

# Comparisons in the Behavior of Stable Copper(II), Silver(II), and Gold(II) Complexes in the Gas Phase: Are There Implications for Condensed-Phase Chemistry?

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**Abstract:** Experiments conducted in the gas phase have led to the formation of a series of stable gold(II) complexes with nitrogen- and oxygen-containing ligands. Such complexes are very rare in condensed-phase chemistry. However, there is also a significant group of potential ligands, for example, H<sub>2</sub>O and NH<sub>3</sub>, for which stable complexes could not be formed. There are strong similarities between these observations and earlier results presented for silver(II), but both metal ions behave markedly different from copper(II). As a group the majority of successful gold(II) ligands are characterized by being good  $\sigma$  donor– $\pi$  acceptor molecules; however, it is also possible to understand the ability of individual ligands to stabilize the metal ion in terms of a simple electrostatic model. Application of the latter reveals a semiquantitative trend between the physical properties of a ligand, e.g. ionization energy, dipole moment, and polarizability, and the ligand's ability to stabilize either Cu(II), Ag(II), or Au(II). The model successfully accounts for the preference of Cu(II) for aqueous chemistry, in comparison to the complete absence of such behavior on the part of Ag(II) and Au(II). Ligands from recent examples of stable condensed-phase gold(II) complexes appear to meet at least one of the criteria identified from the model.

## Introduction

In condensed-phase inorganic chemistry, the group 11 transition metals exhibit considerable differences with respect to the formation of stable oxidation states under aqueous conditions.<sup>1</sup> Copper(I) can only exist in very dilute solution or in the presence of a ligand with a stereochemistry that can preferentially chelate the ion. The most common oxidation state is copper(II), while copper(III) complexes are very rare and may only exist in the solid state.<sup>1</sup> In contrast, Ag(I) is the predominant oxidation state for aqueous silver ions.<sup>1</sup> Stable silver(II) complexes can be prepared, but are readily reduced,<sup>2,3</sup> and silver(III) occurs very rarely. Finally, gold(I) has no aqueous chemistry, but undergoes immediate disproportionation to give metallic gold and gold(III).<sup>4</sup> Mononuclear gold(II) complexes are comparatively rare;<sup>4</sup> however, conditions under which the oxidation state is thought to exist are the following: (i) as a transient intermediate in the redox reaction between Au(I) and Au(III);<sup>4</sup> (ii) in bi- and polynuclear compounds;<sup>4,5</sup> and (iii) in mononuclear complexes where a good  $\sigma$  donor– $\pi$  acceptor ligand can stabilize the metal.<sup>4,6</sup> Complexes in the latter category are thought to involve extensive electron delocalization from the metal to the ligand.<sup>4,6</sup>

Factors responsible for the stability of a particular oxidation state are a subtle combination of atomic and molecular properties, with the latter involving coordination number, solvation

energy, and the degree of electron delocalization to the ligands. Valence shell relativistic stabilization (and radial contraction) of s and p orbitals is at a maximum for the group 11 metals and increases down the group.<sup>7</sup> As a consequence, the first ionization energy (IE) of gold (9.22 eV) is significantly larger than that of either silver (7.57 eV) or copper (7.72 eV). However, the same relativistic effect also destabilizes (and extends) d orbitals,<sup>8</sup> which means that the second IE of gold (20.51 eV) is close to that of copper (20.29 eV), which are both much lower than that of silver (21.49 eV).<sup>4</sup> These results would suggest that gold(II) complexes should be easier to stabilize than those of silver(II). However, d orbital expansion also gives gold a comparatively low third ionization energy which leads to a preference for Au(III).<sup>4</sup> In addition to energy differences between ions, ionic radius is also an important factor as this has a strong influence on solvation energy, and will also affect the positions of any surface crossings which may connect oxidation states. For the M(II) oxidation state, the radii follow

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the order  $\text{Au} > \text{Ag} > \text{Cu}$ , which would give  $\text{Cu(II)}$  the largest solvation energy. The different energies of all these oxidation states determine the ease with which complexes can disproportionate into high and low oxidation levels.

Most isolated metal ions in a high charge state are unlikely to be stable in the presence of a single ligand or solvent molecule, e.g.  $\text{Cu(II)/H}_2\text{O}$  or  $\text{Ag(II)/NH}_3$ . The difference in ionization energy between  $\text{M(I)}$  and the ligand will be such that charge transfer is exothermic leading to a reduction of the metal ion. The circumstances responsible for such behavior have been discussed by Tonkyn and Weishaar,<sup>9,10</sup> and a similar quantitative treatment is presented later in this paper in an analysis of results for a wide range of metal–ligand complexes. Only with the development of a larger solvent or ligand shell do the familiar oxidation states appear in a stable form, e.g.  $\text{Cu(II)}$  in  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ .<sup>11</sup> However, some oxidation states cannot remain stable in the presence of certain types of ligand no matter how many there are of these, and for others stability can only be achieved by modifying the solvent conditions, e.g. pH.<sup>12</sup> At a molecular level it is comparatively straightforward to describe the process of oxidation and reduction as involving a crossing of potential energy surfaces,<sup>9,10,13</sup> and for the types of complexes of interest here the primary curve crossing process involves ligand-to-metal charge (electron) transfer (LMCT). We have recently demonstrated that it is possible to form stable gold(II) complexes,  $[\text{Au}(\text{pyridine})_n]^{2+}$ ,<sup>14</sup> with a ligand that has been recognized previously as capable of stabilizing silver(II) in the condensed phase.<sup>2,3</sup> These complexes were formed in the gas phase, so that the metal–metal interactions responsible for disproportionation were eliminated. Therefore, the question of stability is only a matter of the metal ion–ligand interaction rather than of metal ions in close proximity.

An extensive experimental study of  $\text{Cu(II)}$  and  $\text{Ag(II)}$  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 these metal cations.<sup>11,15–17</sup> These experiments have now been extended to include  $\text{Au(II)}$ , and the results are presented here. The data are discussed in the wider context of a simple theoretical model which embraces copper, silver, and gold in the form of  $[\text{M} \cdot \text{L}_n]^{2+}$  complexes, and relates stability to underlying electrostatic interactions between metal ions and ligands. The model reveals features of  $\text{Cu(II)}$  which could account for the predominance of the ion in aqueous chemistry, compared with the total absence of both  $\text{Ag(II)}$  and  $\text{Au(II)}$ .

## Experimental Section

Details of the pick-up technique used to prepare  $[\text{ML}_n]^{2+}$  complexes have been described in earlier publications.<sup>16,17</sup> For the results presented here, gold vapor was generated from a Knudsen effusion cell operating at 1500 °C and crossed with a cluster beam composed of the ligands of interest together with argon acting as a heat sink. Neutral  $[\text{Au} \cdot \text{L}_n]$  species entered the ion source of a VG ZAB-E high-resolution, double-

focusing mass spectrometer where they were ionized by 100 eV electron impact to form  $[\text{Au} \cdot \text{L}_n]^{2+}$  ions. Since the doubly charged metal ions are prepared already encapsulated in a solvent environment,  $[\text{M} \cdot \text{L}_n]^{2+}$  complexes are observed for all of those ligands which are capable of stabilizing  $\text{M}^{2+}$ . For each particular  $[\text{M} \cdot \text{L}_n]^{2+}$  complex, the experimental conditions were optimized to maximize signal intensity. Therefore, since we have no absolute scale on which to base intensity measurements, comparisons between  $\text{Au(II)}$ ,  $\text{Ag(II)}$ , and  $\text{Cu(II)}$  complexes are made in terms of stability rather than intensity. However, it is evident from the experiments that the intensities of the  $[\text{Au} \cdot \text{L}_n]^{2+}$  ions are frequently 1 or 2 orders of magnitude lower than the corresponding copper or silver complexes.<sup>16,17</sup> This observation could be indicative of  $[\text{Au} \cdot \text{L}_n]^{2+}$  ions being much less stable than either their  $\text{Cu(II)}$  or  $\text{Ag(II)}$  counterparts; however, ion intensity could equally well be influenced by the route taken to prepare the complexes. For example, at the pick-up stage the vapor pressure of gold may not be as high as the other two metals. Second, neutral gold may not be incorporated into the  $\text{L}_n\text{--Ar}_m$  clusters as efficiently as other metals at the pick-up stage, and finally, there may be differences in ionization cross-section for the three metals.

## Results and Discussion

Figure 1 shows plots of the relative intensities of three of the systems studied,  $[\text{Au} \cdot (\text{CO}_2)_n]^{2+}$ ,  $[\text{Au} \cdot (\text{CH}_3)_2\text{CO}]_n^{2+}$ , and  $[\text{Au} \cdot (\text{pyridine})_n]^{2+}$ . From distributions such as these, two important quantities can be recorded: (i)  $n_{\text{min}}$ , the minimum number of ligands required to stabilize a multiply charged metal ion, and (ii)  $I_{\text{max}}$ , the  $[\text{M} \cdot \text{L}_n]^{2+}$  complex with the highest intensity. It has frequently been observed that  $I_{\text{max}}$  correlates remarkably well with metal ion coordination in the solid state.<sup>16,18</sup> The minimum number of ligands required to stabilize the double charge,  $n_{\text{min}}$ , 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 (solvation energy). For example, pyridine is acting here as a  $\sigma$  donor– $\pi$  acceptor ligand via a lone pair on the nitrogen atom and an unoccupied  $\pi^*$  orbital. Similar results have been recorded for gas-phase complexes of  $\text{Cu}^{2+}$  and  $\text{Ag}^{2+}$  with pyridine,<sup>15–17</sup> and for both these ions, direct comparisons can be made between  $I_{\text{max}}$  and condensed-state coordination complexes containing four pyridine molecules.<sup>1</sup> Therefore in this context, gas-phase  $\text{Au(II)}$  would appear to be little different from either  $\text{Cu(II)}$  or  $\text{Ag(II)}$ .

Table 1 presents a summary of those ligands for which an attempt was made to prepare stable  $[\text{Au} \cdot \text{L}_n]^{2+}$  ions. The formation of complexes containing acetone, 2-butanone, and 2-pentanone as ligands demonstrates that oxygen can coordinate to  $\text{Au(II)}$  in the same way that sulfur atoms do in several of the existing solid-state compounds.<sup>4,5</sup> The presence of a carbonyl group in each of the molecules helps it to fulfill the role of a  $\sigma$  donor– $\pi$  acceptor ligand. Similarly, both pyridine and acetonitrile will also act as  $\sigma$  donor– $\pi$  acceptor ligands. The data on benzene match those seen previously for  $\text{Cu(II)}$  and  $\text{Ag(II)}$ , in that the  $[\text{Au} \cdot (\text{benzene})_2]^{2+}$  ion dominates the mass spectrum, and the stability of this ion is interpreted as being due to a sandwich structure. For copper(II), a condensed-phase analogue exists where the  $\pi$  electrons of benzene successfully ligate with the metal ion.<sup>19,20</sup> While unexpected, the success of  $\text{CO}_2$  in stabilizing doubly charged metal ions has been noted previously,<sup>16,17</sup> and has been attributed to the high ionization energy of the molecule, which minimizes the energy difference that has to be accounted for in terms of solvation energy.

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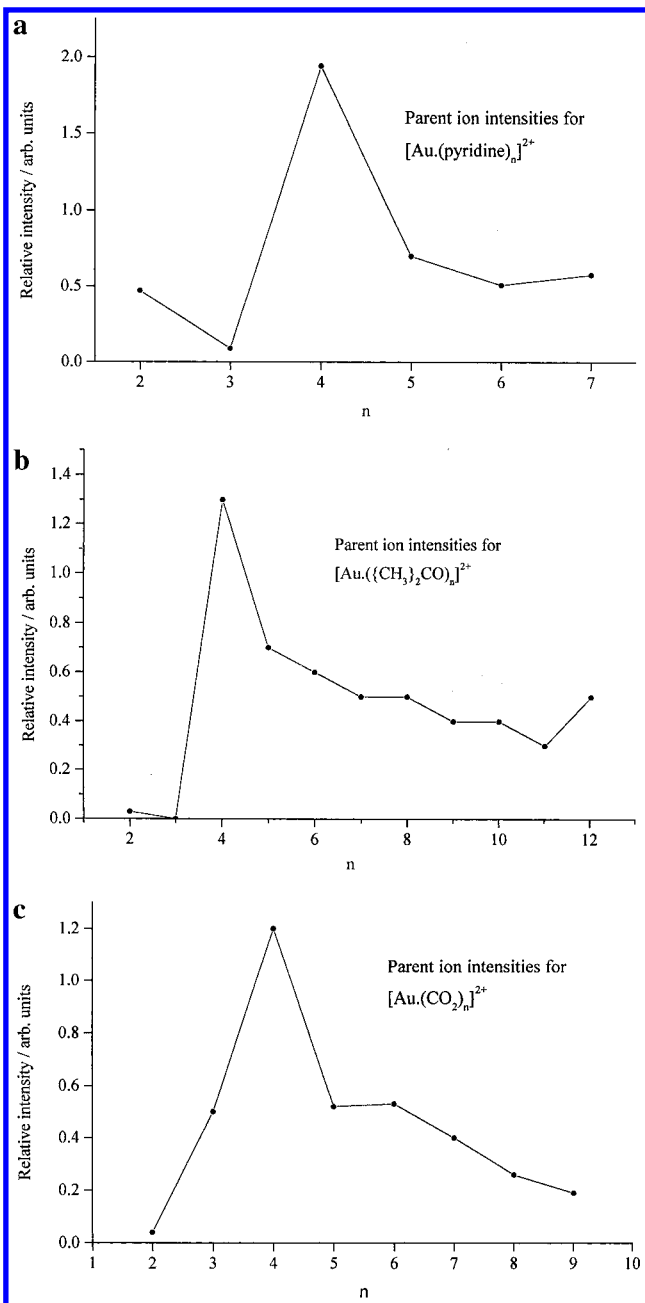
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**Figure 1.** Intensity distributions recorded for examples of stable  $[\text{Au}\cdot\text{L}_n]^{2+}$  complexes plotted as a function of  $n$ : (a)  $[\text{Au}\cdot(\text{pyridine})_n]^{2+}$ ; (b)  $[\text{Au}\cdot(\{\text{CH}_3\}_2\text{CO})_n]^{2+}$ ; and (c)  $[\text{Au}\cdot(\text{CO}_2)_n]^{2+}$ .

In addition to the ligands that succeed in stabilizing Au(II), it can be seen from Table 1 that there are also a large number of molecules for which no stable  $[\text{Au}\cdot\text{L}_n]^{2+}$  ions could be observed. In particular, it should be noted that water and several other hydrogen bonded solvents were incapable of stabilizing the metal ion, a pattern of behavior which would clearly equate with the absence of any Au(II) aqueous chemistry.<sup>4</sup> To place the data presented in Table 1 in the context of the other two metals for which results have been presented, it is sufficient to note that Cu(II) forms stable complexes with all the ligands except  $\text{NO}$ ,<sup>17</sup> and the silver(II) results match those shown for gold(II),<sup>16</sup> but with small differences in  $n_{\min}$  and  $I_{\max}$ . Contrary to some of the expectations expressed in the Introduction, gold(II) appears to have much more in common with silver(II) than copper(II).

**Model Calculations of  $[\text{M}\cdot\text{L}_n]^{2+}$  Stability.** From the experimental data it is evident that there exists a clear distinction

**Table 1.** Dipole Moments, Polarizabilities, and Ionization Energies of the Solvents Tested as Potential Ligands for Doubly Charged Gold Complexes (values taken from the *CRC Handbook of Chemistry and Physics*, 77th ed., 1996–97)

ligand	dipole moment, $\mu/\text{D}$	polarizability, $\alpha/\text{\AA}^3$	IE/eV	Au(II) IE = 20.51 eV	
				$n_{\min}$	$I_{\max}$
pyridine ( $\text{C}_5\text{H}_5\text{N}$ )	2.21	9.18	9.25	2	4
acetonitrile ( $\text{C}_2\text{H}_3\text{N}$ )	3.92	4.40	12.19	4	4
benzene ( $\text{C}_6\text{H}_6$ )	0	10.32	9.25	2	2
carbon dioxide ( $\text{CO}_2$ )	0	2.91	13.77	3	4
acetone ( $\text{C}_3\text{H}_6\text{O}$ )	2.88	6.39	9.70	4	4
2-butanone ( $\text{C}_4\text{H}_8\text{O}$ )	2.78	8.13	9.51	4	4
2-pentanone ( $\text{C}_5\text{H}_{10}\text{O}$ )		9.93	9.38	4	4
tetrahydrofuran ( $\text{C}_4\text{H}_8\text{O}$ )	1.75		9.41	3	5/6
water ( $\text{H}_2\text{O}$ )	1.85	1.45	12.61		
ammonia ( $\text{NH}_3$ )	1.47	2.26	10.16		
methanol ( $\text{CH}_3\text{O}$ )	1.70	3.29	10.85		
ethanol ( $\text{C}_2\text{H}_6\text{O}$ )	1.69	5.41	10.47		
ethylene ( $\text{C}_2\text{H}_4$ )	0	4.25	10.51		
dioxane ( $\text{C}_4\text{H}_8\text{O}_2$ )	0	8.6	9.19		
nitrogen dioxide ( $\text{NO}_2$ )	0.32	3.02	9.75		
nitric oxide ( $\text{NO}$ )	0.16	1.70	9.26		

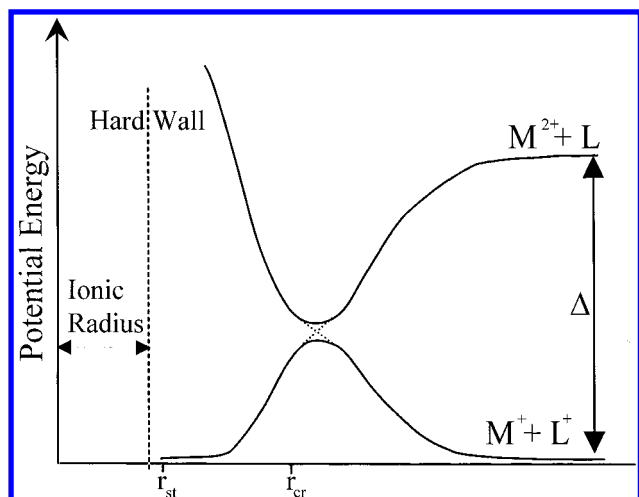
in behavior between Cu(II) on one hand and Ag(II) and Au(II) on the other. Since Cu(II) is the only one of these doubly charged ions to exhibit a stable aqueous chemistry, an attempt has been made to quantify our understanding of these patterns of behaviour. This has been achieved by examining the stability, with respect to charge transfer (LMCT), of each  $[\text{M}\cdot\text{L}_n]^{2+}$  complex as a function of the number ( $n$ ) and nature of the ligands. To account for the relative stabilities of  $[\text{M}\cdot\text{L}_n]^{2+}$  and  $[\text{M}^+\cdot\text{L}_n^+]$  units for these different metals, there are two important energy terms which need to be taken into consideration, and these are (a) the absolute stability of  $[\text{M}\cdot\text{L}_n]^{2+}$  relative to the  $[\text{M}^+\cdot\text{L}_n^+]$  dissociation limit and (b) the crossing point of the two surfaces. For Cu, Ag, and Au as  $\text{M}^{2+}$  ions, the  $d^9$  configuration means that both surfaces are doublets and so there is an avoided crossing.

In the absence of detailed ab initio data covering all of the ligand/metal combinations listed in Table 1, a simple model based on electrostatic interactions is proposed, which utilizes the polarizabilities and, where appropriate, the dipole moments of the ligand species.<sup>21</sup> The model makes the following assumptions: (i) there is a scalar quantity,  $r$ , that defines the M–L distance, and no account is taken of other geometric factors; (ii) L has a point dipole ( $\mu$ ) and an isotropic polarizability ( $\alpha$ ) (all energies are represented by point interactions); (iii) there are no attractive L–L terms, so that for dipolar ligands the geometry of  $\text{ML}_2$  is linear (for nonpolar ligands this will be a poor approximation); (iv) the polarizability and dipole moment of  $\text{L}^+$  and L are the same (this is certainly not the case for small ligands, such as  $\text{H}_2\text{O}$ ); and (v) the polarizabilities of  $\text{M}^+$  and  $\text{M}^{2+}$  are the same. The only other important parameter is  $\Delta$ , which is the difference in ionization energy between  $\text{M}^+$  and L. The ionic radius of each doubly charged ion is taken as a measure of short-range exchange repulsion and is represented as a hard wall. However, the latter plays no part in the calculations outlined above. Data relevant to these calculations are given in Table 1. The model has been applied previously to  $[\text{Mg}\cdot\text{L}_n]^{2+}$  complexes,<sup>22</sup> where it was successful in accounting for a significant variation in the abilities of different ligands to stabilize the  $\text{Mg}^{2+}$  ion. Here the emphasis is different, in that

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**Figure 2.** Schematic representation of the potential energy curves derived from the various attractive and repulsive interactions which contribute to the electrostatic model discussed in the text. The model is used to comment on the relative stabilities of Cu(II), Ag(II), and Au(II) complexes. For the case of  $[M \cdot L_2]^{2+}$  complexes, the two asymptotes are  $M^{2+} + 2L$  and  $M^+ + L^+ + L$ .

we hope to establish why similar ligands behave differently for different metals. Data are presented only for singly and doubly ligated ions to show trends, but the model can clearly be extended to include larger numbers of ligands.

Taking charge to be in units of  $e$ , dipole moment in Debye (D), polarizability in  $\text{\AA}^3$ , and  $r$  in  $\text{\AA}$ , interaction energies ( $E$ ) in eV for various metal–ligand combinations are as follows:

#### 1 Ligand:

$$E(M^{2+}-L) = \Delta - 6.0\mu/r^2 - 28.8\alpha/r^4 \quad (1)$$

$$E(M^+-L^+) = 14.4/r - 3.0\mu/r^2 - 14.4\alpha/r^4 \quad (2)$$

#### 2 Ligands

$$E(M^{2+}-L_2) = \Delta - 12.0\mu/r^2 - 57.6\alpha/r^4 \quad (3)$$

$$E(M^+-L_2^+) = 14.4/r - 6.0\mu/r^2 - 21.6\alpha/r^4 \quad (4)$$

The numerical factors contain the conversion terms necessary to give the energies in units of electronvolt. The combination represented by eq 4 has a double degeneracy as charge transfer can be to either ligand; however, any splitting of this degeneracy would be small, but the symmetric component would mix with the  $M^{2+}$  state. The most important point to note is that the long-range electrostatic interactions are based on charge localized structures and not on configurations of the form  $L^{1/2+}-M^+-L^{1/2+}$ .

From these equations, two important distances are calculated.  $r_{st}$  is the distance at which  $E(M^{2+}-L)$  and  $E(M^{2+}-L_2)$  are zero, and  $r_{cr}$  is the distance at which the energies represented by eqs 1 and 2 or 3 and 4 become equal (the positions of the avoided crossings). These terms are illustrated in Figure 2, where they are placed in relation to a hard-wall representing the repulsive interaction between the metal ion and the ligands. The exact position of the repulsive wall is unknown, but can be estimated from a consideration of the results presented below. What is important for the stability of any  $[M \cdot L_n]^{2+}$  combination is that the repulsive wall be located at a distance that is shorter than  $r_{cr}$ . However, the relationship between stability and the position of  $r_{st}$  is less clear. Table 2 presents a summary of values

**Table 2.** Summary of Calculated Values for  $r_{st}$  and  $r_{cr}$  for  $[Cu \cdot L]^{2+}$  and  $[Cu \cdot L_2]^{2+}$  in Association with a Series of Smaller Ligands

ligand	L		L <sub>2</sub>	
	$r_{st}/\text{\AA}$	$r_{cr}/\text{\AA}$	$r_{st}/\text{\AA}$	$r_{cr}/\text{\AA}$
NO <sup>a</sup>	1.46	1.74	1.75	2.02
NO <sub>2</sub> <sup>a</sup>	1.72	1.96	2.06	2.29
NH <sub>3</sub>	1.73	2.02	2.13	2.38
H <sub>2</sub> O	1.77	2.38	2.24	2.73
Ar <sup>b</sup>	1.79	3.32	2.13	3.47
C <sub>2</sub> H <sub>4</sub>	1.88	2.12	2.23	2.48
CO <sub>2</sub>	1.89	2.58	2.25	2.88

<sup>a</sup> Ligands which fail to form stable complexes with Cu(II).<sup>17</sup> <sup>b</sup> A detailed discussion of complexes formed between argon and Cu(II) will be presented elsewhere.<sup>23</sup>

calculated for  $r_{st}$  and  $r_{cr}$  for Cu(II) in association with some of the smaller ligands identified in Table 1. These data cover ligands with a range of physical properties, which makes it very unlikely that they would all be capable of stabilizing Cu(II). Also shown is the effect of increasing the number of ligands from one to two where both  $r_{st}$  and  $r_{cr}$  are shifted by approximately 0.5  $\text{\AA}$ , which is very significant in terms of the position of the repulsive wall. Of the ligands listed in Table 2, the calculations yield comparatively small values of  $r_{st}$  and  $r_{cr}$  for NO and NO<sub>2</sub>, which suggests that neither of these ligands is likely to stabilize Cu(II), a result that is supported by the absence of any experimental evidence of such complexes. We would therefore consider these two results to act as benchmarks in our evaluation of the more extensive data set recorded for doubly charged metal ions of all three group 11 transition metals. At the other extreme, the calculations indicate that CO<sub>2</sub> and argon are capable of stabilizing Cu(II) in the form of either  $[Cu \cdot CO_2]^{2+}$  or  $[Cu \cdot Ar]^{2+}$ , and this is again confirmed by the experimental observations.<sup>17,23</sup> As confirmation that the model reproduces the essential physics of a metal ion–ligand interaction, it should be noted that the location of the surface crossing identified for  $[Cu \cdot Ar]^{2+}$  is within 0.1  $\text{\AA}$  of that determined from ab initio calculations.<sup>23</sup> For the majority of ligands, at least two are required to stabilize Cu(II). The success of CO<sub>2</sub> as a ligand results from a combination of high ionization energy (comparatively small value for  $\Delta$ ) and moderately high polarizability. Likewise, argon appears to benefit from  $\Delta$  having a small value, but also gains stability by creating a metastable state.<sup>23</sup> The CO<sub>2</sub> results act as a further benchmark, in that they define a successful ligand.

If comparisons are going to be made between dications involving all three group 11 metals, then the values calculated for  $r_{st}$  and  $r_{cr}$  need to be normalized with respect to some measure of the hard wall radii. Within the series Cu(II), Ag(II), and Au(II) the position of the hard wall should reflect the magnitude of the ionic radius; however, since this value depends on the coordination number, there is no quantitative data appropriate for these calculations. For a coordination number of six, the ionic radii are 0.73  $\text{\AA}$  for Cu<sup>2+</sup> and 0.94  $\text{\AA}$  for Ag<sup>2+</sup>, but no value is available for Au<sup>2+</sup>. An estimate of the radius of Au<sup>2+</sup> = 1.05  $\text{\AA}$  can be made from the average of the ionic radii of Pt<sup>2+</sup> = 0.94  $\text{\AA}$  and Hg<sup>2+</sup> = 1.16  $\text{\AA}$  (for 6-coordinate systems). This approach includes the effect of the lanthanide contraction, and more importantly relativistic effects, which result in a radial contraction of the gold 6s orbital.<sup>7,8</sup> The above value is approximately 20% smaller than that estimated from an extrapolation of the ratios of the radii of Cu<sup>+</sup>/Cu<sup>2+</sup> and Ag<sup>+</sup>/

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**Table 3.** Comparisons of  $r_{\text{st}}$  and  $r_{\text{cr}}$  for  $[\text{M}\cdot\text{L}_n]^{2+}$  Complexes Consisting of the Metal Ions Cu(II), Ag(II), and Au(II) in Association with a Selection of the Ligands Given in Table 1

ligand	Cu(II) <sup>a</sup> $r^{2+} = 0.73 \text{ \AA}^b$		Ag(II) <sup>b</sup> $r^{2+} = 0.94 \text{ \AA}^b$		Au(II) <sup>c</sup> $r^{2+} = 1.05 \text{ \AA}^b$	
	$r_{\text{st}}/\text{\AA}$	$r_{\text{cr}}/\text{\AA}$	$r_{\text{st}}/\text{\AA}$	$r_{\text{cr}}/\text{\AA}$	$r_{\text{st}}/\text{\AA}$	$r_{\text{cr}}/\text{\AA}$
pyridine	2.12	2.18	1.84	1.85	1.79	1.83
acetonitrile	2.30	2.51	1.94	2.07	1.94	2.13
benzene	1.96	2.07	1.70	1.76	1.63	1.73
CO <sub>2</sub>	1.51	2.11	1.21	1.68	1.17	1.76
acetone	2.05	2.12	1.75	1.78	1.70	1.77
2-butanone	2.15	2.20	1.85	1.86	1.80	1.85
thf	2.07	2.15	1.79	1.83	1.74	1.80
H <sub>2</sub> O	1.51	1.99	1.19	1.56 <sup>a</sup>	1.16	1.62 <sup>a</sup>
NH <sub>3</sub>	1.40	1.65	1.12	1.30 <sup>a</sup>	1.06	1.29 <sup>a</sup>
methanol	1.65	1.89	1.35	1.53 <sup>a</sup>	1.30	1.53 <sup>a</sup>
C <sub>2</sub> H <sub>4</sub>	1.50	1.75	1.23	1.42 <sup>a</sup>	1.16	1.40 <sup>a</sup>
dioxane	1.84	1.96	1.56	1.65 <sup>a</sup>	1.50	1.61 <sup>a</sup>
NO <sub>2</sub>	1.32	1.55 <sup>a</sup>	1.06	1.24 <sup>a</sup>	0.99	1.21 <sup>a</sup>
Xe <sup>c</sup>	1.67	2.21	1.36	1.76	1.33	1.84

<sup>a</sup> Ligands which fail to form stable complexes.<sup>14,15</sup> <sup>b</sup> Ionic radius, which has been subtracted to yield the data given below. <sup>c</sup> The model has been applied to xenon to draw comparisons with experimental data on the stability of  $[\text{Au}\cdot\text{Xe}_4]^{2+}$  given in ref 24.

$\text{Ag}^{2+}$ , which matches the contraction seen in some Au–L bond lengths when compared with their Ag–L counterparts. To provide a comparison of calculated data for all three metals the estimated ionic radii,  $r^{2+}$ , have been subtracted from the respective values for  $r_{\text{st}}$  and  $r_{\text{cr}}$ .

The results shown in Table 3 incorporate the above approximation for all three metal ions in association with a selection of ligands chosen from Table 1. Taking the NO<sub>2</sub> data as our benchmark, it can be seen that  $r_{\text{cr}} \approx 1.6 \text{ \AA}$  probably represents a lower limit, below which the crossing point is too close to the potential minimum to support bound states of the form  $[\text{M}\cdot\text{L}_n]^{2+}$ . If this limit is applied to the remaining data set, then it can be seen quite clearly that for copper(II) all ligands forming stable complexes have values of  $r_{\text{cr}} \geq 1.6 \text{ \AA}$ . In contrast, there is a distinct group of ligands which the experiments have demonstrated are unable to form stable  $[\text{M}\cdot\text{L}_n]^{2+}$  complexes with either Ag(II) or Au(II), and where the ligands, for the most part, satisfy the condition  $r_{\text{cr}} \leq 1.6 \text{ \AA}$ . In particular, water and the related hydrogen-bonded solvents, ammonia and methanol, fall within this latter category. There is some slight overlap between values calculated for unstable silver(II)/dioxane complexes and those for copper(II)/ammonia where the complexes are known to be stable.<sup>15</sup> However, given the approximations in the model, the correlation between  $r_{\text{cr}}$  and experimental observations across the three metals is remarkable. In effect, the calculations conclude that Ag(II) and Au(II) complexes should undergo proton transfer (hydrolyze!) under aqueous conditions. In contrast, Cu(II) is predicted to be stable under similar circumstances, which is exactly what is observed. In addition, it can be seen from the calculated data on all stable complexes that the positions of the curve crossings,  $r_{\text{cr}}$ , for silver(II) and gold(II) are very similar, and are all located closer to the potential minimum than for copper(II) with the same ligands. Thus, the

silver(II) and gold(II) complexes are predicted to be less stable than those of copper(II) with respect to reduction, which again is precisely what is observed.<sup>1</sup> As a final “calibration” of the model, it has been applied to  $[\text{Au}\cdot\text{Xe}_2]^{2+}$ , which follows from the recent preparation and isolation of  $[\text{Au}\cdot\text{Xe}_4]^{2+}[\text{Sb}_2\text{F}_{11}]_2$  by Seidel and Seppelt.<sup>24</sup> The calculated results are given at the bottom of Table 3, where it can be seen that the model shows xenon to fit well into the pattern of ligands capable of stabilizing Au(II) in the gas phase. Given that argon is also capable of stabilizing Au(II),<sup>23</sup> it is probably safe to assume that krypton would be equally as effective.

From an examination of those ligands which are successful at stabilizing all three metals in the (II) oxidation state, the majority appear to fall into the category of being  $\sigma$  donor– $\pi$  acceptor ligands. Thus, although the model does not take explicit account of ligand molecular orbitals, the presence of a  $\pi$  system and/or lone pair electrons is reflected in the physical properties of dipole moment and/or polarizability. In the absence of a dominant contribution from either of these two properties, then a comparatively high ionization energy could also be the mark of a successful ligand, and CO<sub>2</sub> would appear to be a prime example of such behavior. It is interesting to note that recent successes in forming stable Au(II) complexes in the condensed phase<sup>6b,24</sup> have come through the use of SbF<sub>6</sub>. Although the ionization energy of this species is not known, an estimate based on other heavily fluorinated molecules,<sup>25</sup> for example SF<sub>6</sub>, would suggest a value in the range 14–15 eV. Therefore, in addition to the properties discussed by Seidel and Seppelt,<sup>24</sup> the model presented above would also suggest that, in part, the high IE of SbF<sub>6</sub> contributes to the stabilization of condensed-phase Au(II) complexes.

## Conclusion

Experiments conducted in the gas phase have shown that with ligands that are capable of forming  $\sigma$  donor– $\pi$  acceptor bonds, the doubly charged ions of copper, silver, and gold behave similarly with regard to coordination, but both silver(II) and gold(II) are more difficult to stabilize. However, for other, mainly hydrogen-bonded solvents, copper behaves very differently from either silver or gold, in that ions of the latter two metals are incapable of forming stable  $[\text{M}\cdot\text{L}_n]^{2+}$  complexes. This pattern of behavior is accounted for in terms of a simple electrostatic model of the competing charge-transfer interactions between ions and ligands. A large dipole moment and a high ionization energy would appear to be desirable characteristics in a ligand that can successfully stabilize the Ag(II) and Au(II) oxidation states.

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