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# Selective Extraction of Gold by Niacin

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**ABSTRACT:** Gold recovery using a sustainable and inexpensive method has tremendous environmental and economic implications. We developed a highly cost-effective and sustainable method of gold extraction in which aqueous  $Au^{3+}$  is precipitated selectively as it is complex with the biomolecule niacin, having an overall formula,  $[AuCl_4]^-[2Niacin + H]^+$ , abbreviated as I. This selective precipitation occurs from mixtures of  $Au^{3+}$  with  $Ni^{2+}$ ,  $Cu^{2+}$ , and  $Zn^{2+}$  along with commonly occurring alkali ( $Na^+/K^+$ ) and alkaline earth ( $Mg^{2+}/Ca^{2+}$ ) metal ions. From single-crystal studies, it was confirmed that electrostatic attraction and supramolecular interactions are the reasons for such co-precipitation, which was also confirmed by spectroscopy. Using the method, about 96.5% of gold was extracted in 2 min from electronic waste composed of Au, Cu, and Ni. This method was also employed to extract gold from nanomaterial waste generated in laboratories. Niacin, being inexpensive and renewable, costing ~US\$ 6000 per ton in the local market, the method may be used for cost-effective, selective and sustainable extraction of gold from diverse raw materials.

KEYWORDS: selective recovery of gold, gold-niacin complex, precipitation, electronic/nanowastes, sustainable chemistry

# INTRODUCTION

Noble metals are well-known in view of their exceptional physical and chemical properties.<sup>1–9</sup> Among them, gold is more popular since ancient times. The most universally used method for recovery of gold includes treatment of the ore with highly toxic sodium cyanide, which results in the formation of the soluble coordination complex,  $Au(CN)_2^{-.10,11}$  Gold is also extracted with highly toxic mercury.<sup>12</sup> This is currently the largest source of mercury pollution worldwide.<sup>13,14</sup> In this context, a sustainable, inexpensive, and efficient method for the recovery of gold from mines, as well as chemical and electronic wastes, is highly desirable.

As gold reserves are reducing day by day, it is necessary to recover gold from waste materials including nano- and electronic wastes to meet the growing demand. Gold is one of the precious metals used in electronic devices due to its corrosion resistance and high electrical conductivity. About 300 tonnes of gold are utilized every year in electronic products.<sup>15</sup> A recent report suggested that recovery of metals from electronic waste is more cost-effective than the mining of ores.<sup>16</sup>

Gold-based nanotechnology industries, such as highefficiency compact storage devices, medical diagnostics, photovoltaics, imaging, etc., are expected to expand significantly.<sup>17,18</sup> The worldwide market value of gold nanoparticles (AuNPs) was projected to be 1.34 billion US dollars in 2014.<sup>19</sup> The market for gold-based nanotechnologies is estimated to rise drastically by 2022. As a result, about 20 000 kg of gold will enter the nanotechnology industry by this time.<sup>19</sup>

Many methods have been reported for the recovery of gold. Recently, Yang et al. used pyridine and *N*-bromosuccinimide to leach gold in solution, which could replace the well-known toxic methods of gold extraction like alkaline cyanide.<sup>20</sup> Stoddart et al. utilized different cyclodextrins where  $\alpha$ -cyclodextrin showed efficient binding to AuBr<sub>4</sub><sup>-</sup> to form a precipitate.<sup>21</sup> Liu et al. have synthesized different types of macrocyclic tetralactam receptors, which formed host–guest complexes with square planar complexes of noble metal halides such as AuCl<sub>4</sub><sup>-</sup>, AuBr<sub>4</sub><sup>-</sup>, PdCl<sub>4</sub><sup>-</sup>, etc.<sup>22</sup> Guo et al. selectively

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recovered gold using carbon nitride based on a photoreduction method.<sup>23</sup> Pati et al. recovered gold from nanowastes using Stoddart and co-worker's gold recovery method.<sup>24</sup> Recently, a green method was developed where noble metals like silver and copper were brought into solution from their metallic state using different types of carbohydrates.<sup>25,26</sup> Different types of covalent organic frameworks (COFs) and metal–organic frameworks (MOFs) were also used to capture gold ions selectively from aqueous solutions.<sup>27–29</sup> Cucurbit[6]uril was utilized to extract gold with an efficiency of 99.2% via coprecipitation.<sup>30</sup> Yang et al. captured gold with high adsorption capacity and selectivity using a protein membrane.<sup>31</sup> Love et al. used simple primary amides to extract gold selectively from electronic wastes.<sup>32</sup> Different types of methods used previously in the literature for gold extraction and their efficiencies are listed in Table S1.

Herein, we report the rapid co-precipitation of  $[AuCl_4]^-[2Niacin + H]^+$ , abbreviated as I, in water from gold-containing acidic mixtures by niacin. Electrostatic and supramolecular interactions such as hydrogen bonding and van der Waals (vdW) interactions are responsible for such complexation, as revealed by single-crystal studies. This phenomenon is highly selective for  $AuCl_4^-$  and excludes other commonly coexisting ions such as  $Ni^{2+}$ ,  $Fe^{3+}$ ,  $Pt^{2+}$ ,  $Cu^{2+}$ , and  $Zn^{2+}$  present in such solutions, along with alkali (Na<sup>+</sup>/K<sup>+</sup>) and alkaline earth (Mg<sup>2+</sup>/Ca<sup>2+</sup>) metal ions and Al<sup>3+</sup>. X-ray photoelectron spectroscopy (XPS) and Raman studies also supported the formation of I. Using this method, gold was recovered from various waste samples, including electronic waste.

# MATERIALS AND METHODS

**Chemicals.** Niacin, CuCl<sub>2</sub>·2H<sub>2</sub>O, FeCl<sub>3</sub>·6H<sub>2</sub>O, K<sub>2</sub>PtCl<sub>4</sub>, HAuCl<sub>4</sub>· $3H_2O$ , ZnCl<sub>2</sub>, NaCl, AlCl<sub>3</sub>, and MgCl<sub>2</sub> were purchased from Sigma-Aldrich and used without further purification. Ethanol, HCl, and HNO<sub>3</sub> were purchased from Rankem. Milli-Q water was used throughout the experiment.

**Crystallization of I.** Briefly, 1 mL of  $HAuCl_4$  (27 mM) and 1 mL of a saturated solution of niacin (125 mM) were mixed. NaCl (100 mg) was added to slow down the precipitation. The solution was kept for slow evaporation at room temperature. After 2 days, yellow crystals suitable for X-ray crystallographic analysis were obtained.

**Crystallization of Cu(H<sub>2</sub>O)**<sub>4</sub>(Niacin)<sub>2</sub>. Briefly, 1 mL of CuCl<sub>2</sub> (27 mM) and 1 mL of a saturated solution of niacin (125 mM) were mixed. The solution was kept for slow evaporation at room temperature. After 3 days, blue crystals were obtained. The crystal structure of this system has been reported previously.<sup>33</sup>

**Instrumentation.** X-ray Crystallography. Single-crystal X-ray data collection was performed using a Bruker D8 VENTURE APEX3 diffractometer using Mo K $\alpha$  ( $\lambda = 0.71073$  Å) radiation. Indexing was performed using APEX3. The program, SAINT-v8.37A, was used for integrating the data collection frames. Absorption correction was performed by a multiscan method implemented in SADABS. The structure was solved using SHELXT-2018/2 and refined using SHELXL-2018/3 (full-matrix least-squares on F2) contained in WinGX v2018.3. Crystal data and refinement conditions are listed in Table S1. The crystal data have been deposited in the Cambridge Structural Database (CCDC no. 1989872).

More details on instrumentation are provided in the Supporting Information (SI).

#### RESULTS AND DISCUSSION

Niacin is nicotinic acid and is a form of vitamin  $B_3$ , an essential human nutrient. It is produced industrially, and the sales were reported to be 31 000 tons in 2014.<sup>34</sup> Upon addition of a

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saturated solution of niacin (125 mM, 2 mL) in water to an aqueous solution (1 mL, 27 mM) of  $HAuCl_4$  at room temperature, a light yellow precipitate, labeled as I, appeared within a few minutes (Figure 1). The initial gold concentration



**Figure 1.** Formation and co-precipitation of I after mixing a saturated solution (2 mL) of niacin with HAuCl<sub>4</sub> (27 mM, 1 mL). The light yellow of the liquid meniscus in the bottle on the right is due to reflection from the precipitate.

in this experiment was about 5139 ppm. After addition of niacin, the concentration of gold was reduced to 2.9 ppm. Therefore, about 99.9% of gold was recovered using this method (Table S2). Data corresponding to the selectivity for gold using this precipitation method are presented later.

The  $pK_a$  values of niacin are 2.0 and 4.85. Gold is generally extracted in acidic solutions, and the pH of the HAuCl<sub>4</sub> solution used was 1. After addition of niacin, the pH of the solution became 3. It was important to ensure that such a process occurs even at low concentrations for the process to be useful for gold recovery. It was confirmed that niacin had the ability to precipitate gold down to 320 ppb (Table S2), although complete precipitation was not observed.

Compound I was crystallized using slow evaporation of water. The crystal structure of I is presented in Figure 2A(i), where two niacin molecules interact with one  $AuCl_4^-$ . A simple representation of the crystal structure is shown in Figure 2A(ii). The crystal system is monoclinic with a space group P21/n (Table S3 and Figure 2B). Expanded views of the unit cell in X, Y, and Z directions are presented in Figure S1. The layered structure of I along the Y axis is evident from Figure 3A. In the crystal, AuCl<sub>4</sub><sup>-</sup> and a dimer of niacin molecules (with a proton link) act as the anion and the cation, respectively. The overall formula of the complex is  $[AuCl_4]^-[2Niacin + H]^+$ . The proton is shared between two carboxylic groups of two niacin molecules (Figure 2A). Two  $pK_a$  values (mentioned above) support the zwitterionic structure of niacin in the crystal structure, as the pH of the solution was 3. UV-vis spectra of [AuCl<sub>4</sub>]<sup>-</sup> (blue) and I (red) in dimethylformamide  $(\overline{D}MF)$  were obtained (Figure S2). A characteristic transition at around 320 nm was seen in I, which supported the presence of [AuCl<sub>4</sub>]<sup>-</sup> in the crystal structure. Thus, two niacin molecules are required to precipitate one molecule of AuCl<sub>4</sub><sup>-</sup>. The required amount is about 1.25 g of niacin (equivalent to US\$ 0.0084) per gram of gold.

Looking at the chemical formula, it can be confirmed that electrostatic interactions are present in the crystal structure. Strong H-bonding and vdW interactions are also responsible



**Figure 2.** (A) (i) Crystal structure of I and (ii) Chemdraw representation of I. Color codes for the atoms are shown nearby. Note that the color of the H atom is white. (B) Expanded view  $(5 \times 5 \times 5)$  of the unit cell of I. (C) Van der Waals interactions between halide ions of adjacent  $[AuCl_4]^-$  units. (D) H-bonding interaction between O atom of the carboxylic group and H attached to N.



Figure 3. (A) Packing view of the crystal from the Y axis showing a layered structure. (B) Different noncovalent interactions such as H…Cl, Cl…Cl, Cl…Cl, and H…O present in the unit cell, with specific distances.

for such a complexation. VdW interactions between Cl atoms in the lattice are presented in Figure 2C, which operate in the diagonal direction of the unit cell. Similarly, H-bonding interactions between the O atom of the carboxylic group and H connected to N are presented in Figure 2D. Different types of H-bonding interactions were observed in the crystal (Figure 2D). Such kinds of self-organized and patterned structures are reminiscent of  $\beta$ -sheet and  $\alpha$ -helix in proteins and also in the recently reported Au<sub>103</sub> and Au<sub>246</sub> nanoclusters.<sup>35–37</sup> Expanded views of [AuCl<sub>4</sub>] and [2Niacin + H]<sup>+</sup> in *X*, *Y*, and *Z* directions are presented in Figures S3 and S4, respectively. Different kinds of noncovalent interactions present in the crystal are shown in Figure 3B with specific distances. Noncovalent interactions between the hydrogen atoms of the aromatic ring and chlorines are also present in the crystal (Figure 3B).

To understand the distinct difference in the gold complex, the crystal structure of niacin with copper was also obtained (Figure S5). This complex dissolves in water, and its structure is already known.<sup>33</sup> The overall formula of the complex is  $Cu(H_2O)_4(Niacin-H)_2$ . Here, copper formed a coordination bond with niacin through the N center of the heterocycle. There is a negative charge on the oxygen atom of the carboxylic acid group of niacin. This causes the overall charge to be zero. Such covalent bond formation is absent in I because gold is a soft center while N and O are hard centers in niacin. The presence of various types of noncovalent interactions that are specific in the case of [AuCl<sub>4</sub>]<sup>-</sup> resulted in the precipitation of the complex. Complexes of niacin and such molecules with precious and transition metals have been reported, 38,39 although the structure of the gold complex and its selective precipitation have not been studied.

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Figure 4. XPS data of oxygen (A), nitrogen (B), and carbon (C). The shift in the binding energies confirmed possible interactions in I. Data for pure niacin are also presented. The expanded Raman spectra of I are shown in Figure 3(D,F). (D) C=N and C=O stretching in I and niacin. About 12 and 8 cm<sup>-1</sup> shifts were observed for I compared to niacin alone, for C=N and C=O, respectively. (F) Au-Cl stretching in I and HAuCl<sub>4</sub>.

An XPS study was performed to reveal the interactions in the complex. Significant changes in binding energies were observed for oxygen and nitrogen in the complex, compared to free niacin. In the case of O 1s, a new peak appeared for I along with a ~0.5 eV chemical shift, compared to free niacin (Figure 4A), which could be due to the sharing of hydrogen between carboxylic groups of the two niacin molecules. Similarly, a chemical shift of about 1.6 eV was observed for N 1s in the complex compared to free niacin (Figure 4B). This could be due to the presence of a positive charge on N and H-bonding interactions (Figure 2D). These data confirmed the presence of strong interactions in the complex. The binding energy of C 1s was also influenced by these interactions (Figure 4C).

To get further insights into bonding, Raman spectroscopy was performed. Peak shifts of 12 and 8 cm<sup>-1</sup> were observed for C=N and C=O vibrations, respectively, in I compared to free niacin, which is also supported by XPS and single-crystal XRD data (Figure 4D). There were two types of Au-Cl stretching for HAuCl<sub>4</sub>. This is due to Au-Cl (348 cm<sup>-1</sup>) in AuCl<sub>4</sub><sup>-</sup> and Au-Cl (326 cm<sup>-1</sup>) in AuCl<sub>3</sub>(OH)<sup>-</sup> (Figure 4F, HAuCl<sub>4</sub>). Note that the spectrum of HAuCl<sub>4</sub> was measured in ambient air, which resulted in the water of hydration as the salt is hygroscopic. As the crystal structure of I does not have any OH attached to gold, only one Au-Cl stretching band appeared (Figure 4F). Both XPS and Raman spectroscopy are in good agreement with the single-crystal XRD data of I.

To test the selectivity of the process, an equimolar mixture of HAuCl<sub>4</sub>, CuCl<sub>2</sub>, and ZnCl<sub>2</sub> (27 mM each) was prepared by mixing the corresponding salts. After adding a saturated solution of niacin, precipitation of the gold complex occurred immediately, but copper and zinc were still in solution (Figure S6). The precipitate was examined using scanning electron microscopy/energy-dispersive spectroscopy (SEM/EDS) mapping to confirm the efficiency of the method for selectivity toward gold. SEM images revealed the formation of mesoflower-type of structures for the precipitate. SEM images of the precipitate are provided in Figure S7A,B. SEM/EDS confirmed the presence of N, O, Cl, Au, Cu, and Zn (Figure S7D). Au (10.11%), Zn (0.51%), and Cu (0.12%) were quantified by EDS mapping from the co-precipitate. About 94% pure gold was extracted using this method after one-time treatment of niacin. The elemental analysis of the precipitate is provided in Figure S7D. Elemental maps of copper, gold, and zinc are shown in Figure S7E. A detailed analysis of the solution after precipitation by inductively coupled plasma mass spectrometry (ICP MS) also confirmed the efficiency of extraction (Table S4). Similarly, niacin solution (125 mM) was added separately

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Figure 5. Gold-recovery flow chart using niacin.



Figure 6. Recovery of gold from a central processing unit. (A) The CPU was treated with HCl and HNO<sub>3</sub> (3:1) to dissolve the metals. The resulting solution (blue) was treated with a saturated solution of niacin yielding a precipitate. (B) Percentage removal of various metals evaluated by ICP MS.

to 27 mM solutions of  $PtCl_4$ ,  $AlCl_3$ , and  $FeCl_3$  at pH 3 (Figure S8). No precipitation was observed.

A process of gold recovery using this approach is presented in Figure 5. After precipitation, I can be separated from impurities by filtration. The recovered I can be reduced using a reductant such as sodium metabisulfite  $(Na_2S_2O_5)$  to recover gold metal (see above). The remaining residual gold in the impurities and unused niacin (liquid phase) can be recycled. Preconcentration is necessary for precipitation when the concentration falls below 320 ppb, as mentioned earlier.

Gold was recovered from electronic waste and laboratory nanowaste. A used central processing unit (CPU) of a computer was treated with 5 mL of aqua regia (HCl and HNO<sub>3</sub> in a 3:1 volume ratio) to dissolve the metals (Figure 6A). The solution was heated for 2 h to remove excess acids, yielding 2 mL of a blue solution. More amounts of niacin were required to adjust the pH to 3 if excess acid was present in the solution. Note that precipitate (I) is soluble in HCl. To avoid such issues, excess acids were removed. The solution contained 770 ppm of Ni<sup>2+</sup>, 22 320 ppm of Cu<sup>2+</sup>, and 25 ppm Au<sup>3+</sup> by ICP MS analysis (Table S5). A saturated solution of niacin (125 mM) in tap water (4 mL) containing common ions was added, and the pH of the solution changed to 3. After the treatment with niacin, about 96.5% of gold was recovered within 2 min (Table S5). The removal of different metals is presented in Figure 6B. Hence, it is established that niacin is highly efficient for the recovery of gold from electronic wastes.

A simulated nanowaste consisting of citrate-reduced AuNPs was synthesized. The colloidal AuNPs were precipitated using NaCl-induced aggregation, and the precipitate was dissolved using aqua regia. The niacin-based separation was carried out as before. The clear yellow solution became turbid just after addition of niacin, and the pH of the solution changed to 3. The reaction mixture was filtered through a Whatman filter paper. The precipitate was added to about 50 mM solution of Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> to recover gold. All stages involved in the recovery process were performed at room temperature (Figure S9).

Recovery was also attempted under certain extreme conditions. About 1 ppm of the gold solution was prepared in the presence of 160 000 ppm NaCl and 50 000 ppm MgCl<sub>2</sub>. This method also has the ability to extract gold in such conditions (Table S6). This indicated that this process could be effective in collecting gold from extreme saline solutions.

The solvent can play a key role in such a process. An equimolar mixture of  $HAuCl_4$  and  $CuCl_2$  (27 mM) in ethanol (1 mL) was prepared. In this case, precipitation of the copperniacin complex was observed, while gold was retained in the solution, as shown in Figure S10. Separation of  $HAuCl_4$  and  $CuCl_2$  can also be achieved in ethanol using niacin. Further optimization of the method and experimental parameters is ongoing in our laboratories to expand this process to more realistic applications.

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#### CONCLUSIONS

In summary, we discovered a method for the fast precipitation of gold in water by a simple biomolecule, niacin. The crystal structure of I revealed the presence of strong electrostatic, Hbonding, and vdW interactions in the crystal. Such types of interactions could be the main reason for selective precipitation of I. Raman spectroscopy and XPS were employed to support the single-crystal XRD data. This method is highly selective for gold. Trace amounts of gold could be recovered from complex mixtures of ions in water. This method was employed for the selective extraction of gold from electronic and chemical wastes. Extraction of gold may be achieved using  $HCl/H_2O_2^{30}$  or pyridine and *N*-bromosuccinimide<sup>20</sup> instead of aqua regia, and Au<sup>3+</sup> in the solution may be precipitated with niacin, making the process more sustainable.

# ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.0c07409.

Experimental details; packing of the crystal structure; separation of gold; SEM images and elemental mapping; recovery from nanowaste; crystal data and CIF files; and X-ray crystallographic data of I (PDF)

Gold\_niacin (CIF)

Copper\_niacin (CIF)

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#### Notes

The authors declare no competing financial interest.

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