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^{19}F, ^{1}H-HOESY and PGSE NMR Studies of Neutral Trinuclear Complexes of Au^{I} and Hg^{II}: Evidence for Acid−Base Stacking in Solution

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The trinuclear cyclic basic Au^{I} compounds $[Au(\mu\text{-}C^2,N^3\text{-bzim})]_3$ (bzim = 1-benzylimidazolate), **1**, and $[Au(\mu\text{-}C,N\text{-}C(OEt){=}N\text{-}C_6H_4\text{-}CH_3)]_3$, **2**, have been shown to stack with the trinuclear Hg^{II} acid complex $[Hg(\mu\text{-}C,C\text{-}C_6F_4)]_3$, **3** (Charts 1 and 2).[1a] Stacking processes of similar compounds are well-known in the solid state but only indirect and uncertain indications of their existence in solution have been reported.[1b,2] Seeking direct evidence for the acid−base interactions of complexes **1** or **2** with **3** in solution, we have performed ^{19}F, ^{1}H-HOESY (Heteronuclear Overhauser Effect Spectroscopy) and PGSE (Pulsed Field Gradient Spin−Echo) NMR measurements. The two methodologies afford complementary information; the existence and structure of supramolecular adducts can be deduced from HOESY experiments[3] while the size and nature of the adducts can be explored by PGSE measurements.[4] In addition, supporting data based on electronic spectroscopy were sought. *This work represents the first direct evidence for solution stacking* of **1** or **2** with **3**.

All NMR measurements were performed in tetrahydrofuran-d_8 at room temperature (294 K). The choice of solvent was dictated by the very low solubility of the adducts (**1**/**3** and **2**/**3**) in common organic solvents with the exception of THF and DMSO. The latter should be better for PGSE measurements (due to its high viscosity), but the adducts slowly decompose in DMSO. Solutions in THF-d_8 were prepared from solid starting materials (**1**, **2**, and **3**) and isolated solid **1**/**3** and **2**/**3** adducts (each with mole ratios of both 1:1 and 1:2). Moreover, solutions of in situ synthesized **1**/**3** or **2**/**3** aggregates were also investigated. The measurements were performed at different concentrations (1.5−29 mM) using tetraethylorthosilicate (TEOS) and tetramethylsilane (TMS) as internal references (see below).

Chart 1. Structures of **1**, **2**, and **3**

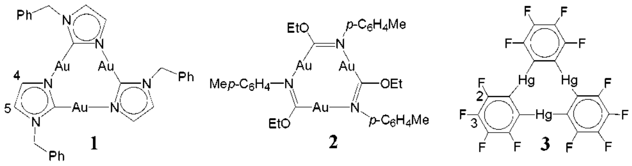
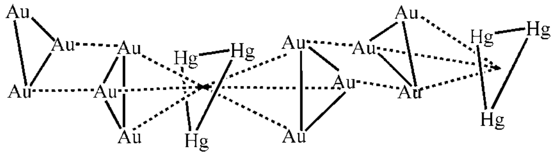


Chart 2. Metal Atom Arrangement in Stacks of **1** or **2** with **3**



The ^{19}F, ^{1}H-HOESY NMR measurements showed the presence of intermolecular cross-peaks for solutions of both **1**/**3** and **2**/**3** adducts. In particular, intermolecular interactions were observed in **1**/**3** between F2 from **3**, on the one hand, and the CH_2, H4, H5, and *o*-H protons from **1**, on the other (Figure 1).[5] Weak intermolecular contacts were also observed between the same protons and F3. In adduct **2**/**3**, F2 interacts with the CH_2 protons of the OEt group and with the *o*-H protons. These observations are consistent with the X-ray data, which show several short H−F distances (3.2−4.0 Å) for **1**/**3** and **2**/**3** adducts.[1a] We conclude that aggregates of **1** or **2** with **3** do exist in solution. The classical NMR approach for investigating intermolecular interactions leads to inconclusive results. In fact, the maximum chemical shift difference, ppm units, between the adduct and free molecules is 0.14 for H5, 0.38 for H4, 0.23 for CH_2, 0.78 for F2, and 1.30 for F3 in the case of **1**/**3** adducts while it is practically zero (<0.05 ppm) for **2**/**3** adducts (see the Supporting Information).

The PGSE NMR measurements[6] were performed by using the standard stimulated echo pulse sequence.[4] As known from the literature,[4] there is a linear dependence of log(I), where I = resonance intensity, on G^2, where G = gradient field strength, using a constant waiting time. The slope of the log(I) vs G^2 plot is proportional to the self-diffusion coefficient of the diffusing particle (D), which is related to the hydrodynamic radius of the particle.[7] By knowing D, an estimation of the particle hydrodynamic radius, consequently the volume, can be obtained by measuring the solution viscosity or approximating it as that of the solvent. Alternatively, an internal standard of known volume can be used and only the ratio between self-diffusion coefficients of the species and the reference is considered. In such a way, the results are not affected by changes in the solution viscosity. An example of the intensity trends as a function of the square of the gradient strength is presented in Figure 2. Table 1 summarizes the data from the PGSE measurements. Two additional considerations were made in order to check the quality of the results. First, the ratios between the two standard translational self-diffusion coefficients (D_{TEOS}/D_{TMS}) should be constant and, from the data shown in Table 1, it appears that the maximum deviation is less than 3%. Second, the aggregate size can be estimated by the ratio V_{agg}/V_{tr}, where V_{agg} represents the volume of the **1**/**3** or **2**/**3** adduct while V_{tr} represents the volume of **1** or **2** alone, which are assumed not to aggregate in solution in the absence of **3**. The very similar D/D_{TEOS} or D/D_{TMS} values for **1**

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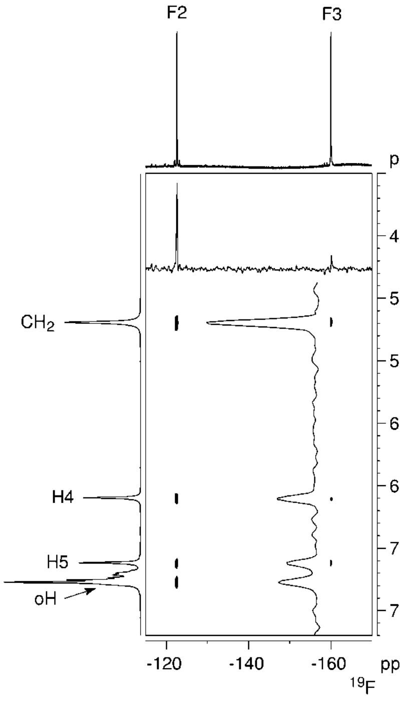

Figure 1. Section of a ^{19}F, ^1H-HOESY NMR spectrum of **1**/**3** adduct (9.6 mM) at 376.63 MHz. Intermolecular NOEs are shown between F2 and the CH_2, H4, H5 ,and *o*-H protons, and between F3 and the CH_2, H4, and H5 protons (labels follow Chart 1). The 1D traces relative to the F2 column and CH_2 row are shown on the right and top of the section, respectively.

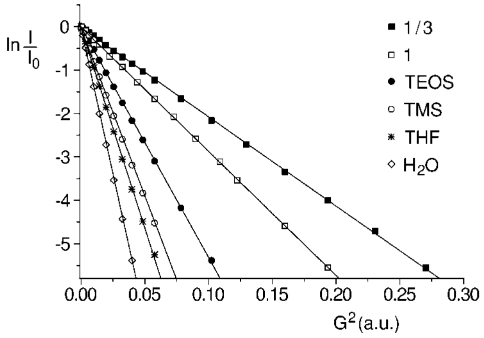

Figure 2. Plot of $\ln(I/I_0)$ vs G^2 for the CH_2 protons of the **1**/**3** adduct (18 mM), TEOS (CH_3), THF (OCH_2), TMS, H_2O, and the CH_2 protons of **1** (1.5 mM). The largest species has the smallest slope thus the smallest diffusion coefficient. The mean deviations of the average slope values, determined for individual resonances for each species, are less than 5%.

and **2** at different concentrations (see Table 1) support the conclusion that the compounds do not aggregate by themselves (contrary to the solid-state structure of **2** and similar compounds[8]). The "V_{agg}/V_{tr}" ratios were calculated as "$\{(D_{\mathbf{1}\text{ or }\mathbf{2}}/D_{TEOS})/(D_{\mathbf{1/3}\text{ or }\mathbf{2/3}}/D_{TEOS})\}^3$". This ratio was always higher than 2 for **1**/**3** solutions while the theoretical[9] values for the "Au_3Hg_3" and "$Au_3Hg_3Au_3$" adducts are 1.7 and 2.7, respectively. Thus both adducts are likely to be present in solution. Meanwhile, an "Au_3Hg_3" **2**/**3** adduct has a theoretical V_{agg}/V_{tr} value of 1.7 (compared to 1 for free molecules of **2**). The experimental values of V_{agg}/V_{tr} for **2**/**3** solutions (1.08−1.29) indicate a smaller tendency for **2** than **1** to aggregate with **3**. Thus, **2**/**3** solutions exhibit equilibrium between the "Au_3Hg_3" adduct and free molecules of **2** and **3**.

Electronic spectra also support the conclusion that acid−base adducts form in solution. The absorption energy for the **1**/**3** adduct is substantially red shifted from the energies for either **1** or **3** alone, due to metallophilic interactions in solution. For example, at 0.5 absorbance value in 10 mM solutions, the absorption energy for the **1**/**3** adduct is red-shifted from the corresponding energies for **1** and **3** by 5.8 × 10^3 and 4.0 × 10^3 cm^{-1}, respectively.

Table 1. PGSE Results for **1**, **2**, and Their Adducts with **3**

concn, mM	species	D/D_{TEOS}	D/D_{TMS}	D_{TEOS}/D_{TMS}	D_{tr}/D_{agg}[a]	V_{agg}/V_{tr}
1.5	**1**	0.520	0.355	0.683		
17	**1**	0.527	0.358	0.679		
1.9	**2**	0.511	0.349	0.682		
29	**2**	0.516	0.352	0.681		
4.4[b]	**1/3**	0.413	0.280	0.678	1.26	2.02
3.2[c]	**1/3**	0.408	0.275	0.673	1.28	2.12
9.6[d]	**1/3**	0.389	0.265	0.680	1.34	2.40
18[b]	**1/3**	0.384	0.265	0.689	1.35	2.45
9.0[d]	**2/3**	0.502	0.343	0.684	1.03	1.08
8.2[b]	**2/3**	0.505	0.342	0.677	1.02	1.08
13[c]	**2/3**	0.476	0.322	0.676	1.09	1.29

[a] D_{tr} and D_{agg}: self-diffusion coefficients of **1** or **2** and of the **1/3** or **2/3** aggregates, respectively. [b] Dissolved adducts with a 2:1 mole ratio. [c] Dissolved adducts with a 1:1 mole ratio. [d] Solutions of **1** or **2** mixtures with **3** (mole ratios 1:1.3).

In conclusion, this paper reports unprecedented direct evidence for supramolecular assembly in solutions of **1**/**2** and **2**/**3**. Intermolecular NOEs in the ^{19}F, ^1H-HOESY NMR spectra indicate the stacked structure of adducts. PGSE NMR measurements indicate that a mixture of "Au_3Hg_3" and "$Au_3Hg_3Au_3$" aggregates is present in **1**/**3** solutions, while **2**/**3** adducts exhibit only "Au_3Hg_3" aggregate and free **2** and **3** units.

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Supporting Information Available: Further detailed NMR results and measurement description (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) Details of NMR measurements are in the Supporting Information.

(7) According to the Stoke−Einstein equation, $D = (kT)/(6\pi\eta r_H)$, where η = solution viscosity and r_H = hydrodynamic radius of the diffusing particles.

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(9) Theoretical V_1, V_2, V_3, and related aggregate volumes were calculated from X-ray data[1a] and the van der Waals atomic radii: $V_{\mathbf{1}} = 432.8$ Å^3, $V_{\mathbf{2}} = 470.3$ Å^3, $V_{\mathbf{3}} = 331.4$ Å^3, $V_{\mathbf{1/3}} = 756.4$ Å^3, $V_{\mathbf{2/3}} = 797.9$ Å^3.

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