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Dinuclear gold(III) pyrazolato complexes – Synthesis, structural characterization and transformation to their trinuclear gold(I) and gold(I/III) analogues

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ABSTRACT

The reaction of $AuCl_3py$ with Na(pz*) (pz* = pyrazolato, or substituted pyrazolato anion) yields stable dinuclear [*cis*-$Au^{III}Cl_2$(μ-pz*)]$_2$ complexes. In the presence of a base, the latter undergo reduction with concomitant transformation of the dinuclear Au^{III}_2-structure to trinuclear $Au^{III}_2Au^{I}$, $Au^{III}Au^{I}_2$ (containing *trans* $Au^{III}Cl_2$-centres) and Au^{I}_3 species.

1. Introduction

Interest in Au^{III} chemistry has recently been rekindled by articles describing the catalytic redox activity of gold [1]. Mononuclear Au^{III}-centres in contact with the surface of a MgO-support have been identified as the catalytically active species in the hydrogenation of ethylene [2]. Some homogeneous Au^{III}-catalyzed alkyne hydration processes have also been reported [3]. Even more provocative has been the report that the gold-sequestering methanotrophic bacterium *Micrococcus luteus* contains a trinuclear gold active-centre, which cycles between the Au(I) and Au(III) oxidation states as it converts methane to methanol [4]. Following up on that report, $AuCl_4^-$ has been shown to catalyze the air-oxidation of alkanes [5]. Consequently, our discovery of unusual redox properties in the chemistry of trinuclear gold pyrazolates has prompted us to further investigate this system [6]. The Au^{I}-complex [Au(μ-pz*)]$_3$ (pz* = substituted pyrazolate anion) undergoes a six-electron oxidation to its corresponding Au^{III}-analogue [*trans*-$AuCl_2$(μ-pz*)]$_3$ upon treatment with neat *aqua regia*, which surprisingly leaves the nine-membered $(Au–N–N)_3$ metallacycle intact. Subsequently, the fully oxidized Au_3Cl_6-species undergoes spontaneous stepwise reductions, through the mixed-valent $Au^{I}Au^{III}_2Cl_4$ and $Au^{I}_2Au^{III}Cl_2$-species, back to the fully reduced Au^{I}_3 starting complex. Each reductive step proceeds with a formal Cl_2-elimination, accompanied by chlorination of the pyrazole 3,5-alkyl substituents [6]. The presence of electron-releasing/withdrawing substituents around the pyrazole rings was proposed as an important factor in tuning this behavior, suggesting that appropriately substituted derivatives might further stabilize the oxidized forms. An additional mixed-valent $Au^{I}_2Au^{III}Cl_2$-pyrazolate, prepared by the reaction of $AuCl_3py$ and $Na(3,5\text{-}Ph_2\text{-}pz)$, has been known for several years [7].

A second issue in synthetic Au^{III}-pyrazolate chemistry has been the paucity of structural data for complexes of *cis*-geometry, which is, in contrast, the commonly observed geometry for all other d^8-metal pyrazolates, including Pd^{II}, Pt^{II}, Rh^{I}, Ir^{I} and Ru^{0} [8–12]. The existence of a *cis* dinuclear gold pyrazolate, prepared by the action of *aqua regia* on [Au^{I}(μ-pz*)]$_3$, had been proposed by Bonati et al. in 1984, based on analytical and spectroscopic evidence [13]. However, a subsequent reinvestigation that included X-ray structural data, failed to identify this isomer, the only product characterized being a mixed-valent $Au^{I}_2Au^{III}Cl_2$-species [7b]. An additional report on the synthesis of *cis*-[Me_2Au(μ-3,5-Me_2-pz)]$_2$ was not supported by X-ray data [14]. The first crystallographically characterized example of *cis*-gold(III) pyrazolate complex – *cis*-$Au^{III}_2Cl_4$(μ-pz)$_2$ – appeared in the literature recently [15]. The latter, as well as the related complex of 3-Me-pz, are potent *in vitro* cytocides, adding to the growing list of Au^{III} antitumour agents [16].

In order to better understand the redox and coordination chemistry-controlling factors of gold pyrazolates, we are now extending our studies [6,7,17] to include a wider variety of pyrazole ligands, namely the parent unsubstituted pyrazole (pzH), as well as the peripherally-substituted 4-Me-pzH, 3,4,5-Me_3-pzH, and 4-I-3,5-Me_2-pzH. Herein we report the synthesis, characterization, redox

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solution chemistry, molecular and crystal structures of three new dinuclear Au^{III}-pyrazolates, along with some related trinuclear mixed-valent Au$^{I/III}$-complexes, and the ^{1}H NMR study of a dinuclear-to-trinuclear complex transformation.

2. Experimental

2.1. Materials and methods

All reactions were performed under nitrogen atmosphere with the use of standard Schlenk line techniques. All solvents, unless noted, were dried and distilled under N$_2$ by standard methods prior to use. Pyrazole and 4-Me-pzH from commercial sources were used as received, while 3,4,5-Me$_3$-pzH, 4-I-3,5-Me$_2$-pzH and AuCl$_3$py were prepared by literature methods [18–20]. Sodium pyrazolates were prepared by deprotonation of the corresponding pyrazoles with NaH in THF, followed by crushing out of the product with hexane and vacuum drying. C, H, N analyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN, USA). ^{1}H NMR spectra were recorded on a Bruker Advanced DRX-500 spectrometer.

2.2. Synthesis of [Au$_2^{III}$Cl$_4$(μ-pz)$_2$] (**1**)

To AuCl$_3$py (0.05 mmol, 19 mg) was added Na(pz) (0.05 mmol, 4.5 mg) in 3 ml CH$_2$Cl$_2$–THF (2:1). The resulting mixture was stirred for 20 min and filtered. The filtrate was allowed to slowly evaporate yielding, within one week, pale yellow crystals of **1**, whose crystal structure was shown by X-ray diffraction to be identical to the recently published one [15]. Yield: 5%. The major product of this reaction is insoluble [Au^I(μ-pz)]$_3$ [17].

2.3. Synthesis of [Au$_2^{III}$Cl$_4$(μ-4-Me-pz)$_2$] (**2**)

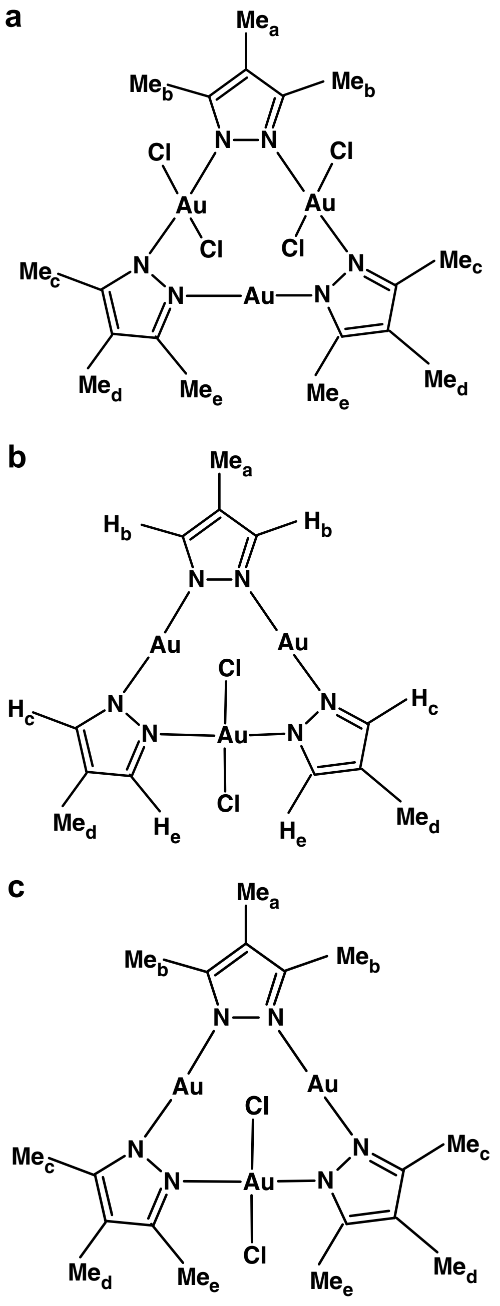
This complex was prepared similarly to **1** using Na(4-Me-pz) instead of Na(pz). X-ray quality red needles of **2** and orange blocks of **2** · **THF** were obtained in 15% yield by the same technique. *Anal.* Calc. for C$_8$H$_{10}$Cl$_4$N$_4$Au$_2$: C, 13.75; H, 1.43; N, 8.02. Found: C, 13.98; H, 1.51; N, 8.16%. ^{1}H NMR (CDCl$_3$, ppm): 2.19 (s, 3H, 4-Me), 7.74 (s, 2H, 3,5-pz).

2.4. Synthesis of [Au$_2^{III}$Cl$_4$(μ-3,4,5-Me$_3$-pz)$_2$] (**3**)

This complex was prepared similarly to **1** using Na(3,4,5-Me$_3$-pz) instead of Na(pz). Red crystalline solid of **3** was obtained in 40% yield. X-ray quality crystals are obtained by diffusion of hexane into a CH$_2$Cl$_2$ solution of **3** at 5 °C. *Anal.* Calc. for C$_{12}$H$_{18}$Cl$_4$N$_4$Au$_2$: C, 19.10; H, 2.39; N, 7.43. Found: C, 19.08; H, 2.37; N, 7.39%. ^{1}H NMR (CD$_2$Cl$_2$, ppm): 1.98 (s, 3H, 4-Me), 2.38 (s, 6H, 3,5-Me$_2$).

2.5. Reduction of **3** in the presence of Et$_3$N

Et$_3$N (2 ml of a 0.01 M CH$_2$Cl$_2$ solution, 0.02 mmol) was added to a CH$_2$Cl$_2$ solution of **3** (7.5 mg, 0.01 mmol), and after 30 min of stirring the mixture was allowed to slowly evaporate. Orange thin plates of [Au^{I}Au$_2^{III}$Cl$_4$(μ-3,4,5-Me$_3$-pz)$_3$] (**4**) and small orange prismatic crystals of [Au$_2^I$Au^{III}Cl$_2$(μ-3,4,5-Me$_3$-pz)$_3$] (**5**), along with some **3** resulted within 1–2 days. If the reaction mixture is kept for 2 days, the colour of the solution fades, becoming eventually colourless. Evaporation of the solution affords small colourless prismatic crystals of [Au(μ-3,4,5-Me$_3$-pz)]$_3$ (**6**). ^{1}H NMR of **4** (CD$_2$Cl$_2$, ppm): 2.05 (s, 6H, 4-Me$_d$), 2.09 (s, 3H, 4-Me$_a$), 2.34 (s, 6H, 3,5-Me$_e$), 2.40 (s, 6H, 3,5-Me$_c$), 2.48 (s, 6H, 3,5-Me$_b$). See Scheme 1a for ^{1}H NMR assignment.



Scheme 1.

2.6. Reaction of AuCl$_3$py with excess Napz*

AuCl$_3$py (0.05 mmol, 19 mg) and Napz* (0.15 mmol) were added to 5 ml of 2:1 CH$_2$Cl$_2$–THF (pz* = pz$^-$ or 4-Me-pz$^-$) and the resulting mixture was stirred for 30 min. During this time, the initial orange yellow solutions turned to pale yellow (for pz* = pz), or colourless (for pz* = 4-Me-pz). After filtration, the filtrate was allowed to evaporate until crystals appeared on the wall of the reaction vessel, which were then analyzed by X-ray diffraction. From the reaction of AuCl$_3$py + 3 Na(4-Me-pz), colourless polyhedra were obtained, which proved to be the known complex, [Au^I(μ-4-Me-pz)]$_3$ [15]. From the reaction of AuCl$_3$py + 3 Napz, two kinds of crystals, colourless square prisms, as the major mixture component, and a minor product, isolated as a few yellow rectangular plates, were obtained. The colourless crystals proved by unit cell