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

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

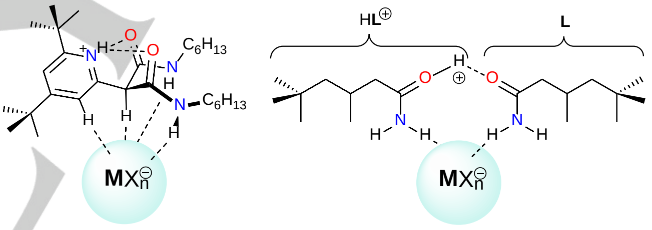
**Abstract:** Waste electrical and electronic equipment (WEEE) such as mobile phones contain a plethora of metals of which gold is by far the most valuable. Here we describe a simple primary amide that achieves the selective separation of gold from a mixture of metals typically found in a mobile phone 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 $AuCl_4^-$ anions through hydrogen bonding in the organic phase, as shown by EXAFS, mass spectrometry measurements and computational calculations, and supported by distribution coefficient analysis. We anticipate that the fundamental chemical understanding gained here is 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 billion 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 favours 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,[7] the development of which relied on an understanding of the coordination and supramolecular chemistry.

In contrast, the chemistry that underpins the recovery of gold by solvent extraction is poorly understood. Commercial reagents such as MIBK (methyl-*iso*-butylketone), DBC (dibutylcarbitol), 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.

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



$$MX_n^{m-} + y\,\mathbf{L} + m\,H^+ \rightleftharpoons [MX_n(H\mathbf{L})_m(\mathbf{L})_{y-m}] \qquad \text{Eq. 1}$$

**Figure 1.** Organisation of protonated receptors for metalate extraction. Left: receptor used in the extraction of $MCl_4^{2-}$ with M = Co, Zn from X-ray crystal structural data for M = Zn;[11] right: receptor $H\mathbf{L}_2^+$ used in this work for the extraction of $AuCl_4^-$ from MD calculations.

We have now exploited this concept using the simple primary amide **L** (Figure 1), prepared from commercially available $ClC(O)CH_2CH(Me)CH_2Bu^t$ and $NH_3$, for the extraction of $HAuCl_4$. While tertiary amides have been examined in gold recovery [12] and in some cases exploited commercially in platinum group metal and f-block metal recovery,[8] primary amides are 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 shows the pattern expected according to the Hofmeister series (Figure 2).

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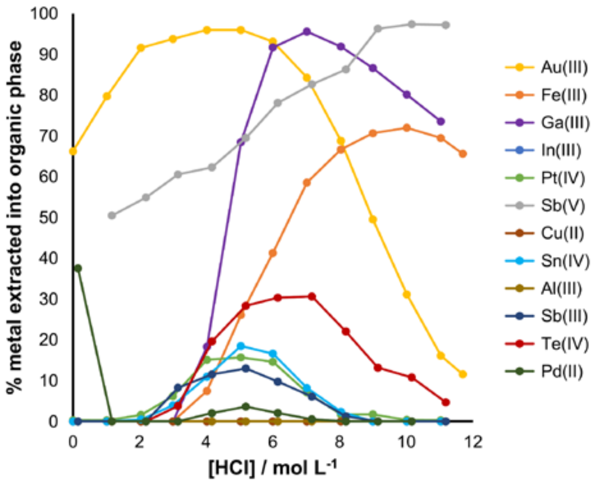

**Figure 2.** Extractions from single-metal solutions of varying concentrations of aqueous HCl into toluene using the amide **L**. Conditions: 0.01 M of the metal salt dissolved in varying concentrations of HCl (2 mL) contacted with 0.1 M of **L** in toluene (2 mL) at 20 ºC for 1 h. No transfer of Zn(II), 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) at zero [HCl] is likely due to inner-sphere coordination of **L**.

The distribution coefficient (*D* = [Au(org)]/[Au(aq)]) for Au at 2 M HCl is high (*D* = 15.1) compared with potential contaminants such as Fe (0, as $FeCl_4^-$), Sn ($4.5x10^{-3}$ as $SnCl_6^{2-}$), and Cu (0, as $CuCl_4^{2-}$), with only Sb (1.2, as $SbCl_6^-$) showing appreciable extraction. As the [HCl] is increased, Au extraction peaks at 4 M, then drops, typical of competitive chloride extraction. These data contrast to those of the commercial reagents MIBK and DBC (Supporting Information, Figure S1) which show significant extraction of other metalates.[9a] Significantly, unlike MIBK and DBC and most other selective Au extractants, the addition of water to the metal-loaded organic phase results 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 2M HCl mixed-metal solution of concentrations representative of the dissolution of mobile phone e-waste (Figure 3).

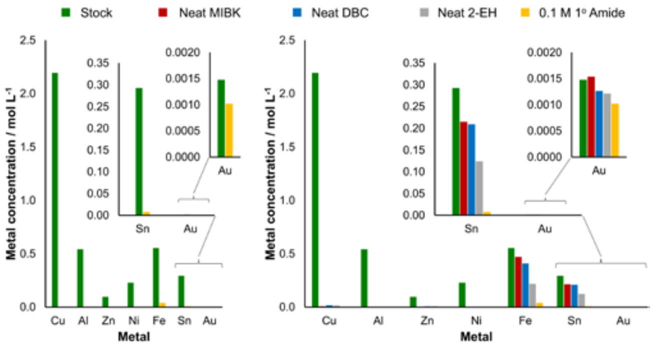

**Figure 3.** Concentrations of metals extracted into a 0.1 M toluene solution of **L** (2 mL) on contacting with an aqueous acidic mixed-metal feed (2 M HCl, 2 mL, left) and comparison to undiluted commercial reagents (right). Aqueous metal concentrations are representative of those found in a standard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

Even in the presence of high concentrations of other metals, **L** remains highly selective for Au, extracting 82% of the Au present. While some Fe (6.4 %) and Sn (2.7%) are extracted, no Cu is 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-ethylhexanol in toluene lead 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, e.g. DBC extracts 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.

The identity of the Au species in the organic phase was probed. Slope analyses of log *D* against log [**L**] plots, (SI Figure S2) give **L**:Au ratios from 2.5 to 3.0, depending on the initial concentration of Au in aqueous solution. For other metals, e.g. $Fe^{3+}$ and $Ga^{3+}$, similar slope analyses give **L**:M ratios of 3.0 for all concentrations. It is therefore clear that simple 1:1 ion pairs, e.g. (H**L**)$AuCl_4$ 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 (SI Figure S3).

Further insight into the solution structure of the extracted species was gained from an EXAFS study (SI Figure S4). The chlorine-phase-shift-corrected FT-EXAFS shows one intense peak at 2.28 Å attributed to the chloride neighbours. The position and symmetry of this peak is consistent with a homoleptic $AuCl_4^-$ anion,[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 is observed at 2.7 Å and may be produced by back scattering from N or O atoms on the ligand as it hydrogen bonds to the outer-sphere of the $AuCl_4^-$ anion. Fitting the EXAFS data with a two-shell Au-Cl and Au-O model results 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 give either an O or 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 below.

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

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

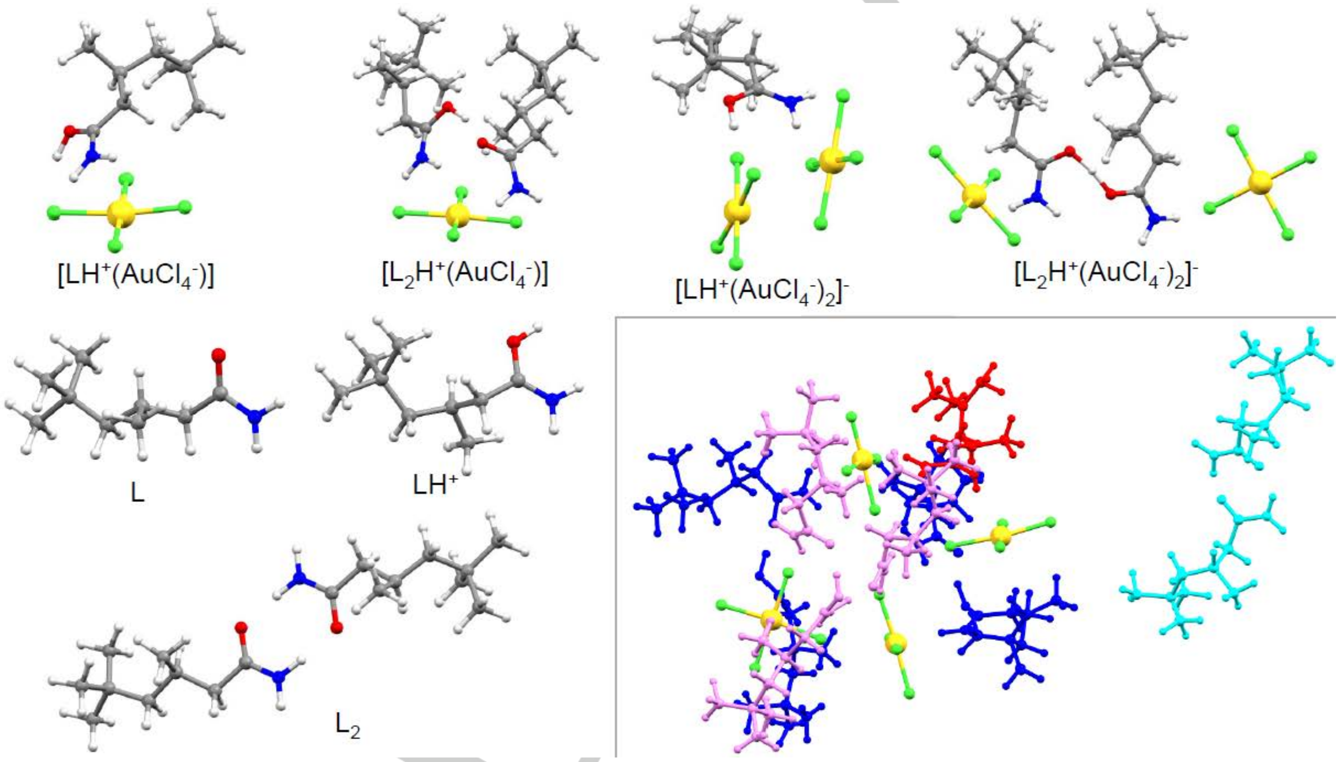

**Figure 4.** Structures of L/$HAuCl_4$ aggregates obtained from QM and MD calculations. The MD calculations on the 10:4 **L**:$HAuCl_4$ system display several amide bridged entities, including [(H**L**)($AuCl_4$)$_2$]$^-$ (red), [(H**L**$_2$)($AuCl_4$)$_2$]$^-$ (dark blue), [(H**L**$_3$)($AuCl_4$)$_2$]$^-$ (magenta), and (**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 between **L** and **L**H$^+$ with the $AuCl_4^-$ anion 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 $AuCl_4^-$ anion,[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 draws 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]

## Experimental Section

Full synthetic and experimental procedures are provided in the Supporting Information.

## Acknowledgements

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**Keywords:** metal recovery • recycling • supramolecular • chemical structure • precious metals

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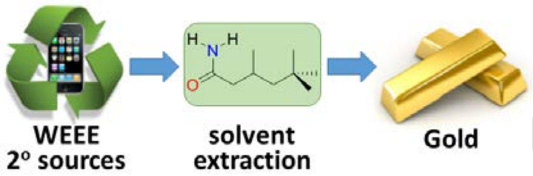
## Entry for the Table of Contents

## COMMUNICATION

A simple primary amide is shown to be an effective reagent for the selective recovery of gold by solvent extraction from a mixture of metals representative of those in a mobile phone and is achieved through the formation of dynamically assembled hydrogen-bonded amide/$AuCl_4$ clusters.



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