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Article

# Density Functional Theory-Based Prediction of Some Aqueous-Phase Chemistry of Superheavy Element 111. Roentgenium(I) Is the ‘Softest’ Metal Ion

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A previous approach (Hancock, R. D.; Bartolotti, L. J. *Inorg. Chem.* **2005**, *44*, 7175) using DFT calculations to predict log $K_1$ (formation constant) values for complexes of $NH_3$ in aqueous solution was used to examine the solution chemistry of Rg(I) (element 111), which is a congener of Cu(I), Ag(I), and Au(I) in Group 1B. Rg(I) has as its most stable presently known isotope a $t_{1/2}$ of 3.6 s, so that its solution chemistry is not easily accessible. LFER (Linear free energy relationships) were established between $\Delta E$(g) calculated by DFT for the formation of monoammine complexes from the aquo ions in the gas phase, and $\Delta G$(aq) for the formation of the corresponding complexes in aqueous solution. For $M^{2+}$, $M^{3+}$, and $M^{4+}$ ions, the gas-phase reaction was $[M(H_2O)_6]^{n+}(g) + NH_3(g) = [M(H_2O)_5NH_3]^{n+}(g) + H_2O(g)$ (1), while for $M^+$ ions, the reaction was $[M(H_2O)_2]^+(g) + NH_3(g) = [M(H_2O)NH_3]^+(g) + H_2O(g)$ (2). A value for $\Delta G$(aq) and for $\Delta E$ for the formation of $M = Cu^{2+}$ in reaction 1, not obtained previously, was calculated by DFT and shown to correlate well with the LFER obtained previously for other $M^{2+}$ ions, supporting the LFER approach used here. The simpler use of $\Delta E$ values instead of $\Delta G$(aq) values calculated by DFT for formation of monoamine complexes in the gas phase leads to LFER as good as the $\Delta G$-based correlations. Values of $\Delta E$ were calculated by DFT to construct LFER with $M^+ = H^+$, and the Group 1B metal ions $Cu^+$, $Ag^+$, $Au^+$, and $Rg^+$, and with $L = NH_3$, $H_2S$, and $PH_3$ in reaction 3: $[M(H_2O)_2]^+(g) + L(g) = [M(H_2O)L]^+(g) + H_2O(g)$ (3). Correlations involving $\Delta E$ calculated by DMol3 for $H^+$, $Cu^+$, $Ag^+$, and $Au^+$ could reliably be used to construct LFER and estimate unknown log $K_1$ values for Rg(I) complexes of $NH_3$, $PH_3$, and $H_2S$ calculated using the ADF (amsterdam density Functional) code. Log $K_1$ values for Rg(I) complexes are predicted that suggest the Rg(I) ion to be a very strong Lewis acid that is extremely ‘soft’ in the Pearson hard and soft acids and bases sense.

## Introduction

The chemistry of the monovalent Group 1B metal ions (Cu(I), Ag(I), and Au(I)) is interesting, since they are very ‘soft’ in the HSAB (hard and soft acids and bases) sense of Pearson.[1] In addition, the chemistry of Au(I) is dominated by relativistic effects[2−5] (RE), which appear to be responsible for the covalence of Au−L bonds and its accompanying softness. The solution chemistry of Au(I) suggests that it is by far the softest metal ion,[6] which means that Au−L bonding is very covalent. Indeed, Au(I) is at the center of an ‘island of electronegativity’, with the highest electronegativity[7] known for any metallic element. It has been estimated[8] that RE increase the electronegativity of Au by at least 0.5. Au(I) is central to the HSAB classification, and expectations of how soft a metal ion might be relate largely

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to how close it is to Au in the periodic table. This raises the question of what the aqueous-phase chemistry might be like for Rg(I), the heaviest member of Group 1B. Rg is a superheavy element[9−11] (SHE), elements of which run from element 104 (Rf) onward and at present are confirmed[10] as being synthesized as far as Rg (element 111). The SHE following Lr (element 103, the heaviest actinide) are not f-block elements[9−11] but belong to d-block groups and then main groups of elements as one progresses along the seventh period. Thus, Rf belongs to Group 4b (Ti, Zr, and Hf), while Rg is thought to belong to Group 1B. The SHEs include element 114, which had been expected[12] to be at the center of an island of stability, with elements with $t_{1/2}$ of the order of years. The half-life of $^{274}$Rg, the most stable isotope of Rg produced until recently,[10,11] is only 6 ms. Only one atom at a time of the SHEs can be synthesized,[10,11] ranging from a few atoms per hour for Rf to only about one per day for Rg. At the present time, direct chemical study, using single atoms, of up to element 108 (Hs) has been achieved,[10,11,13] with $t_{1/2} = 14$ s for $^{269}$Hs, with the gas-phase generation of $HsO_4$. The latter is analogous to $OsO_4$, supporting the placement of Hs in Group 8B with Fe, Ru, and Os. It appears that chemical properties may be deduced directly only for elements with isotopes with $t_{1/2}$ of at least several seconds. In the future, more stable isotopes of Rg may be produced,[14,15] leading to direct study of its chemistry. There is already a report[10,11,14,15] of observation of an isotope of Rg with $t_{1/2}$ of 3.6 s, and one may anticipate[14] Rg isotopes with $t_{1/2}$ of the order of up to 1 min. Prediction of its solution chemistry could aid in designing appropriate experiments for studying the chemistry of Rg(I). Of course, Rg(I) is of considerable interest in relation to how its softness in the HSAB sense would relate to that of Au(I). Numerous wave-mechanical studies[16−24] on Rg(I) show that RE are even more important for Rg(I) than Au(I), so that one might expect from this alone that Rg(I) would be very soft. Such calculations can be used to predict gas-phase properties of Rg compounds, but so far have not been used to predict those of Rg(I) species in aqueous solution in any detail.

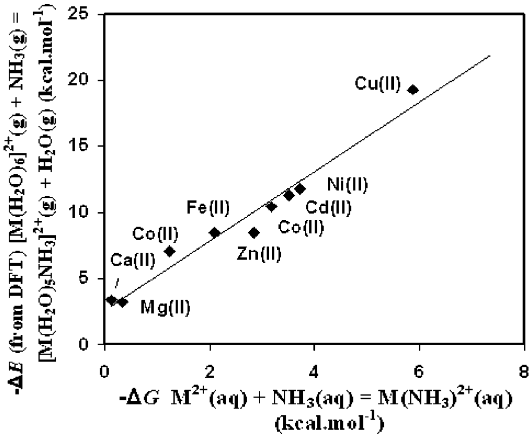

**Figure 1.** Δ$E$ (corrected for zero point energy) for the formation of $[M(H_2O)_5NH_3]^{2+}$ complexes calculated by DFT in the gas phase (eq 1) plotted against experimental Δ$G$(aq) values in aqueous solution.[27] The correlation coefficient ($R$) for the least-squares best-fit line drawn in is 0.981.

In recent work[25,26] it has been shown that density functional theory (DFT) calculations of Δ$G$(g) for gas-phase reactions of the type in eq 1 correlate well with Δ$G$(aq) for the corresponding equilibria in aqueous solution.[27] These LFER (linear free energy relationships) thus allow for prediction of unknown Δ$G$(aq) values, and hence log $K_1$ values, for formation of ammonia complexes in aqueous solution. Thus, it was possible[25,26] to predict log $K_1(NH_3) = 1.46$ for $Lr^{3+}$ and 2.29 for $Am^{3+}$, consistent with their resembling Lanthanides, but with somewhat greater covalence, as indicated by the higher log $K_1(NH_3)$ values. Log $K_1(NH_3)$ for $La^{3+}$ and $Lu^{3+}$ were similarly estimated[25] to be smaller at 0.27 and 0.99, respectively.

$$[M(H_2O)_6]^{2+}(g) + NH_3(g) \rightarrow [M(H_2O)_5NH_3]^{2+}(g) + H_2O(g) \quad (1)$$

It has been noted that Δ$E$ for eq 1 correlates as well with Δ$G$(aq) values, as does Δ$G$(g), so in the present work, Δ$E$ values were used to draw up the correlations, with the added advantage that these are easier to calculate. In the previous study,[25,26] values of Δ$E$ and Δ$G$(g) were not obtained for the Cu(II) complex of ammonia because of difficulty in obtaining a well-energy-minimized structure. This difficulty has since been overcome, and the results of the DFT calculations on Cu(II) with $NH_3$ in eq 1 are available as Supporting Information. The LFER for Δ$E$ for divalent metal ions in eq 1, versus the Δ$G$(aq) values, now including Cu(II), is presented in Figure 1. The LFER has a correlation coefficient ($R$) of 0.981, showing the excellent relationship between Δ$E$ in the gas phase and the Δ$G$(aq) values[27] for formation of the corresponding complexes in aqueous solution. Figure 1 gives one some confidence that the

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predictions of the solution chemistry of Rg(I) made here will be quite reliable.

In this paper the $\Delta G$(g) and $\Delta E$(g) values for eq 2 are calculated by DFT for L = $NH_3$, $PH_3$, and $SH_2$ with M = H(I), Cu(I), Ag(I), and Au(I), and $\Delta E$(g) values for Rg(I) and LFER are established with $\Delta G$(aq) values for related equilibria for H(I), Cu(I), Ag(I), and Au(I) in aqueous solution.[27] These LFER are then used to predict $\Delta G$(aq) values for the aqueous phase equilibria for Rg(I) and also the corresponding log $K_1$ values.

$$[M(H_2O)_2]^+(g) + L(g) = [M(H_2O)L]^+(g) + H_2O(g) \tag{2}$$

The ADF (amsterdam density functional) code[28] was used for calculations involving Rg(I) since the DMol3 code[29] used previously has not been set up to deal with elements beyond Lr (element 103). To ensure that the results from the ADF code were comparable with those obtained with DMol3, calculations were carried out for Au(I) using both codes.

## Computational Method

The calculations on the H(I), Cu(I), Ag(I), Au(I), and Cu(II) complexes employing DMol3[29] were carried out as described previously.[25] The ADF calculations on Au(I) and Rg(I) complexes were performed with version 2005.01b of the code.[28,30−33] Scalar relativistic corrections[28] were included via the ZORA to the Dirac equation.[34,35] The valence basis sets were taken from the ADF ZORA/TZP directory and employ uncontracted, Slater-type functions of primarily triple-$\zeta$ quality. The frozen core approximation was used; Au(4d), Rg(5d), O(1s), N(1s), S(2p), and P(2p). The local density parametrization of Vosko, Wilk, and Nusair[36] was employed in conjunction with the PBE[37] gradient corrections. The ADF numerical integration parameter was set to 6.0 in all calculations, and the energy gradient convergence criterion was set to $4.5 \times 10^{-4}$ au/Å in geometry optimizations. The SCF convergence criterion was set to $1 \times 10^{-7}$.

## Results and Discussion

The values of $\Delta E$ calculated for eq 2 for H(I), Cu(I), Ag(I), Au(I), and Rg(I) and L = $NH_3$ are seen in Table 1. The agreement in $\Delta E$ obtained for Au(I) using the DMol3[29] and ADF[28] codes is most encouraging. Similar good agreement is obtained by these two codes for Au(I) for the reactions where L = $H_2S$ and $PH_3$, shown in Tables 2 and 3. The good agreement for the Au(I) complexes using the two codes encourages one to believe that one may reliably include the results obtained for Rg(I) using the ADF code with the results obtained using DMol3 for the other M(I) ions. What Figure 2 shows is a good LFER for M(I) ions for $\Delta E$(g) for eq 2 with L = $NH_3$, against $\Delta G$(aq) for formation of the corresponding complexes in aqueous solution, with $R$ = 0.989. The correlation allows one to estimate $\Delta G$ for the formation of the $NH_3$ complex of Rg(I) in solution as 22 kcal/mol, which in turn leads to log $K_1(NH_3)$ = 13.1. The latter is higher than the highest reported[27] log $K_1(NH_3)$ values of, for example, log $K_1(NH_3)$ = 9.7 for Pd(II), 8.8 for Hg(II), or 9.22 with H(I).

**Table 1.** Values of $\Delta E$ (kcal/mol) Calculated for Group 1B Metal Ions and the Proton by DFT (eq 2), for Formation of Complexes with $NH_3$, with Experimental Values of $\Delta G$(aq) and log $K_1$ for Formation of the Corresponding Complexes in Aqueous Solution[27]

| Lewis acid | $H^+$ | $Cu^+$ | $Ag^+$ | $Au^+$ | $Rg^+$ |
|---|---|---|---|---|---|
| | | | $\Delta E$ ($NH_3$) (DFT) | | |
| DMol3$^a$ | −26.77 | −19.89 | −16.96 | −28.14 | |
| DMol3 (ZPE)$^a$ | −24.77 | −18.90 | −16.04 | −27.05 | |
| ADF | | | | −27.52$^b$ | −33.80$^b$ |
| ADF (ZPE) | | | | −26.80$^b$ | −33.17$^b$ |
| $\Delta G$ ($NH_3$) (aq) | −12.63 | −8.09 | −4.52 | −13.1$^c$ | −17.9$^d$ |
| log $K_1(NH_3)$ | 9.22 | 5.93 | 3.31 | 9.6$^c$ | 13.1$^d$ |

$^a$ Reference 25. ZPE = $\Delta E$ corrected for zero point energy. $^b$ This work. $^c$ Estimated previously.[6,25,26] $^d$ Estimated from Figure 2.

**Table 2.** Values of $\Delta E$ (kcal/mol) Calculated by DFT (eq 2) for Complex Formation of Group 1B Metal Ions and the Proton with $SH_2$ as Ligand, with Experimental or Predicted Values of $\Delta G$(aq) and log $K_1$ for Formation of the Corresponding Thioether ($SR_2$ Below, Which Is $S(CH_2CH_2OH)_2$) Complexes in Aqueous Solution[27]

| Lewis acid | $H^+$ | $Cu^+$ | $Ag^+$ | $Au^+$ | $Rg^+$ |
|---|---|---|---|---|---|
| | | | $\Delta E$ ($SH_2$) (DFT) | | |
| DMol3$^a$ | 6.75 | −7.22 | −7.44 | −19.80 | |
| DMol3 (ZPE)$^a$ | 5.66 | −7.36 | −7.24 | −19.96 | |
| ADF | | | | −19.49 | −25.21 |
| ADF (ZPE) | | | | −19.86 | −25.69 |
| $\Delta G$ ($SR_2$) (aq) | 8.0 | −4.91 | −4.82 | −12.4$^b$ | −17.9$^c$ |
| log $K_1(SR_2)$ | −5.9$^d$ | 3.6$^e$ | 3.53 | 9.1$^b$ | 13.1$^c$ |

$^a$ This work. ZPE = $\Delta E$ corrected for zero point energy. $^b$ Estimated previously.[6] $^c$ Estimated Figure 3. $^d$ Reference 38. $^e$ Hancock, R. D.; Tice, K. E. To be published.

**Table 3.** Values of $\Delta E$ (kcal/mol) Calculated by DFT (eq 2) for Complex Formation of Group 1B Metal Ions and the Proton with $PH_3$ as Ligand, with Experimental or Predicted Values of $\Delta G$ and log $K_1$ for Formation of the Corresponding Phosphine ($(C_6H_5)_2P(C_6H_4SO_3^-$, DPPS) Complexes in Aqueous Solution[27]

| Lewis acid | $H^+$ | $Cu^+$ | $Ag^+$ | $Au^+$ | $Rg^+$ |
|---|---|---|---|---|---|
| | | | $\Delta E$ ($PH_3$) (DFT) | | |
| DMol3$^a$ | −1.67 | −14.77 | −14.49 | −35.22 | |
| DMol3 (ZPE)$^a$ | −2.54 | −14.69 | −14.29 | −34.98 | |
| ADF | | | | −33.81 | −46.48 |
| ADF (ZPE) | | | | −34.12 | −46.96 |
| $\Delta G$ ($PR_3$) (aq) | −0.86 | −7.86 | −11.12 | −28.1$^c$ | −37.3$^d$ |
| log $K_1(PR_3)$ | 0.63 | 5.76 | 8.15 | 20.6$^c$ | 27.3$^d$ |

$^a$ This work. ZPE = $\Delta E$ corrected for zero point energy. $^b$ This work. $^c$ Estimated previously.[6,25,26] $^d$ Estimated by eq 2.

Soft ligands with S-donors and P-donors are of particular interest with soft metal ions because of the complexes of very high stability formed.[27] It has been found that an important aspect of correlations such as those shown in Figures 1 and 2 is the contribution of polarizability[38−41] to the thermodynamics of complex formation in the gas phase.

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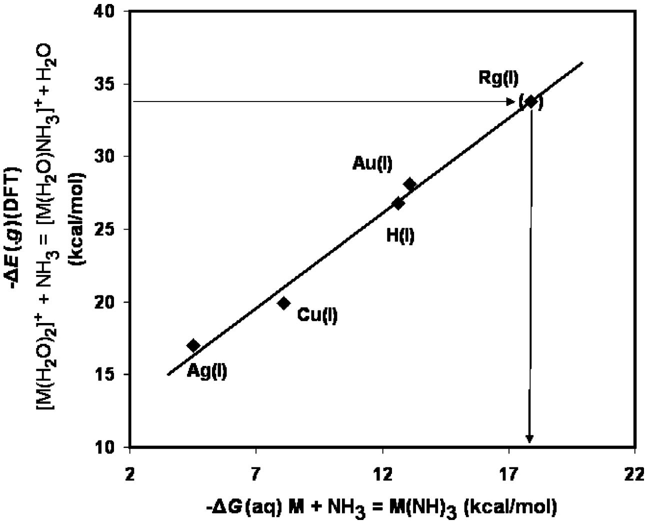

**Figure 2.** LFER between $\Delta E$ (corrected for zero point energy) calculated for eq 2 for the formation of $[M(H_2O)NH_3]^+$ complexes in the gas phase versus $\Delta G$(aq) for the formation of the corresponding complexes in aqueous solution. The correlation coefficient for the least-squares best-fit line excluding the point for Rg(I) is 0.989. The arrows indicate the estimation of $\Delta G$(aq) for the formation of the Rg(I)/ammonia complex in aqueous solution.

Polarizability effects stabilize complex ions formed in the gas phase by distribution of the charge over the whole complex ion and are size-dependent. Thus, complexes formed by cations such as $H^+$ or $Li^+$ are stabilized simply by the size of the ligand, and conversely, the smaller the metal ion, the greater is its response to polarizability effects. In the gas phase, $\Delta G$ of protonation of amines increases very strongly along the series $NH_3 < CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$[38]. The latter effect is largely due to polarizability, with a much smaller contribution from inductive effects. In solution, polarizability effects are quenched due to H-bonding, which distributes charge over the solvent in the vicinity of the cation or anion. Thus, in aqueous solution[27] the differences in basicity along the above series of mono-amines is small. Use of waters of solvation on metal ions in the form of $[M(H_2O)_6]^{n+}$ or $[M(H_2O)_5NH_3]^{n+}$ species in the gas phase in eq 1 in the form of 'clusters'[25,26] is an attempt to minimize polarizability effects by decreasing differences in size of the Lewis acids. For replacement of a water on $M^{2+}$ by $NH_3$ in eq 1, the contributions of polarizability effects are minimal because the difference in size between $H_2O$ and $NH_3$ is small. For ligands that are significantly larger than the coordinated $H_2O$ molecule that is displaced, such as $(CH_3)_2S$ or $(CH_3)_3P$, one could reduce the contribution of polarizability effects by adding more water molecules to the metal aqua ion in the gas phase, which would be the addition of a second sphere of water molecules. This approach is being examined, but clearly it would be computationally much more demanding. Work with the 2-coordinate $[M(H_2O)L]^+$ ions of Group 1B suggests that the one or two waters present are insufficient to quench polarizability effects. Thus, if one uses $(CH_3)_2S$ or $(CH_3)_3P = L$ for DFT calculations in eq 2, $\Delta E$ for the small proton is much too large compared to $\Delta E$ for the large Group 1B metal ions, which it seems reasonable to attribute to polarizability effects. A simpler approach to minimizing polarizability effects is to use models of $R_2S$ and $R_3P$ ligands that are not very different in size from the $H_2O$ displaced in the complex-formation reaction. Thus, $SH_2$ and $PH_3$ have been used in the gas-phase DFT calculations of $\Delta E$ for eq 2 for comparison with $\Delta G$ of formation of $SR_2$ ($R = -CH_2CH_2OH$) (thiodiethanol, TDE) and $PR'_2R''$ complexes ($R' =$ phenyl, $R'' = C_6H_4SO_3^-$, DPPS) in aqueous solution.[27]

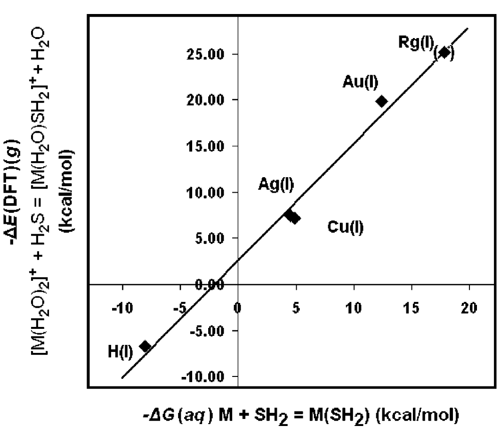

**Figure 3.** LFER between $\Delta E$ (corrected for zero point energy) calculated for eq 2 for the formation of $[M(H_2O)SH_2]^+$ complexes in the gas phase versus $\Delta G$ for the formation of thioether complexes in aqueous solution (ref 27 and Table 2). The correlation coefficient ($R$) for the least-squares best-fit line excluding the point for Rg(I) is 0.989.

In Figure 3 is shown the correlation between $\Delta E$ calculated in the gas phase for formation of $SH_2$ complexes and aqueous-phase values of $\Delta G$(aq) for the formation of TDE ($SR_2$) complexes. Excellent linearity is obtained, with $R = 0.989$, allowing for estimation of $\Delta G$(aq) for the formation of $[Rg(H_2O)R_2S]^+$ of $-17.9$ kcal/mol, and hence $\log K_1 = 13.1$. A similar correlation to Figure 2 is obtained for $PH_3$ as ligand (not shown), where the solution thermodynamics refer to the sulfonated phosphine ligand diphenylphosphinosulfonic acid[27,42−44] (DPPS). The relationship leads to eq 3, which fits the data with $R = 0.994$.

$$\Delta E(\mathrm{DFT, g}) = 1.185\Delta G(\mathrm{aq}) + 2.3483 \qquad (3)$$

The value of $\Delta E$ for the formation of the phosphine complex of Rg(I) in Table 3 of $-46.48$ kcal/mol thus leads to a predicted $\log K_1$ for Rg(I) with DPPS of 27.3. It has been suggested[45] from ab initio studies that Rg(I) will be a highly unstable oxidation state. The very high $\log K_1$ values with soft ligands here suggests that, like Au, the monovalent state will be strongly stabilized by ligands such as phosphines, as well as other soft ligands such as $CN^-$. It does not appear[46] that an actual value of the standard reduction

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potential, $E°$, has been estimated for $Rg^+$(aq). However, one may estimate from the values[47] of $E°$ for the other Group 1B $M^+$(aq) ions that $E°$ for $Rg^+$(aq) might be about +3.2 V:

| metal ion: | $Cu^+$ (aq) | $Ag^+$ (aq) | $Au^+$ (aq) | $Rg^+$ (aq) |
|---|---|---|---|---|
| $E°$ (V) | +0.52 | +0.80 | +1.69 | ∼+3.2 |

It is not clear that $E°$ for $Rg^+$(aq) can be obtained accurately as above from a simple progression involving the known values for the other Group 1B $M^+$ ions since REs cause the ionic radius of $Rg^+$ to contract[10,11] to be similar to that of the smallest Group 1B cation, $Cu^+$, which would make $Rg^+$ have a higher hydration energy, possibly leading to a lower $E°$. A reviewer has pointed out that $Rg^+$ has a $6d^87s^2$ configuration,[48] as compared to the $5d^{10}$ configuration of $Au^+$, and that the relativistic contraction of $Rg^+$ is entirely due to the 7s contraction. If, for purposes of the present discussion, $E°$ for $Rg^+$(aq) is considered to be about +3.2 V and that log $\beta_2$(L) for Group 1B $M^+$ ions[27] tends to be about 2 × log $K_1$(L), one can estimate the following $E°$ values for Rg(I) complexes:

$$[Rg(NH_3)_2]^+\ (aq) + e^- \rightarrow Rg(s) + 2NH_3(aq) \qquad E° = +1.8\ V \quad (4)$$

$$[Rg(PR_3)_2]^+\ (aq) + e^- \rightarrow Rg(s) + 2PR_3(aq) \quad E° = -0.1\ V \quad (PR_3 = \text{DPPS, diphenylphosphinobenzenesulfonic acid}) \quad (5)$$

The log $K_1$ values for the Ag(I) and Rg(I) complexes with DPPS are 8.15 and 27.3 (Table 3). By simple proportion, with[27] log $\beta_2$ = 20.5 for $[Ag(CN)_2]^-$, one might expect log $\beta_2$ for $[Rg(CN)_2]^-$ to be about 67, which would yield

$$[Rg(CN)_2]^-\ (aq) + e^- \rightarrow Rg(s) + 2CN^-(aq) \quad E° = -0.8\ V \quad (6)$$

Assuming $E°$ for the $Rg^+$(aq) ion to be very high, as estimated above, only the more powerfully complexing ligands such as phosphines and $CN^-$ would form stable complexes with Rg(I) in aqueous solution. Complexes with more weakly complexing ligands such as $R_2S$, $NH_3$, or $Cl^-$ would be very unstable, particularly to disproportion into the more stable[45] Rg(III) species plus metallic Rg. This would resemble, for example, $[AuCl_2]^-$, which in aqueous solution disproportionates[49] into $[AuCl_4]^-$ and metallic gold. Equation 6 suggests that, like Au, metallic Rg would dissolve readily in dilute $CN^-$ solutions in the presence of air.

**Table 4.** Softness of Group 1B Metal Ions Calculated Following the Method of Pearson and Mawby[50] and the Wag Angles ($\theta$) Calculated Here by DFT for the Group 1B $[M(H_2O)_2]^+$ Ions

| Lewis acid | H(I) | Cu(I) | Ag(I) | Au(I) | Rg(I) |
|---|---|---|---|---|---|
| softness,[a] $S$ | 0.062 | 0.743 | 0.864 | 1.252 | 1.375 |
| wag angle[b] ($\theta$) (deg) | 38.8 | 32.8 | 33.6 | 47.7 | 56.6 |

[a] The softness parameter ($S$) for each Lewis acid is given by the ratio of the DFT calculated $\Delta E$ values for eq 2, namely $\Delta E(L = PH_3)/\Delta E(L = NH_3)$, as discussed in the text. [b] The wag angle ($\theta$) is the angle between the plane containing the coordinated water molecule and the M−O bond (see Figure 4).

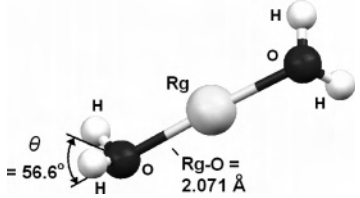

**Figure 4.** Structure of the Rg(I) aqua ion generated here by DFT, showing the large value of the wag angle ($\theta$).

The soft nature of Rg(I) can be judged from its predicted very high log $K_1$ values with soft ligands. One can quantify this using the approach of Pearson and Mawby,[50] where hardness/softness of metal ions is quantified using gas-phase heats of formation of halide complexes. Thus, the hardness parameter, $I_P$, for any metal ion is effectively the ratio of the gas-phase heat of formation of the metal ion complex with a very hard halide ion ($F^-$) to that of a very soft ion ($I^-$). An analogous approach here gives a softness parameter (Table 4) that is the ratio of $\Delta E$ in the gas phase for formation of the $PH_3$ complex compared to that for the $NH_3$ complex in Tables 1 and 3.

It has also been suggested[25] that the wag angle ($\theta$) between the plane containing the coordinated water molecule and the M−O bond (see Figure 4) increases with increasing covalence in the M−O bond. Thus, for very ionic bonding, $\theta$ is zero, while for covalent bonding, it approaches the 54.7° expected for a regular tetrahedron. It is interesting to note that the values for $\theta$ predicted for the Group 1B ions are consistent with the idea that the bonding in Rg(I) complexes is very covalent and that Rg(I) would be the softest member of Group 1B.

The DFT calculations of $\Delta E$ for eq 2 with L = $NH_3$, $H_2S$, and $PH_3$ are encouraging in that they reproduce the subtleties of HSAB behavior seen in aqueous solution. Thus, with the hard[1] $NH_3$ ligand, log $K_1$ for the hard $H^+$ ion is much greater than $Cu^+$, which is greater than for the softer[6] $Ag^+$ ion. With the soft $H_2S$ and $PH_3$ ligands, this order of preference is reversed, as would be expected, and is that observed[27] in aqueous solution, where the proton now forms the least stable complex. The behavior of Au(I) and Rg(I) reflects the fact that not only are they very soft but they are also stronger Lewis acids than the other M(I) ions. The authors anticipate carrying out studies of the kind reported here for Rg(I) with other SHEs, such as Rf(IV) in comparison to other M(IV) ions or Mt(III) compared to other M(III) ions, with a view

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to making more extensive predictions of the aqueous chemistry of these elements.

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**Supporting Information Available:** Structures of Au(I) and Rg(I) complexes generated by DFT and discussed here, tables of $\Delta E$ and $\Delta E$(ZPE) for reaction 2 reported here, and DFT calculated values of $\Delta G$ and $\Delta E$ for complexation of $Cu^{2+}$(g) with $NH_3$(g) (eq 1). This material is available free of charge via the Internet at http://pubs.acs.org.

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