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# Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

## Synthesis and characterization of novel gold(III) complexes with polydentate N-donor ligands based on the pyridine and triazole heterocycles



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#### ARTICLE INFO

Article history: Received 14 March 2013 Accepted 8 April 2013 Available online 17 April 2013

Keywords: Gold(III) Chloro-complexes N-donor ligands Pyridine Triazole

### ABSTRACT

The coordination chemistry towards the Au(III) metal centre of the pyridine-triazole ligands 2-[(4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl]pyridine (**pytz**<sup>Ph</sup>) and 2-[(4-pentyl-1*H*-1,2,3-triazol-1-yl)methyl]pyridine (**pytz**<sup>Pent</sup>) has been explored and complexes having formulae AuCl<sub>3</sub>(pytz<sup>Ph</sup>) (1<sup>Ph</sup>) and AuCl<sub>3</sub>(pytz<sup>Pent</sup>) (1<sup>Pent</sup>) have been isolated and characterised. Reaction of 1<sup>Ph</sup> with AgClO<sub>4</sub> allowed the preparation of the compound [AuCl<sub>2</sub>(pytz<sup>Ph</sup>)](ClO<sub>4</sub>) (2<sup>Ph</sup>). Reaction of 1<sup>Ph</sup> and 1<sup>Pent</sup> with K[AuCl<sub>4</sub>]·2H<sub>2</sub>O led to the formation of the salts [Hpytz<sup>Ph</sup>][AuCl<sub>4</sub>] (3<sup>Ph</sup>) and [Hpytz<sup>Pent</sup>][AuCl<sub>4</sub>] (3<sup>Pent</sup>).

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Polydentate N-donor ligands play a fundamental role in the coordination chemistry of gold(III). Some examples of species commonly present in the coordination sphere of this metal centre are polyfunctional amines such as ethylenediamine, diethylenetriamine and their derivatives, amido-ligands usually obtained from the deprotonation of the corresponding amines, pyridine-based compounds such as 2,2'-bipyridine, 1,10-phenantroline, 2,2':6':2"-terpyridine and 2,3,5,6-tetrakis(2-pyridinyl)pyrazine, a number of ligands containing imine moieties or 5-membered heterocycles such as pyrazoles, oxazoles and imidazoles [1].

The catalytic properties of many gold complexes, in particular as far as activation of unsaturated compounds and of the C-H bond is concerned, make the coordination chemistry of gold a current field of research [2]. Moreover, the synthesis of novel complexes is nowadays prompted by the anti-tumoral, anti-bacterial, anti-viral and anti-rheumatoid properties exhibited by several coordination compounds of gold [3].

The heterocycle 1,2,3-triazole is present in various polydentate N-donor ligands [4]. The relative abundance of triazole-based coordinating moieties can be ascribed to the ease of their preparation, usually based on the copper-catalysed Huisgen reaction between an organic azide and an alkyne [5]. The coordination chemistry of polydentate neutral ligands containing pyridine and triazole moieties towards some square-planar d<sup>8</sup> metal centres has been recently studied. In particular, 2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)pyridine and 2-[(4-phenyl-

1*H*-1,2,3-triazol-1-yl)methyl]pyridine (**pytz**<sup>Ph</sup>) have been recently used for the preparation of novel halogeno-, allyl- and homoleptic Pd(II) and Pt(II) complexes [6]. However, in the case of the isoelectronic gold(III) centre the only reported compound is the salt [**Hpytz**<sup>Ph</sup>][AuCl<sub>4</sub>], which has also been structurally characterised [6c].

Our recent studies have been aimed at extending the coordination chemistry of the ligand **pytz**<sup>Ph</sup> towards gold(III) and in this communication we wish to report the synthesis and a preliminary study on the reactivity of the complexes having formula  $AuCl_3(pytz^{Ph})$  ( $1^{Ph}$ ) and  $[AuCl_2(pytz^{Ph})](ClO_4)$  ( $2^{Ph}$ ). Furthermore, we have also expanded this study to ligands having an aliphatic substituent instead of a phenyl ring on the triazole moiety, by synthesising the species 2-[(4-pentyl-1*H*-1,2,3-triazol-1-yl)methyl]pyridine (**pytz**<sup>Pent</sup>).

The ligand **pytz**<sup>Ph</sup> was prepared by reacting 2-(azidomethyl)pyridine with phenylacetylene according to a literature procedure [6]; **pytz**<sup>Pent</sup> was obtained analogously by reacting 2-(azidomethyl)pyridine with 1-heptyne in THF/H<sub>2</sub>O. Details about the synthesis and characterization of **pytz**<sup>Pent</sup> are collected in the Supplementary file.

Neutral complexes having general formula AuCl<sub>3</sub>(pytz<sup>R</sup>) (R = Ph, Pent) were synthesised by adding a slight excess of the appropriate ligand dissolved in methanol to an aqueous solution of K[AuCl<sub>4</sub>]·2H<sub>2</sub>O (see Scheme 1). While [AuCl<sub>3</sub>(pytz<sup>Ph</sup>)] (1<sup>Ph</sup>) immediately precipitates as a pale yellow solid, AuCl<sub>3</sub>(pytz<sup>Pent</sup>) (1<sup>Pent</sup>) was obtained as a yellow oil after removal of the solvent at reduced pressure. Yields were >95% in both the cases. Displacement reactions on gold(III) bromocomplexes as precursors [7] led instead to quite unstable species, which quickly decomposed with the formation, among all, of the [AuBr<sub>2</sub>]<sup>-</sup> anion.



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Scheme 1. Synthesis of 1<sup>Ph</sup>, 1<sup>Pent</sup>, 2<sup>Ph</sup>, 3<sup>Ph</sup> and 3<sup>Pent</sup>.

Characterization data for **1**<sup>Ph</sup> and **1**<sup>Pent</sup> are reported in Table S1. Details about the characterization methods are collected in the Supplementary file. Elemental analysis data are in agreement with the proposed formulae. Conductivity measurement on acetone solutions confirmed that both the products are neutral.

In the aromatic region of the <sup>1</sup>H NMR spectrum of **1**<sup>Pent</sup> (see Supplementary file) only one set of resonances for the pyridine and triazole rings is present and one singlet attributable to the methylene group is observable at 6.00 ppm (the corresponding <sup>13</sup>C NMR resonance falls at 59.2 ppm). In the aliphatic region the signals of the pentyl chain are easily observable. There is no meaningful change among the <sup>1</sup>H NMR spectra of **1**<sup>Pent</sup> recorded in the range 298–193 K. In particular, the  $-CH_2-$  signal remains a sharp singlet, this suggesting the coordination of the N-donor ligand to the gold centre through only one nitrogen atom. The <sup>1</sup>H NMR resonance of pyridine-H<sub>6</sub> proton is 8.58 ppm, a value close to the 8.56 ppm of the free ligand. On the contrary, the chemical shift of triazole-H<sub>5</sub> is meaningfully high-frequency shifted with respect to **pytz**<sup>Pent</sup>, this suggesting the interaction of the ligand with Au(III) through the triazole moiety.

In order to better give insight into the coordination mode of the ligand towards the AuCl<sub>3</sub> fragment, we optimised the possible isomers of  $\mathbf{1}^{Pent}$  (coordination through pyridine-N, triazole-N<sub>2</sub> and triazole-N<sub>3</sub>) by DFT calculations (computational details are reported in the Supplementary file). The species where the ligand is bonded to the gold centre by the triazole-N<sub>3</sub> atom (Fig. 1) is significantly more stable than the other isomers, in agreement with the experimental NMR observations.

The <sup>1</sup>H NMR spectrum of  $1^{Ph}$  is considerably different from that of  $1^{Pent}$ . The presence of two sets of signals suggests the presence of two isomers, namely  $1^{Ph}a$  and  $1^{Ph}b$ , in the relative molar ratio of 0.8:1. In particular, in the aromatic region eight signals attributable to two *ortho*-substituted pyridine rings are observable together with two singlets corresponding to the hydrogen atoms in position 5 of two triazole moieties. Two singlets in the spectral region between 6.6 and 6.0 ppm are also present, which correspond to two distinct methylene groups and have been attributed to the proper isomer by NOESY experiments. As for  $1^{Pent}$ , no meaningful change of the NMR spectra was observed by lowering the temperature to 193 K. The presence of two

isomers of  $\mathbf{1}^{\mathbf{Ph}}$  is confirmed also by the <sup>13</sup>C {<sup>1</sup>H} NMR spectrum. In particular, two resonances at 153.1 and 147.7 ppm have been attributed to the pyridine carbon atom in position 6, while two signals at 124.1 and 123.6 ppm correspond to the triazole-CH. The methylene groups give two signals at 55.8 and 54.3 ppm. It is to be noted that the <sup>1</sup>H NMR chemical shift value of the pyridine-H<sub>6</sub> in  $\mathbf{1}^{\mathbf{Pent}}$  (8.58 ppm) is closer to that reported for the  $\mathbf{1}^{\mathbf{Ph}}\mathbf{b}$  isomer of the phenyl-substituted derivative (8.85 ppm), this suggesting a similar coordination mode. The chemical shift of the same proton in  $\mathbf{1}^{\mathbf{Ph}}\mathbf{a}$  is instead quite high-frequency shifted (9.43 ppm) and implies the coordination of the ligand by the pyridine nitrogen atom.

From DFT calculations the isomers of  $\mathbf{1}^{\mathbf{Ph}}$  with the Au-N<sub>3</sub>(triazole) or the Au-N(pyridine) bonds resulted the most stable and have comparable energies, while the coordination through the triazole-N<sub>2</sub> has been excluded. The most stable isomers are probably the species observed by means of NMR spectroscopy and the optimised geometries are reported in Fig. 1.

The apparently higher coordinating ability of the triazole moiety in **pytz**<sup>Pent</sup> with respect to **pytz**<sup>Ph</sup> is fairly attributable to the increased basicity induced by the alkyl group. In fact, the computed proton affinity (PA) for the triazole-N<sub>3</sub> in **pytz**<sup>Pent</sup> is about 3 kcal mol<sup>-1</sup> higher than that calculated for the same nitrogen atom in **pytz**<sup>Ph</sup>. In this connection it is noteworthy that a similar PA difference has been computed in the past between 3-methyl-pyridine and pyridine [8].

The complexes  $1^{ph}$  and  $1^{Pent}$  were reacted with one equivalent of AgClO<sub>4</sub> in CH<sub>3</sub>NO<sub>2</sub> with the aim of preparing coordination compounds in which the N-donor ligands act as bidentate, but only with the phenyl-substituted ligand it was possible to isolate in high yield (ca. 90%) the compound [AuCl<sub>2</sub>(pytz<sup>Ph</sup>)](ClO<sub>4</sub>) ( $2^{Ph}$ ) (see Scheme 1).

The relevant characterization data are collected in Table S1. Elemental analysis data for  $2^{Ph}$  are in agreement with the proposed formulation and the complex behaves as 1:1 electrolyte in CH<sub>3</sub>NO<sub>2</sub> [9]. The IR spectrum shows signals attributable to the C=N and Cl-O stretchings and in the far-IR region a band at 370 cm<sup>-1</sup> and a shoulder around 378 cm<sup>-1</sup> have been attributed to the Au-Cl stretching [10].

The <sup>1</sup>H NMR spectrum of  $2^{Ph}$  in  $(CD_3)_2CO$  at 298 K shows in the aromatic region four signals attributable to the pyridyl moiety alongside the singlet corresponding to the triazole-H<sub>5</sub> proton and the



**Fig. 1.** DFT-optimised structures of the most stable isomer of  $1^{Pent}$  and of the two most stable isomers of  $1^{Ph}$  ( $1^{Ph}a$  and  $1^{Ph}b$ ). Selected calculated bond lengths (Å) for  $1^{Pent}$ : Au-N = 2.046, Au-Cl(*trans*-N) = 2.315, AuCl(*cis*-N) = 2.344, 2.344; for  $1^{Ph}a$ : Au-N = 2.081, Au-Cl(*trans*-N) = 2.317, AuCl(*cis*-N) = 2.346, 2.346; for  $1^{Ph}b$ : Au-N = 2.053, Au-Cl(*trans*-N) = 2.313, AuCl(*cis*-N) = 2.344, 2.345. The geometries of all the considered isomers are reported in the Supplementary file.

resonances due to the phenyl ring. At room temperature the  $- CH_2$ bridge appears as a singlet centred at 6.90 ppm. The signal of the methylene group becomes an AB quartet for temperatures below 252 K and the  ${}^2J_{\text{HH}}$  coupling constant is 15.8 Hz at 203 K ( $\Delta \nu = 28$  Hz) (see Supplementary file). The presence of an AB spin system at low temperature confirms that in  $2^{\text{Ph}}$  the ligand is coordinated to the gold centre through both the pyridine and the triazole groups. However, the presence of a singlet at room temperature suggests that a quite fast dissociation of one of the N-donor moieties occurs; the mechanism likely implies reversible displacement of an N-donor heterocycle by a molecule of acetone [11]. From variable-temperature NMR data the  $\Delta G^{\ddagger}$ value for such a reaction was estimated to be 12  $\pm$  1 kcal mol<sup>-1</sup> [12].

Unfortunately, we were unable to collect crystals suitable for X-Ray diffraction. DFT calculations are however in agreement with the experimental data and the optimised structure of the cation of  $2^{Ph}$  is reported in Fig. 2. The only stable minimum is that in which coordination of the N-donor ligands occurs through the pyridine-N and the triazole N<sub>2</sub> atoms, as already observed for Pd(II) and Pt(II) complexes of the same ligand [6]. The optimisation of starting structures in which the triazole moiety is bonded through the N<sub>3</sub> atom led to the same minimum above described.

In the case of  $1^{\text{Pent}}$  the reaction with AgClO<sub>4</sub> led to a scarcely stable product, which quickly decomposes with the formation, among all, of the [AuCl<sub>2</sub>]<sup>-</sup> anion. The different behaviour with respect to  $1^{\text{Ph}}$  can be tentatively ascribed to the greater basicity of the triazole moiety in **pytz**<sup>Pent</sup> with respect to **pytz**<sup>Ph</sup>.

Finally, we tried to synthesise binuclear complexes by reacting  $1^{Ph}$  and  $1^{Pent}$  with a second equivalent of the AuCl<sub>4</sub><sup>-</sup> anion. In a typical experiment, an acetone solution containing the proper complex and a stoichiometric amount of K[AuCl<sub>4</sub>]·2H<sub>2</sub>O was heated to reflux for six hours. Standard workup (see Supplementary Information) allowed to obtain  $3^{Ph}$  as a yellow solid, while  $3^{Pent}$ , the product of

the reaction between  $\mathbf{1}^{Pent}$  and  $K[AuCl_4] \cdot 2H_2O$ , was isolated as a yellow oil.

Characterization data, collected in Table S1, do not support the formation of neutral binuclear complexes. **3**<sup>Ph</sup> and **3**<sup>Pent</sup> behave as electrolytes in acetone solution and elemental analysis data do not match the values expected for species having general formula  $(AuCl_3)_2(\mu$ -pytz<sup>R</sup>). <sup>1</sup>H NMR spectra show in both the cases only one set of resonances and the  $-CH_2$ - signal is a sharp singlet. The <sup>1</sup>H NMR spectra do not meaningfully change on cooling the sample to 193 K. To understand the nature of **3**<sup>Ph</sup>, X-Ray diffraction data were collected from a single crystal obtained by slow cooling a saturated acetone/diethylether solution of the complex. It was found that **3**<sup>Ph</sup> is a pyridinium salt of formulation [Hpytz<sup>Ph</sup>][AuCl<sub>4</sub>], having the solid-state structure already observed by Crowley and Kilpin [6c], which obtained the same compound by reacting **pytz**<sup>Ph</sup> with tetrachloroauric acid. The close analogy of the characterization data between **3**<sup>Pent</sup> and **3**<sup>Ph</sup> suggests that also **3**<sup>Pent</sup> is an ionic compound having formula [Hpytz<sup>Pent</sup>][AuCl<sub>4</sub>].

In summary, pyridine-triazole ligands revealed to be able to form neutral and ionic mono-nuclear gold(III) chloro-complexes. Very interestingly, the coordination mode of these polydentate N-donor ligands and the formation of the complexes appear to be strongly influenced by small changes of basicity caused by the introduction of alkyl- of aryl-substituents on the triazole moiety.

#### Appendix A. Supplementary material

Characterization data (Table S1). Details about the synthesis and characterization of the ligand **pytz<sup>Pent</sup>** and the coordination compounds are collected in the Supplementary file, together with the description of the computational methods used for the simulations and selected NMR spectra. Pictures of all the DFT-optimised isomers of



Fig. 2. DFT-optimised structure of the cation of  $2^{Ph}$ . Selected calculated bond lengths (Å): Au-N(pyridine) = 2.096, Au-N<sub>2</sub>(triazole) = 2.059, Au-Cl(trans-N-pyridine) = 2.311,  $AuCl(trans-N_2-triazole) = 2.302.$ 

 $\mathbf{1}^{\mathbf{Ph}}$  and  $\mathbf{1}^{\mathbf{Pent}}.$  Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2013.04.015.

#### References

- [1] (a) M.A. Cinellu, in: F. Mohr (Ed.), Gold Chemistry, Applications and Future Directions in the Life Sciences, Wiley-VCH, Weinheim, 2009;
  - (b) M.C. Gimeno, A. Laguna, in: J.A. McCleverty, T.J. Mejer, D.E. Fenton (Eds.), Comprehensive Coordination Chemistry II, vol. 7, Cap. 6.7, Elsevier, Amsterdam, 2004;
  - (c) R.J. Puddephatt, in: G. Wilkinson (Ed.), Comprehensive Coordination Chemistry, vol. 5, Cap. 55, Pergamon, Oxford, 1997;
  - (d) M. Serratrice, M.A. Cinellu, L. Maiore, M. Pilo, A. Zucca, C. Gabbiani, A. Guerri, I. Landini, S. Nobili, E. Mini, L. Messori, Inorg. Chem. 51 (2012) 3161;
  - (e) M.A. Cinellu, L. Maiore, G. Minghetti, F. Cocco, S. Stoccoro, A. Zucca, M. Manassero, C. Manassero, Organometallics 28 (2009) 7015;
  - (f) M. Bortoluzzi, E. De Faveri, S. Daniele, B. Pitteri, Eur. J. Inorg. Chem. (2006) 3393
- [2] (a) In: A.S.K. Hashmi, D.F. Toste (Eds.), Modern Gold Catalyzed Synthesis, Wiley-VCH, Weinheim, 2012;
  - (b) A.S.K. Hashmi, M. Rudolph, Chem. Soc. Rev. 37 (2008) 1766;
  - (c) A.S.K. Hashmi, Chem. Rev. 107 (2007) 3180;
  - (d) A. Arcadi, Chem. Rev. 108 (2008) 3266;
  - (e) Z. Li, C. Brouwer, C. He, Chem. Rev. 108 (2008) 3239;
  - (f) N. Marion, S.P. Nolan, 37 (2008) 1776.
- (g) T.C. Boorman, I. Lardosa, Chem. Soc. Rev. 40 (2011) 1910. [3]
  - (a) V. Milacic, Q.P. Dou, Coord. Chem. Rev. 253 (2009) 1649;
  - (b) M. Navarro, Coord. Chem. Rev. 253 (2009) 1619;
  - (c) R.W.-Y. Sun, C.-M. Che, Coord. Chem. Rev. 253 (2009) 1682;
  - (d) I. Ott, Coord. Chem. Rev. 253 (2009) 1670;

- (e) C.F. Shaw III, Chem. Rev. 99 (1999) 2589;
- C. Gabbiani, M.A. Cinellu, L. Maiore, L. Massai, F. Scaletti, L. Messori, Inorg. (f)
- Chim. Acta 393 (2012) 115; (g) C. Gabbiani, F. Scaletti, L. Massai, E. Michelucci, M.A. Cinellu, L. Messori,
- Chem. Commun. 48 (2012) 11623; (h) M. Serratrice, F. Edafe, F. Mendes, R. Scopelliti, S.M. Zakeeruddin, M. Grätzel,
- I. Santos, M.A. Cinellu, A. Casini, Dalton Trans. 41 (2012) 3287; (i) L. Maiore, M.A. Cinellu, S. Nobili, I. Landini, E. Mini, C. Gabbiani, L. Messori, J.
- Inorg. Biochem. 108 (2012) 123.
- [4] H. Struthers, T.L. Mindt, R. Schibli, Dalton Trans. 39 (2010) 675.
  - (a) R. Huisgen, Proc. Chem. Soc. (October 1961) 357;
  - (b) H.C. Kolb, M.G. Finn, K.B. Sharpless, Angew. Chem. Int. Ed. 40 (2001) 2004; (c) C.W. Tornøe, C. Christensen, M. Meldal, J. Org. Chem. 67 (2002) 3057;
  - V.V. Rostovtsev, L.G. Green, V.V. Fokin, K.B. Sharpless, Angew. Chem. Int. Ed. (d) 41 (2002) 2596.
- [6] (a) D. Urankar, B. Pinter, A. Pevec, F. De Proft, I. Turel, J.I. Koŝrmlj, Inorg. Chem. 49 (2010) 4820:
  - E. Amadio, M. Bertoldini, A. Scrivanti, G. Chessa, V. Beghetto, U. Matteoli, R. (b) Bertani, A. Dolmella, Inorg. Chim. Acta 370 (2011) 388; (c) K.J. Kilpin, J.D. Crowley, Polyhedron 29 (2010) 3111.
- [7] L. Cattalini, G. Chessa, G. Michelon, B. Pitteri, M.L. Tobe, A. Zanardo, Inorg. Chem. 24 (1985) 3409.
- (a) M. Bortoluzzi, G. Paolucci, G. Annibale, B. Pitteri, Polyhedron 28 (2009) 1079; [8] (b) M. Bortoluzzi, G. Paolucci, B. Pitteri, Polyhedron 29 (2010) 767. W. Geary, Coord. Chem. Rev. 7 (1971) 81.
- [0]
- K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th ed. John Wiley and Sons, New York, 1986. [10]
- J. Ribas Gispert, Coordination Chemistry, Wiley-VCH, Weinheim, 2008. [11]
- H. Friebolin, Basic One-and Two-Dimensional NMR Spectroscopy, Wiley-VCH, [12] Weinheim, 2011.