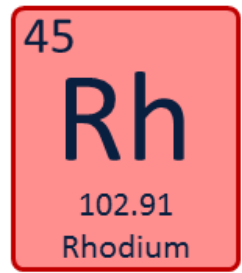




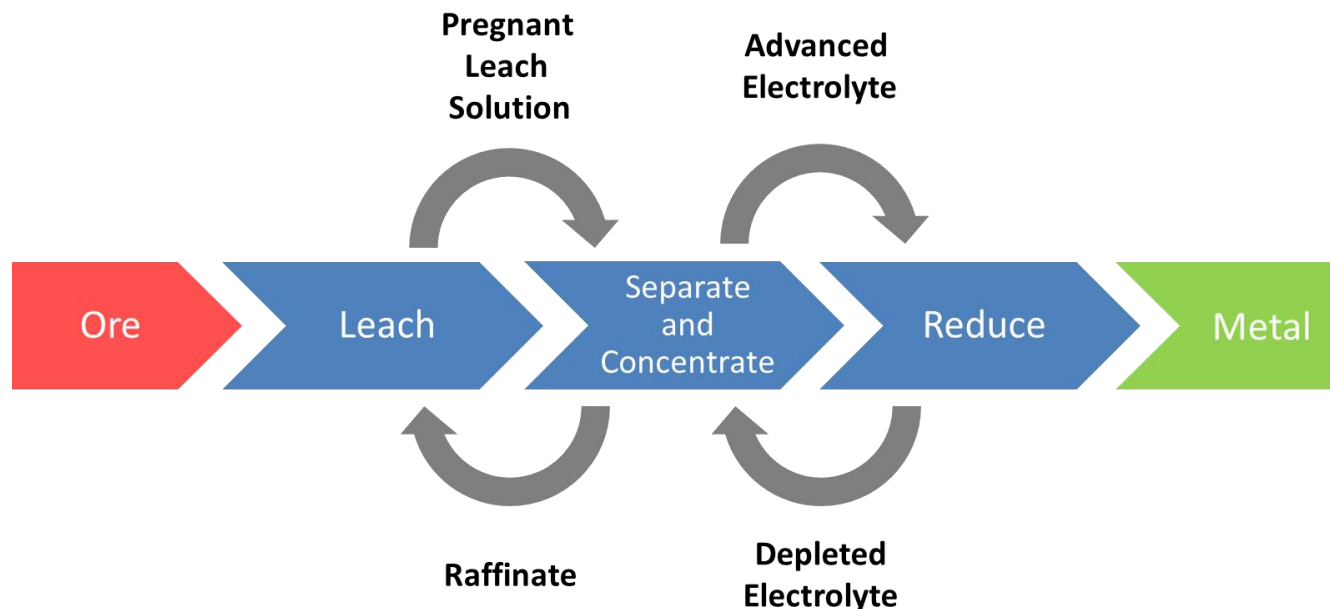
Understanding rhodium solvent extraction: a mode of action study

Rebecca M. Nicolson, Ross J. Gordon, Jason B. Love,
Peter A. Tasker, and Carole A. Morrison

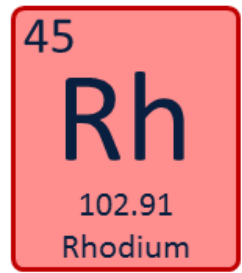
Rhodium and its recovery



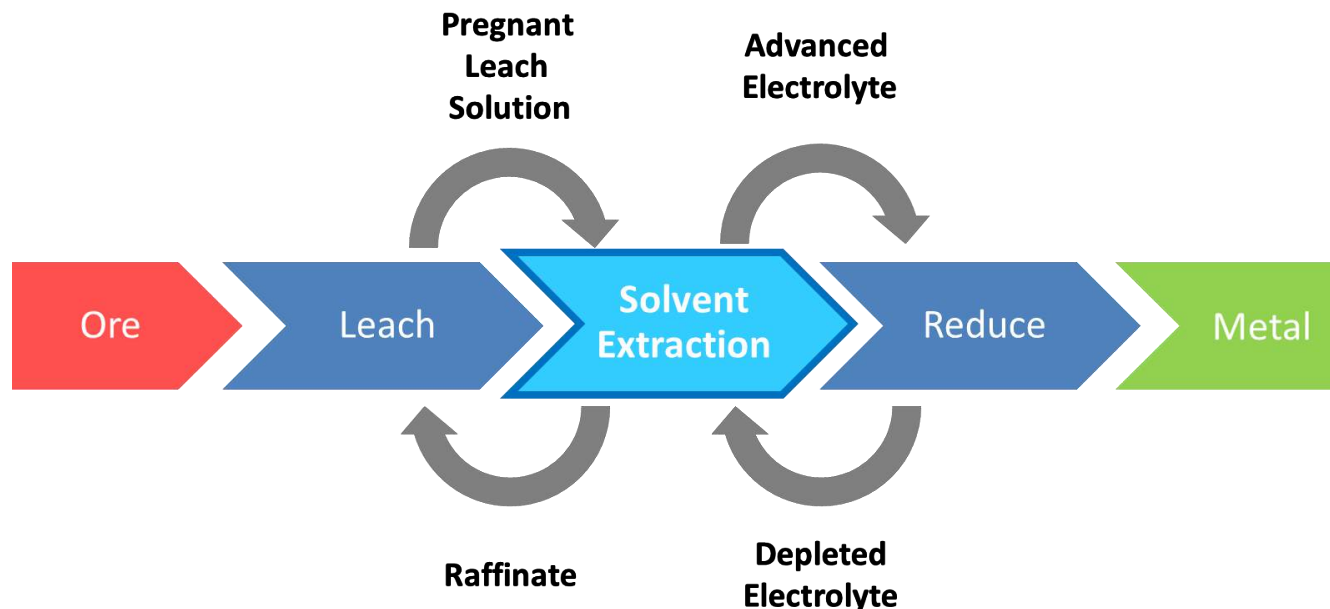
- Rh is a useful, valuable metal. **\$30,000 per kg**
- It can be obtained from platinum ores or recycled from secondary sources.
- Current recovery methods employ a precipitation step; this is undesirable and solvent extraction would be preferred.



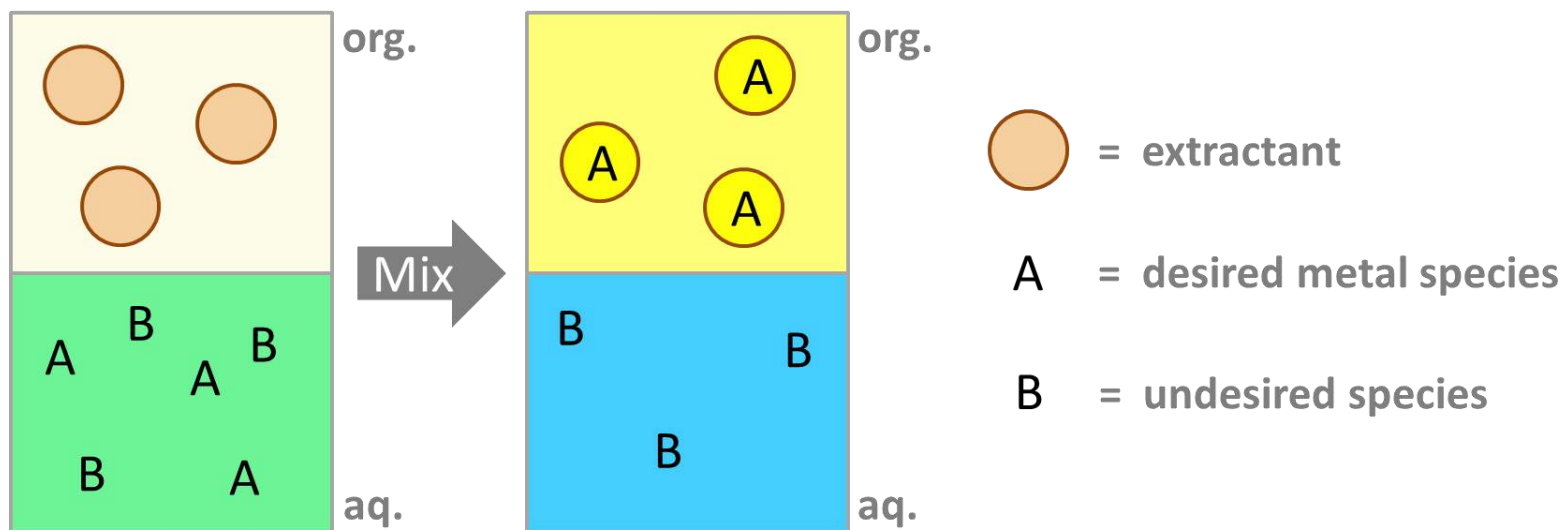
Rhodium and its recovery



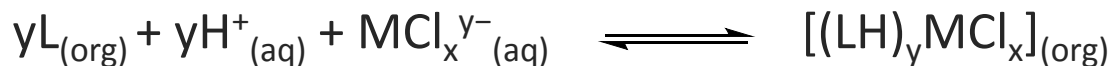
- Rh is a useful, valuable metal. **\$30,000 per kg**
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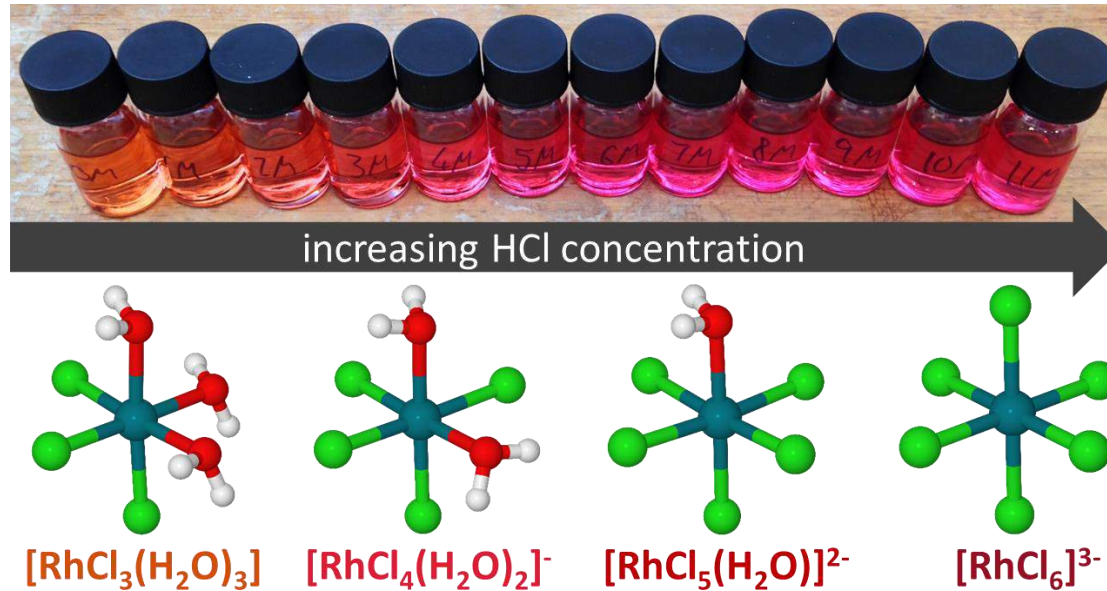
Solvent extraction (SX)



- Transfer of species from aqueous solution into an immiscible organic solution
- Precious metals are often extracted from HCl solutions, as chloridometalates, MCl_x^{y-} e.g. RhCl_6^{3-}
 - ▶ Chloridometalate SX – anion exchange:



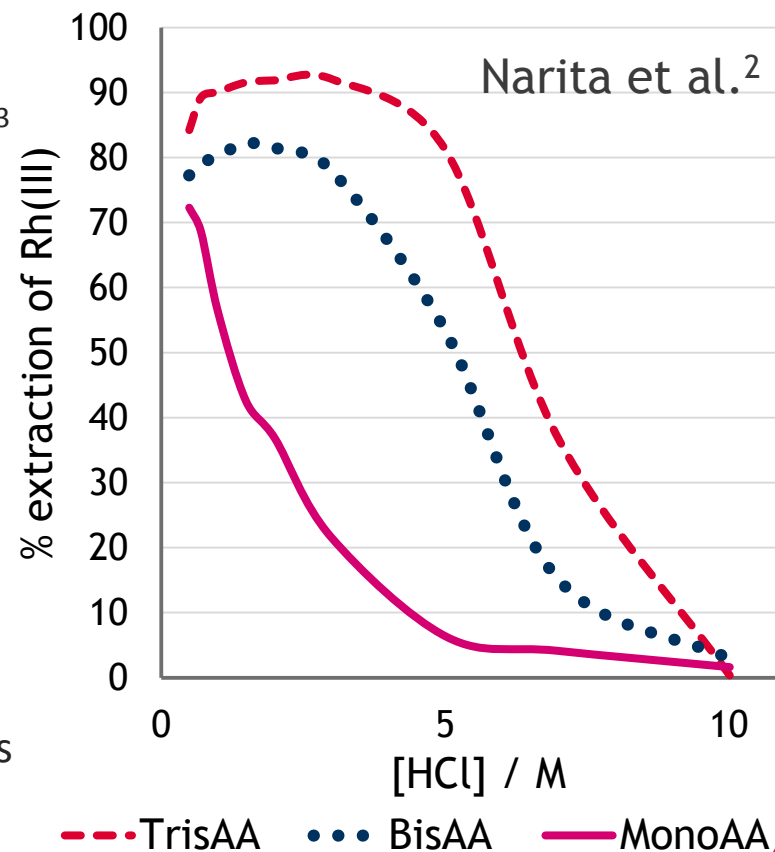
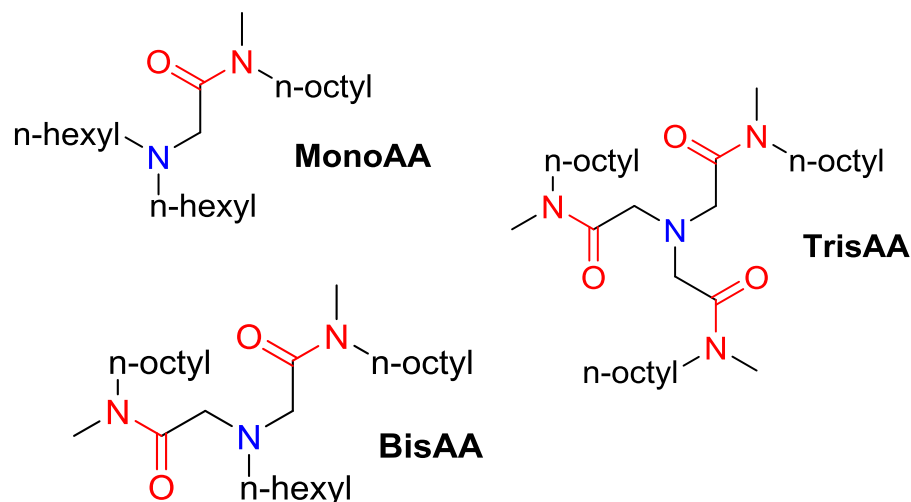
SX of Rh from HCl solution



- Rh is present in HCl solution as a variety of complexes, the concentration of each changing with the chloride concentration
- The mixture makes Rh difficult to extract, as the target complex is not present at 100%
- In addition, highly charged and/or highly hydrated complexes are more difficult to extract (Hofmeister bias)
 - ▶ Because their hydration shell is more difficult to displace

Rh extractants

- Currently, there is no commercial reagent for the SX of Rh
- Many ligands have been shown to be poor extractants for Rh chloridometalates from high [HCl] solutions – successful extraction usually requires treatment with some other reagent¹
- However, successful extraction has recently been reported using amido-amine extractants^{2,3}

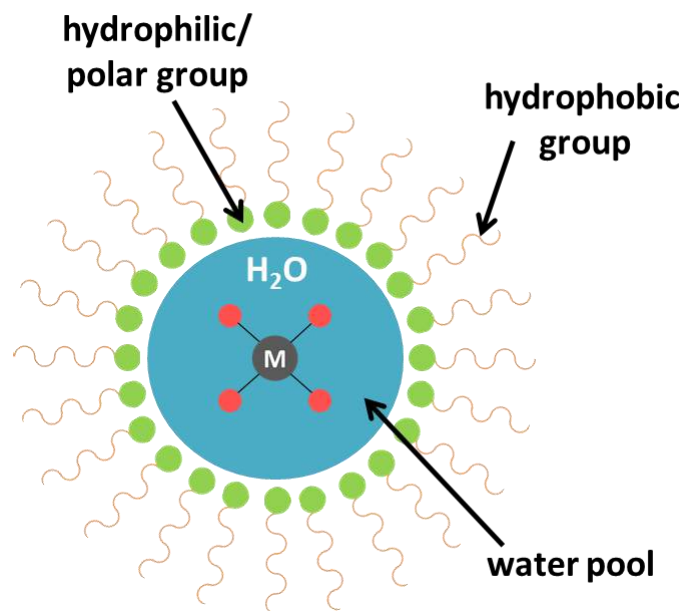
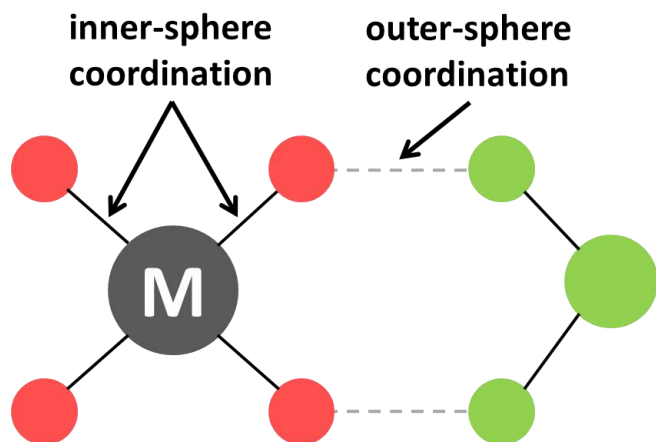
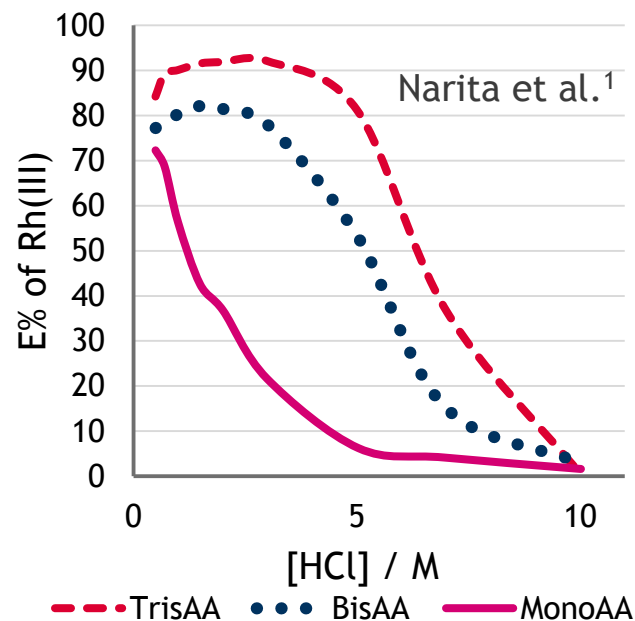


- Understanding how these successful extractants work is key to developing further, improved Rh extractants

1. Benguerel, E.; Demopoulos, G. P.; Harris, G. B., *Hydrometallurgy* **1996**, 40, 135-52.
 2. Narita, H.; Morisaku, K.; Tanaka, M., *Chem. Commun. (Cambridge, U. K.)* **2008**, 5921-5923.
 3. Narita, H.; Morisaku, K.; Tanaka, M., *Solvent Extr. Ion Exch.* **2015**, 33, 407-417.

Mode of action

- Narita et al. concluded that their ligands:^{1,2}
 - extracted $[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$
 - worked via an ion-pair mechanism
 - may hydrogen-bond to the *aquo* ligand
 - and that BisAA and TrisAA have a feature, that MonoAA lacks, which makes them better extractants

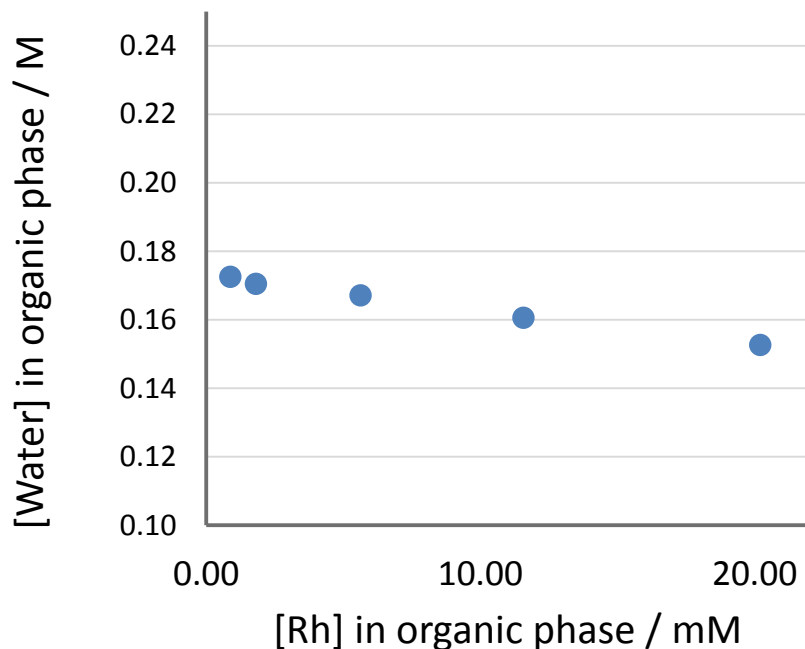


Aims

Understand the mode of action of MonoAA, BisAA and TrisAA in Rh solvent extraction

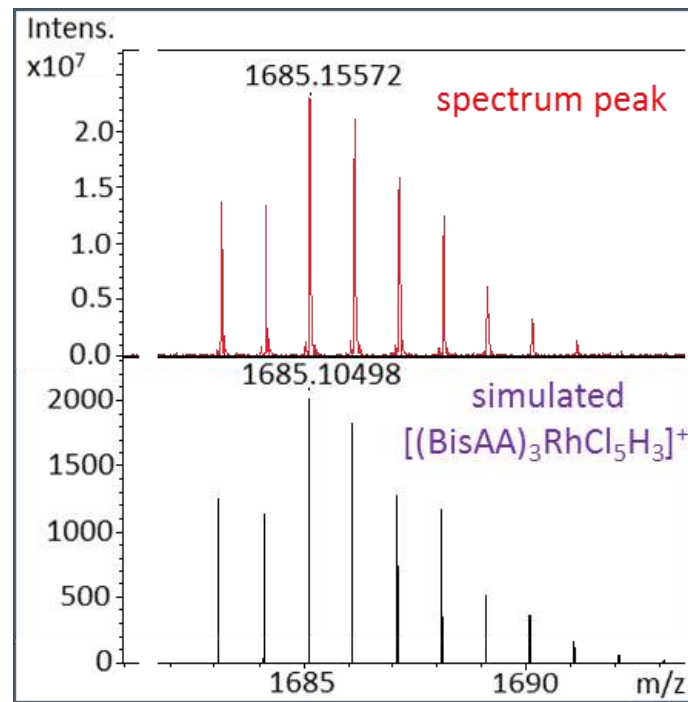
- Conduct some preliminary extraction experiments and analysis (using BisAA)
- Use QM calculations to:
 - ▶ visualise the extracted complexes
 - ▶ determine formation and exchange energies
 - ▶ explore the differences in behaviour between MonoAA, BisAA and TrisAA

Conclusions from experimental work



- Water content of organic phase essentially constant with increasing Rh concentration

→ suggests that extraction is not via a micelle mechanism



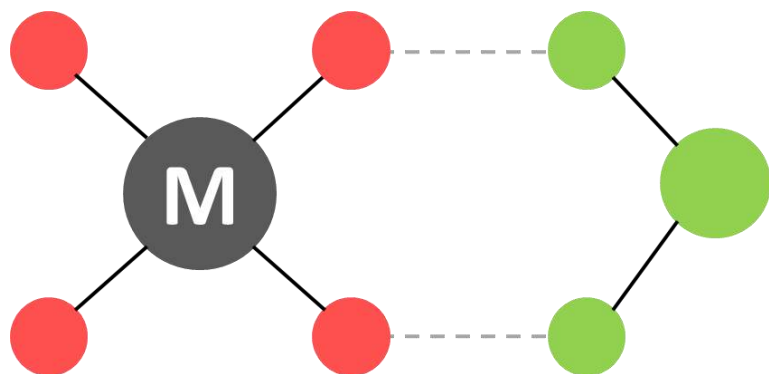
- ESI-MS identified the main extracted species to be:



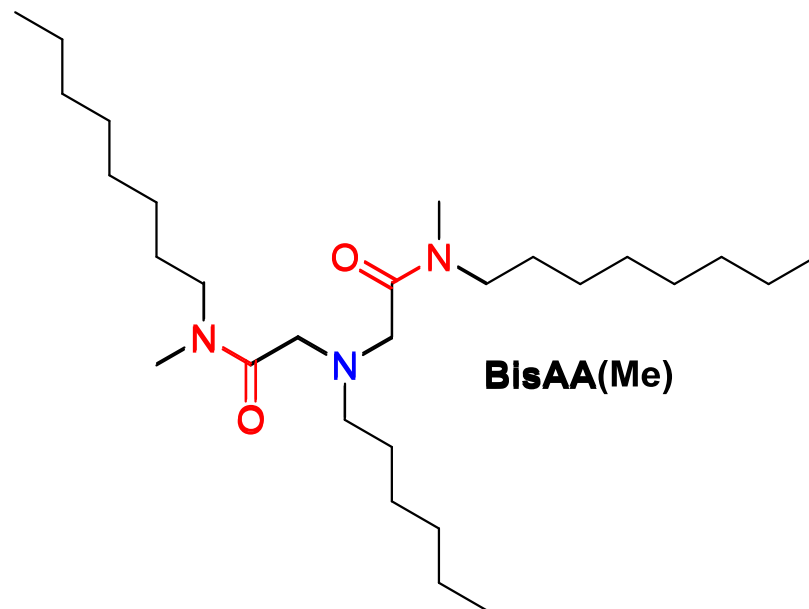
→ at least one ligand in the outer-sphere

Modelling

- Modelling ion-pair extraction mode based on experimental findings
- Use versions of the ligands with truncated R-groups for modelling

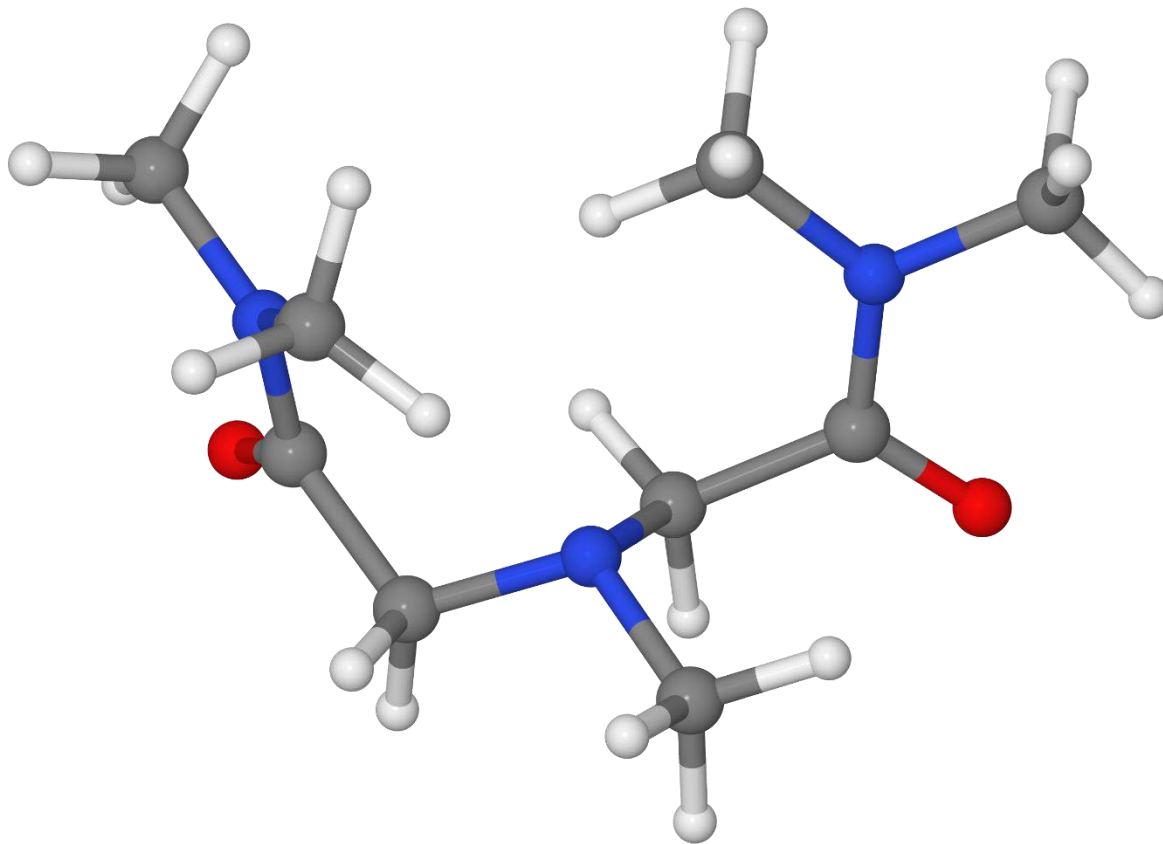


- Structures to model:
 - ▶ $[(\text{RhCl}_5(\text{H}_2\text{O}))(\text{LH})_2]$ complex
 - ▶ $[\text{Cl}(\text{LH})]$ complex
 - ▶ all species required for formation energies



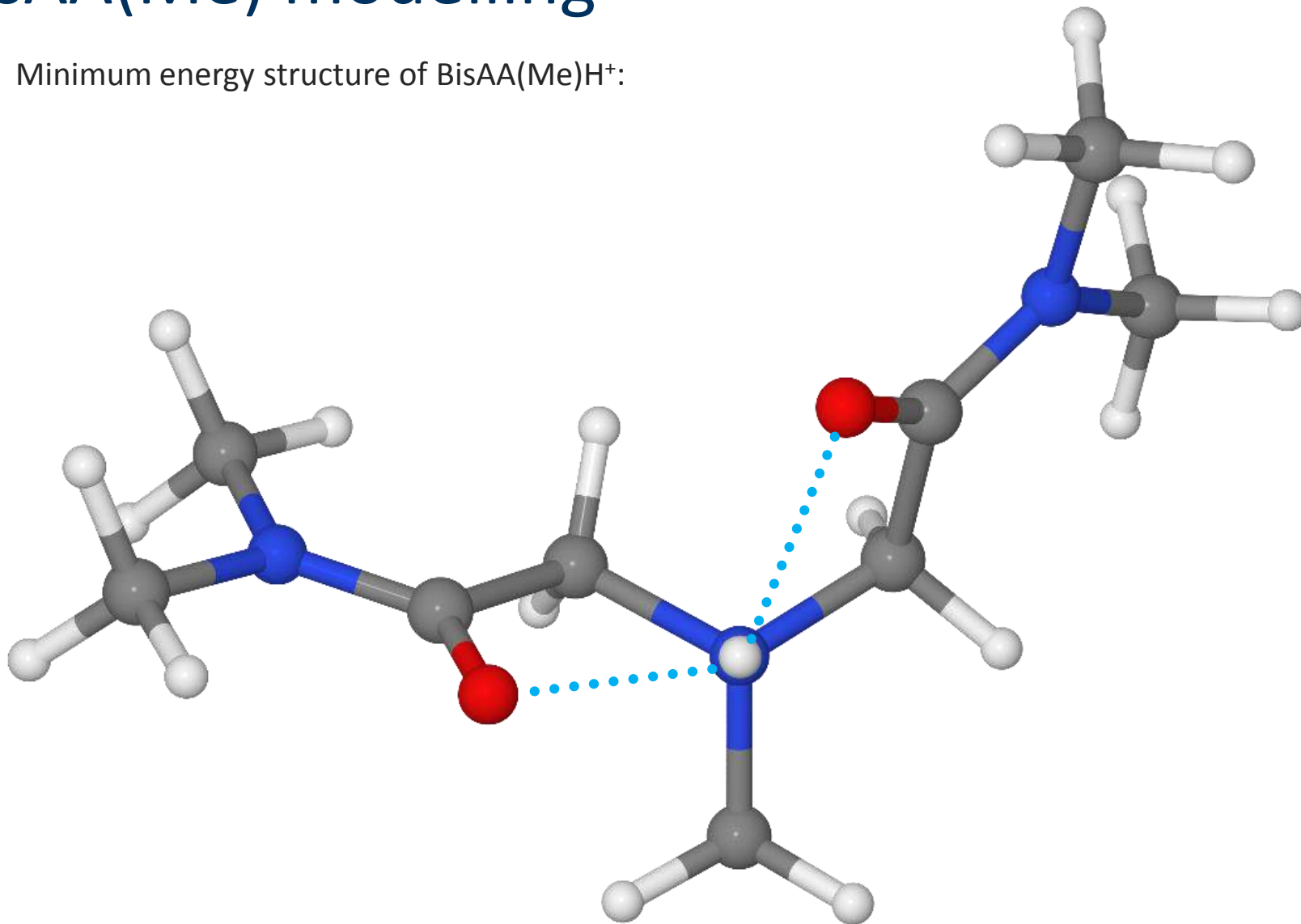
BisAA(Me) modelling

- Minimum energy structure of BisAA(Me):



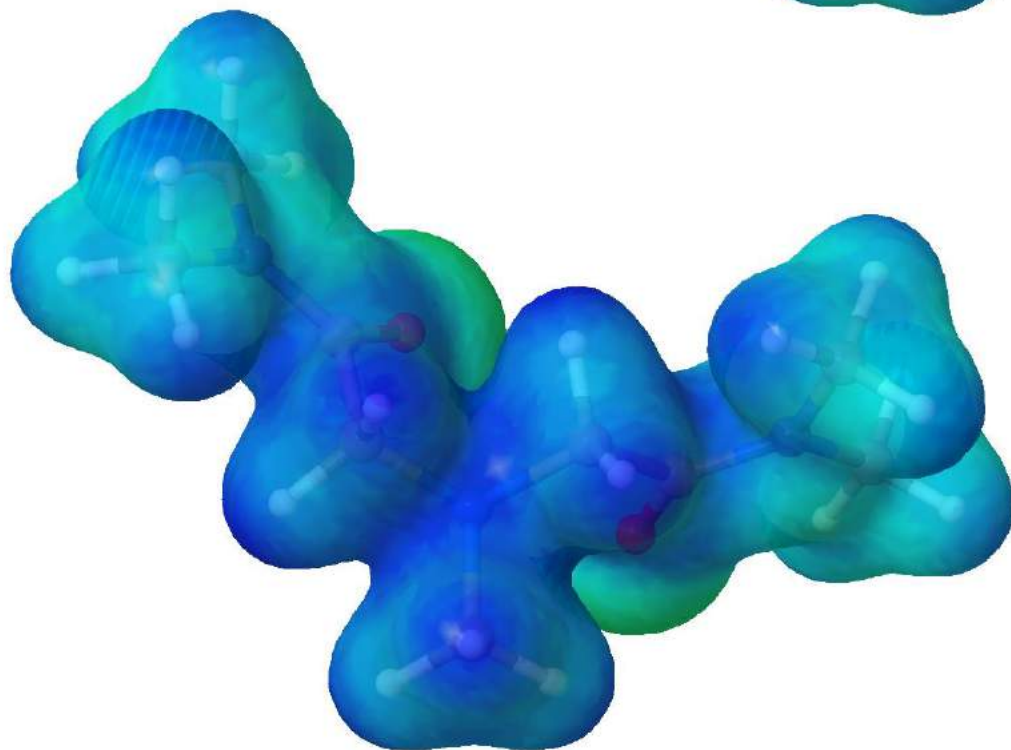
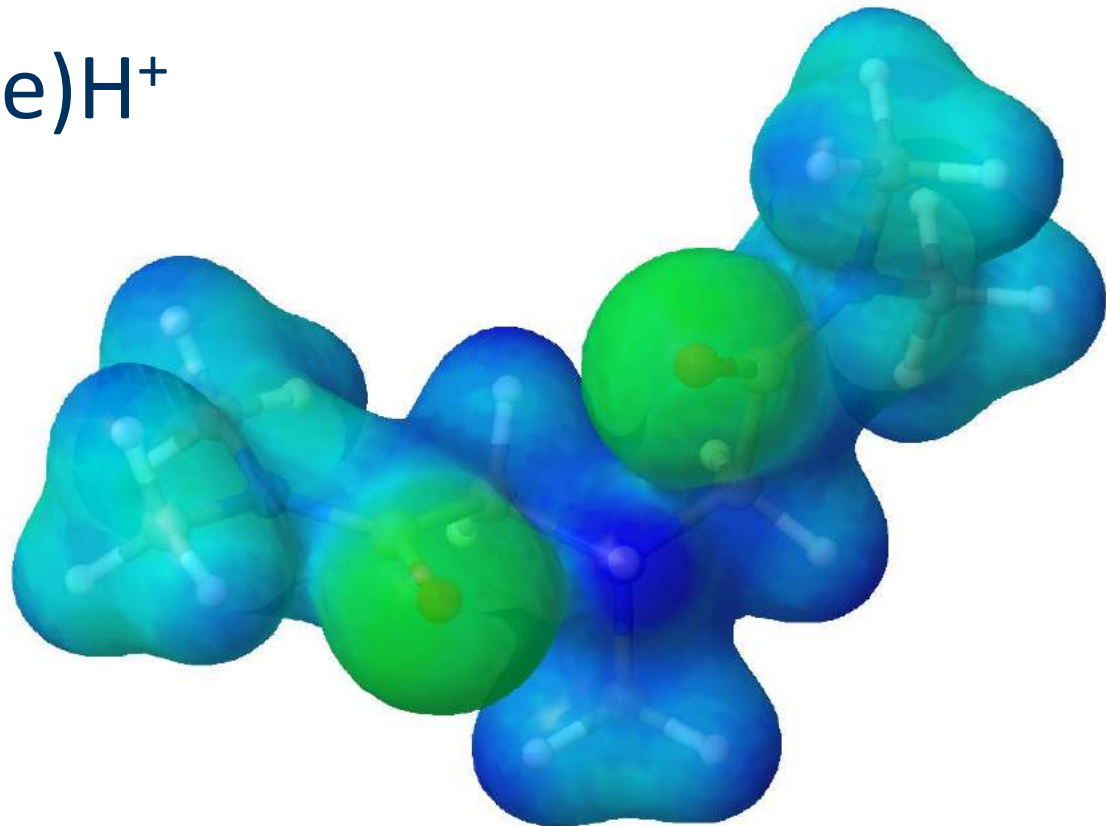
BisAA(Me) modelling

- Minimum energy structure of BisAA(Me)H⁺:



Binding of BisAA(Me)H⁺

- Electrostatic potential plots show areas of positive charge (blue) and relatively negative charge (green)
 - ▶ Proton very positive
 - ▶ Amide O atoms negative
 - ▶ “Back” of ligand also positive

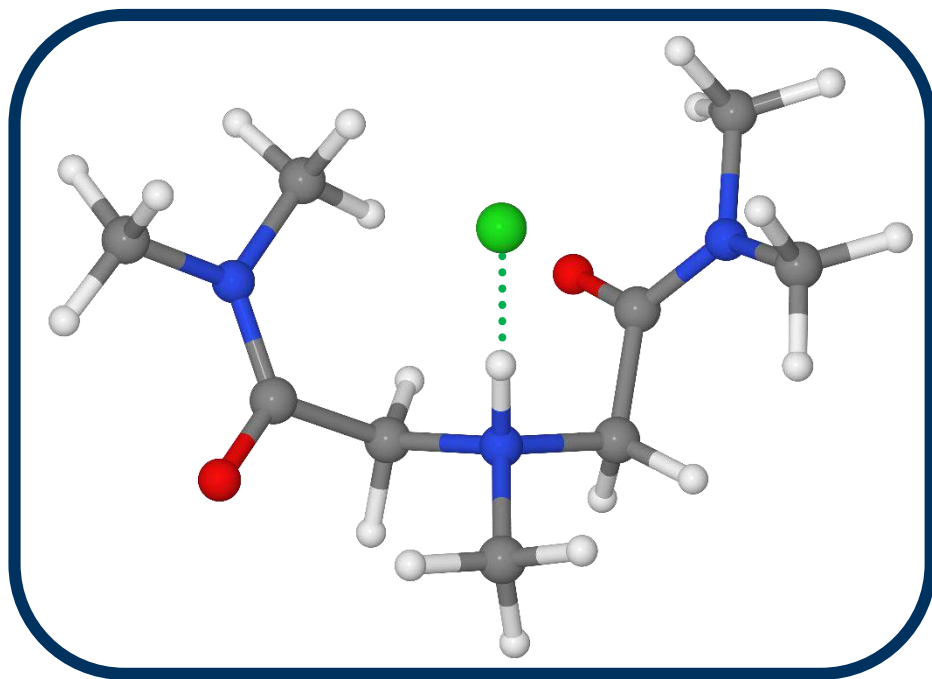


It is possible that the back of the ligand, an area of diffuse positive charge, could bind to the anions

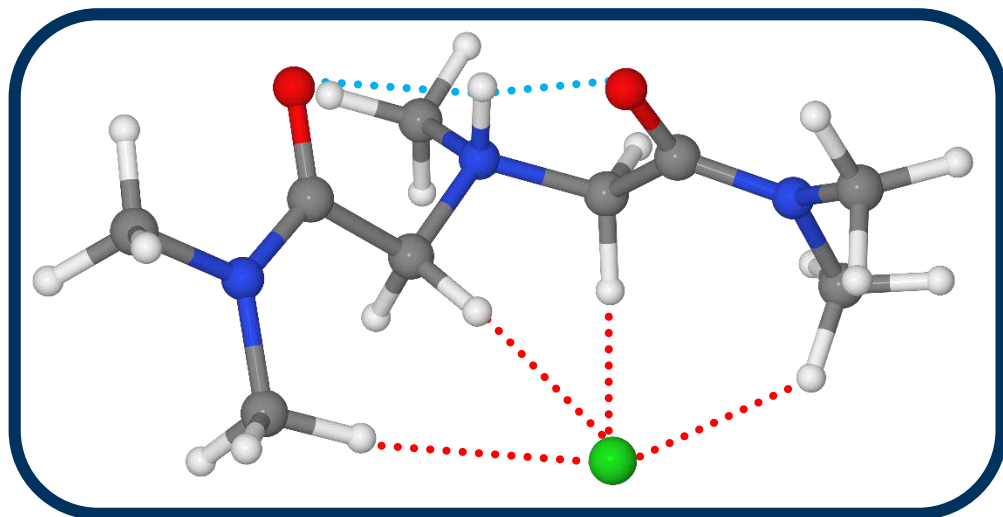
BisAA(Me) modelling

- Possible [Cl(BisAA(Me)H)] structures:

BUT
only 2 kJ mol⁻¹ higher



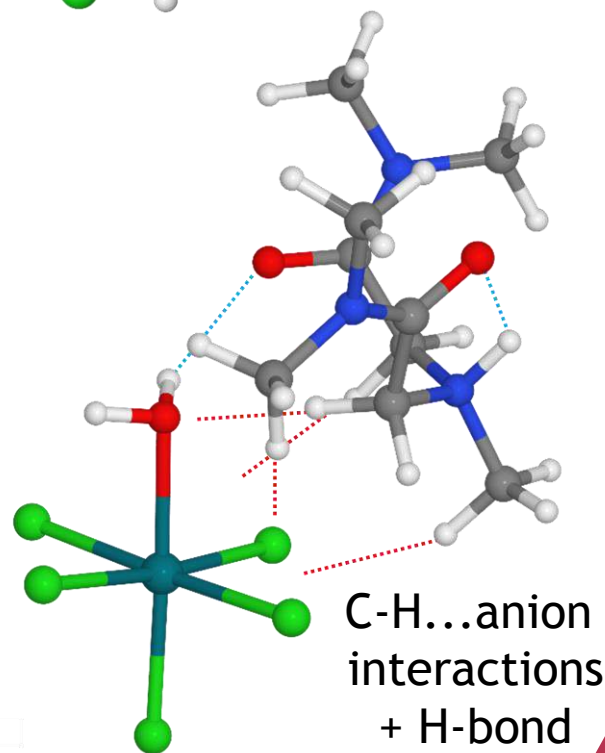
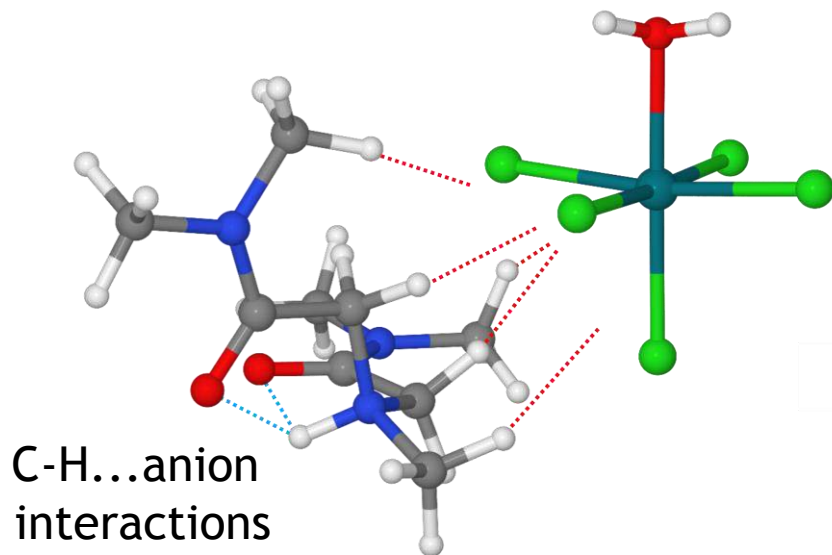
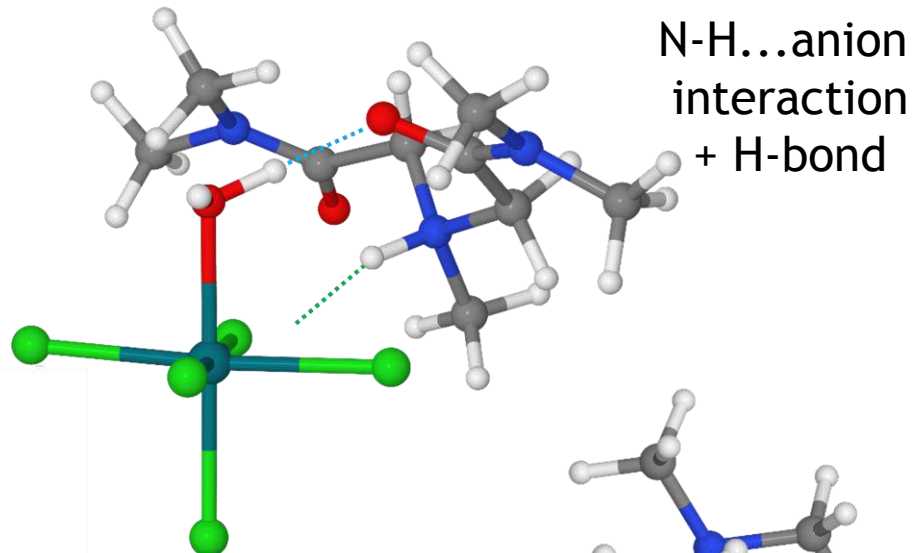
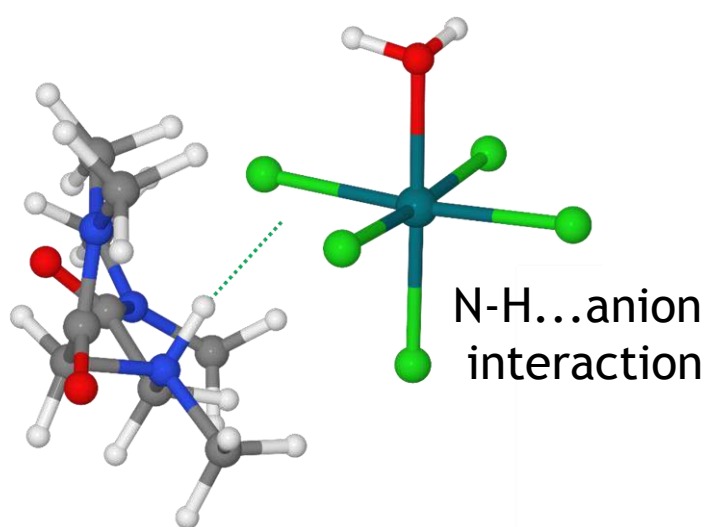
Lowest energy structure



**Likely that both
exist in solution**

BisAA(Me) modelling

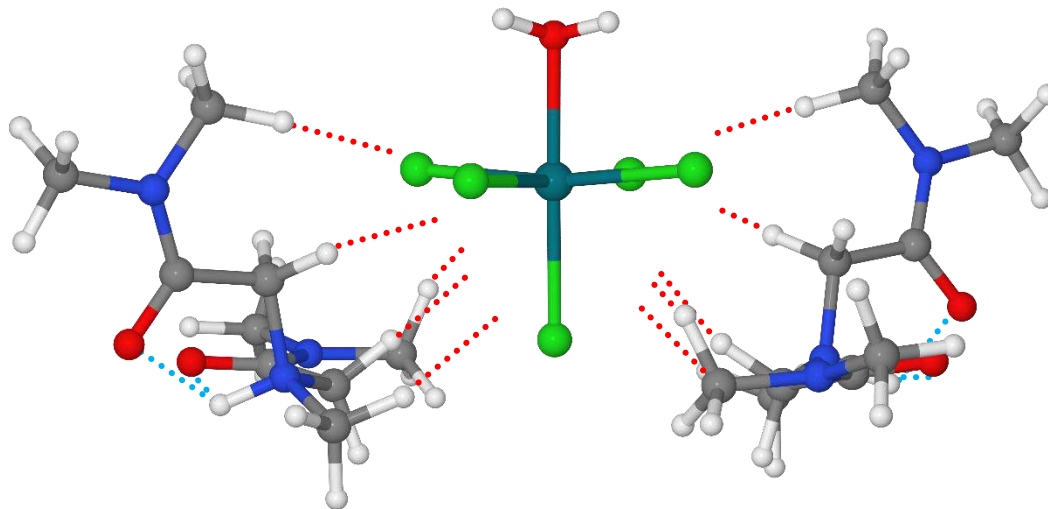
- There are a number of possible $[(\text{RhCl}_5(\text{H}_2\text{O}))(\text{BisAA}(\text{Me})\text{H})_2]$ binding modes:



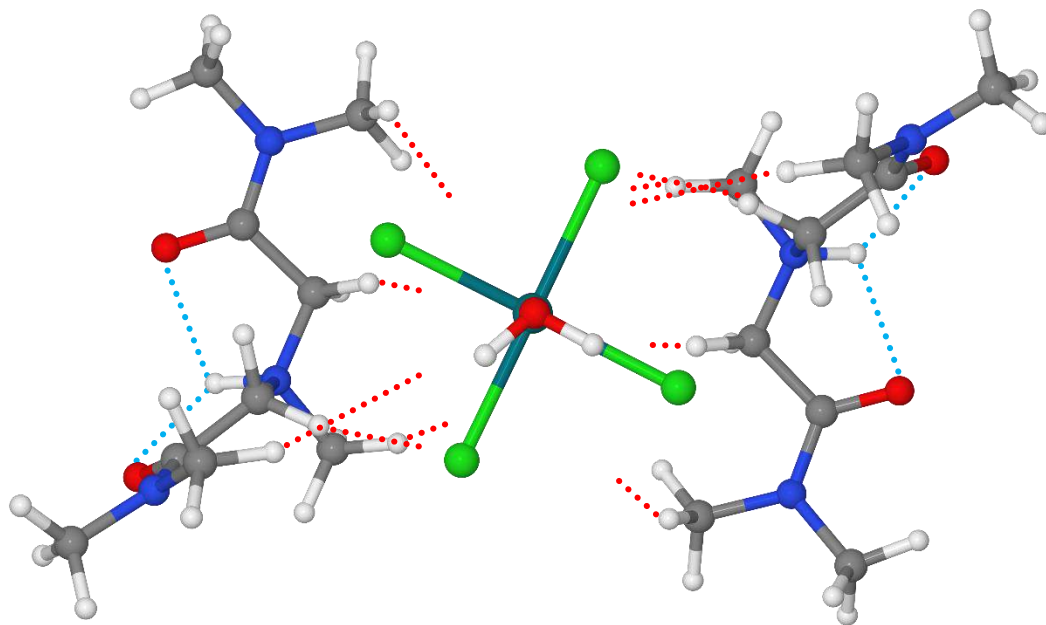
BisAA(Me) modelling

- Lowest energy structure of $[(\text{RhCl}_5(\text{H}_2\text{O}))(\text{BisAA}(\text{Me})\text{H})_2]$:

Side view:



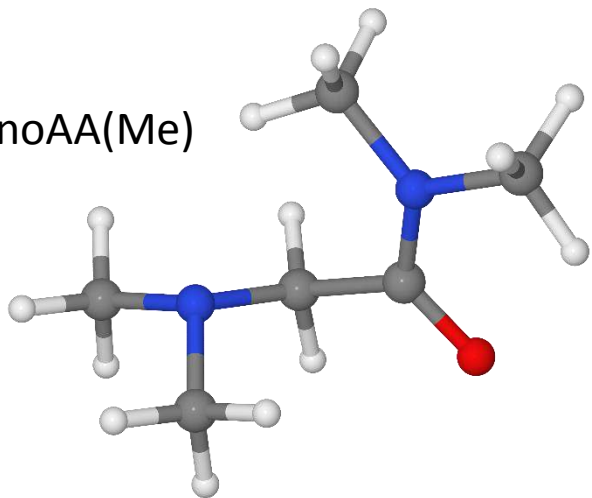
Top view:



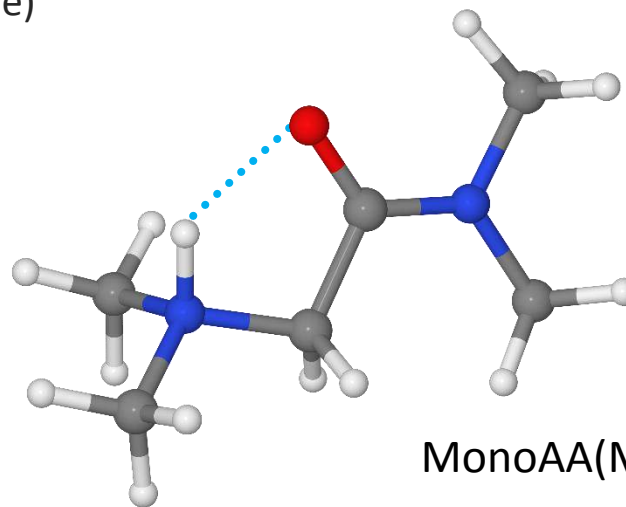
MonoAA(Me) modelling

- The same process was carried out for MonoAA(Me)

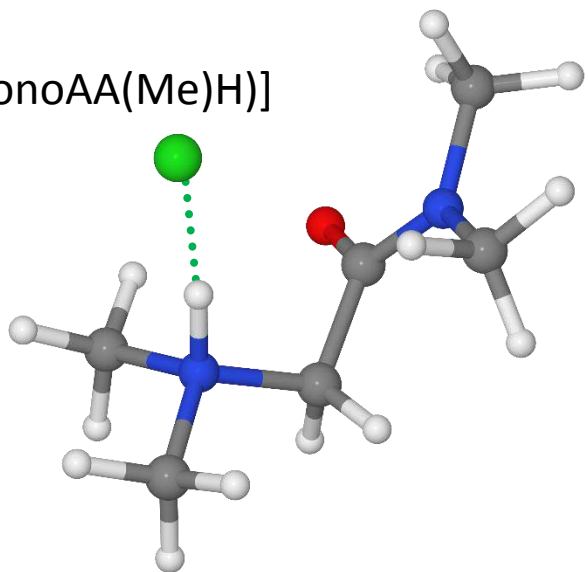
MonoAA(Me)



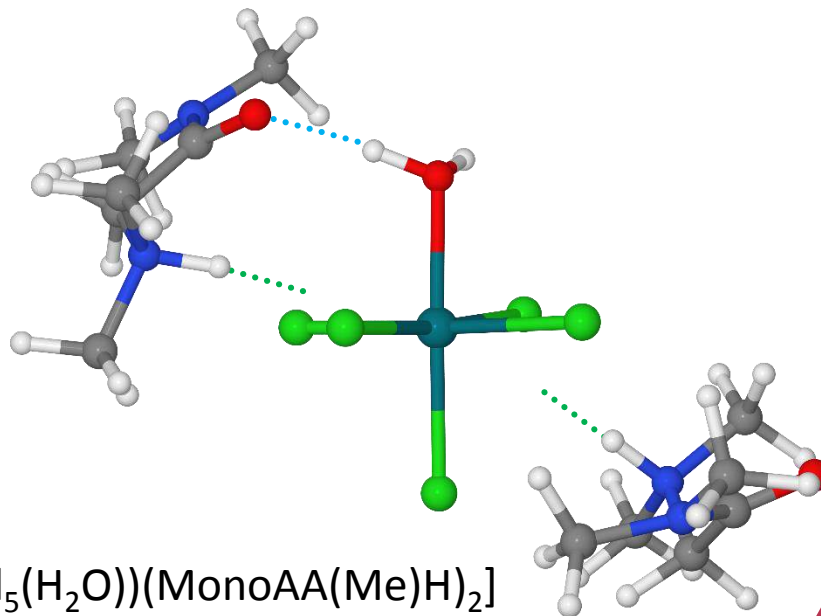
MonoAA(Me)H⁺



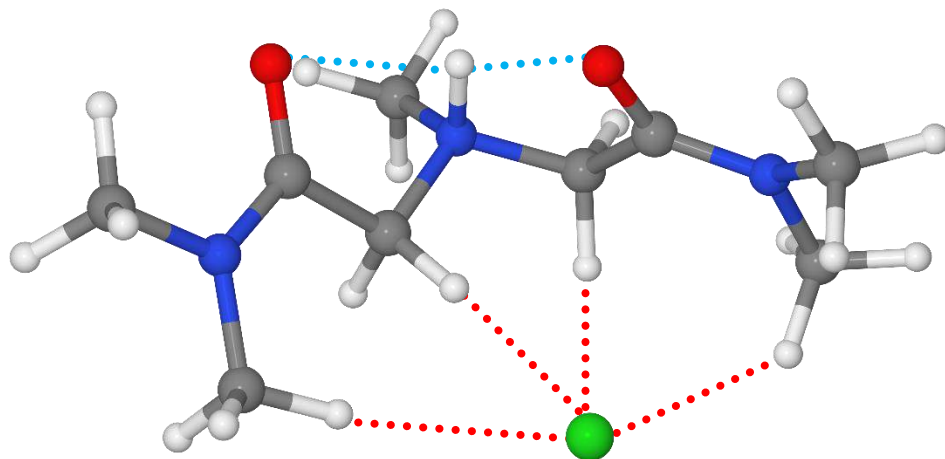
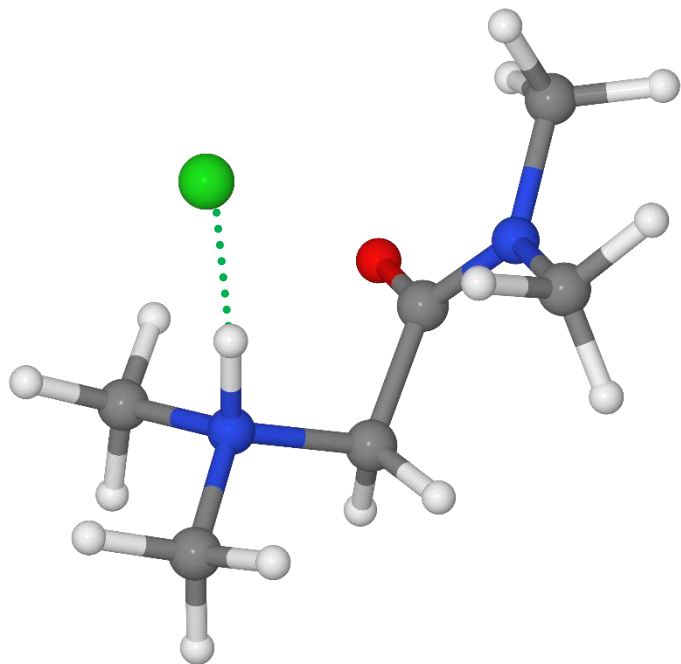
[Cl(MonoAA(Me)H)]



[(RhCl₅(H₂O))(MonoAA(Me)H)₂]



Comparing Mono and Bis – Structures



- With MonoAA(Me)H⁺:

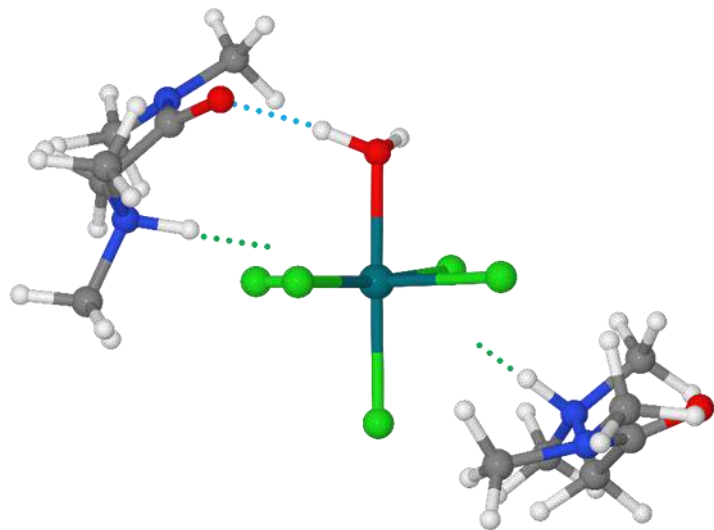
- ▶ N-H...Cl interaction
- ▶ no intra-ligand H-bond

- With BisAA(Me)H⁺:

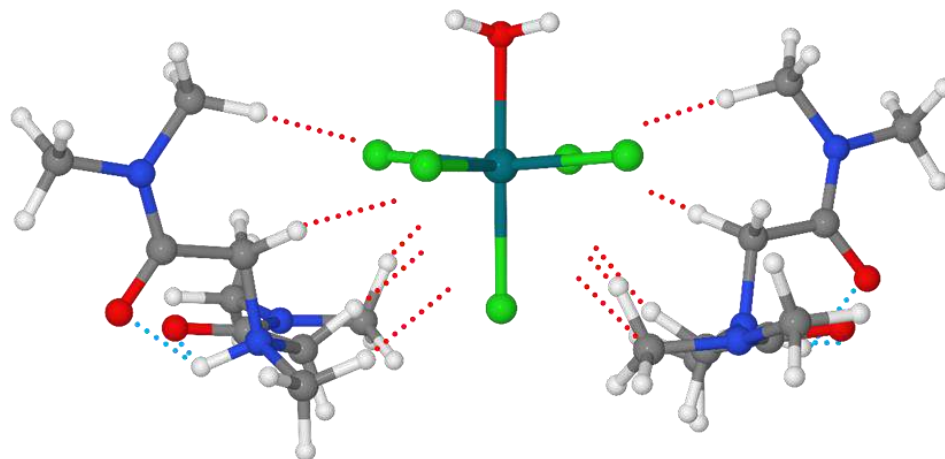
- ▶ C-H... Cl interactions
- ▶ intra-ligand H-bonding

MonoAA(Me)H⁺ and BisAA(Me)H⁺ interact with chloride in **different** ways

Comparing Mono and Bis – Structures



- With MonoAA(Me)H⁺:
 - ▶ both ligands have a N-H...anion interaction
 - ▶ one amide O forms a H-bond with the *aquo* ligand
 - ▶ no intra-ligand H-bonds



- With BisAA(Me)H⁺:
 - ▶ both ligand have C-H... anion interactions
 - ▶ there is no *aquo* ligand to amide O H-bonding
 - ▶ both ligands have intra-ligand H-bonding

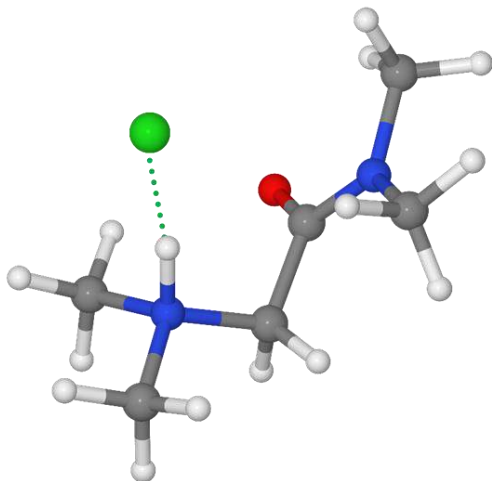
MonoAA(Me)H⁺ and BisAA(Me)H⁺ interact with
[RhCl₅(H₂O)]²⁻ in **different** ways

Comparing Mono and Bis – Structures

- MonoAA(Me)H⁺ and BisAA(Me)H⁺ have **different anion binding sites**
- This is likely due to differing numbers of possible intra-ligand H-bonds
 - ▶ MonoAA(Me)H⁺ only has one potential H-bond → **smaller energy penalty to disrupt**
 - ▶ BisAA(Me)H⁺ has two potential H-bonds → **larger energy penalty to disrupt**

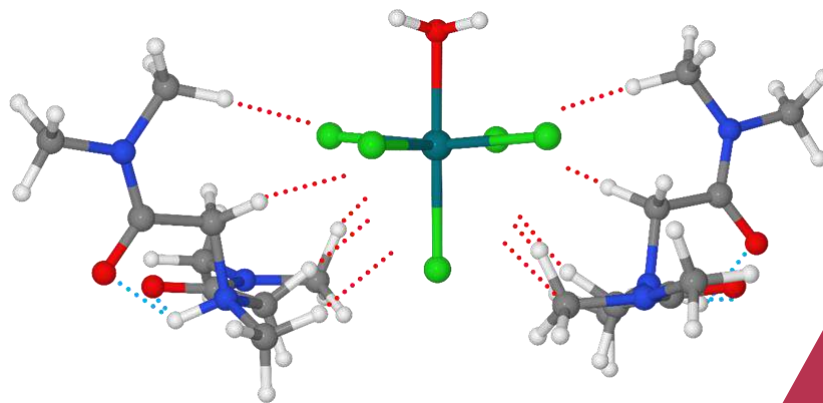
MonoAA(Me)H⁺ binding site:

- N-H...anion interaction
- “Hard” interaction
- Favours binding of “hard” anions, e.g. chloride

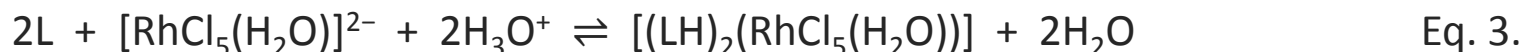


BisAA(Me)H⁺ binding site:

- C-H...anion interaction
- “Soft” interaction
- Favour bindings of “soft” anions, e.g. [RhCl₅(H₂O)]²⁻



Comparing Mono and Bis – Energies



Process	Ligand	Gibbs Free Energy / kJ mol ⁻¹ #
Eq. 1	Mono	-116.4
	Bis	-117.5
Eq. 2	Mono	-133.1
	Bis	-128.1
Eq. 3	Mono	-250.6
	Bis	-259.5
Eq. 4	Mono	15.6
	Bis	-3.3

- The following points can be summarised:

M06/LANL2TZ,6-311+G**

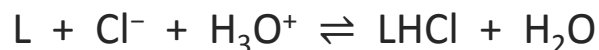
PCM(SCRF, solvent=chloroform or water)

BSSE corrected for using Counterpoise

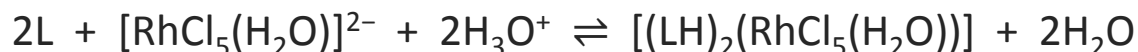
Comparing Mono and Bis – Energies



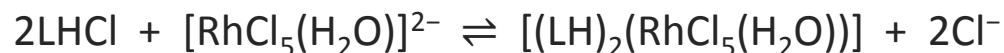
Eq. 1.



Eq. 2.



Eq. 3.



Eq. 4.

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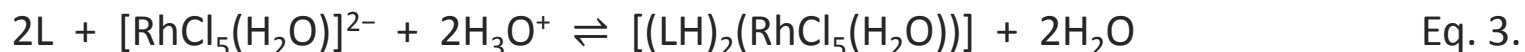
- Protonation energies of the two molecules are comparable

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- The following points can be summarised:
 - Protonation energies of the two molecules are comparable
 - Association with chloride is more favourable for MonoAA(Me) than BisAA(Me)

M06/LANL2TZ,6-311+G**

PCM(SCRF, solvent=chloroform or water)

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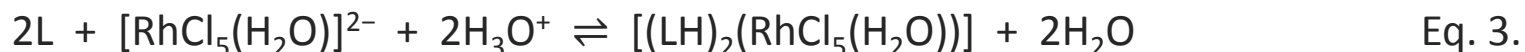
- The following points can be summarised:
 1. Protonation energies of the two molecules are comparable
 2. Association with chloride is more favourable for MonoAA(Me) than BisAA(Me)
 3. Association with the Rh species is more favourable for BisAA(Me) than MonoAA(Me)

M06/LANL2TZ,6-311+G**

PCM(SCRF, solvent=chloroform or water)

BSSE corrected for using Counterpoise

Comparing Mono and Bis – Energies



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Eq. 4	Mono	15.6
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- The following points can be summarised:
 1. Protonation energies of the two molecules are comparable
 2. Association with chloride is more favourable for MonoAA(Me) than BisAA(Me)
 3. Association with the Rh species is more favourable for BisAA(Me) than MonoAA(Me)
 4. Exchange of chloride for Rh species is more favourable for BisAA(Me) than MonoAA(Me)

M06/LANL2TZ,6-311+G**

PCM(SCRF, solvent=chloroform or water)

BSSE corrected for using Counterpoise

Comparing Mono and Bis – Energies

More **favourable association with chloride** using MonoAA(Me)

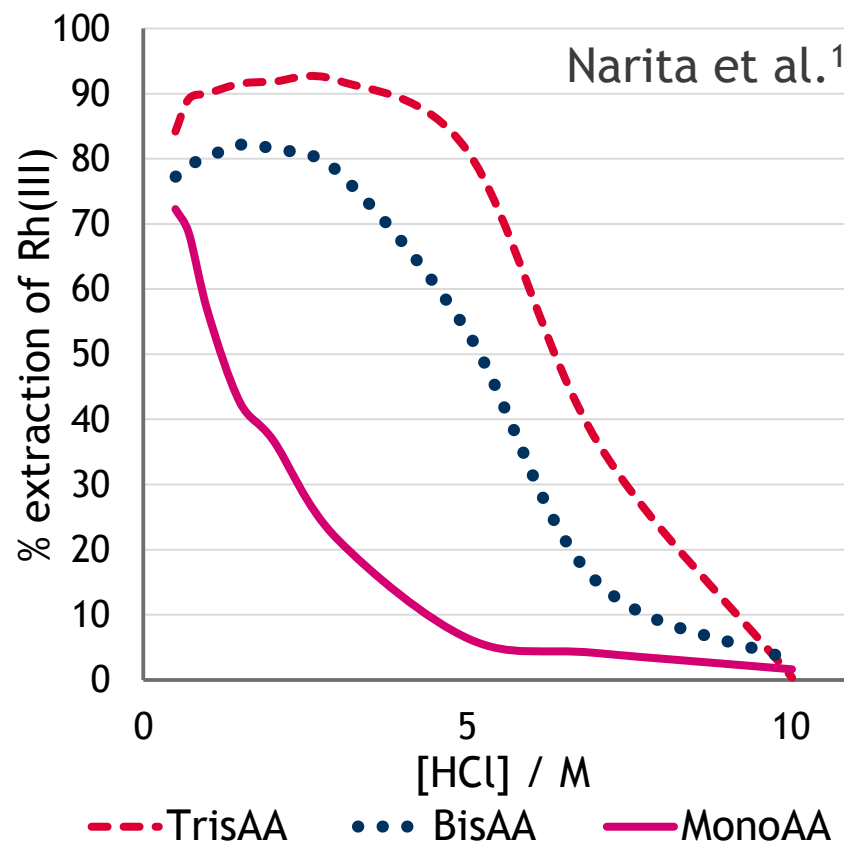
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Rh extraction decreasing with increasing HCl concentration using **MonoAA**

More **favourable association with Rh** using BisAA(Me)

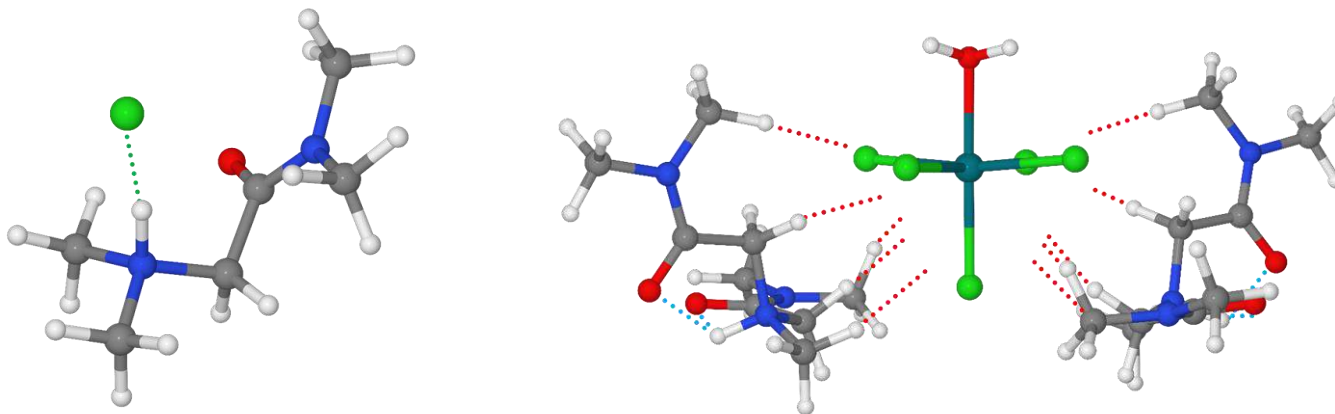
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the **extraction of Rh remaining high** to start and only decreasing with much higher [HCl] using **BisAA**



Conclusions

- QM calculations have shown:
 - ▶ protonated MonoAA(Me) and BisAA(Me) have **different binding sites**
 - ▶ less competition with chloride using BisAA → **BisAA is a more selective extractant**
 - ▶ stronger association with $[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$ using BisAA → **BisAA is a stronger extractant**



QM modelling supports and rationalises the experimental results

- This mode of action study has provided important insight into the extraction mechanism
 - ▶ This information can help design new reagents

Acknowledgements



- Dr Carole Morrison
- Prof Jason Love
- Prof Peter Tasker
- Innis Carson
- Euan Doidge
- Dr Mary Healy
- Jamie Hunter
- Dr Kirsty MacRuary
- Dr David Rodgers



- Dr Ross Gordon
- Dr Emma Schofield



Ongoing work

- QM calculations for the TrisAA(Me) systems

