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Rhodium remains a high value platinum group metal that has key applications in electronics, catalysts, and batteries. To provide a useful tool for Rh isolation, a novel tridentate ligand utilizing soft N and S donors was designed to specifically extract Rh. The synthesis, complexation kinetics, and liquid–liquid extraction studies were performed to explore the overall process and recovery of Rh from chloride media†

Platinum group metals (PGMs) occur in mixed ores with rhodium present in low concentrations (0.4–10 ppb) in the earth's crust.<sup>1,2</sup> Rhodium is the most extensively used metal in catalytic applications (e.g., oxidation of ammonia to nitric acid, automobile catalytic converters) and is resistant to aerial oxidation and insoluble in all acids, including aqua regia.<sup>1,3,4</sup> In an alternative source, rhodium is also produced in sufficient quantities (0.47 kg t<sup>-1</sup> initial heavy metal) during the fission process of <sup>235</sup>U in nuclear reactors.<sup>4,5</sup> Classical methods for rhodium purification are time consuming and inefficient due repetition of precipitation and dissolution steps in chloride media.<sup>1,3,6,7</sup> Current commercial processing involves dissolution of relative high rhodium content ores in a potassium bisulfate melt before further treatment to ensure adequate purity.<sup>1</sup> Low abundance, high demand, and extensive processing make rhodium the most expensive PGM.

After initial separation, PGMs dissolution typically occurs in a chloride media by hydrochloric acid to generate water soluble metal chloride complexes.<sup>1,6</sup> Depending on the oxidation states, group 9 and 10 metals can exist as 4 coordinate square planar or 6 coordinate octahedral complexes complicating the exact species and charge in aqueous solution. Rhodium(III) is typically observed in the octahedral geometry and can accommodate up to six ligands in the primary coordination

sphere to yield six different complexes starting from  $\text{Rh}(\text{OH}_2)_6^{3+}$ . In chloride media, these complexes vary in conformations and overall charge from cationic (+3) to anionic (-3) based on increasing  $[\text{Cl}^-]$ .<sup>8</sup> At relative low  $[\text{Cl}^-]$ , cationic species ( $[\text{Rh}(\text{OH}_2)_5\text{Cl}]^{2+}$ ,  $[\text{Rh}(\text{OH}_2)_4\text{Cl}_2]^+$ ) are observed that transition through the neutral  $\text{Rh}(\text{OH}_2)_3\text{Cl}_3$  complex eventually to anionic complexes  $[\text{Rh}(\text{OH}_2)_n\text{Cl}_{6-n}]^{n-3}$ , ( $n = 0, 1, 2$ ) at  $>1$  M  $[\text{Cl}^-]$ .<sup>6,8,9</sup> The complex nature of rhodium speciation in chloride media, presents a unique challenge in rhodium extractions, where multiple species can be observed at a single  $[\text{Cl}^-]$ .<sup>6,8-10</sup>

Two general strategies, ion pairing and coordination complexation, have been utilized to extract Rh(III) from chloride media.<sup>11</sup> Ion pairing mechanisms have been studied primarily with the tertiary and quaternary amines.<sup>12-16</sup> Comparison of three tertiary amines for coordination (Alamine 304-1, Alamine 308, Alamine 336) and a quaternary ammonium salt for ion pairing (Aliquat 336) showed better extraction through ion pairing with Aliquat 336 (~80%).<sup>13</sup> Mixed mechanism extractions, initial ion pairing followed by coordination, have been proposed with *N*-octylaniline<sup>12</sup> and sulfoxides during long extraction equilibrium times.<sup>17,18</sup>

To address the slow kinetics of Rh(III) and complex chloride speciation, several studies have focused on improving these limitations by the addition of reducing agent ( $\text{SnCl}_2$ ) to access the substitution labile Rh(I) oxidation state.<sup>6,11,14-17</sup> Extraction strategies with tributylphosphate<sup>19</sup> (coordination complexation) and Kelex 100<sup>20</sup> (ion pairing) continue to be effective in the presence of  $\text{SnCl}_2$ . However, the addition of reducing agent may have unforeseen redox implications on the complex matrix of nuclear waste. An alternative strategy utilizes soft donor ligands to more effectively complex Rh(III) without a reducing agent.<sup>21</sup> Herein, a soft donor (S, N) tridentate ligand was designed to generate a single neutral ( $\text{RhLCl}_3$ ) species from chloride media. The solvent extraction and complexation kinetics of the ligand system were also evaluated.

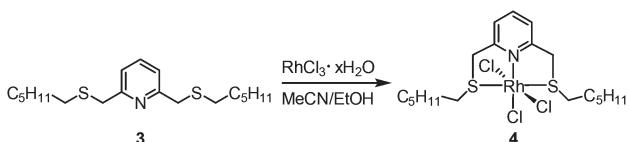
The ligand 3 was prepared by alkylation (S<sub>N</sub>2) of 2,6-bis(bromo-methyl)pyridine, 1, with 1-hexanethiol, 2, in excellent yields after purification (86%) (Scheme S1†). ESI-MS characterization of 3 confirmed the parent ion  $[\text{M} + \text{H}]^+$  (340.2). <sup>1</sup>H NMR ana-

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†Electronic supplementary information (ESI) available: Experimental details, characterization, crystallography, all bond distances and angles. CCDC 1441290. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt04876a



Scheme 1 Synthesis of *mer*-[RhCl<sub>3</sub>(3)] (4).

lysis exhibited symmetric multiplets for the hexyl groups. Most notably, the py-CH<sub>2</sub>-S protons appear as a singlet (3.79 ppm) and the S-CH<sub>2</sub>-CH<sub>2</sub> protons as a triplet (2.46 ppm). <sup>13</sup>C NMR also confirmed a symmetric molecule with the largest shifts adjacent to the thioether.

The formation of *mer*-[RhCl<sub>3</sub>(3)], 4, was observed in near quantitative yields (95%) by reacting the ligand 3 with a slight excess of RhCl<sub>3</sub>·xH<sub>2</sub>O (Scheme 1). ESI-MS (neg. mode) confirmed single ligand incorporation into the complex with an [M]<sup>-</sup> ion (548.0 *m/z*). In positive mode, the sodium adduct of the parent ion (572.0 *m/z* [M + Na]<sup>+</sup>) was detected as the primary peak, but Cl<sup>-</sup> dissociation ions were also observed in the spectrum corresponding to loss of one (511.9 *m/z*), two (440.1 *m/z*), or three Cl<sup>-</sup> (476.0 *m/z*). <sup>1</sup>H NMR of the complexed ligand exhibited a general downfield shift compared to the free ligand. Closest to the rhodium center, the py-CH<sub>2</sub>-S exhibited splitting from a singlet in the free ligand to a multiplet (4.87–4.60 ppm) that resembles an AB<sub>q</sub>. The S-CH<sub>2</sub>-CH<sub>2</sub> also displayed increased splitting from a triplet in the free ligand (2.46 ppm) to a multiplet (3.54–3.06 ppm). <sup>13</sup>C NMR indicated a symmetric molecule with the expected peaks. Single crystals of 4, grown by slow evaporation of an ethanol solution, were analyzed by X-ray diffraction and determined to pack in the *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> space group with one molecule in the asymmetric unit cell (Fig. 1).<sup>‡</sup> The

rhodium center exists as a distorted octahedra with ligand 3 and the three chlorides occupying meridional conformations. The five membered coordination rings in 4 exhibited a constricted bite angle (85–86°) between S-Rh-N, which may account for the non-linear S-Rh-S bond angle (171.63°) and shortened Rh-S bonds (2.3176(7)–2.3283(7) Å) compared to monodentate Rh-S bonds (2.3625(6)–2.4068(6) Å).<sup>22–24</sup>

Metal ligand binding kinetics were studied in ethanol with 3 and RhCl<sub>3</sub>·xH<sub>2</sub>O to evaluate the complexation process by UV spectroscopy, which indicated two distinct processes occurring. The faster process represents approximately 80% of the absorbance change; the rest of the reaction is 100 fold slower (Fig. S1†). However, we will limit our discussion to the faster process, which is pseudo-first order with a *t*<sub>1/2</sub> = 3.02 min at 60 °C with the ligand in 100 fold excess. Evaluation of the concentration dependence shows that the reaction is quite complex but the data were reasonably modelled with a concentration dependent (first order in ligand, second order overall) and a concentration independent process. Further analysis of the ligand concentration dependence yielded an apparent second order rate constant of 0.22 ± 0.03 M<sup>-1</sup> s<sup>-1</sup> and an additional first order, ligand independent, contribution of 8.6 ± 2.8 × 10<sup>-4</sup> s<sup>-1</sup> at 60 °C (Fig. 2). The temperature dependences of the data are presented through Eyring plots (Fig. S2†) and yielded activation parameters that were drastically different ( $\Delta H^\ddagger = 189 \pm 20$  and  $56 \pm 14$  kJ mol<sup>-1</sup>;  $\Delta S^\ddagger = 309 \pm 39$  and  $-134 \pm 93$  J mol<sup>-1</sup> K, second and first order reactions respectively).

Solvent extraction studies with RhCl<sub>3</sub>·xH<sub>2</sub>O in the aqueous phase and 3 in 1-pentanol as the organic phase were conducted at room temperature. An inversion rotator (55 rpm) was found critical to optimize contact between the two phases during the extraction. Two time points, 24 h and 7 d, were examined to determine rhodium extraction with 3 at room temperature. The 24 h point was conducted to compare with previous rhodium extraction studies,<sup>13,25</sup> while 7 d accommodated the very slow kinetics of Rh(m). At each time point, the [Rh]<sub>(aq)</sub> was analyzed by ICP-OES to determine the distribution

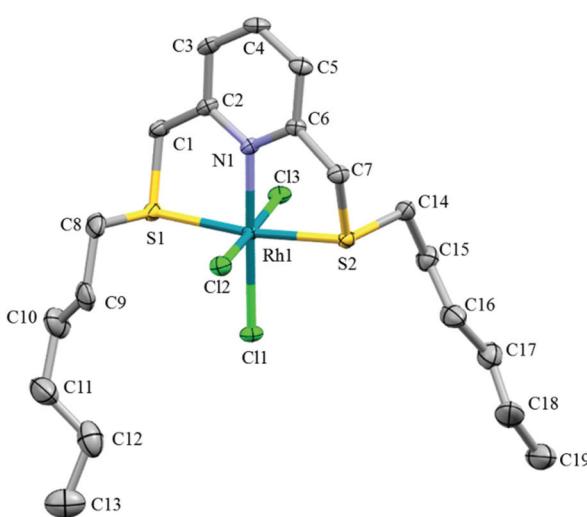


Fig. 1 X-ray structure of 4 is displayed with 30% ellipsoid probability. Hydrogen atoms were omitted and only one disordered hexyl chain (C(8)–C(13)) were shown to improve clarity. Selected bond angles (°): N(1)-Rh(1)-S(1) 85.68(7), N(1)-Rh(1)-S(2) 86.01(7), S(1)-Rh(1)-S(2) 171.63(3), and distances (Å): Rh(1)-N(1) 2.011(2), Rh(1)-S(1) 2.3283(7), Rh(1)-S(2) 2.3176(7), Rh(1)-Cl 2.3439(7)-2.3568(7).

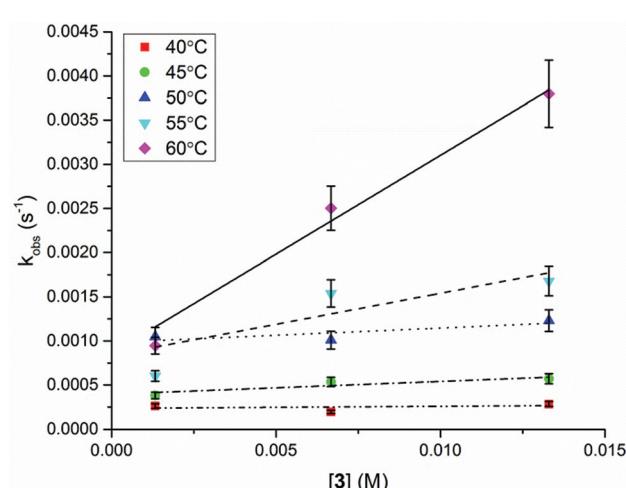


Fig. 2 Apparent rate constants for the formation of 4.

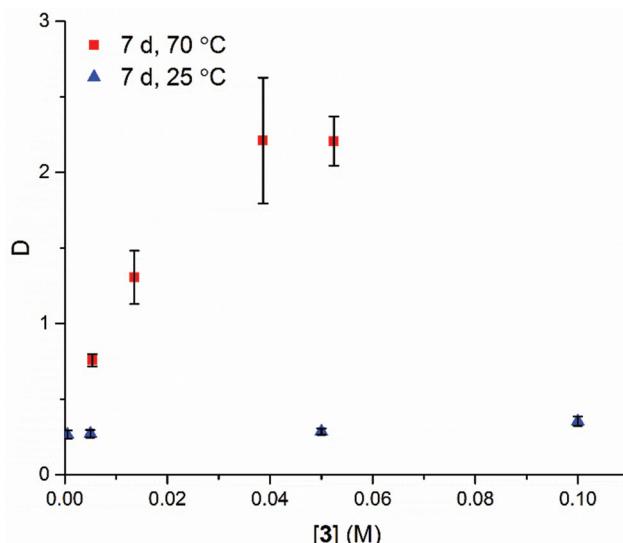


Fig. 3  $D$  values for the extraction of rhodium from aqueous solutions with **3** after 7 d at room temperature or 70 °C.

ratio ( $D$ ) between the phases. At 24 h, the concentration of 3 (0.5 mM–0.1 M) had minimal effect on the  $D$  values ( $0.21 \pm 0.02$  to  $0.25 \pm 0.02$ ) observed across the range (Table S1†).

At 7 d, similar results were observed with a modest increase in  $D$  values ( $0.26 \pm 0.03$  to  $0.36 \pm 0.03$ ) (Table S1†). Based on the temperature dependent kinetic data, an extraction study based on ligand concentration (0.005–0.05 M) was conducted at 70 °C to assess the impact of temperature on the distribution ratio at 7 d (Fig. 3). At the higher temperature, a clear trend of increased  $D$  values with respect to ligand concentration was observed (Table S2†). At 0.005 M, the  $D$  value at 70 °C increased from  $0.26 \pm 0.03$  (25 °C) to  $0.76 \pm 0.04$ . At higher ligand concentrations, the  $D$  values increased to  $2.21 \pm 0.16$  indicating a significant improvement of the elevated temperature extractions.  $D$  values observed at 70 °C were consistent with values reported in literature without reducing agents.<sup>13</sup>

In summary, a novel soft donor (N, S) tridentate ligand was prepared and found to effectively coordinate  $\text{RhCl}_3$  to form a well-defined neutral complex, *mer*-[ $\text{RhCl}_3$ (**3**)] (**4**). Kinetics studies revealed a multifaceted complexation mechanism with a clear temperature dependence on the rate of formation. The influence of temperature was observed in the solvent extraction studies, where  $D$  values obtained at 70 °C were significantly higher than room temperature values. Overall, the data suggests the feasibility of this strategy for rhodium complexation in chloride media without the presence of ancillary reducing agents.

## Acknowledgements

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## Notes and references

‡ Crystal data for **4**,  $\text{C}_{19}\text{H}_{33}\text{Cl}_3\text{NRhS}_2$ ,  $M_r = 548.84$  g mol<sup>-1</sup>, orthorhombic, space group  $P2_12_12_1$ ,  $a = 8.2408(13)$  Å,  $b = 12.5927(19)$  Å,  $c = 23.083(4)$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 2395.4(6)$  Å<sup>3</sup>,  $T = 173(2)$  K,  $Z = 4$ ,  $\mu(\text{MoK}\alpha) = 0.71073$  Å, 28 087 reflections measured, 5486 independent reflections ( $R_{\text{int}} = 0.0320$ ). The final  $R(F)$  values were 0.0245 ( $I > 2\sigma(I)$ ). The final  $wR(F^2)$  values were 0.0567 ( $I > 2\sigma(I)$ ). The final  $R(F)$  values were 0.0268 (all data). The final  $wR(F^2)$  values were 0.0578 (all data). The goodness of fit on  $F^2$  was 1.029. All experimental details are listed in Table S3,‡ and all bond lengths (Å) and angles (°) are listed in Table S4.‡ CCDC deposition number: 1441290.

- 1 W. P. Griffith, *The Chemistry of the Rarer Platinum Metals (Os, Ru, Ir, and Rh)*, Interscience Publishers, London, New York, 1967.
- 2 V. M. Goldschmidt, *Geochemistry*, Oxford, Clarendon Press, 1954.
- 3 R. S. Dickson, *Organometallic Chemistry of Rhodium and Iridium*, Academic Press, New York, 1983.
- 4 H. J. Ache, L. H. Baetsle, R. P. Bush, A. F. Nechaev, V. P. Popik and Y. Ying, Feasibility of Separation and Utilization of Ruthenium, Rhodium and Palladium from High Level Waste, V. IAEA Report Technical Report Series No. 308, IAEA, Vienna, 1989.
- 5 G. R. Choppin, J.-O. Liljenzen and J. Rydberg, in *Radiochemistry and Nuclear Chemistry*, ed. G. R. C.-O. and L. Rydberg, Butterworth-Heinemann, Woburn, 3rd edn, 2002, pp. 583–641, DOI: 10.1016/B978-075067463-8/50021-2.
- 6 E. Benguerel, G. P. Demopoulos and G. B. Harris, *Hydrometallurgy*, 1996, **40**, 135–152.
- 7 J. S. Forrester and G. H. Ayres, *J. Phys. Chem.*, 1959, **63**, 1979–1981.
- 8 W. C. Wolsey, C. A. Reynolds and J. Kleinberg, *Inorg. Chem.*, 1963, **2**, 463–468.
- 9 G. Levitin and G. Schmuckler, *React. Funct. Polym.*, 2003, **54**, 149–154.
- 10 D. T. Richens, *The Chemistry of Aqua Ions*, John Wiley & Sons, Chichester, 1997.
- 11 J. G. H. du Preez and C. Viviers, *Solvent Extr. Ion Exch.*, 2003, **21**, 815–826.
- 12 S. S. Kolekar and M. A. Anuse, *Talanta*, 2002, **58**, 761–771.
- 13 P. P. Sun, J. Y. Lee and M. S. Lee, *Mater. Trans.*, 2011, **52**, 2071–2076.
- 14 P. Malik and A. P. Paiva, *Solvent Extr. Ion Exch.*, 2008, **26**, 25–40.
- 15 N. G. Afzaletdinova, Y. I. Murinov, S. Y. Khazhev, S. O. Bondareva and R. R. Muslukhov, *Russ. J. Inorg. Chem.*, 2010, **55**, 460–467.
- 16 D. V. Chavan and P. M. Dhadke, *J. Chem. Technol. Biotechnol.*, 2002, **77**, 925–932.
- 17 N. G. Afzaletdinova and Y. I. Murinov, *Russ. J. Appl. Chem.*, 2010, **83**, 1570–1575.
- 18 N. G. Afzaletdinova and Y. I. Murinov, *Russ. J. Inorg. Chem.*, 2011, **56**, 1143–1152.
- 19 L. Zou, J. Chen and X. Pan, *Hydrometallurgy*, 1998, **50**, 193–203.

20 M. S. Alam and K. Inoue, *Hydrometallurgy*, 1997, **46**, 373–382.

21 N. Li, M. Struttman, C. Higginbotham, A. J. Grall, J. F. Skerlj, J. F. Vollano, S. A. Bridger, L. A. Ochrymowycz, A. R. Ketring, M. J. Abrams and W. A. Volkert, *Nucl. Med. Biol.*, 1997, **24**, 85–92.

22 A. J. Blake, G. Reid and M. Schroder, *J. Chem. Soc., Dalton Trans.*, 1989, 1675–1680, DOI: 10.1039/DT9890001675.

23 E. A. Shusharina, I. A. Druzhinina, V. V. Tatarchuk and S. A. Gromilov, *J. Struct. Chem.*, 2010, **51**, 987–990.

24 M. Venkatesh, N. Goswami, W. A. Volkert, E. O. Schlemper, A. R. Ketring, C. L. Barnes and S. Jurisson, *Nucl. Med. Biol.*, 1996, **23**, 33–40.

25 B. Raju, J. R. Kumar, J.-Y. Lee, H.-S. Kwon, M. L. Kantam and B. R. Reddy, *J. Hazard. Mater.*, 2012, **227–228**, 142–147.

