



Enhancing the reprocessing of spent nuclear fuel; ways to recycle and reuse materials from the fission process



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Introduction

Nuclear power provides one of the cleanest energy sources for the United States, capable of supporting the ever-increasing demand for electricity. Fission byproducts remaining in spent nuclear fuel after electricity generation have potential applications if they can be recycled from the fuel elements. Platinum group metals (e.g., Pt, Ag, Pd, Ir, Ru, Rh), detected in quantities greater than what is found in the earth's crust, can be reclaimed for applications in catalysts, solar cells, electronics, batteries, etc. by using various extraction methods. Although no industrial extraction process has been reported to date, liquid-liquid extraction methods show promise in metal extraction.

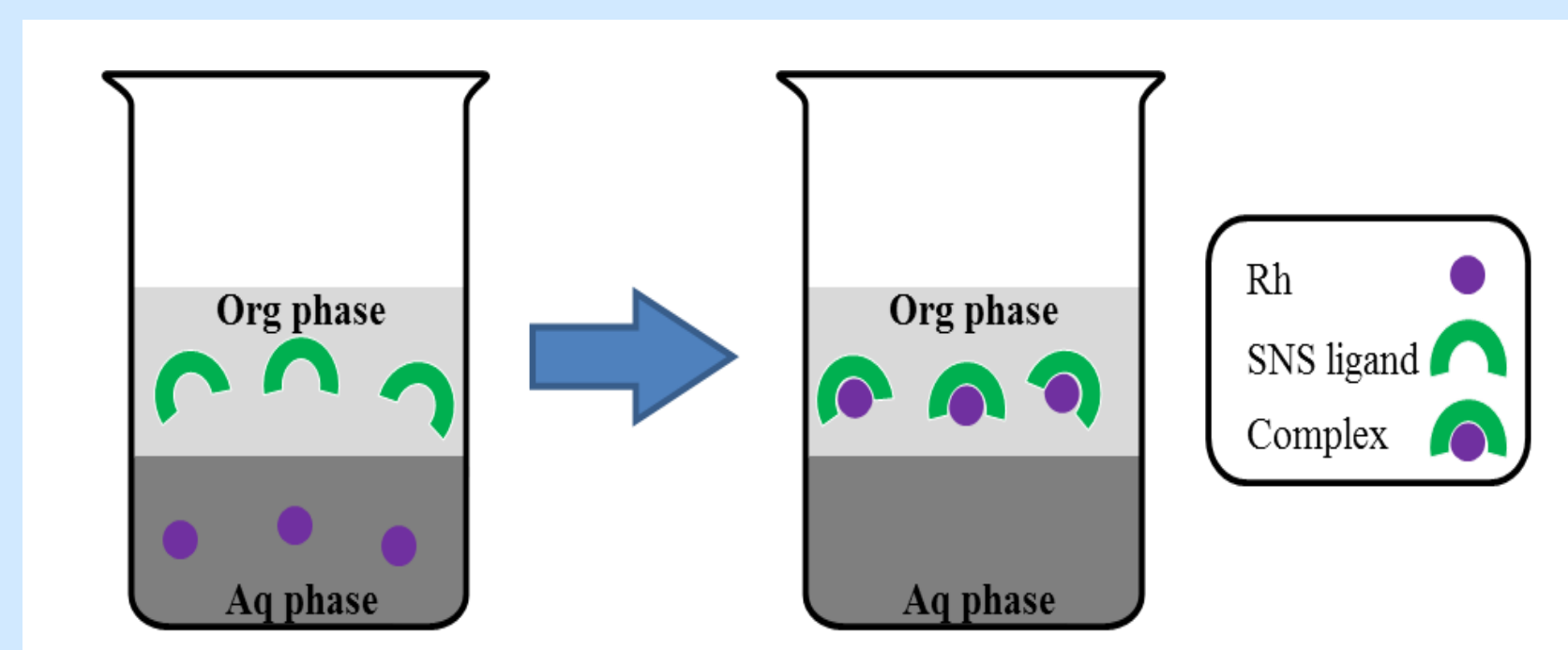
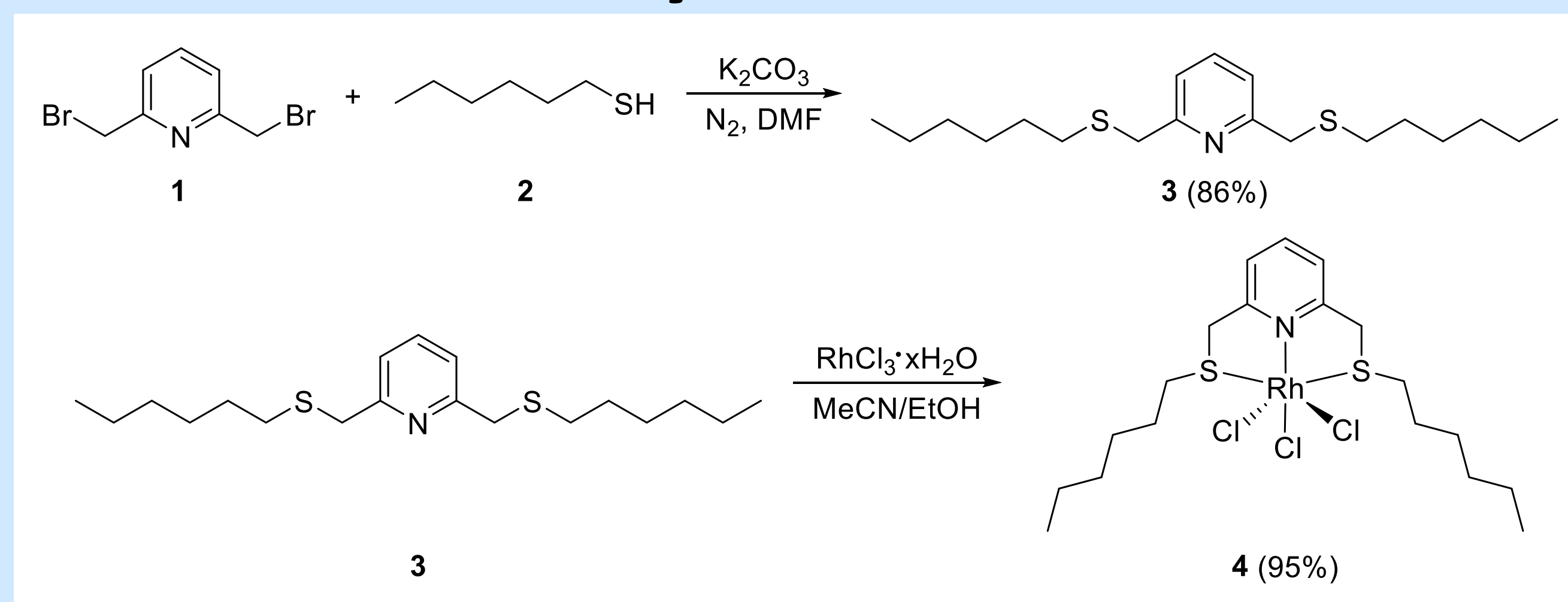


Figure 1. Extraction of Rh from aqueous phase to organic phase utilizing SNS ligand extractant.

In this Work:

- Complex *mer*-Rh(SNS)Cl₃ was synthesized in excellent yields and fully characterized
- Complexation kinetics were explored to determine ΔH^\ddagger and ΔS^\ddagger
- Liquid-liquid extraction of Rh was investigated with the tridentate ligand (SNS)

Synthesis



Synthesis of 3.

1 (0.7906 g, 2.98 mmol) was dissolved in dry DMF (20 mL). K₂CO₃ (1.237 g, 8.95 mmol) and **2** (2.105 mL, 14.91 mmol) were added while stirring. The reaction was heated under N₂(g) to 60 °C for 3 h. 100 mL of H₂O was added to the reaction mixture and was extracted with CHCl₃ (3 x 50 mL). The combined organic layers were then washed with H₂O (5 x 100 mL), dried over MgSO₄, and filtered before solvent was removed under vacuum. The crude oil was purified by silica column chromatography (hexanes:chloroform gradient 0-100%) to yield a yellow oil (0.8685 g, 86%) upon concentration. λ_{max} (CH₂Cl₂)/nm (ϵ /dm³ mol⁻¹ cm⁻¹): 273 (2,850). ν_{max} /cm⁻¹: 2954.2, 2923.3, 2854.1, 1589.2, 1572.7, 1450.8, 747.8. m/z 340.2 (M+H⁺, 100%).

Synthesis

Synthesis of 4.

3 (0.0641 g, 0.19 mmol) was dissolved in 4% v/v ACN/EtOH (15 mL) and RhCl₃ (2.819 mL, 0.0703 ± 0.1 M, 0.20 mmol) was added drop-wise while stirring. Reaction was heated at 60 °C for 12 h. Solvent was removed under vacuum and the resulting oil was dissolved in dichloromethane (20 mL) and washed with water (3 x 15 mL). It was then washed with brine (1 x 15 mL) and dried over MgSO₄, filtered, and dried under vacuum overnight to yield an orange solid. **4** was recrystallized by slow evaporation of EtOH to yield orange crystals (0.0986 g, 95%). λ_{max} (EtOH)/nm (ϵ /dm³ mol⁻¹ cm⁻¹): 240 (21,480); 370 (1,241). ν_{max} /cm⁻¹: 2954.8, 2921.1, 2852.6, 1463.4, 1391.5, 787.2. m/z 548.0 (M⁺, 100%).

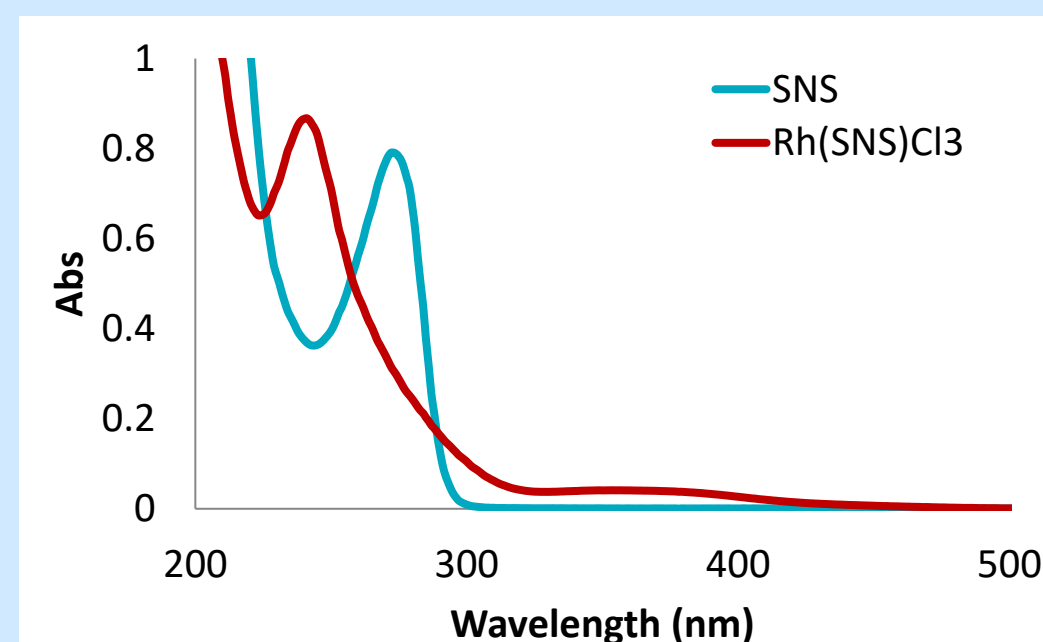


Figure 2. UV-Vis comparison of **3** (blue) and **4** (red) in ACN.

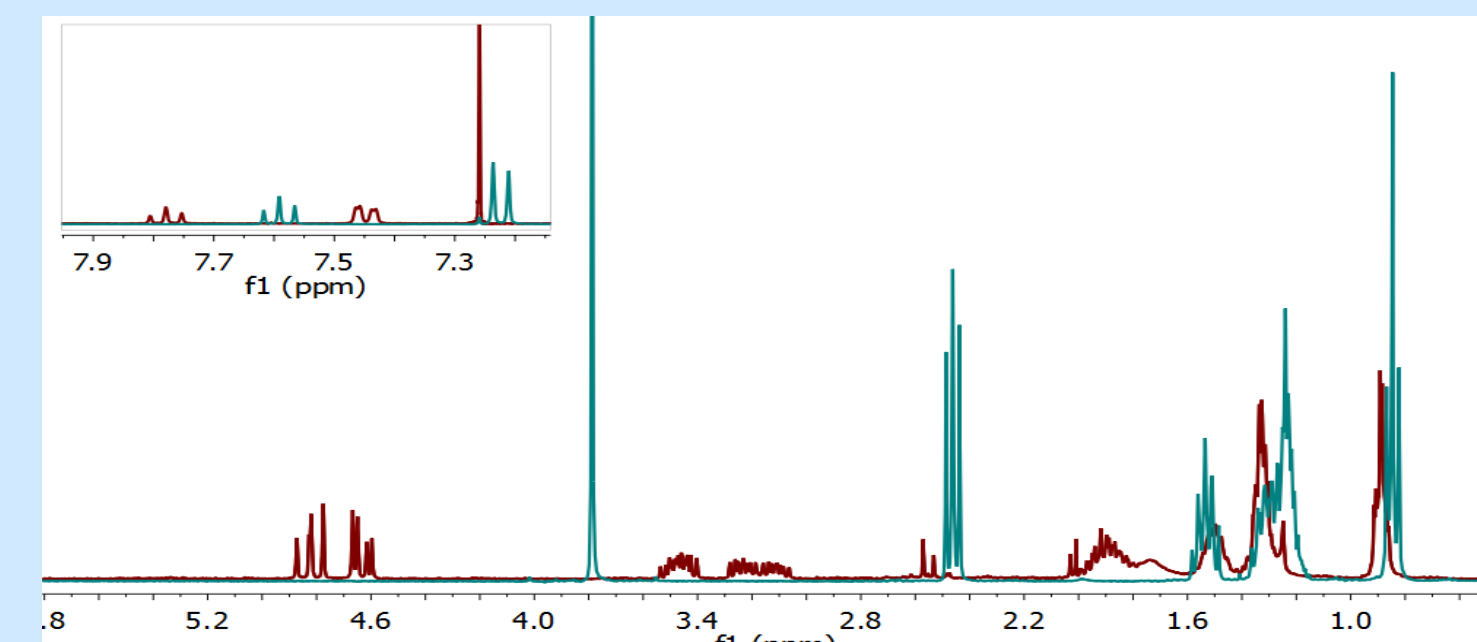


Figure 3. ¹H NMR comparison of **3** (blue) and **4** (red) in CDCl₃.

Crystal Structure

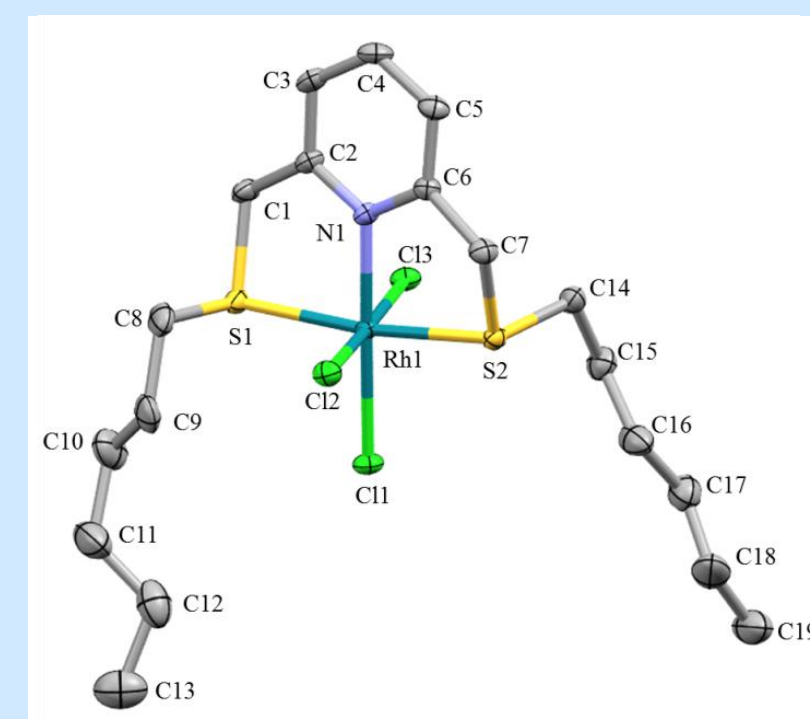


Figure 4. X-ray structure of **4** with hydrogen atoms omitted for clarity. Ellipsoids drawn at 30% probability.

Rh(1)-N(1)	2.011(2)	S(2)-Rh(1)-Cl(2)	82.52(3)
Rh(1)-S(2)	2.3176(7)	S(1)-Rh(1)-Cl(2)	96.52(3)
Rh(1)-S(1)	2.3283(7)	N(1)-Rh(1)-Cl(3)	87.77(7)
Rh(1)-Cl(2)	2.3439(7)	S(2)-Rh(1)-Cl(3)	97.28(3)
Rh(1)-Cl(3)	2.3497(7)	S(1)-Rh(1)-Cl(3)	83.32(3)
Rh(1)-Cl(1)	2.3568(7)	Cl(2)-Rh(1)-Cl(3)	177.50(3)
N(1)-Rh(1)-S(2)	86.01(7)	N(1)-Rh(1)-Cl(1)	179.12(8)
N(1)-Rh(1)-S(1)	85.68(7)	S(2)-Rh(1)-Cl(1)	93.54(3)
S(2)-Rh(1)-S(1)	171.63(3)	S(1)-Rh(1)-Cl(1)	94.78(3)
N(1)-Rh(1)-Cl(2)	89.72(7)	Cl(2)-Rh(1)-Cl(1)	90.96(3)
		Cl(3)-Rh(1)-Cl(1)	91.54(3)

Table 1. Bond distances (Å) and angles (°) of **4**.

Complexation Kinetics

Data was collected on a Varian Cary 50 UV-Vis spectrometer fitted with a Quantum Northwest temperature control system with a water bath, and reactions were run inside sealable 10 mm quartz cuvette with 5x2 mm micro stir bars. Reaction progress was monitored by examining the absorbance change at 370 nm with an averaging time of 0.10s for 17-24h utilizing a four stage progression with constant [Rh]=1.3E-4 M and ligand concentration in excess to achieve pseudo first order kinetics. Studies were carried out at 40, 45, 50, 55, and 60 °C. All data was fit to a sum of two exponentials using nonlinear least-squares analysis.

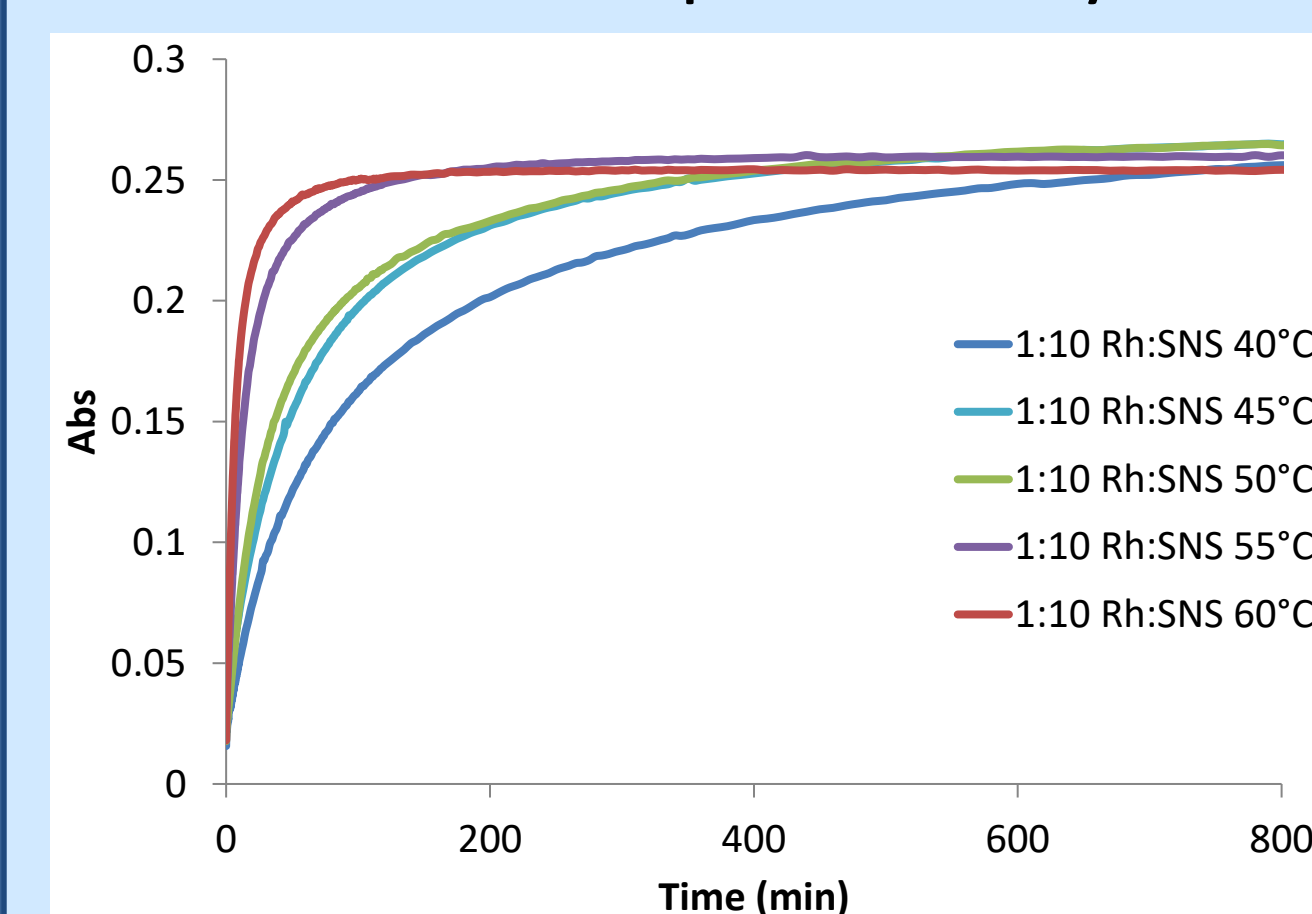


Figure 5. Absorbance data at $\lambda=370$ nm as a function of time.

	E_a (KJ/mol)
k_1	160 ± 50
k_2	80 ± 50

Table 2. Activation energies (E_a) for process one (k_1) and process two (k_2).

M:L	$\Delta H^\ddagger k_1$ (KJ/mol)	$\Delta H^\ddagger k_2$ (KJ/mol)	$\Delta S^\ddagger k_1$ (J/mol-K)	$\Delta S^\ddagger k_2$ (J/mol-K)
1:10	56	82	-36	26
1:50	110	90	134	55
1:100	105	85	33	-53

Table 3. ΔH^\ddagger and ΔS^\ddagger values for process one (k_1) and process two (k_2).

Extraction Study

Liquid-liquid extraction experiments were performed in quadruplicate at room temperature with ligand concentrations of 0.0005-0.1 M in pentanol (1 mL) and 0.0005 M Rh in 18 MΩ H₂O (1 mL). The extractions were rotated for up to 8 days. The concentration of Rh in the aqueous phase was measured using inductively coupled plasma optical emission spectrometry (ICP-OES). The distribution value, D, was calculated using equations

$$D = \frac{[M]_{org}}{[M]_{aq,init}} \quad (1) \quad [M]_{org} = [M]_{aq,init} - [M]_{aq} \quad (2)$$

where $[M]_{aq,init}$ and $[M]_{aq}$ are the initial and final concentrations of metal ions, respectively, in the solution.

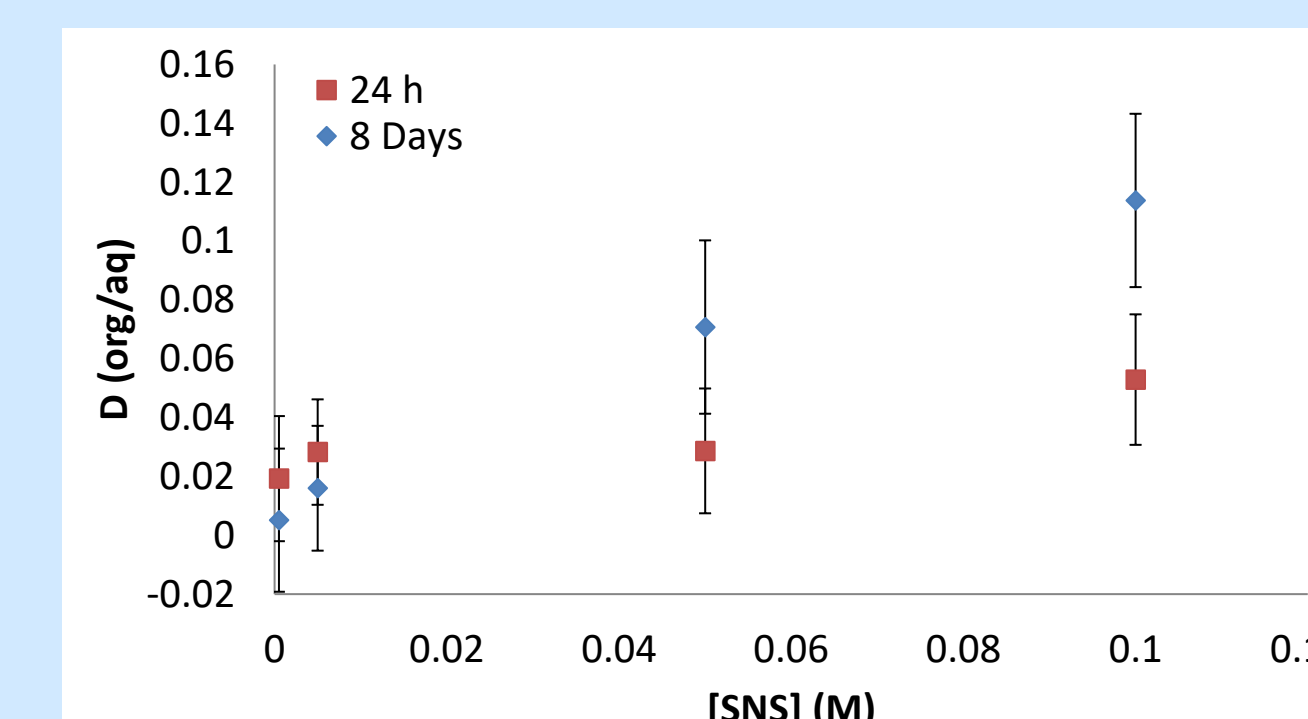


Figure 6. D values for the extraction of RhCl₃ with SNS ligand.

[SNS]	D (24h)	D (8d)
0.0005	0.02±0.02	0.01±0.02
0.005	0.03±0.02	0.02±0.02
0.05	0.03±0.02	0.07±0.03
0.1	0.05±0.02	0.11±0.03

Table 4. D values for the extraction of RhCl₃ with SNS ligand at 24h and 8 days.

Conclusions

- SNS ligand (**3**) was synthesized in good yields (86%)
- Rh(SNS) complex (**4**) was synthesized in excellent yields (95%)
- Crystal structure of **4** was obtained and analyzed
 - 4** shown to pack in the P2₁2₁2₁ space group with one molecule in the asymmetric unit cell
 - 4** exists in a distorted octahedral geometry
 - Chloride and SNS ligand coordinate meridinally
- Kinetics study shows a two process complex mechanism
 - One process dependent on ligand concentration
 - One process independent on ligand concentration
- Extraction of RhCl₃ with SNS ligand was observed to give low distribution values
 - 0.11±0.03 (10% extraction) for the 0.1 M concentration of the ligand at the 7 day period.
 - 8 day extractions yielded significantly higher distribution values than 24 h extractions at 0.05 M and 0.1 M ligand concentrations

Future Work

- Elevated temperature extractions
- Second generation ligands which offer faster complexation and better distribution values have been synthesized

Acknowledgments

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