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# A Gold-197 Mössbauer Investigation of some Diazole Adducts of Gold(I) Chloride

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## Abstract

The Mössbauer parameters of $L_nAuCl$ complexes (L is an imidazole, $n = 1$ or 2; L is 3,5-dimethylpyrazole, $n = 2$) are reported and discussed. They are shown to provide evidence on bonding and on two-coordination in the solid state.

## Introduction

In preceding papers of ours [1, 2] some adducts between gold(I) chloride and various neutral azoles were reported and characterized through the usual analytical and spectroscopic techniques. In the case of diazoles with pyrazoles, adducts such as bis(3,5-dimethyl- or -3-methyl-5-phenyl-pyrazole)-chlorogold(I) were found to be monomer (*i.e.* three-coordinated) in chloroform solution where others, e.g. (3,5-dimethylpyrazole)chlorogold, were found to be associated [2]. With imidazoles [1] both 1:1 and 1:2 adducts of gold chloride were obtained and were found to be insufficiently soluble for molecular weight determinations. These could be carried out only for bis(2-iso-propylimidazole)chlorogold(I) where a concentration-dependent intermolecular association was put into evidence by osmometry in chloroform solution. On the other hand, different gold(I) compounds, namely those deriving from the corresponding azolato anions, were shown to contain two-coordinated gold(I) by means of X-ray crystal structure determinations as well as by Mössbauer spectra [3]: for example in the cases of tris-(pyrazolato-*N,N'*)trigold(I) [4], polymeric (2-phenylimidazolato-*N,N'*)gold(I) [1], or tri(cyclo-hexyl) phosphine(2-iso-propylimidazolato-*N*)gold(I) [5]. Any information on the metal coordination in the adducts between gold(I) chloride and simple azoles may be useful in trying to understand the biologically relevant [6] interaction between gold(I) nuclei and purines, nucleosides, or nucleotides.

In view of all this, of the difficulties with the commonly available techniques, and in the absence of X-ray crystal structure determinations we resorted to Au-197 Mössbauer spectroscopy [7]. Here our results concerning some adducts between gold(I) chloride and diazoles are reported and compared with the few data available for reference compounds [3, 8, 9]

## Results and Discussion

The Mössbauer parameters such as *IS*, *QS*, and *LW*, that is isomer shift, quadrupole splitting and average half width, respectively, are reported in Table I together with pertinent literature data. Our compounds exhibit a typical Mössbauer spectrum, shown in Fig. 1 for (2-methylimidazole)$_2$-$AuCl \cdot H_2O$: it consists of a quadrupole-split doublet, where the linewidth is close to the minimum value (1.89 mm/s). A narrow linewidth is in agreement with the presence of only one distinguishable gold site, while broad lines (e.g. 3–4 mm/s) suggest the presence of similar environments for the coordination centers, as indeed found by the recent X-ray crystal structure determination carried out on **XI**, [(py)Au(py)][ClAuCl] [10].

The parameters characterizing our compounds lie in ranges (*IS*: 1.3–2.3; *QS*: 7.1–7.9 mm/s) which are typical of gold(I) complexes, even if in **VIII**, **IX** or **X** minor components, due to gold(III), were found, because of decomposition either upon prolonged standing or upon irradiation. Similarly, the presence of metallic gold as impurity was reported [8] for **VI**. Amongst all the compounds listed the less positive *IS* values are reached for **VI**, **XI**, and **XII**, and the most positive values for the $L_2AuCl$

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TABLE I. $^{197}$Au Mössbauer Parameters at 4.2 K

| Formula[a] | | IS[b] | QS[b] | LW[b] | Calculated QS | | Note |
|---|---|---|---|---|---|---|---|
| | | | | | N–Au–N | N–Au–Cl | |
| $(ImH)_2AuCl$ | (I) | 2.15(2) | 7.69(2) | 1.89(6) | −8.36 | −7.26 | c |
| $(2\text{-}MeimH)_2AuCl\cdot H_2O$ | (II) | 2.18(2) | 7.83(2) | 2.20(5) | −8.36 | −7.26 | |
| $(2\text{-}i\text{-}PrimH)_2AuCl$ | (III) | 2.32(1) | 7.89(1) | 1.91(2) | −8.36 | −7.26 | |
| $(1,2\text{-}Me_2\text{-}im)_2AuCl$ | (IV) | 2.21(3) | 7.76(3) | 1.89(9) | −8.36 | −7.26 | |
| $(3,5\text{-}Me_2pzH)_2AuCl\cdot H_2O$ | (V) | 1.67(2) | 7.50(2) | 1.90(2) | −8.36 | −7.26 | |
| $(ino)_2AuCl$ | (VI) | 0.80(2) | 6.54(2) | 2.19(2) | | −7.26 | d, ref. 8 |
| $(guo)_2AuCl$ | (VII) | 1.14(10) | 6.44(10) | 4.60(10) | | −7.26 | ref. 8 |
| $(1\text{-}Meim)AuCl$ | (VIII) | 1.94(3) | 7.18(3) | 1.9(3) | −8.36 | −7.26 | e,c |
| $(1\text{-}PhCH_2im)AuCl$ | (IX) | 1.3(2) | 7.6(2) | 1.9(2) | −8.36 | −7.26 | f |
| $(benzimH)_3Au_2Cl_2$ | (X) | 1.79(1) | 7.52(1) | 2.00(4) | −8.36 | −7.27 | c,g |
| $(pyridine)AuCl$ | (XI) | 1.06(10) | 6.75(10) | 3.34(10) | −8.36 | −7.26 | ref. 9 |
| $(Cy_2NH)AuCl$ | (XII) | 0.90(10) | 6.48(10) | 2.00(10) | | −7.26 | ref. 9 |

[a] ImH, imidazole; imH, a substituted imidazole; pzH, a pyrazole; benzimH, benzimidazole; ino, inosine; guo, guanosie; Cy, cyclohexyl. [b] *IS*, *QS* and *LW* are isomer shift, quadrupole splitting, and average linewidth, respectively, in mm/s; reference is Au/Pt; literature references to Au were converted to this scale by subtracting 1.23 mm/s. [c] The infrared spectrum of the sample was the same before and after the recording of the Mössbauer spectrum. [d] Metallic gold was also present in the sample (*IS*, −1.21; *QS*, 0). [e] Minor Au(III) absorptions with *IS*, 0.0(1); *QS*, 5.4(1); *LW*, 1.9(3). [f] Minor Au(III) absorptions with *IS*, 0.6(3) *QS*, 4.8(3); *LW*, 1.9(4). [g] Minor Au(III) absorptions with *IS*, 1.23 (8); *QS*, 2.47(8); *LW*, 1.9(3).

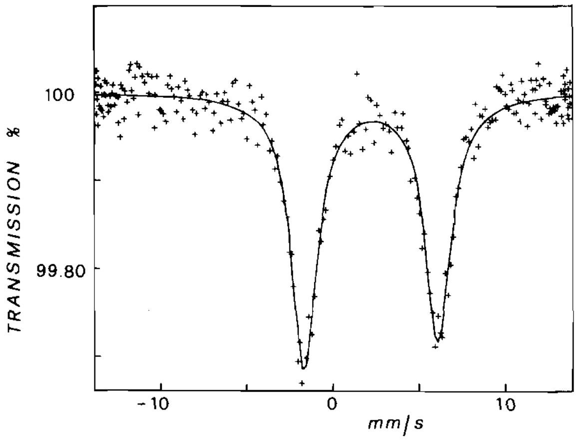

Fig. 1. Mössbauer spectrum of $(2\text{-methylimidazole})_2AuCl\cdot H_2O$ at 4.2 K.

compounds I–IV. Combined infrared and Mössbauer literature data plus an X-ray crystal structure determination [9, 10] support a simple structure for compounds **XI** and **XII**, which contain linearly coordinated gold(I) linked through two $sp_z$ orbitals to chlorine and to the nitrogen ligands. Consequently the *IS* values for the compounds I–IV are in agreement with a two-coordinate gold(I) site.

Additional evidence in favour of linearly coordinated gold(I) atoms may be found in the agreement between the experimental *QS* values and those calculated according to the *pqs* (partial quadrupole splitting) model. To this end the literature *pqs* were used, namely: −1.54(2) for chloride, −1.70(2) for bis(cyclo-hexylamine), −1.82(3) for pyridine, −1.71(4) for inosine, and −1.65(10) for guanosine. Besides, the *pqs* of 2-iso-propylimidazole (QH), −2.09(5), was derived from the splitting observed in the spectrum of $(Ph_3P)Au(Q)$ [3], a molecule closely related to $(Cy_3P)Au(Q)$ which was shown to contain linear gold(I) and no Au•••Au interaction through an X-ray crystal structure determination [5]. Taking advantage of the fact that the Mössbauer parameters are scarcely influenced by substitution on the ring or by exchange of a pyrazolyl with an imidazolyl or a triazolyl group [3, 11], it is then also possible to assume for imidazole, benzimidazole and 3,5-dimethylpyrazole the same *pqs* as for the Q ligand. By use of these data the electric quadrupole splittings corresponding to a linear N–Au–N or N–Au–Cl coordination were calculated; they are listed in Table 1. In addition, the Cl–Au–Cl geometry, with a calculated splitting of (−)6.16 mm/s [12], may be excluded for our compounds. Therefore in the solid state, ionic structures such as $[L_2Au][AuCl_2]$ or $[L_4Au]\cdot[AuCl_2]$ can be ruled out for the LAuCl and for the $L_2AuCl$ species, respectively, where L is an imidazole or pyrazole; for the last type of compounds other ionic structures such as [L–Au–L] [Cl] are excluded because the experimental values of *QS* (7.69–7.89 mm/s) are lower than the calculated values (8.3–8.5 mm/s). Independently, ionic structures were also excluded by conductivity measurements for the species present in solution [1, 2].

By comparison, it is known [7b, 13], that in the homogeneous series of compounds $L_nAuX$ ($n$ = 1–4;

X is a monovalent group such as chlorine; L is triphenylphosphine) the value of *IS* decreases with increasing *n*, that is when the coordination number increases. Since in our compounds the value of *IS* is fairly constant (1.3–2.3 mm/s) and lies on the higher side of the values reported for assumed (**VI**, **VII**, **XII**) or proved (**XI** [10]) two-coordinated gold compounds, it is not unlikely that the gold atom has the same coordination in all of them, although additional supporting evidence would be welcomed for a few, e.g. **IX** or **X**.

Therefore, only the N–Au–Cl arrangement seems to be in agreement with all the data discussed, even if nearly all our compounds have a formula with a (potential ligand)/gold ratio higher than two. This last piece of experimental evidence may be rationalized by assuming that only chloride and one nitrogen ligand coordinate to gold, and that any remaining ligand (water or diazole) is hydrogen bonded to the chloride. Where such a bonding is not possible, as in compound **IV**, bis(1,2-dimethylimidazole)chlorogold, the additional molecule may be clathrated in the lattice, a frequent occurrence with solvent molecules in the chemistry of gold (e.g. [5] and refs. therein) or with imidazoles in coordination chemistry [14]. Since both formation of hydrogen bonds or clathration (or any form of placement outside the first coordination sphere) involve much lower energy gain than the formation of a dative bond, slight variations of the experimental conditions used for preparing, or isolating, our compounds may afford either 1:1 or 1:2 adducts, or a hydrated rather than a anhydrous sample, or different crystalline modifications, as indeed found in some cases.

## Experimental

The compounds were prepared as described in refs. 1 and 2. Their identity and purity was checked through C,H,N analyses and comparison of the infrared and proton NMR spectra with those already reported. These data show that the sample actually used of compound **II** (Found: C, 23.07; H, 3.07; N, 13.28% and **V** (Found: C, 27.15; H, 4.07; N, 12.65%) contains one molecule of water, and that the sample of compound **IX** used is a 1:1 adduct (Found: C, 30.90; H, 2.74; N, 7.05%), while past preparations afforded a 1:2 adduct. It should be pointed out that all these preparations are deceitfully simple. For example in the case of **X**, tris(benzimidazole)dichlorodigold(I), two apparently identical preparations afforded two samples with nearly identical analyses (Found: C, 30.29 or 30.57; H, 2.42 or 2.25; N, 10.20 or 10.30% respectively) but having somewhat different infrared spectra (e.g.: a band at 3450 $cm^{-1}$ was present only in one sample): a different crystalline form may be the explanation here exactly as it was in the case of imidazole complexes of platinum(II) [15].

The $^{197}Pt$ activity feeding the 77.3 keV Mössbauer transition was produced by irradiation of enriched $^{196}Pt$ metal. Both source and absorber were kept at 4.2 K; a sinusoidal velocity waveform and an intrinsic Ge detector were used. The reported shifts are given with respect to the Au(Pt) source. Absorbers with a $^{197}Au$ content of 50–200 $mg/cm^2$ were used.

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