laguna and J. Vicente, *J. Organomet. Chem.*, 1977, **131**, 471.
2 J. Vicente, M. T. Chicote, R. Guerrero, P. G. Jones and M. C. Ramírez de Arellano, *Inorg. Chem.*, 1997, **36**, 4438.
3 J. Vicente, M.-T. Chicote, M.-D. Abrisqueta, R. Guerrero and P. G. Jones, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1203.
4 R. B. Bradbury, N. C. Hancox and H. H. Hatt, *J. Chem. Soc.*, 1947, 1394.
5 K. Findeisen, H. Heitzer and K. Deehnicke, *Synthesis*, 1981, 702.
6 G. Goemar, M. Bernhardt and W. Haubold (Leuna-Werke A.-G.), DE 4,216,056, 1993 (*Chem. Abstr.*, 1994, **120**, 245138a).
7 A. Balogh, J. Durmis, K. M., J. Sabados, M. Collak, M. Magura and M. Holko, Cs 235,379, 1987 (*Chem. Abstr.* 1988, **108**, 167494z).
8 R. Ballardini, V. Borzatta, M. T. Gandolfi and R. Scrima, *Res. Discl.*, 1993, **354**, 701.
9 K. Sasaki, O. M. and K. Myake (Sumitomo Chemical Co), JP 07,291,931, 1995 (*Chem. Abstr.*, 1996, **124**, 202290j).
10 G. Shimada (Daicel Chemical Industries, Ltd.), JP 03,188,066, 1989 (*Chem. Abstr.*, 1992, **116**, 41319t).
11 Y. Fukuda (Kyowa Yuka Kk), JP 05,117,242, 1991 (*Chem. Abstr.*, 1993, **119**, 180817d).
12 I. Dragutan, S. Serban, P. Obloja, D. Nistor and V. Dragutan (Combinatul Petrochimic, Pitesti), Rom. RO 96,131, 1987 (*Chem. Abstr.*, 1990, **113**, 172048q).
13 I. Dragutan, S. Servan, P. Obloja, D. Nistor and V. Dragutan (Combinatul Petrochimic, Pitesti), Rom. RO 96,132, 1987 (*Chem. Abstr.*, 1990, **113**, 212011f).
14 M. Inaba and Y. Inui (Mitsubishi Petrochemical Co., Ltd.), JP 01,233,271, 1989 (*Chem. Abstr.*, 1990, **112**, 55627w).
15 R. Kinishi and M. Kasagi (Yoshitomi Pharmaceutical Industries, Ltd.), JP 62,132,859, 1985 (*Chem. Abstr.*, 1987, **107**, 198104f).
16 K. Sakanashi and Y. Azaki (Yoshitomi Pharmaceutical Industries, Ltd.), JP 62,167,763, 1987 (*Chem. Abstr.*, 1988, **108**, 150314t).
17 R. Kinishi (Yoshitomi Pharmaceutical Industries, Ltd.), JP 63,10,761, 1988 (*Chem. Abstr.*, 1988, **109**, 92800f).
18 Z. Ma, Q. Huang and J. M. Bobbit, *J. Org. Chem.*, 1993, **58**, 4837.
19 W. Schneider, A. Bauer and H. Schmidbaur, *J. Chem. Soc., Dalton Trans.*, 1997, 415; W. Schneider, A. Bauer, A. Schier and H. Schmidbaur, *Chem. Ber.*, 1997, **130**, 1417.
20 W. Schneider, K. Angermaier and H. Schmidbaur, *Z. Naturforsch., Teil B*, 1996, **51**, 801.
21 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1987, S1.

Communication 9/04777H