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Abstract: The recycling of tantalum (Ta) is becoming increasingly important due to the criticality of its supply from a conflict mineral. It is used extensively in modern electronics, such as in capacitors, and so electronic waste is a potentially valuable secondary source of this metal. However, the recycling of Ta is difficult, not least because of the challenges of its leaching and subsequent separation from other metals. In this work, we show that Ta(V) halides, such as $TaCl_5$ and TaF_5, which can potentially be accessed from Ta metal upon acid halide leaching, can be recovered by solvent extraction using a simple primary amide reagent. The need for high halide concentrations in the aqueous phase implies the formation of the hexahalide salts $[TaX_6]^-$ (X = F, Cl) and that an anion-swing mechanism operates. While extraction of the fluorides is poor (up to 45%), excellent extraction under chloride conditions is found (>99%) and presents an alternative route to Ta recycling.

Keywords: tantalum; solvent extraction; WEEE; recycling; chemical separation

1. Introduction

The third-row transition metal element tantalum is critical to modern consumer technologies, finding extensive use as a component in capacitors for the microelectronics industry. Approximately 40% of the world's tantalum production is used in this application, but its recycling is limited, at only 1% [1]. This is surprising, as electronic waste (e-waste) is becoming one of the fastest growing waste categories worldwide [2,3]. Furthermore, it was found that metal recovery from secondary resources is gradually becoming more cost-effective than virgin mining, especially as the volume of e-waste is projected to increase substantially; over the next few decades, new technologies will become cheaper and more accessible, driving up the rate of device obsolescence [4,5]. With the best estimates suggesting that only 20% of e-waste is properly recycled [5], the development of sustainable, efficient hydrometallurgical techniques for the recovery of these critical resources offers huge potential to reduce the environmental impact of e-waste, lower energy costs, and move towards a more circular economy [6]. However, this depends on the availability of inexpensive reagents for both leaching and separation processes.

The status of tantalum as a metal derived from a conflict mineral [7], combined with its low abundance in the earth's upper crust means there is a need to design a sustainable closed-loop process to recycle tantalum from waste capacitors. Due to its very low solubility in typical mineral acids such as HCl, H_2SO_4, and HNO_3 compared with other d-block elements, current hydrometallurgical processes for tantalum involve the use of highly corrosive and toxic solutions of concentrated HF, combined with H_2SO_4 or HCl in order to generate soluble anionic metalates, such as $[TaF_6]^-$ and $[TaF_7]^{2-}$ [8–11].

As such, it is evident that there is a need to develop more sustainable processes which can not only efficiently recycle tantalum from secondary sources but do so using milder reagents [12–15].

Recent efforts towards fluoride-free tantalum recovery processes have focused on alkaline matrices to generate polyoxotantalates that are recovered at elevated temperatures by solvent extraction [16–18]. Ionic liquids (ILs) have also been investigated as potential extractants for tantalum recovery. Methylisobutylketone (MIBK)-derived ILs were shown to efficiently extract $[TaF_7]^{2-}$ from concentrated sulfuric acid solutions with excellent selectivity for tantalum over other, potentially interfering metals [19]. In this case, it was thought that this enhanced extraction compared with MIBK alone could be due to greater solubility of water in the IL phase, overcoming the prerequisite to displace the hydration sphere prior to transport of the metalate into nonpolar solvents.

To our knowledge, there are very few reports that describe the extraction of tantalum from chloride-based media; acids such as HCl were tested in the extraction of TaF_5, but in these cases, significant solubility issues were seen [20]. Despite the limited speciation data available for tantalum in halide acids, previous theoretical studies have postulated that $TaCl_5$ could behave in a similar manner to TaF_5 in aqueous solution, so forming halidometalates such as $TaCl_6^-$ in the presence of excess chloride ion [21,22].

We have shown previously that the primary amide, **L** (Figure 1), forms hydrophobic supramolecular assemblies with metalates, including $[AuCl_4]^-$, which allows for e-waste separations using anion-exchange solvent extraction processes [23]. In this work, we describe the transport of tantalum as its halometalate $TaCl_6^-$ into a toluene organic phase using the simple primary amide reagent **L** from acidic solutions in the presence of chloride. Subsequent back extraction (stripping) of the metalate into a fresh aqueous phase is possible with water or dilute HCl.
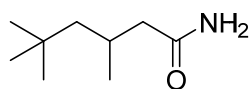

Figure 1. Structure of 3,5,5-trimethylhexanamide **L**.

2. Experimental

2.1. Materials and Instruments

Unless otherwise stated, all solvents and reagents were purchased from Sigma-Aldrich, Fisher scientific UK, Alfa Aesar (Heysham, UK), Acros Organics (Geel, Belgium), or VWR international (Lutterworth, UK) and used without further purification. Deionised water was produced using a Milli-Q purification system. The syntheses of 3,5,5-trimethylhexanamide, **L** and $[H(C_{11}H_{23}NO)_2]_2[SnCl_6]$ were carried out according to the literature [23,24].

ICP-OES analysis was carried out on a Perkin Elmer Optima 8300DC Inductively Coupled Plasma Optical Emission Spectrometer. Samples in 1-methoxy-2-propanol were taken up by peristaltic pump at a rate of 2.0 mL min^{-1} into a Gem Tip cross flow nebuliser and a glass cyclonic spray chamber. Argon plasma conditions were: 1500 W RF forward power; argon gas flows of 17, 1.0, and 0.50 L min^{-1} for plasma, auxiliary, and nebuliser flow, respectively. ICP-OES calibration standards were obtained from SCP science.

Karl-Fischer water content determinations were carried on a Metrohm 831 KF Coloumeter with Hydranal Coulomat AG as the reagent mixture.

2.2. Preparation of TaCl$_5$ and TaF$_5$ Solutions

A 0.12 M stock solution of TaX$_5$ (X = F, Cl) was prepared in 12 M HCl at 25 °C. This stock solution was then diluted to 0.01 M TaX$_5$ in 1 M HCl with varying solutions of lithium chloride in deionised water. A colourless precipitate formed over several weeks in dilute HCl solutions of TaCl$_5$, and so solutions were used immediately after diluting from the 12 M stock solution. A colourless precipitate

formed overnight from stock solutions of TaF$_5$ in 12 M HCl, and so solutions were therefore diluted and used immediately.

2.3. General Solvent Extraction Procedure

An aqueous solution of TaX$_5$ (0.01M, X = F, Cl) in 1 M HCl, 0-11 M LiCl (2 mL) was contacted with a toluene organic phase (2 mL) containing 3,5,5 trimethylhexanamide **L** (0.1 M) and stirred (1 h, 1000 rpm, 25 °C). The phases were separated physically, and samples from the organic phase taken and diluted with 1-methoxy-2-propanol for ICP-OES analysis. Samples of the stock solution were analysed by ICP-OES to confirm mass balance and percentage extraction. Samples of the post extraction aqueous phase could not be analysed by ICP-OES due to the high salt content suppressing the tantalum wavelengths. Samples from relevant phases were also taken for water concentration determination and NMR analysis as required.

2.4. NMR Data for [H(C$_{11}$H$_{23}$NO)$_2$]$_2$[SnCl$_6$].

^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ_H 10.17 (s, broad, 1H), 3.27 (s, 6H, NCH$_3$), 2.76 (dd, 2H, CH$_2$CO, *J* = 14.2, 6.7 Hz), 2.65 (dd, 2H, CH$_2$CO, *J* = 14.2, 8.7 Hz), 2.18-2.08 (m, 2H, CH(CH$_3$)), 1.32 (dd, 2H, CH$_2$(CH$_3$)$_3$, *J* = 14.1, 3.3 Hz), 1.21 (dd, 2H, CH$_2$(CH$_3$)$_3$, *J* = 14.1, 7.1 Hz), 1.05 (d, 6H, CH(CH$_3$), *J* = 6.6 Hz), 0.90 (s, 18H, C(CH$_3$)$_3$).

^{13}C{^{1}H} NMR (C$_6$D$_6$, 126 MHz, ppm): δ_C 176.34, 50.65, 41.33, 38.90, 31.09, 29.99, 28.12, 22.39.

3. Results and Discussion

3.1. Solvent Extraction of Tantalum Pentachloride

The dissolution of TaCl$_5$ in HCl only occurs at high concentrations of HCl (12 M). Initial solvent extraction procedures were therefore developed by contacting a 0.1 M solution of **L** in toluene with a 0.01 M solution of TaCl$_5$ in 12 M HCl. However, at this high HCl concentration, no appreciable tantalum extraction is seen, and it is likely that the amide **L** is instead protonated and transported into the aqueous phase (Figure 2). Upon addition of LiCl to the TaCl$_5$ solution at 12 M HCl, the concentration of Cl$^-$ is increased further, although this results in the out-gassing of HCl from the solution. Under these conditions, low to moderate quantities (30%–50%) of Ta are transferred to the organic phase (Figure 2), although **L** is likely still being lost to the aqueous phase as a result of its high acidity.

To minimize the loss of **L** to the aqueous phase while maximising Ta transfer, the acid concentration was diluted to 1 M HCl in conjunction with varying total chloride concentration through the addition of LiCl; no precipitation of Ta is seen under these conditions. In extraction experiments, no loss of **L** from the organic phase is seen (by ^{1}H NMR spectroscopy) and Ta is completely extracted between 7 and 11 M LiCl (Figure 3). As tantalum begins to be extracted at 3–6 M LiCl, small quantities of a precipitate forms which dissolve at higher LiCl concentrations. Quantitative ^{1}H NMR analysis of this third phase dissolved in deuterated dimethyl sulfoxide shows that no **L** from the organic phase is present, and ICP-OES analysis shows it comprises tantalum and lithium only, so is potentially LiTaCl$_6$ or a similar complex. Furthermore, **L** does not transfer significant quantities (<10 ppm) of Li into the organic phase, as the concentrations of **L** or LiCl are varied.
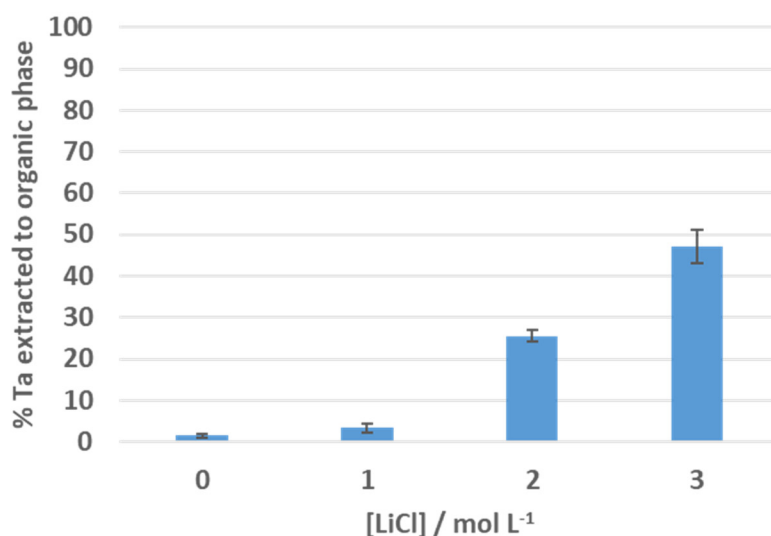
Figure 2. Extraction of tantalum from aqueous solutions of $TaCl_5$ in 12 M HCl with varying concentrations of LiCl into a toluene solution of **L**. Conditions: $TaCl_5$ (0.01 M) in 12 M HCl with 0–3 M LiCl (2 mL) stirred with **L** (0.1 M) in toluene (2 mL); phases contacted for 1 h at RT with magnetic stirring. Experiments performed in duplicate and reported as an average.
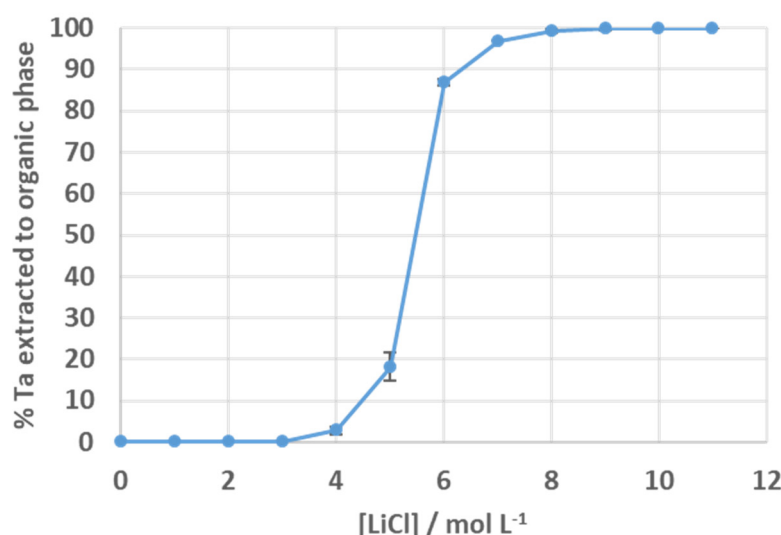

Figure 3. Transport of tantalum from aqueous solutions of $TaCl_5$ in 1 M HCl with varying concentrations of LiCl into a toluene solution of **L**. Conditions: 0.01 M $TaCl_5$ diluted in 1 M HCl, 1–11 M [LiCl] (2 mL), stirred with **L** (0.1 M) in toluene (2 mL); phases contacted for 1 h at RT with magnetic stirring. Interpolation used to aid the eye only. Experiments performed in duplicate and reported as averages.

The need for high levels of LiCl to promote Ta extraction suggests that either the formation of the anion $TaCl_6^-$ is a prerequisite for transport into the organic phase, or a salting-out effect is operating. To understand this, experiments were undertaken which vary the concentration of BF_4^- (using $NaBF_4$) as a non-coordinating anion instead of Cl^- and show that negligible Ta transfer to the organic phase occurs. This confirms that $TaCl_5$ is not simply "salting-out" to the organic phase and that a source of chloride is necessary to drive $[TaCl_6]^-$ formation; even so, the high salt content may aid extraction by reducing the concentration of free water in the aqueous phase [25]. Importantly, Ta was readily back-extracted (~80%) from the organic phase to a fresh aqueous phase with either water or 1 M HCl; a white precipitate forms with water, while no precipitate is immediately observed in the strip solution with 1 M HCl.

3.2. Structure Elucidation

From the data above, it is apparent that Ta is transported into the organic phase as its ion pair [H**L**][**L**]$_n$[TaCl$_6$]. To further interrogate the organic-phase speciation, slope analysis of Log D against Log [**L**] was carried out (Figure 4), which results in a **L**:Ta ratio of approximately 2 (slope of 1.71 ± 0.13), suggesting the formation of an ion pair such as [H**L**$_2$][TaCl$_6$] in the organic phase. This type of behaviour is similar to that seen previously for Au extraction using **L** in which experimental and computational analysis showed that two amides chelate a proton through the oxygen atoms to form a charge-diffuse cation that can interact with diffusely charged metalate anions through classical (N-H$\cdots$X) and non-classical (C-H$\cdots$X) hydrogen bonds [23,24].
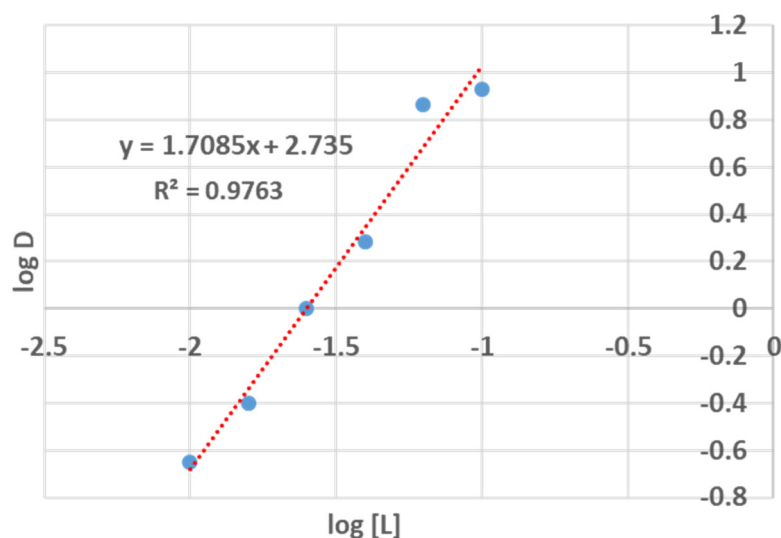

Figure 4. Slope analysis for the transport of Ta with **L**. Conditions: 2 mL 0.01 M TaCl$_5$ in 1 M HCl, 11 M LiCl, contacted with 2 mL of 0.01 to 0.1 M **L** in toluene for 1 h at RT with magnetic stirring.

Direct structural characterisation of the extracted species has so far proven inconclusive, although ^{1}H NMR studies provide an indication as to how the receptor [H**L**$_2$]$^+$ is interacting with the metalate (Figure 5). As the concentration of tantalum in the organic phase increases, the two signals at 4.61 and 6.46 ppm associated with the NH$_2$ protons coalesce and shift downfield to 9.63 ppm. Variable temperature NMR spectra (Figure S1) reveal an additional signal that is attributable to associated water or hydronium, which coalesces with the amide protons upon Ta loading. There is also a large downfield shift of the signals at 1.59 and 1.87 ppm, associated with the diastereotopic CH$_2$ protons adjacent to the amide group, to 2.49 and 2.56 ppm respectively. These changes in the ^{1}H NMR spectra for Ta-loaded **L** are similar to those seen for the solid third phase formed between [SnCl$_6$]$^{2-}$ and a tertiary amide version of **L** (Figures S2 and S3). In this latter case, the solid-state structure showed that the two amide ligands chelate the single proton through the amido oxygen atoms, with the cation subsequently interacting with the outer-sphere of the [SnCl$_6$]$^{2-}$ octahedron through non-classical C-H hydrogen bonds [24,26,27]. The similarity in the ^{1}H NMR spectra for Ta/**L**, and also a relatively large downfield shift of the carbonyl carbon from 174 ppm to 180 ppm in the ^{13}C NMR spectrum (Figure S4) upon Ta loading strongly suggest that a similar structure is formed in the organic phase, with no direct interaction of the amido-oxygen donor with the Ta centre; i.e., an amide complex such as TaCl$_5$(**L**) is not formed.
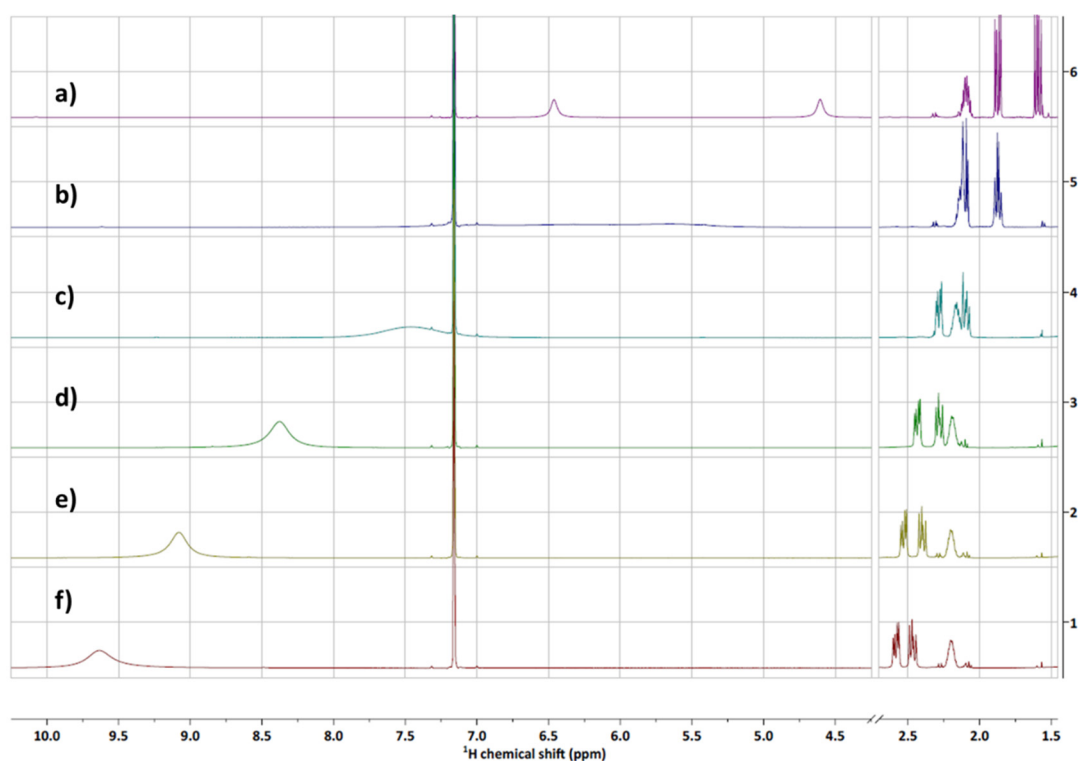
Figure 5. ^{1}H NMR spectra of (**a**) 0.1 M **L** in C_6D_6; then 0.1 M **L** in C_6D_6 after contact with 0.01 M $TaCl_5$ in 1 M HCl and: (**b**) 5 M LiCl; (**c**) 6 M LiCl; (**d**) 7 M LiCl; (**e**) 8 M LiCl; (**f**) 9 M LiCl.

Karl-Fischer titrations were undertaken to determine the role of water in the extracted species. It is seen that as more tantalum transfers to the organic phase, the concentration of water does not significantly increase, ruling out a micellar extraction mechanism (Figure 6). However, at even higher concentrations of **L** where the concentration of tantalum in the organic phase does not change, more water is transported, suggesting that water transport into the organic phase is associated with the concentration of **L**.
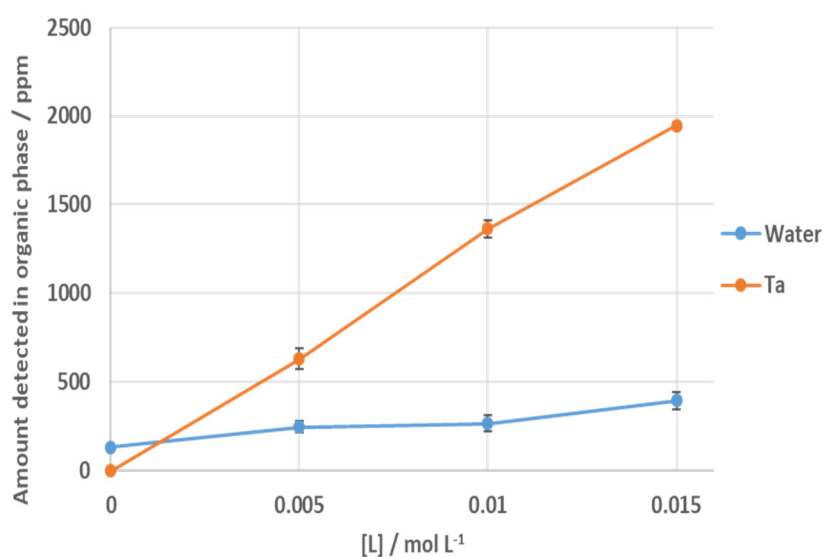

Figure 6. Karl-Fischer water measurements (1.0 mL samples from organic phase analysed for H_2O; concentrations of Ta and H_2O are on the same scale). Interpolation used to aid the eye only. Experiments performed in duplicate and reported as an average.

During the slope analysis and Karl-Fischer titrations, a solid precipitate is seen at concentrations of **L** below 0.02 M, with more precipitate forming at lower concentrations of **L**. As with above, quantitative analysis of the organic phases by ^{1}H NMR spectroscopy shows that the ligand concentration remains constant (i.e., no loss of **L** to solid 3rd phase or the aqueous phase); furthermore, this phenomenon was irreproducible in the absence of either TaCl$_5$ or **L**.

3.3. Solvent Extraction of Tantalum Fluoride

As current commercial processes for tantalum recovery involve the use of hydrogen fluoride to leach the metal as its fluoride salts, it is important to compare how the chloride process described above would compare with its fluoride equivalent. However, all attempts to extract TaF$_5$ instead of TaCl$_5$ were unsuccessful under the conditions used, with negligible extraction seen between 0–12 M HCl and 0–18 M H$_2$SO$_4$ with **L**; at high acid concentrations **L** is lost to the aqueous phase. When the HCl concentration is 1 M and the concentration of LiCl is varied, optimal extraction of the tantalum is 45% at 5 M LiCl before trending downwards upon further increase of LiCl (Figure 7).
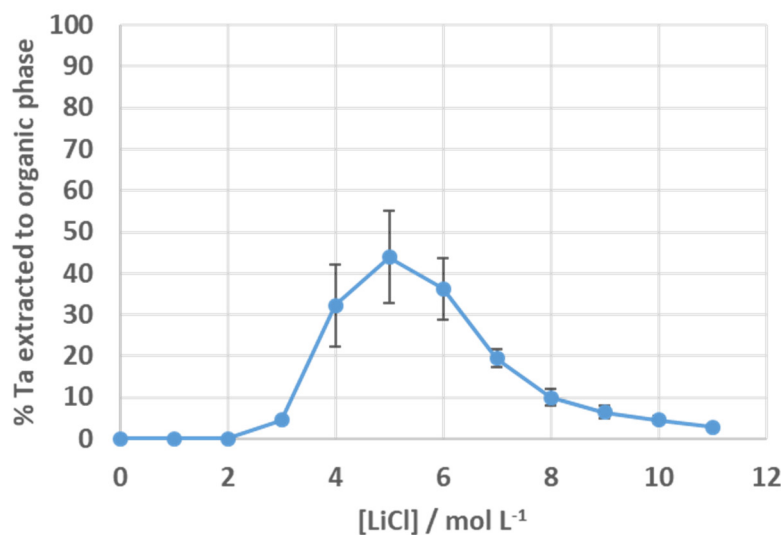

Figure 7. Extraction of tantalum from aqueous solutions of TaF$_5$ in 1 M HCl with varying concentrations of LiCl into a toluene solution of **L**. Conditions: 0.01 M TaF$_5$ diluted in 1 M HCl, 1–11 M [LiCl] (2 mL), stirred with **L** (0.1 M) in toluene (2 mL); phases contacted for 1 h at RT with magnetic stirring. Interpolation used to aid the eye only. Experiments performed in duplicate and reported as averages.

In these experiments, no solid third phase forms at any stage, and quantitative ^{1}H NMR experiments confirm that no amide is lost to the aqueous phase. These data contrast with the experiments using TaCl$_5$, perhaps because potential fluorometalates such as [TaF$_6$]$^-$ or [TaF$_5$Cl]$^-$ that would be formed in the aqueous phase, are smaller and have more charge dense anions with respect to [TaCl$_6$]$^-$, and therefore will have higher hydration energies. Poor Ta extraction at high LiCl concentrations is likely to result from the competitive transport of chloride by **L** into the organic phase.

4. Conclusions

The simple primary amide, **L**, shows excellent performance for tantalum recovery by solvent extraction under high chloride conditions. The extraction mechanism is identified as similar to that seen for the recovery of gold by **L,** in which charge-diffuse protonated receptors are formed that preferentially interact with the charge diffuse monoanionic metalate [AuCl$_4$]$^-$ [23,24]. ^{1}H and ^{13}C NMR data are consistent with a strong outer-sphere interaction between [H**L**$_2$]$^+$ and [TaCl$_6$]$^-$. In contrast, amide **L** is a poor reagent of choice when attempting to transport TaF$_5$ under high chloride conditions, likely due to a combination of competitive chloride extraction and significantly weaker interactions

between $[HL_2]^+$ and more charge-dense species in the aqueous phase, such as $[TaF_5Cl]^-$. This latter aspect is evident from a comparison of the X-ray crystal data for $[TaCl_6]^-$ and $[TaF_6]^-$, which shows a 1 A decrease in the diameter of the Ta complex moving from chloride to fluoride [28,29]. It is therefore anticipated that **L** would be a poor extractant for Ta when employed under solely fluoride conditions, in which species such as $[TaF_6]^-$ and even the dianion $[TaF_7]^{2-}$ may be present. Even so, the process described here represents an alternative, fluoride-free route to recycling Ta from waste electronics, using milder reagents than the current commercial methods.

Supplementary Materials: The following are available online at http://www.mdpi.com/2075-4701/10/3/346/s1. Figure S1: Variable temperature ^{1}H NMR spectra of 0.1 M **L** in d_8-toluene after contact with 0.01 M $TaCl_5$ in 1 M HCl and 9 M LiCl from $-40\,^\circ$C to 60 $^\circ$C. Presence of additional water or hydronium signal is revealed amongst the signals assigned to the amide protons (between 8.5 ppm and 10 ppm) when the sample is cooled. Y-axes are offset for clarity. Figure S2: ^{1}H NMR spectra of a $C_{11}H_{23}NO$ (top) and $[H(C_{11}H_{23}NO)_2]_2[SnCl_6]$ (bottom) in $CDCl_3$. Figure S3: $^{13}C\{^1H\}$ NMR spectra of a $C_{11}H_{23}NO$ (top) and $[H(C_{11}H_{23}NO)_2]_2[SnCl_6]$ (bottom) in $CDCl_3$. Figure S4: $^{13}C\{^1H\}$ NMR spectra of 0.1 M **L** in C_6D_6 (top) and 0.1 M **L** in C_6D_6 after contact with 0.01 M $TaCl_5$ in 1 M HCl and 9 M LiCl (bottom).

References

1.　European Commission: Critical raw materials fact sheets. Available online: https://ec.europa.eu/info/index_ en (accessed on 13 January 2020). [CrossRef]

2.　Ogunseitan, O.A.; Schoenung, J.M.; Saphores, J.D.M.; Shapiro, A.A. The electronics revolution: From E-wonderland to E-wasteland. *Science* **2009**, *326*, 670–671. [CrossRef]

3.　Rao, M.D.; Singh, K.K.; Morrison, C.A.; Love, J.B. Challenges and opportunities in the recovery of gold from electronic waste. *RSC Adv.* **2020**, *10*, 4300–4309. [CrossRef]

4.　Zeng, X.; Mathews, J.A.; Li, J. Urban mining of E-waste is becoming more cost-effective than virgin mining. Environ. *Sci. Technol.* **2018**, *52*, 4835–4841. [CrossRef]

5.　Baldé, C.P.; Forti, V.; Gray, V.; Kuehr, R.; Stegmann, P. The Global E-waste Monitor-2017, 2017. United Nations University (UNU), International Telecommunication Union (ITU) & International Solid Waste Association (ISWA), Bonn/Geneva/Vienna. Available online: https://www.itu.int/en/ITU-D/Climate-Change/Documents/ GEM%202017/Global-E-waste%20Monitor%202017%20-%20Executive%20Summary.pdf (accessed on 13 January 2020).

6.　Velenturf, A.P.M.; Jopson, J.S. Making the business case for resource recovery. *Sci. Total Environ.* **2019**, *648*, 1031–1041. [CrossRef]

7.　Young, S.B. Responsible sourcing of metals: certification approaches for conflict minerals and conflict-free metals. *Int. J. Life Cycle Assess.* **2018**, *23*, 1429–1447. [CrossRef]

8.　Nete, M.; Purcell, W.; Nel, J.T. Hydrometallurgical separation of niobium and tantalum: A fundamental approach. *JOM* **2016**, *68*, 556–566. [CrossRef]

9.　Zhu, Z.; Cheng, C.Y. Solvent extraction technology for the separation and purification of niobium and tantalum: A review. *Hydrometallurgy* **2011**, *107*, 1–12. [CrossRef]

10.　Kabangu, M.J.; Crouse, P.L. Separation of niobium and tantalum from Mozambican tantalite by ammonium bifluoride digestion and octanol solvent extraction. *Hydrometallurgy* **2012**, *129–130*, 151–155. [CrossRef]

11.　Nguyen, T.H.; Lee, M.S. A review on the separation of niobium and tantalum by solvent extraction. *Miner. Process. Extr. Metall. Rev.* **2019**, *40*, 265–277. [CrossRef]

12.　Nelson, J.J.M.; Schelter, E.J. Sustainable inorganic chemistry: metal separations for recycling. *Inorg. Chem.* **2019**, *58*, 979–990. [CrossRef] [PubMed]

13. Debnath, B.; Chowdhury, R.; Ghosh, S.K. Sustainability of metal recovery from E-waste. *Front. Environ. Sci. Eng.* **2018**, *12*, 2. [CrossRef]

14. Love, J.B.; Miguirditchian, M.; Chagnes, A. New insights into the recovery of strategic and critical metals by solvent extraction: The effects of chemistry and the process on performance. In *Ion Exchange and Solvent Extraction: Changing the Landscape in Solvent Extraction*; Moyer, B.A., Ed.; CRC Press: Boca Raton, FL, USA, 2019; Volume 23, pp. 1–44. ISBN 9781315114378.

15. Wilson, A.M.; Bailey, P.J.; Tasker, P.A.; Turkington, J.R.; Grant, R.A.; Love, J.B. Solvent extraction: The coordination chemistry behind extractive metallurgy. *Chem. Soc. Rev.* **2014**, *43*, 123–134. [CrossRef] [PubMed]

16. Deblonde, G.J.P.; Bengio, D.; Beltrami, D.; Bélair, S.; Cote, G.; Chagnes, A. A fluoride-free liquid-liquid extraction process for the recovery and separation of niobium and tantalum from alkaline leach solutions. *Sep. Purif. Technol.* **2019**, *215*, 634–643. [CrossRef]

17. Deblonde, G.J.P.; Weigel, V.; Bellier, Q.; Houdard, R.; Delvallée, F.; Bélair, S.; Beltrami, D. Selective recovery of niobium and tantalum from low-grade concentrates using a simple and fluoride-free process. *Sep. Purif. Technol.* **2016**, *162*, 180–187. [CrossRef]

18. Deblonde, G.J.P.; Chagnes, A.; Bélair, S.; Cote, G. Solubility of niobium(V) and tantalum(V) under mild alkaline conditions. *Hydrometallurgy* **2015**, *156*, 99–106. [CrossRef]

19. Turgis, R.; Arrachart, G.; Michel, S.; Legeai, S.; Lejeune, M.; Draye, M.; Pellet-Rostaing, S. Ketone functionalized task specific ionic liquids for selective tantalum extraction. *Sep. Purif. Technol.* **2018**, *196*, 174–182. [CrossRef]

20. Ungerer, M.J.; Van Der Westhuizen, D.J.; Lachmann, G.; Krieg, H.M. Comparison of extractants for the separation of TaF_5 and NbF_5 in different acidic media. *Hydrometallurgy* **2014**, *144–145*, 195–206. [CrossRef]

21. Ungerer, M.J.; van Sittert, C.G.C.E.; van der Westhuizen, D.J.; Krieg, H.M. Molecular modelling of tantalum penta-halides during hydrolysis and oxidation reactions. *Comput. Theor. Chem.* **2016**, *1090*, 112–119. [CrossRef]

22. Ungerer, M.J.; van Sittert, C.G.C.E.; van der Westhuizen, D.J.; Krieg, H.M. DFT modelling of tantalum pentafluoride extraction with phosphorus-based extractants–A molecular dynamics study. *J. Phys. Chem. Solids* **2019**, *135*, 109121. [CrossRef]

23. Doidge, E.D.; Carson, I.; Tasker, P.A.; Ellis, R.J.; Morrison, C.A.; Love, J.B. A simple primary amide for the selective recovery of gold from secondary resources. Angew. *Chem. Int. Ed.* **2016**, *55*, 12436–12439. [CrossRef]

24. Doidge, E.D.; Kinsman, L.M.M.; Ji, Y.; Carson, I.; Duffy, A.J.; Kordas, I.A.; Shao, E.; Tasker, P.A.; Ngwenya, B.T.; Morrison, C.A.; et al. Evaluation of simple amides in the selective recovery of gold from secondary sources by solvent extraction. *ACS Sustain. Chem. Eng.* **2019**, *7*, 15019–15029. [CrossRef]

25. Nash, K.L. A review of the basic chemistry and recent developments in trivalent f-element separations. *Solvent Extr. Ion Exch.* **1993**, *11*, 729–768. [CrossRef]

26. Carson, I.; MacRuary, K.J.; Doidge, E.D.; Ellis, R.J.; Grant, R.A.; Gordon, R.J.; Love, J.B.; Morrison, C.A.; Nichol, G.S.; Tasker, P.A.; et al. Anion receptor design: Exploiting outer-sphere coordination chemistry to obtain high selectivity for chloridometalates over chloride. *Inorg. Chem.* **2015**, *54*, 8685–8692. [CrossRef]

27. Turkington, J.R.; Bailey, P.J.; Love, J.B.; Wilson, A.M.; Tasker, P.A. Exploiting outer-sphere interactions to enhance metal recovery by solvent extraction. *Chem. Commun.* **2013**, *49*, 1891–1899. [CrossRef]

28. Bartalucci, N.; Bortoluzzi, M.; Pampaloni, G.; Pinzino, C.; Zacchini, S.; Marchetti, F. Stable coordination complexes of α-diimines with Nb(V) and Ta(V) halides. *Dalton Trans.* **2018**, *47*, 3346. [CrossRef]

29. Kiyota, Y.; Kadoya, T.; Yamamoto, K.; Iijima, K.; Higashino, T.; Kawamoto, T.; Takimiya, K.; Mori, T. Benzothienobenzothiophene-based molecular conductors: High conductivity, large thermoelectric power factor, and one-dimensional instability. *J. Am. Chem. Soc.* **2016**, *138*, 3920–3925. [CrossRef]