

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

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The complex $[\text{Au}(\text{acetone})_2]\text{ClO}_4$ (**3-ClO₄**) (acetone = 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 $[\text{AuCl}(\text{tht})]$ (tht = tetrahydrothiophene); the crystal structure of **3-ClO₄** was determined by X-ray crystallography.

We have recently reported the synthesis of $[\text{Au}(\text{NH}_3)_2]\text{Cl}$ (**1-Cl**) by reacting $[\text{AuCl}(\text{tht})]$ (tht = tetrahydrothiophene) with NH_3 in acetone (Scheme 1).² The reaction of **1-Cl** with TiCF_3SO_3 or AgClO_4 gives, respectively, **1-CF₃SO₃** or **1-ClO₄**. The latter two complexes react with acetone to give the first acetiminogold(I) complexes $[\text{Au}(\text{NH}=\text{CMe}_2)_2]\text{X}$ (**2-CF₃SO₃**, **2-ClO₄**, 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-ClO₄** in a one-pot reaction, using NaClO_4 instead of AgClO_4 , we bubbled NH_3 through an acetone solution containing equimolar amounts of $[\text{AuCl}(\text{tht})]$ and NaClO_4 . However, a suspension formed from which a small amount of **1-Cl** was removed, and from the resulting solution the complex $[\text{Au}(\text{acetone})_2]\text{ClO}_4$ (**3-ClO₄**) (acetone = 2,2,4,4,6-pentamethyl-2,3,4,5-tetrahydropyrimidine) was isolated in 88% yield (Scheme 1).

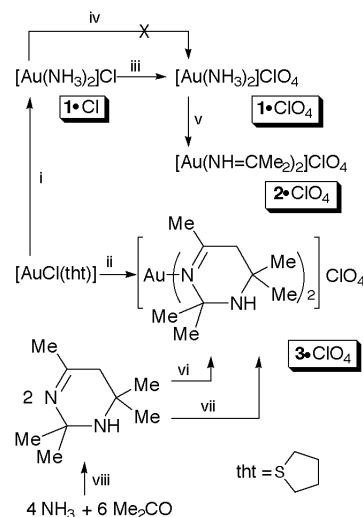
Acetone was first characterized by Bradbury *et al.*⁴ in 1947, based on its molecular refraction and its reduction and hydrolysis products. It has been reported to form among the decomposition products of acetimine $\text{NH}=\text{CMe}_2$,⁵ but it is most frequently obtained from the reaction of acetone 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} Acetone 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 acetone and its derivatives we were rather surprised to find that neither a single acetone complex of any element nor X-ray studies on acetone itself or any substituted acetone had been reported.

In the reaction of NH_3 , $[\text{AuCl}(\text{tht})]$ and NaClO_4 leading to **3-ClO₄**, neither **1-ClO₄** nor **2-ClO₄** were detected. We have independently proved that these two complexes react with acetone solutions of NH_3 to give **3-ClO₄** (Scheme 1) which could explain their absence among the reaction products, if they were formed. These results suggest that acetone forms from the reaction of NH_3 with acetone and replaces tht in $[\text{AuCl}(\text{tht})]$. The displacement of Cl^- by ClO_4^- (from $[\text{AuCl}(\text{tht})]$ or from the possible intermediate $[\text{AuCl}(\text{acetone})]$), or even from the non-isolated **3-Cl** is crucial in the formation of **3-ClO₄** because, as mentioned above, in the absence of NaClO_4 , $[\text{AuCl}(\text{tht})]$ 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 acetone to give **3-Cl** or $[\text{AuCl}(\text{acetone})]$. 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 , $\text{NH}=\text{CMe}_2$ and acetone ligands.

The crystal structure of **3-ClO₄** was determined by X-ray crystallography (Fig. 1).[§] The structure consists of centrosymmetric $[\text{Au}(\text{acetone})_2]^+$ cations and perchlorate anions forming a chain through hydrogen bonds $[\text{N}2\cdots\text{O}2\ 3.26(1)\ \text{Å}$, $\text{H}2\cdots\text{O}2\ 2.46(4)\ \text{Å}$, $\text{N}2-\text{H}2\cdots\text{O}2\ 157(5)^\circ$]. 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 ($\text{Au}\cdots\text{Au}\ 5.921\ \text{Å}$). In the acetone ring the $\text{C}2-\text{C}1-\text{N}1-\text{C}4-\text{N}2$ fragment is planar (mean deviation $0.0052\ \text{Å}$) and makes an angle of 44.7° with the $\text{C}2-\text{C}3-\text{N}2$ plane. The $\text{Au}-\text{N}$ bond distance found in **3-ClO₄** [$2.040(5)\ \text{Å}$] is similar to those found in **2-CF₃SO₃**³ [$2.017(5)$, $2.018(2)\ \text{Å}$] or other complexes containing $\text{Au}-\text{N}(\text{sp}^2)$ bonds (range $1.985-2.07\ \text{Å}$).^{19,20} The bond distances in the acetone rings are similar to those found in compounds with the same hybridization and bond order.²¹ ¹H and ¹³C NMR spectra of **3-ClO₄** 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 [$\delta(\text{Me})_{\text{complex}} - \delta(\text{Me})_{\text{acetone}}$] greater [$0.57\ \text{ppm}$; assigned to methyls on C(6)] than the other one [$0.09\ \text{ppm}$; assigned to methyls on C(4)].[¶]

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Scheme 1 Reagents: i, + 2 NH_3 – tht; ii, + 4 NH_3 + 6 Me_2CO + NaClO_4 – 6 H_2O – NaCl – tht; iii, + AgClO_4 – AgCl ; iv, + NaClO_4 ; v, + 2 Me_2CO – 2 H_2O ; vi, + $[\text{Au}(\text{NH}_2)_2]\text{ClO}_4$ – 2 NH_3 ; vii, + $[\text{Au}(\text{NH}=\text{CMe}_2)_2]\text{ClO}_4$ – $\text{HN}=\text{CMe}_2$; viii, – 6 H_2O .

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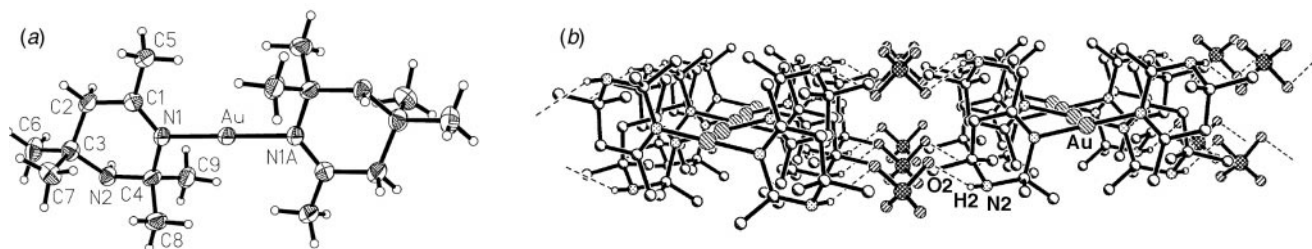


Fig. 1 (a) Crystal structure of the cation **3** showing the atom numbering scheme. Selected bond lengths (Å) and angles (°): Au–N1 2.040(5), N1–C1 1.297(8), C1–C2 1.502(8), C2–C3 1.528(7), C3–N2 1.469(7), N2–C4 1.474(7), C4–N1 1.510(7), N1–C1–C2 122.1(5), C1–C2–C3 112.6(5), C2–C3–N2 108.0(4), C3–N2–C4 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**·ClO₄ showing hydrogen bonds.

Notes and references

§ *Crystal data* for **3**·ClO₄: C₁₈H₃₆AuClN₄O₄, 0.48 × 0.40 × 0.02 mm, monoclinic, *C*2/*c*, *a* = 15.871 (2), *b* = 14.707 (2), *c* = 11.841 (2) Å, β = 123.910 (6)°, *V* = 2293.8 (5) Å³, *Z* = 4, ρ_{calc} = 1.752 Mg m⁻³, 2θ_{max} = 50.0°, Mo–Kα radiation, λ = 0.71073 Å, ω-scans, *T* = 173(2) K, 3514 reflections measured, 1514 reflections observed [*I* < 2σ(*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, *R*1 [*I* > 2σ(*I*)] = 0.0287, *wR*2 (all reflections) = 0.0811, Δρ_{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 NH₃ by removing the solvent at room temperature. δ_H(300 MHz, CDCl₃) 1.12 [s, 6H, C(4)Me], 1.38 [s, 6H, C(2)Me], 1.87 (s, 2 H, CH₂), 1.96 [s, 3H, C(6)Me].

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