SYNTHESIS AND STRUCTURE OF CONDENSATION PRODUCT OF DIMETHYLGLYOXIME ON GOLD MATRIX

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Complex of gold of the composition $[AuL(NO_2)]$ (**1**), where HL is a new tridentate ligand obtained by the condensation of two dimethylglyoxime (H_2DMG) molecules on the matrix of the gold ion, was synthesized and characterized by X-ray structural analysis. It was shown that in the system $H[AuCl_4]\cdot 4H_2O + H_2DMG + Py$, depending on pH of the reaction medium and sequence of addition of components, the final products have unexpected compositions ($[Au^{III}(DMG)ClPy]$, $[AuCl_2Py_2][AuCl_4]\cdot 2[AuCl_3Py]$ or $[Au^{II}L(NO_2)]$). Molecular complex **1** is sustained by the Au···Au···Au intermolecular interactions.

1. Introduction

Recently we have synthesized and investigated by single crystal diffraction technique the dimethylglyoximates of gold, the products of interaction of $H[AuCl_4]\cdot 4H_2O$, H_2DMG with pyridine and the products of interaction of $H[AuCl_4]\cdot 4H_2O$ with the only dimethylglyoxime both in the methanol solution and in the system methanol/water [1, 2]. It was established that in the latter case the final products are $[Au^{III}(HDMG)_2][Au^{III}Cl_4]$ and $[Au^{III}(HDMG)_2][Au^{I}Cl_2]$ [2], where the cation $[Au(HDMG)_2]^+$ is stable and the fragment does not change its configuration owing to the strong intramolecular hydrogen bonds O-H···O between two $HDMG^-$ anions responsible for the formation of a pseudomacrocyclic structure as in the structures of dimethylglyoximates of Co(II), Co(III), Ni(II) and Cu(II), studied in detail in [3-5].

The interaction of $H[AuCl_4]\cdot 4H_2O$ with H_2DMG and Py in different sequence of addition of components resulted in two different products, $[Au^{III}(DMG)PyCl]$ and $[AuCl_2Py_2][AuCl_4]\cdot 2[AuCl_3Py]$ [1]; in the latter case the complex free of H_2DMG has been obtained. The change of the synthetic conditions in the system (different amount of pyridine used) results in a new product $[AuL(NO_2)]$ (**1**), different from the previously reported ones [1].

The subject of this contribution is a new complex $[AuL(NO_2)]$ (**1**), which was synthesized in the system $H[AuCl_4]\cdot 4H_2O + H_2DMG + Py$, where L^- is a new monoanionic tridentate ligand. The oxidation state of gold equal II in **1** is concluded from the condition to balance a single negative charge of the ligand and a single negative charge of a NO_2^- anion. This is an intrigue result, as $[AuL(NO_2)]$ is considered as a mononuclear gold(II) derivative, while known so far gold(II) complexes are usually dinuclear [6-8], formally contain an $[Au_2]^{4+}$ core stabilized by two equal bridging ligands, retaining the gold centres in a close proximity to afford a diauracycle, although the monomeric complexes of gold(II) with dithiolates and dithiocarbamates ions are also known [9, 10]. On the basis of X-ray data and IR, NMR spectra for compound **1** the oxidation state of gold in the complex, the probable mechanism of the ligand formation and the supramolecular aspect of the structure of this complex are discussed.

2. Experimental

2.1. Synthesis of $[Au^{II}L(NO_2)]$ (1)

To a hot solution of $H[AuCl_4]\cdot 4H_2O$ (1.03 g, 2.5 mmol) in methanol (20ml) was added a solution of dimethylglyoxime (0.29 g, 2.5 mmol) in methanol (20 ml) in a molar ratio of 1:1. The reaction temperature is ~ 45°C. A small amount of pyridine was added to the obtained solution (pH ~ 4.5-5.0). The solution was allowed to cool at room temperature. The crystals precipitated within several hours and were air dried. Yield: 0.40 g (38%). *Anal.* Calc. for $C_8H_{12}Au_1N_4O_4$, %: C, 22.60; H, 2.84; N, 13.18. Found: C, 22.33; H, 3.02; N, 12.99.

2.2. X-ray investigation

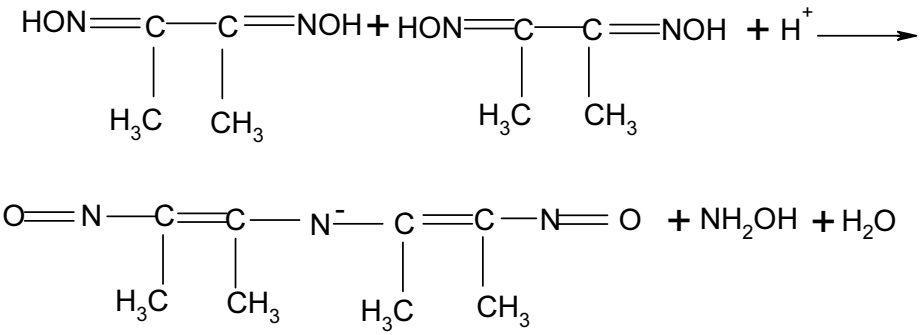
*Crystal data for **1**.* $C_8H_{12}Au_1N_4O_4$, M = 425.18, crystal dimensions 0.30 x 0.10 x 0.10 mm, orthorhombic, space group *Amm*2, a = 3.1980(4), b = 16.089 (1), c = 10.897(1) Å, U = 560.7(1) Å^3, Z = 2, D_c = 2.518 g/cm^3, μ(Mo-K$_\alpha$) = 13.130 mm^{-1}, T = 293(2) K. The majority of the crystals were twinned. The only one selected non-twinned crystal gave the satisfactory set of reflections. The θ-range for data collection is 2.26-27.49°, number of all reflections 2474, number of unique reflections 785, 784 with $I>2\sigma(I)$, number of parameters 56, R_1 = 0.0255, wR_2 = 0.0635 ($I>2\sigma(I)$), R_1 = 0.0256, wR_2 = 0.0635 (all data).

Experimental data for **1** were collected on a Nonius Kappa CCD diffractometer with graphite monochromated Mo Kα radiation using ω rotations with sample to detector distance of 25 mm. Preliminary orientation matrices and unit cell parameters were obtained from the peaks of the first 10 frames, respectively, and refined using the whole data set. The frames were integrated and corrected for Lorentz and polarization effects using DENZO [11]. The scaling as well as the global refinement of crystal parameters was performed by SCALEPACK [11]. Reflections, which were partly measured on previous and following frames, were used to scale these frames on each other. The absorption correction was introduced by semi-empirical method from symmetry equivalent reflections [12]. The structures were solved by a standard direct method using SHELXS-97 and refined by full-matrix least squares based on F^2 using SHELXL-97 [13]. Hydrogen atoms of methyl groups were included in calculated positions and refined with isotropic displacement parameters according to the riding model. ORTEP [14] was used for the molecular drawings.

3. Results and discussion

The new compound $[Au^{II}L(NO_2)]$ (**1**) (Fig. 1) was synthesized upon addition of some amount of pyridine to a mixture of $H[AuCl_4].4H_2O$ and H_2DMG in methanol. The change of the synthetic conditions in the system $H[AuCl_4]\cdot 4H_2O$ - H_2DMG – Py results in this product, different from the previously reported in [1] $[Au^{III}(DMG)PyCl]$ and $[AuCl_2Py_2][AuCl_4]\cdot 2[AuCl_3Py]$. It is proposed that the *pH* of the reaction medium dependent on the different amount of pyridine used, is a decisive factor here, as for $[Au^{III}(DMG)PyCl]$ it is ~ 7.5, while in the case of compound **1** *pH* of the reaction ranges within 4.5 - 5.0.

In the complex $[AuL(NO_2)]$ the new tridentate ligand L^- is a product of condensation of two H_2DMG molecules. The coupling interaction of dimethylglyoxime molecules represents a usual template reaction on a matrix of metal ion with the possible formation of hydroxylamine (scheme).



Another example of condensation is stated for $[Co(DTOH)(DTO)\cdot 2H_2O$ complex [15], where $DTOH_2$ is a diacetylmonooxime thiosemicarbazone, obtained as a product of transamination of one of oxime groups of H_2DMG with thiosemicarbazide in the system Co(II) + H_2DMG + thiosemicarbazide.

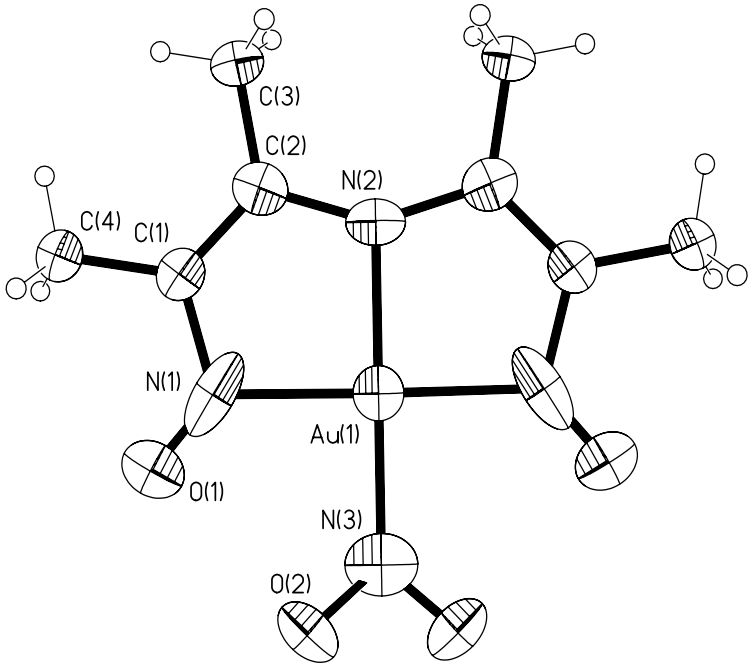


Fig. 1. ORTEP diagram and numbering scheme in **1**.

ORTEP view for complex 1 is depicted in Fig. 1. Complex crystallized in the orthorhombic space group *Amm*2. Compound **1** resides on a mirror plane. To determine the form of the ligand in **1** (neutral molecule or anion, obtained in the result of deprotonation), the NMR spectrum for the sample of **1** dissolved in $DMSO_d6$ was obtained. $DMSO_d6$ is the only solvent suitable for dissolution of **1**. The characteristic peak for NH- group (near 2.0 ppm) in NMR spectrum was not found. This confirms the fact of deprotonation of the coordinated ligand which acts as a monoanion. The analysis of interatomic distances in **1** shows that the ligand is characterized by their essential redistribution (Table 1). The bond distances N-C, C-C, and C-N in the metallocycle in **1** and in the complex of Au(III) with *bis*(2aminoethyl)amine- and *bis*(2aminoethyl)amido-ligand [16, 17] reveals that the ones are extended. The analysis of the bond distances N-O, N-C and C-C in L^- (1.16(1), 1.48(2) and 1.41(2) Å, correspondingly) reveals that they essentially differ from the similar ones in the fully deprotonated DMG^{2-} in the $[Au^{III}(DMG)PyCl]$ [1] (N-O – 1.24(2), 1.26(1) Å, N-C 1.33(2), 1.30(2) Å, C-C 1.45(2) Å).

The templated by the gold ion L^- ligand acts in a chelate mode, and coordinates through a N_3-set of donor atoms with the formation of two symmetric five-membered metallocycles. The interatomic distances Au-N are 2.033(9) and 2.02(2) Å (Table 1). They are comparable with Au-N distances in the typical compound with Au(II), (bis(μ_2-1, 3, 4, 6, 7, 8-hexahydropyrimido(1, 2-a)pyrimidinato)-dichloro-digold(II) $[Au_2(hpp)_2Cl_2]$ (2.062(9), 2.010(11) Å) [6], and slightly differ from the similar ones in asymmetric complex (μ_2-2, 2-diphenyl-2-phosphapropane)-(μ_2-pyridine-2-thiolato-N, S)dibromo-digold(II) (Au-N distances in three independent complexes are 2.147(4), 2.137(4), 2.139(4) Å) [7]. The interatomic distances Au-N in **1** are comparable with the distances in Au(III) complexes with the other deprotonated ligands, chloro - (bis (2-aminoethyl) amido-gold(III) perchclorate (2.05(4), 2.06(4) and 2.01(4) Å) and slightly differ from the similar ones in the complex with neutral ligand, chloro - (bis (2-aminomethyl) amine-gold(III) chloride perchclorate (1.97(2), 2.05(2) and 1.98(2) Å) [16]. The analysis of the above cited literature data reveals that interatomic Au-N distance is sensitive not only to the nature of the coordinated nitrogen atom but also to the ligand geometry. It is impossible to make an unambigous assignement of the Au-N distance to the oxidation state of gold.

Square-planar gold(II) coordination in **1** is formed by N_3-set of donor atoms of L^- ligand and is completed by nitrogen N(3) atom of symmetric anion NO_2^-, which apparently is formed as a result of interaction of hydroxylamine with $H[AuCl_4]$. In the IR spectrum of **1** a series of band frequencies is observed, $\nu_{as}(NO)$ – 1474 cm^{-1}, $\nu_s(NO)$ – 1358 cm^{-1}, $\delta(NO_2$ – 830 cm^{-1}, $\rho(NO_2)$ – 600 cm^{-1}, ν(M-N) – 514 cm^{-1}, that is typical for coordinated to gold NO_2^- group, Au←NO_2^-. The bond Au-N(3) distance of 2.03(3) Å in **1** is shorter than of 2.142 Å found in bis(μ_2-diphenylphosphinodimethylene-C, C)-dinitro-di-gold(II) [8], that might be explained by a greater *trans* influence of N^- in **1** than by the second coordinated Au atom in the last compound, where Au-N(NO_2) bond and a single Au-Au bond are oriented along a common axis.

Table 1. Bond lengths (Å) and angles (deg) for **1**.

Au(1)-N(1)	2.033(9)	N(2)-C(2)	1.48(2)
Au(1)-N(2)	2.02(2)	C(1)-C(2)	1.41(2)
Au(1)-N(3)	2.03(3)	C(1)-C(4)	1.51(2)
O(1)-N(1)	1.16(1)	C(2)-C(3)	1.51(2)
N(1)-C(1)	1.48(2)	N(3)-O(2)	1.21(2)

N(1)-Au(1)-N(2)	89.4(5)	C(2)-C(1)-C(4)	126(1)
N(1)-Au(1)-N(3)	90.6(5)	C(2)-C(1)-N(1)	120(1)
N(1)-Au(1)-N(1)#1	179(1)	C(4)-C(1)-N(1)	115(1)
O(1)-N(1)-C(1)	123(1)	C(1)-C(2)-N(2)	119(2)
O(1)-N(1)-Au(1)	131(1)	C(1)-C(2)-C(3)	125(1)
C(1)-N(1)-Au(1)	106(1)	N(2)-C(2)-C(3)	116(1)
C(2)-N(2)-C(2)#1	147(2)	O(2)-N(3)-O(2)#1	100(2)
C(2)-N(2)-Au(1)	107(1)	O(2)-N(3)-Au(1)	130(1)

Symmetry transformations used to generate equivalent atoms: #1 -*x*+1, -*y*, *z*.

Concluding, the compound **1** represents a molecular complex of gold(II). Complex **1** is composed of the new ligand acting in a monoanionic mode, nitrite anion NO_2^- and gold(II) ion, the oxidation state of the latter being assigned to balance the charge of the coordinated ligand. The reduction of Au^{3+} to Au^{2+} promotes by the hydroxylamine obtained probably in the result of reaction of condensation two molecules of H_2DMG [18].

Oxidation state one and three, as it is stated in [19-21], is typical for gold. It is known that the complexes of Au(I) and Au(III) are diamagnetic; the more characteristic of the former compounds is the linear configuration and, correspondingly, the coordination number of metal atom equal to two, while the overwhelming majority for the latter ones is square-planar configuration with the Au coordination number equal to four. Oxidation state two is very rare for gold, although it is a basic one in copper chemistry. So far, the existence of Au(II) was unambiguously proved in binuclear complexes where the single Au-Au bond with the distances 2.475 – 2.596 Å was registered [6-8]. It is established that many complexes of gold, in which the oxidation state of metal in the empirical formulas formally corresponds to +2, actually represent the mixed-valence Au(I) – Au(III) compounds. Now, alongside with the Au(II) complexes which are formed at intermediate stages of reactions (intermediates) and exist so short that routine physicochemical techniques appear useless for their detection, there are known Au(II) complexes stable enough to be separated and characterized by spectroscopic or X-ray diffractometer techniques [19].

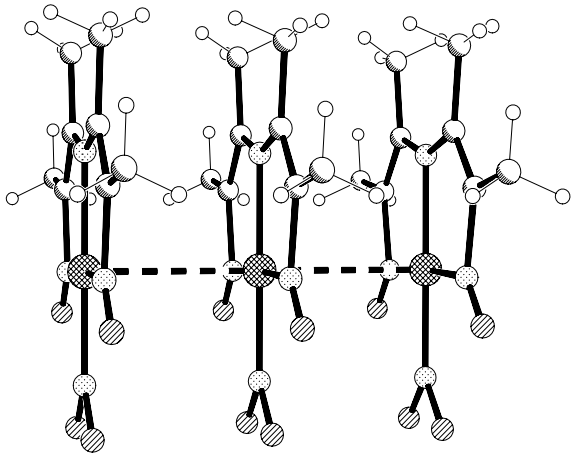


Fig. 2. Solid dashed lines show aurophilic attraction in chains in **1**.

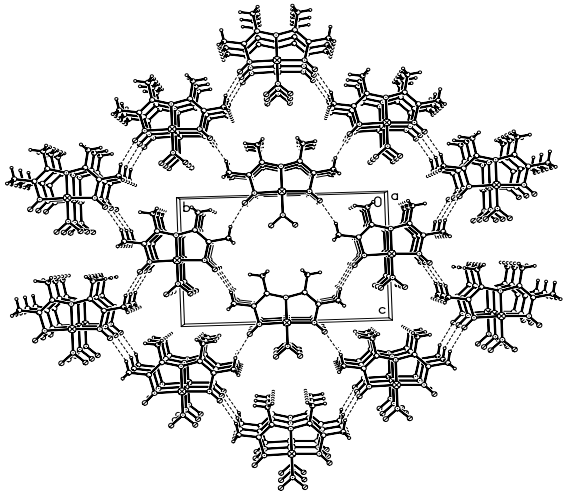


Fig. 3. Fragment of 3D network in **1**.

Complexes, where metal ion exists in $5d^9$ electronic configuration, are paramagnetic ones in the case the contact Au···Au is absent [19]. In monomeric complexes with dithiolate and dithiocarbamate ions [9, 10] stabilization of Au(II) is explained by the delocalization of non-paired electron alongside the unsaturated ligand. Complex **1** is not paramagnetic, that is explained by the availability of shorten Au···Au distances and probably by the delocalization of non-paired electron. As a result of this shorten metal–metal separation, which corresponds to secondary interaction and is in the range typical for aurophilic attraction [22], complexes **1** are packed in the chains in the crystal (Fig. 2).

The Au(II)···Au(II) distance in **1** of 3.198 Å is longer than Au···Au distance in binuclear complexes Au(II), where gold-gold distances are 2.4752 Å [6], 2.547 Å [7], 2.596 Å [8], 2.5679 Å [23], a little longer than the distance observed in metallic gold (2.884 Å) [24], in polynuclear gold(I) complexes containing xanthine derivatives and bis(phosphine) (3.053 Å) [25] and shorter than distance Au^{III}-Au^{I} in $[Au^{III}(HDMG)_2][Au^{I}Cl_2]$ where it is 3.25 Å [2].

Taking into account the weak interactions between chains, C(4)-H···O(1)(1-*x*, 0.5-*y*, -0.5+*z*) (C···O 3.182 Å, ∠CHO 160°) the structure of **1** is a 3*D* grid (Fig. 3).

4. Conclusions

Complex [AuL(NO_2)] (**1**) was obtained in the system H[$AuCl_4$]· $4H_2O$ + H_2DMG + Py under different synthetic conditions (different pH of the reaction medium) than the previously studied [Au^{III}(DMG)PyCl] [1]. The template reaction on a matrix of gold results in an "assembly" of a new ligand through the condensation of two molecules of dimethylglyoximes. Concluding from the complex composition, a single negative charge of the tridentate coordinate ligand and the presence in the complex a monoanion NO_2^- gold in complex **1**is stabilized in an oxidation state +2. Because of the short gold–gold separation, complex, although being in $5d^9$ electronic configuration of metal ion, is not a paramagnetic one. The stabilization in the crystal of molecular mononuclear complexes is achieved through Au···Au intermolecular interactions, which define the crystal architecture. In addition, weak hydrogen bonds of C-H···O and C-H···Cl types significantly contribute to the complex stability.

5. Supplementary material

Crystallographic data for **1** have been deposited with the Cambridge Crystallographic Data Center, CCDC 613391. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK(fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

6. Acknowledgements

We dedicated this article to the memory of academician Nicolae Gerbeleu, one of the creators of template reactions who initiated the study of gold complexes with dimethylglyoxime.

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