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# A Simple Primary Amide for the Selective Recovery of Gold from Secondary Resources

*Euan D. Doidge, Innis Carson, Peter A. Tasker, Ross J. Ellis, Carole A. Morrison, and Jason B. Love**

**Abstract:** *Waste electrical and electronic equipment (WEEE) such as mobile phones contains a plethora of metals of which gold is by far the most valuable. Herein a simple primary amide is described that achieves the selective separation of gold from a mixture of metals typically found in mobile phones by extraction into toluene from an aqueous HCl solution; unlike current processes, reverse phase transfer is achieved simply using water. Phase transfer occurs by dynamic assembly of protonated and neutral amides with* $[AuCl_4]^-$ *ions through hydrogen bonding in the organic phase, as shown by EXAFS, mass spectrometry measurements, and computational calculations, and supported by distribution coefficient analysis. The fundamental chemical understanding gained herein should be integral to the development of metal-recovery processes, in particular through the use of dynamic assembly processes to build complexity from simplicity.*

Gold is a valuable metal resource, not only as jewellery and for investment, but increasingly in modern electronics, medicine, and chemical catalysis.[1] The low abundance of gold in its ores, combined with economic and societal issues associated with mining and separation operations, means that e-waste streams are attractive sources of this metal.[2] The gold content of WEEE is estimated to be 80 times that found in primary mining deposits, representing 3 % of the world mine supply in 2007, and its recovery would decrease the environmental and societal footprint of mining along with potential savings of 17000 t/t in carbon dioxide emissions.[3] Furthermore, current processes for the recovery of gold from WEEE are hazardous, as they often use toxic chemicals such as cyanide. As such, governments worldwide are developing waste-recycling strategies to exploit e-waste through "urban mining",[4] with the market forecasted to have a compound annual growth rate of 20.6 % between 2015 and 2020 from its USD $1.66\times10^9$ value in 2014.[5] These strategies combine metal-leaching, -separation, and -precipitation technologies which increasingly require the use of "green" materials, reagents, and processes for societal and economic acceptance.[6]

The recovery of metals using solvent extraction can offer significant environmental advantages over energy- and capital-intensive pyrometallurgical routes, especially if a single metal is targeted.[7] Selectivity of extraction is achieved by designing a reagent that favors the phase transfer of one metal from a mixed-metal aqueous leach solution to an organic phase.[8] Currently, 25 % of global Cu recovery is carried out by hydrometallurgy using phenolic oxime reagents,[8] the development of which relied on an understanding of the coordination and supramolecular chemistry of copper.

In contrast, the chemistry that underpins the recovery of gold by solvent extraction is poorly understood. Commercial reagents such as MIBK (isobutyl methyl ketone), DBC (diethylene glycol butyl ether), and 2-EH (2-ethylhexanol) recover gold as its metalate $[AuCl_4]^-$ from aqueous HCl by solvent extraction [Eq. (1)], but exhibit selectivity, safety, and mass-balance issues.[9] Recent work has shown that dilute HCl acts as a lixiviant for the metals in printed-circuit boards,[6d] but due to a lack of selectivity the commercial reagents are likely to recover significant quantities of unwanted materials.

$$\mathrm{MX}_n{}^{m-} + y\,\mathbf{L} + m\,\mathrm{H}^+ \rightleftharpoons [\mathrm{MX}_n(\mathrm{H}\mathbf{L})_m(\mathbf{L})_{y-m}] \qquad (1)$$

In studying the solvent extraction of metalates such as $[ZnCl_4]^{2-}$ we found that the organization of the reagent upon protonation, $\mathrm{H}\mathbf{L}^+$ in Equation (1), is crucial for selectivity, not only between metalates but also over chloride which is present in large excess (Figure 1, left).[10]

We have now exploited this concept using the simple primary amide **L** (Figure 1, right), prepared from commercially available $ClC(O)CH_2CH(Me)CH_2t\mathrm{Bu}$ and $NH_3$, for the extraction of $H[AuCl_4]$. While tertiary amides have been examined in gold recovery[12] and in some cases exploited commercially in the recovery of platinum group and f-block metals,[8] the use of primary amides is limited to early examples in f-block chemistry,[13] possibly through an assumed lack of solubility in hydrocarbon solvents. As such, the transfer of a range of metalates/metalloids found in WEEE from single-metal aqueous HCl solutions into a toluene organic phase containing **L** was examined, and showed the pattern expected according to the Hofmeister series (Figure 2).

The distribution coefficient ($D = [\mathrm{Au(org)}]/[\mathrm{Au(aq)}]$) for Au in 2 M HCl is high ($D = 15.1$) compared with those of potential contaminants such as Fe (0, as $[FeCl_4]^-$), Sn ($4.5\times10^{-3}$ as $[SnCl_6]^{2-}$), and Cu (0, as $[CuCl_4]^{2-}$), with only Sb (1.2,

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[*] E. D. Doidge, I. Carson, Prof. P. A. Tasker, Dr. C. A. Morrison, Prof. J. B. Love
EaStCHEM School of Chemistry, University of Edinburgh
Joseph Black Building, The King's Buildings
David Brewster Road, Edinburgh EH9 3FJ (UK)
E-mail: jason.love@ed.ac.uk
Dr. R. J. Ellis
Chemical Sciences and Division
Oak Ridge National Laboratory (USA)

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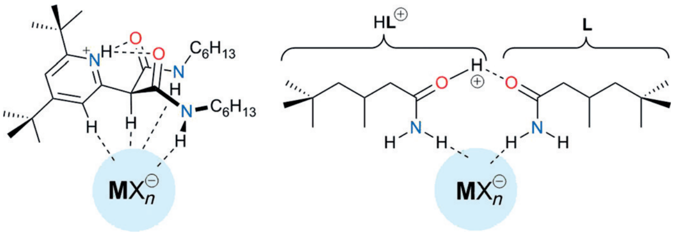

***Figure 1.*** Organization of protonated receptors for metalate extraction. Left: receptor used in the extraction of $[MCl_4]^{2-}$ with M = Co, Zn; structure deduced from an X-ray crystal structure analysis for M = Zn;[11] right: structure of receptor $HL_2^+$ used in this work for the extraction of $[AuCl_4]^-$ from MD calculations.

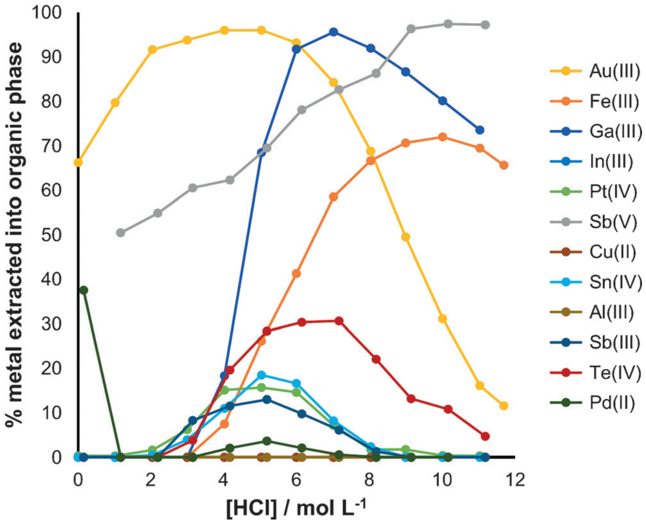

***Figure 2.*** Extractions from single-metal solutions in aqueous HCl of varying concentrations into toluene using amide **L**. Conditions: 0.01 M of the metal salt dissolved in varying concentrations of HCl (2 mL) contacted with 0.1 M of **L** in toluene (2 mL) at 20 °C for 1 h. No transfer of $Zn^{II}$, $Co^{II}$, $Ir^{III}$, and $La^{III}$ in 6 M HCl by 0.1 M toluene solutions of **L** was seen and the loading of $Pd^{II}$ when no HCl was present is likely due to inner-sphere coordination of **L**.

as $[SbCl_6]^-$) showing appreciable extraction. As the concentration of HCl was increased, Au extraction peaked at 4 M, then dropped, typical of competitive chloride extraction. These data contrast with those of the commercial reagents MIBK and DBC (see Figure S1 in the Supporting Information) which show significant extraction of other metalates.[9a] Significantly, unlike with MIBK and DBC and most other selective Au extractants, the addition of water to the metal-loaded organic phase resulted in 88 % back transfer of $[AuCl_4]^-$ into the aqueous phase. This stripping step of the extraction process is important as the use of acid, base, or other reagents such as thiourea, as is required to retrieve aqueous Au solutions from MIBK or DBC solutions, is detrimental to the overall materials balance.

The selectivity of **L** was evaluated by single-point extractions from a 2 M HCl mixed-metal solution of concentrations representative of the dissolution of mobile-phone e-waste (Figure 3). Even in the presence of other metals in high concentrations, **L** remained highly selective for Au, extracting 82 % of the Au present. While some Fe (6.4 %) and Sn (2.7 %) were extracted, no Cu was extracted, which is surprising considering its 2000 times higher concentration. Extractions of the same mixed-metal solution using diluted 0.1 M MIBK, DBC, or 2-EH in toluene led to effectively zero transfer of all metals (e.g. for DBC: Fe 2.4 mM; Sn 0.25 mM; Au 0.098 mM). Only by using neat reagents did any appreciable extraction occur, and then with very poor selectivity, for example, DBC extracted 86 % Au, 72 % Sn, 74 % Fe, 6.8 % Zn, and 0.8 % Cu. It is clear that **L** offers significant advantages over current commercial reagents.

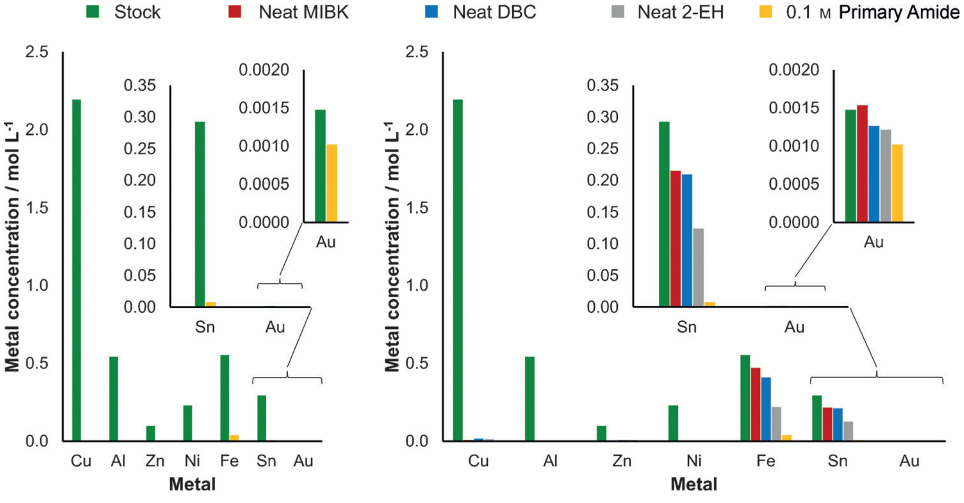

***Figure 3.*** Concentrations of metals extracted into a 0.1 M toluene solution of **L** (2 mL) on contacting with an aqueous acidic mixed-metal feed (2 M HCl, 2 mL, left) and comparison to undiluted commercial reagents (right). Aqueous metal concentrations were representative of those found in a standard mobile phone: Cu 2.37; Al 0.57; Zn 0.11; Ni 0.24; Fe 0.61; Sn 0.28; Au 0.0012 M.

The identity of the Au species in the organic phase was probed. Slope analyses of log*D* against log[**L**] plots (Figure S2) gave **L**:Au ratios from 2.5 to 3.0, depending on the initial concentration of Au in the aqueous solution. For other metals, for example, $Fe^{3+}$ and $Ga^{3+}$, similar slope analyses gave **L**:M ratios of 3.0 for all concentrations. It is therefore clear that simple 1:1 ion pairs, for example, $(HL)[AuCl_4]$, are not the extracted species. Micellar-type species involving water pools as seen in extractions using weak-base reagents such as tributylphosphate[14] can be discounted as Karl Fischer measurements show that no water is transferred into the organic phase on increasing Au extraction (Figure S3).

Further insight into the solution structure of the extracted species was gained from an EXAFS study (Figure S4). The chlorine-phase-shift-corrected FT-EXAFS showed one intense peak at 2.28 Å attributed to the chloride neighbors. The position and symmetry of this peak is consistent with a homoleptic $[AuCl_4]^-$ ion,[15] suggesting that the ligand–metal interaction in solution is indeed outer-sphere. The broad peak at 4.1–4.9 Å is most likely produced by multiple scattering from this dominant Au–Cl correlation. Another peak of significance was observed at 2.7 Å and may be produced by backscattering from N or O atoms on the ligand as it hydrogen bonds to the outer sphere of the $[AuCl_4]^-$ ion. Fitting the EXAFS data with a two-shell Au–Cl and Au–O model resulted in a coordination number for chloride in the inner sphere of 4.0, confirming that the metal species is solely $[AuCl_4]^-$. Fits of the minor feature gave either an O or an N coordination number of around 1.0, at a distance of 2.8 Å. This short Au–O/N interaction could emerge if hydrogen bonding with the edge of the square-planar anion occurs,[16] as is suggested by the interactions seen in the simulations described below.

The speciation in $CH_3CN$ solution was evaluated by positive-ion electrospray mass spectrometry (ESI-MS; Figure S5) in which the dominant gold-containing species have a generic formula $[(H\mathbf{L})_{n+1}(AuCl_4)_n]^+$ down to nanomolar concentrations. The lower-molecular-weight assemblies with $m/z$ 1649 $[(H\mathbf{L})_4(AuCl_4)_3]^+$, $m/z$ 1152 $[(H\mathbf{L})_3(AuCl_4)_2]^+$, and $m/z$ 655 $[(H\mathbf{L})_2(AuCl_4)]^+$ are formed by sequential loss of $[(H\mathbf{L})(AuCl_4)]$ from higher-nuclearity assemblies such as tetranuclear $[(H\mathbf{L})_5(AuCl_4)_4]^+$ ($m/z$ 2146) upon collision-induced decay (tandem MS/MS, He buffer gas). No ions were seen that signified the incorporation of hydroxonium, $H_3O^+$, supporting the Karl Fischer analysis, and the base peak was $H\mathbf{L}_2^+$ ($m/z$ 315), consistent with the structure described in Figure 1.

Further structural corroboration of the extracted species was sought by DFT and MD calculations. The geometry-optimized structure of the hydrogen-bonded dimer $(\mathbf{L})_2$ is 80.5 kJ mol$^{-1}$ more favored than two **L** monomers, consistent with its X-ray crystal structure (Figure S6), and the formation of the protonated hydrogen-bonded dimer $(H\mathbf{L}_2)^+$ is 77.3 kJ mol$^{-1}$ more stable than that of the protonated monomer $(H\mathbf{L})^+$. These protonated extractants form neutral ion pairs with $[AuCl_4]^-$, with $[(H\mathbf{L}_2)(AuCl_4)]$ being energetically more favored than $[(H\mathbf{L})(AuCl_4)]$, and have multiple O–H and N–H sites that promote bridged structures such as in $[(H\mathbf{L})(AuCl_4)_2]^-$ ($-57.2$ kJ mol$^{-1}$) and $[(H\mathbf{L}_2)(AuCl_4)_2]^-$ ($-44.3$ kJ mol$^{-1}$; Figure 4). It is therefore thermodynamically favorable for amide cations associated with one $[AuCl_4]^-$ unit to form a second interaction with another $[AuCl_4]^-$ unit, leading to the higher-order clusters seen by ESI-MS. To investigate supramolecular clustering, a system containing four $[AuCl_4]^-$ ions and ten amide molecules, four of which were protonated (**L**:M ratio of 2.5 as per slope analysis), was studied by classical molecular dynamics techniques and showed a cluster of $8\mathbf{L}:4[AuCl_4]^-$, with the remaining two extractant molecules as the hydrogen-bonded dimer $(\mathbf{L})_2$ (Figure 4). The supramolecular cluster $[(AuCl_4)_4(H\mathbf{L})_4(\mathbf{L})_4]$ is assembled through $(H\mathbf{L})^+$, $(H\mathbf{L}_2)^+$, or $(H\mathbf{L}_3)^+$ bridging amide molecules and results in each $[AuCl_4]^-$ ion being well separated with Au···Au distances of 6.8 to 8.7 Å with no short intermolecular Au···Cl interactions.

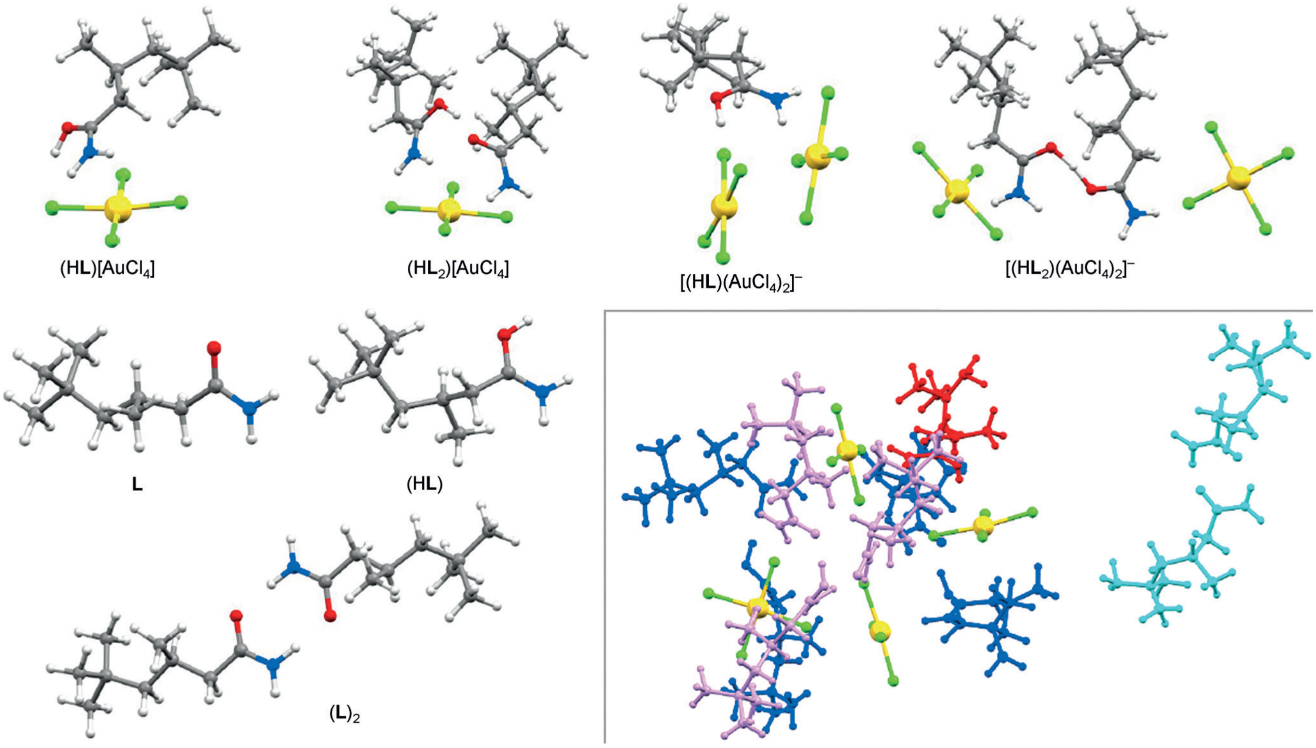

*Figure 4.* Structures of **L**/H[AuCl$_4$] aggregates obtained from DFT and MD calculations. The MD calculations on the 10:4 **L**:H[AuCl$_4$] system displayed several amide-bridged entities, including $[(H\mathbf{L})(AuCl_4)_2]^-$ (red), $[(H\mathbf{L}_2)(AuCl_4)_2]^-$ (dark blue), $[(H\mathbf{L}_3)(AuCl_4)_2]^-$ (magenta), and $(\mathbf{L})_2$ (cyan).

The combination of the above experiments provides clear evidence that simple ion pairing does not occur during the recovery of gold from aqueous HCl by **L**. Instead, bridging hydrogen bonding interactions of **L** and **L**H$^+$ with the $[AuCl_4]^-$ ions leads to the spontaneous formation of supramolecular clusters in the organic phase. Unusually, these assemblies do not arise through aurophilic (Au⋅⋅⋅Au) and/or Au−Cl⋅⋅⋅Au interactions,[17] the former prevalent for Au$^I$ complexes and the latter seen extensively in solid state structures of the $[AuCl_4]^-$ ion,[18] but are generated through hydrogen bonding and Coulombic interactions. The ability of the simple primary amide **L** to form these complex molecular assemblies in the organic phase appears integral to its efficacy in gold recovery and reverse phase transfer and points at parallels with the developments of encapsulation complexes in which intricate entities are assembled in solution using supramolecular interactions such as hydrogen bonding, encapsulation, and soft-templating.[19]

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