STABILISATION OF THE NOVEL GOLD-CATIONS Au^{2+} AND $Au(CO)^{2+}$ IN SUPERACIDS

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The solution of gold tris(fluorosulfate), $Au(SO_3F)_3$, in fluorosulfuric acid, HSO_3F, is a very strong monoprotonic superacid [1]. In this system gold(III) can be reduced under mild conditions by CO [2] or gold metal [3]. The reduction of $Au(SO_3F)_3$ with CO is described by the overall reaction:

$$2\ Au(SO_3F)_3 + 3\ CO \longrightarrow [Au(CO)_2]^+ + SO_3F^- + S_2O_5F_2 + CO_2$$

The action of gold metal on $Au(SO_3F)_3$ in HSO_3F yields the solvated Au^{2+} cation, which has been characterised by ESR spectra. The ESR signal is strongly dependent on the $Au^{2+}/Au(SO_3F)_3$ ratio. From the saturated solution a red-yellow precipitate of diamagnetic $Au[Au(SO_3F)_4]$ is formed at room temperature. Paramagnetic Au^{2+} ions are also generated as lattice defects in solid $Au(SO_3F)_3$ by pyrolysis. The resulting materials are studied by ESR and magnetic susceptibility measurements and represent together with $Au^{2+}_{(solv)}$ the first unambiguous evidence for the existence of true Au^{2+} cations.

In addition, a solid complex is obtained where $[Au(CO)_2]^+$ is stabilised by $Sb_2F_{11}^-$. The linear cation $[Au(CO)_2]^+$ is fully characterized by IR-, Raman- and ^{13}C-NMR-spectroscopy. The CO stretching frequencies for $[Au(CO)_2]^+$ are the highest reported so far. Its force field is compared to those of other carbonyls and the dicyanoaurate(I) ion, $[Au(CN)_2]^-$. The kinetics of the CO-exchange of $[Au(CO)_2]^+$ in HSO_3F-solution has been studied.

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