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Stable Gold(II) Complexes in the Gas Phase

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Summary: Interactions which may cause the disproportionation of noble-metal complexes can be suppressed in the gas phase. Under such circumstances, it is shown that gold(II) is capable of forming stable coordination complexes similar to those seen for Cu(II) and Ag(II).

In condensed-phase coordination chemistry, stable mononuclear gold(II) complexes are comparatively rare.[1] Conditions under which the oxidation state Au(II) is thought to exist are (i) as a transient intermediate in the redox reaction between Au(I) and Au(III),[1] (ii) in bi- and polynuclear compounds,[1,2] and (iii) in mononuclear complexes where a good σ-donor−π-acceptor ligand can stabilize the metal;[1,3] however, complexes of this type are thought to involve extensive electron delocalization from the metal to the ligand.[1,3] Factors responsible for the stability of an oxidation state are a subtle combination of atomic properties and molecular orbital considerations, which influence coordination number, solvation energy, and the degree of electron delocalization.[1,2] At the atomic level, an examination of the second ionization energies of Cu (1958 kJ mol^{-1}), Ag (2074 kJ mol^{-1}), and Au (1980 kJ mol^{-1}) would suggest that gold(II) complexes should be easier to stabilize than those of silver. However, the comparatively low third ionization energy of gold also indicates a preference to form Au(III).[1] In addition, ionic radius is an important factor, as this has a strong influence on solvation energy, and also the position of any surface crossing which may connect oxidation states. For the M(II) oxidation state, the radii follow the order Au > Ag > Cu, which would give Cu(II) the largest solvation energy, and differences here between oxidation states will determine the ease with which complexes can disproportionate into high and low ionization levels.

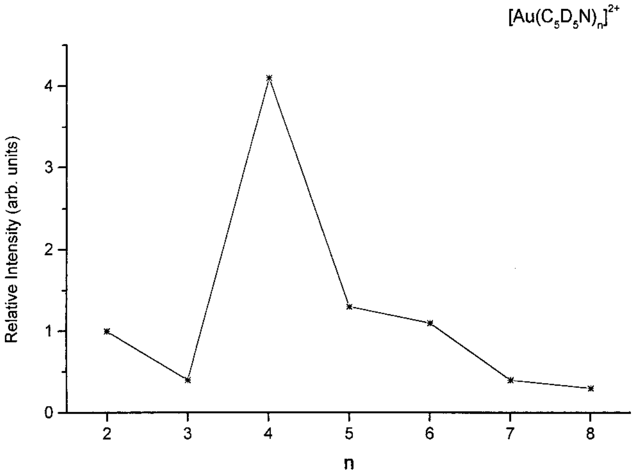

Figure 1. Relative intensities of $[Au(C_5D_5N)_n]^{2+}$ complexes plotted as a function of *n*. Data points represent differences in signal intensity recorded with the shutter on the Knudsen cell open and closed.

Reported here are the preliminary results of a series of experiments designed to identify the factors responsible for stabilizing gold(II) coordination complexes. Using a technique developed in this laboratory,[4−6] transition-metal complexes can be generated and interrogated in the gas phase. An extensive study of Cu(II) and Ag(II) complexed with a very wide range of ligands has revealed significant differences between nitrogen- and oxygen-containing molecules in terms of their ability to stabilize either metal cation.[6−8] In the results presented here, we show that, in the absence of condensed-phase processes which may lead to disproportionation, stable mononuclear Au(II) complexes can also be prepared with ligands more normally associated with Cu(II). In addition, it is shown that the most stable metal−ligand combination conforms to expectation regarding coordination numbers observed for dications of the other two noble metals.[9]

For a given ligand, L, neutral $[Au{\cdot}L_n]$ complexes are prepared using a "pick-up" technique described in earlier publications. Gold vapor generated from a Knudsen effusion cell operating at 1500 °C is crossed with a cluster beam composed of the ligands of interest together with argon acting as a heat sink. Neutral

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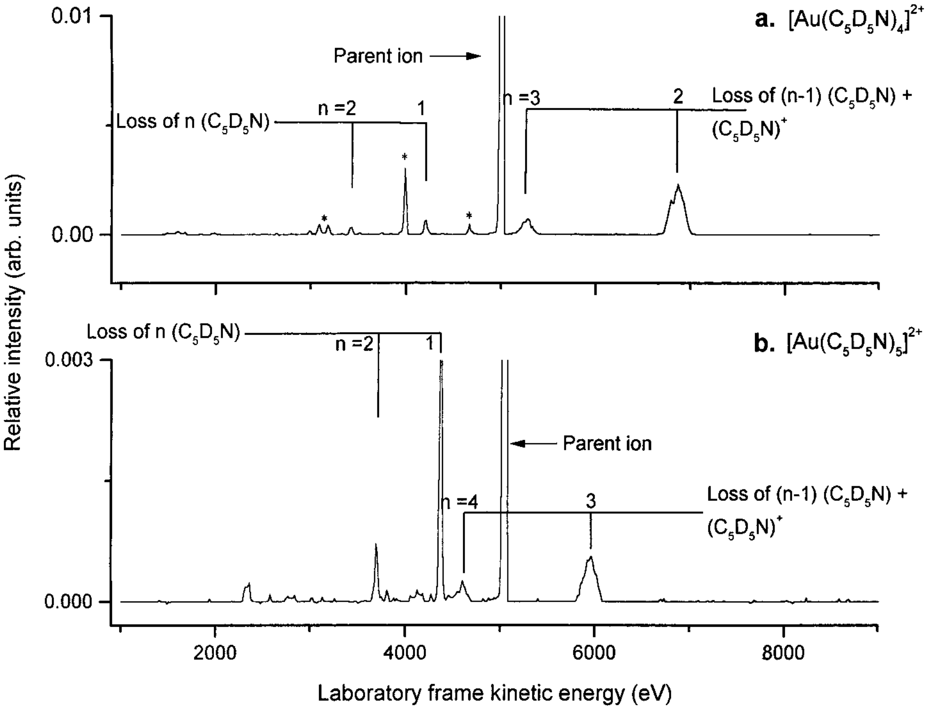

Figure 2. MIKE (mass-analyzed ion kinetic energy) scans of the size-selected cluster ions $[Au(C_5D_5N)_4]^{2+}$ and $[Au(C_5D_5N)_5]^{2+}$ following collisional activation in the presence of air at $\sim 10^{-6}$ mbar, with the ion source operating at a potential of +5 kV. Product ions arising from both the loss of neutral pyridine and charge transfer are identified. The fragments labeled with an asterisk are produced by an unknown ion with the same *m*/*z* value as $[Au(C_5D_5N)_4]^{2+}$. To emphasize the fragment peaks, the intensity scale has been expanded by a factor of 10.

$[Au{\cdot}L_n]$ species enter the ion source of a VG ZAB-E high-resolution, double-focusing mass spectrometer, where they are ionized by electron impact to form $[Au{\cdot}L_n]^{2+}$ ions. This approach to preparing multiply charged complexes circumvents the very considerable problems that are encountered when attempts are made to "grow" such ions from a bare multiply charged metal core. Intensity measurements on individual ions reveal stable metal–ligand combinations, and collision-induced fragmentation patterns are used to confirm the magnitude of the charge and to substantiate its location. A shutter is located at the exit of the Knudsen cell, and this is used to confirm the presence of gold in the complexes and to identify contributions from background impurities.

Figure 1 shows a plot of the relative intensities of $[Au(C_5D_5N)_n]^{2+}$ cluster ions as a function of *n*. These data represent differences in intensity when the oven shutter is open and closed. The deuterated version of this ligand was used in order to avoid mass coincidences between $[Au{\cdot}(C_5H_5N)_n]^{2+}$ complexes and other cluster ions generated as a byproduct of the experimental procedure outlined above. The data contain two important measurements; first, the minimum number of ligands required to stabilize the double charge is 2, and second, the most stable (intense) ion is $[Au(C_5D_5N)_4]^{2+}$. No evidence could be found, either directly from the mass spectrum or indirectly via the fragmentation of a large complex (see below), of a doubly charged complex containing just a single ligand. Where comparisons could be made, an identical pattern of behavior was observed for $[Au(C_5H_5N)_4]^{2+}$ complexes. The minimum number of ligands required to stabilize the double charge reflects a subtle balance between the second ionization energy of the metal ion, the ionization energy of the ligand, the ionic radius, and the ability of the ligand to donate electron density to the ionic core. Pyridine is acting here as a σ-donor–π-acceptor ligand via a lone pair on the nitrogen atom and an unoccupied π^* orbital. Very similar results were recorded for gas-phase complexes of Cu^{2+} and Ag^{2+} with pyridine.[6–8]

The intensity maximum recorded in Figure 1 is considered to demonstrate the presence of a stable coordination complex. In this context, gold(II) again follows the pattern seen for Cu^{2+} and Ag^{2+} and yields $[Au(C_5H_5N)_4]^{2+}$ as the most stable combination. For both copper and silver, direct comparisons can be made with condensed-state coordination complexes which contain four pyridine molecules.[9] Therefore, in this context, isolated gold(II) would appear to be little different from either Cu(II) or Ag(II). However, where gold does exhibit a difference is with regard to the absolute intensities of the $[Au(C_5D_5N)_n]^{2+}$ ions and other similar species, as these are 1 or 2 orders of magnitude lower than the corresponding copper or silver complexes.[6–8] This observation we interpret as indicative of $[Au(C_5D_5N)_n]^{2+}$ ions being much less stable than their Cu(II) or Ag(II) counterparts.

Figure 2 shows two examples of MIKE (mass-analyzed ion kinetic energy) scans of the complexes $[Au(C_5D_5N)_4]^{2+}$ and $[Au(C_5D_5N)_5]^{2+}$, recorded in the presence of $\sim 10^{-6}$ mbar of collision gas.[10] The ZAB-E is a reverse-geometry mass spectrometer, which means that ions prepared in the source first encounter a magnet where they can be selected according to *m*/*z* value. These ions then pass through a small cell and are subjected to collisional excitation before passing into

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[10] Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. In *Metastable Ions*; Elsevier: Amsterdam, 1973.

an electrostatic analyzer. Since any fragmentation is accompanied by a change in kinetic energy and/or charge, it is possible to equate kinetic energies measured in the electrostatic analyzer (as shown in Figure 2) with the *m*/*z* values of any fragment ions. Two principal decay routes can be seen; these are (i) ligand-to-metal electron transfer and (ii) loss of neutral ligands. For $[Au(C_5D_5N)_4]^{2+}$ the dominant electron-transfer step corresponds to the reaction

$$[Au(C_5D_5N)_4]^{2+} \rightarrow Au^+(C_5D_5N)_2 + C_5D_5N + C_5D_5N^+ \quad (1)$$

which leads to the formation of an established gold(I) complex[1] and would equate with linear coordination.[1] A similar pattern of charge transfer is seen in copper(II) and silver(II) complexes with pyridine,[6] but not with the same level of specificity. Similar results are seen in the MIKE scan recorded for $[Au(C_5D_5N)_5]^{2+}$, in that the most intense charge-transfer signal corresponds to formation of $Au^+(C_5D_5N)_2$. The widths of the peaks arising from charge transfer all have associated with them a significant width, which can be attributed to Coulomb repulsion following charge separation. The peaks are comparable in width to those recorded previously for copper(II)– and silver(II)–pyridine complexes[6–8] and are also very similar to those observed for other doubly charged metal complexes,[4] where there is no ambiguity regarding the position of the positive charge and/or any back-donated electrons. We consider these comparisons to provide strong evidence that both positive charges reside on the central metal atom.

Fragmentation signals corresponding to the loss of neutral ligands are very weak for $[Au(C_5D_5N)_4]^{2+}$, which is in contrast to the situation for $[Au(C_5D_5N)_5]^{2+}$, where the loss of one pyridine molecule appears to be a favorable process. Both of these observations serve to confirm the underlying stability of the $[Au(C_5D_5N)_4]^{2+}$ unit.

Results almost identical with those given above have also been recorded for gold(II)–acetone and gold(II)–acetonitrile complexes in the forms $[Au(\{CH_3\}_2CO)_n]^{2+}$ and $[Au(CH_3CN)_n]^{2+}$, respectively.[8] Once again, these ligands have the necessary attributes of lone-pair electrons and vacant π^* orbitals. In contrast, many saturated ligands which readily coordinate with Cu^{2+}, for example, water and ammonia,[8] fail to form stable complexes with Au^{2+}. A detailed comparison of the behaviors of Cu^{2+}, Ag^{2+}, and Au^{2+} with a wide range of ligands is in preparation.[8]

These preliminary results on the gas-phase solvation of gold(II) demonstrate that, in isolation, the ion is capable of forming a stable complex with a ligand (pyridine) that is more normally associated with the chemistry of copper(II) and silver(II). In this respect, gold(II) would appear to follow a pattern of behavior that could be predicted from atomic properties (such as electron configuration, ionization energy, and ionic radius) that are part of a trend established by the other two members of the noble metal series.

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