

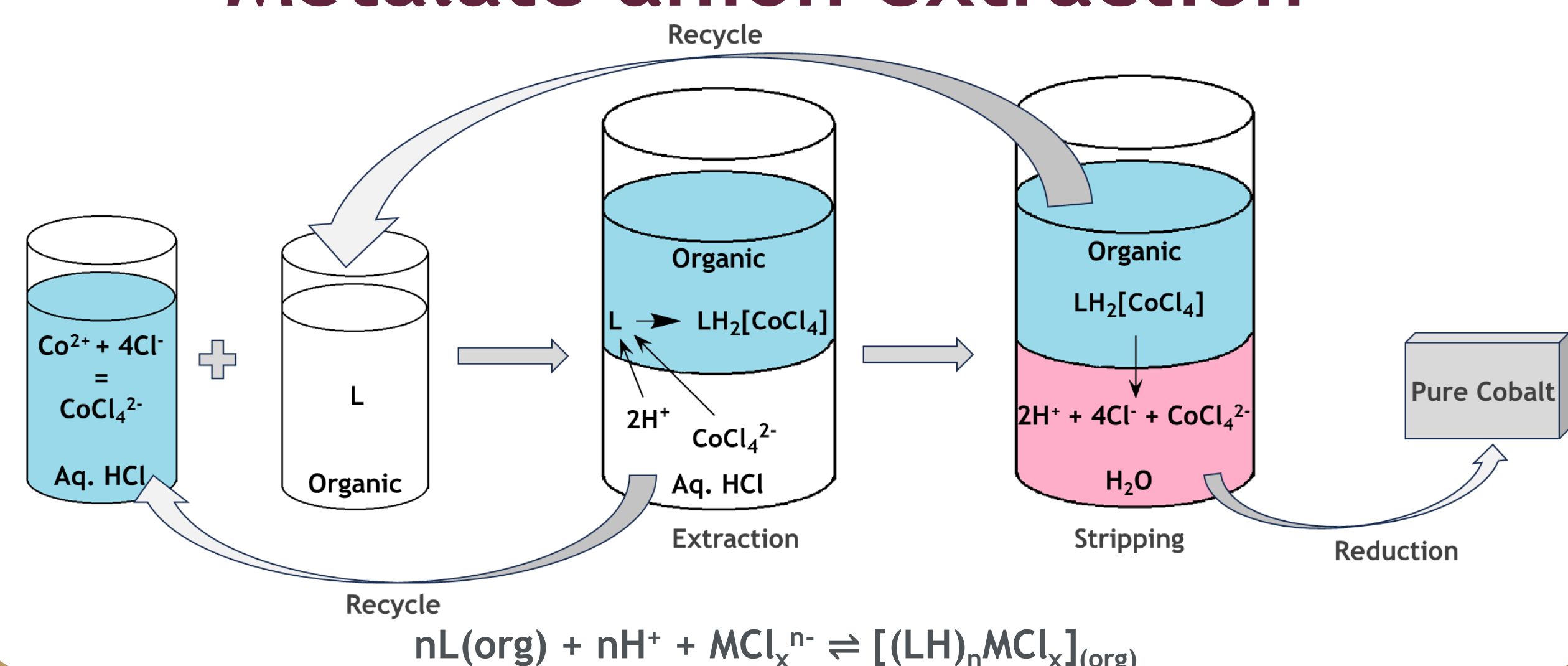
Introduction

Annual demand for Cobalt is expected to nearly double between 2020 and 2030 due to the increased demand for lithium-ion batteries (LIBs) [1]. Recycling of LIB cathodes by means of solvent extraction is an attractive means of recovering Cobalt [2]. NMC cathodes consisting of Ni, Mn and Co are currently the preferred material for electric vehicle batteries [3]. Amine compounds offer a greener route for selective solvent extraction compared to the industry standard phosphorus-based ligands, which also suffers from poor selectivity over Mn [4].

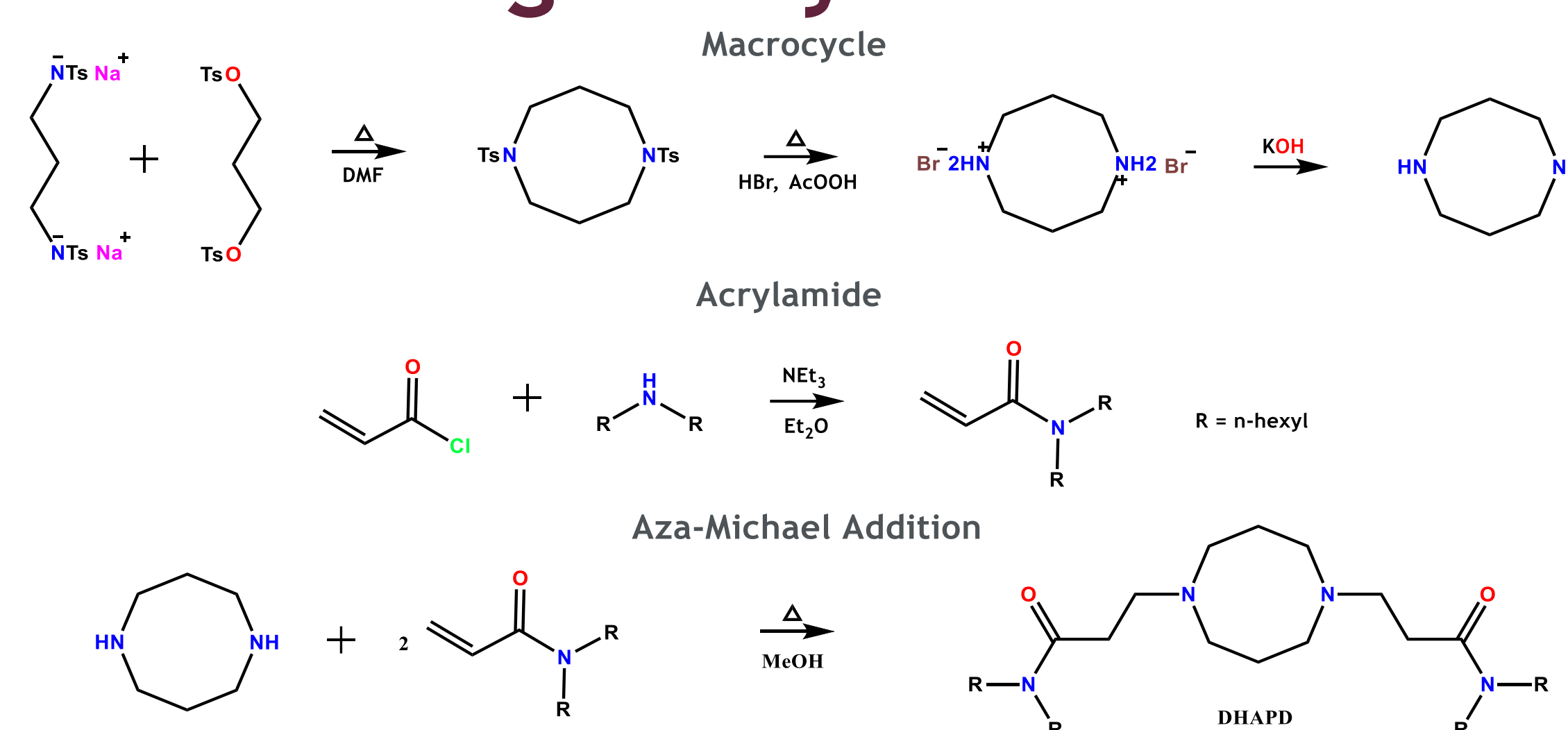
Metalate anion extraction relies on ion pairing between cationic ligands and anionic metal complexes. This is an attractive means of separating Co from Ni and Mn due to the existence of anionic $[\text{CoCl}_4]^{2-}$ in high Cl^- solutions which is not observed for Ni or Mn [5,6]. Tertiary amines can be protonated to form quaternary ammonium species capable of ion pairing with the metalate anion complex [7]. The inclusion of amide groups have been shown to enhance extraction, potentially by stabilizing the positive charge through intramolecular hydrogen bonding [8,9,10].

Several studies have reported on the use of tertiary amines for metalate anion extraction [7-10], however none of them have investigated the use of diamines nor have any macrocyclic ligands been considered. Having two protonatable sites on one molecule could allow for greater materials balance and by incorporating them into cyclic structures not only enhances the stability but forms cavities that may be ideal for the metal complex of interest.

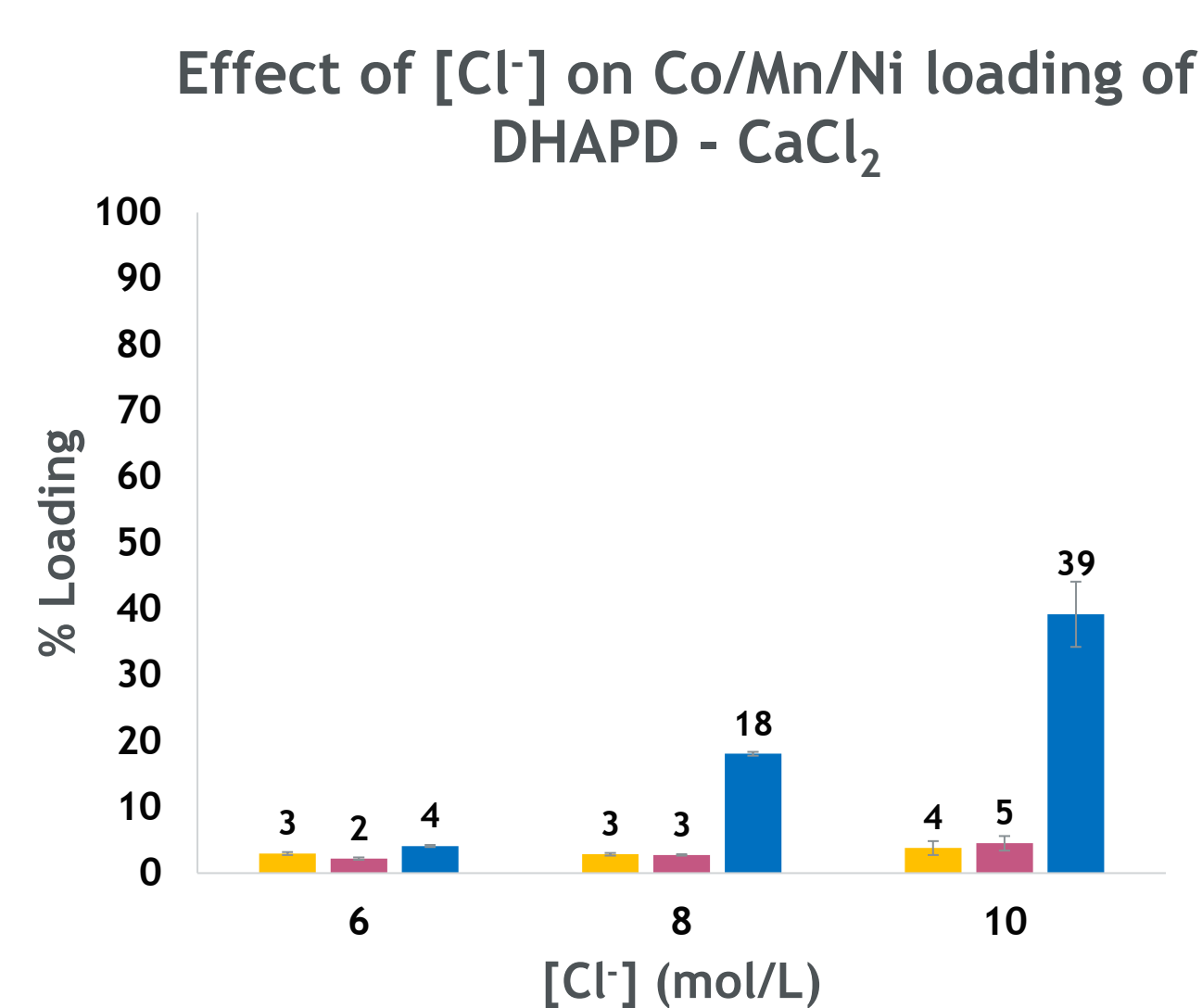
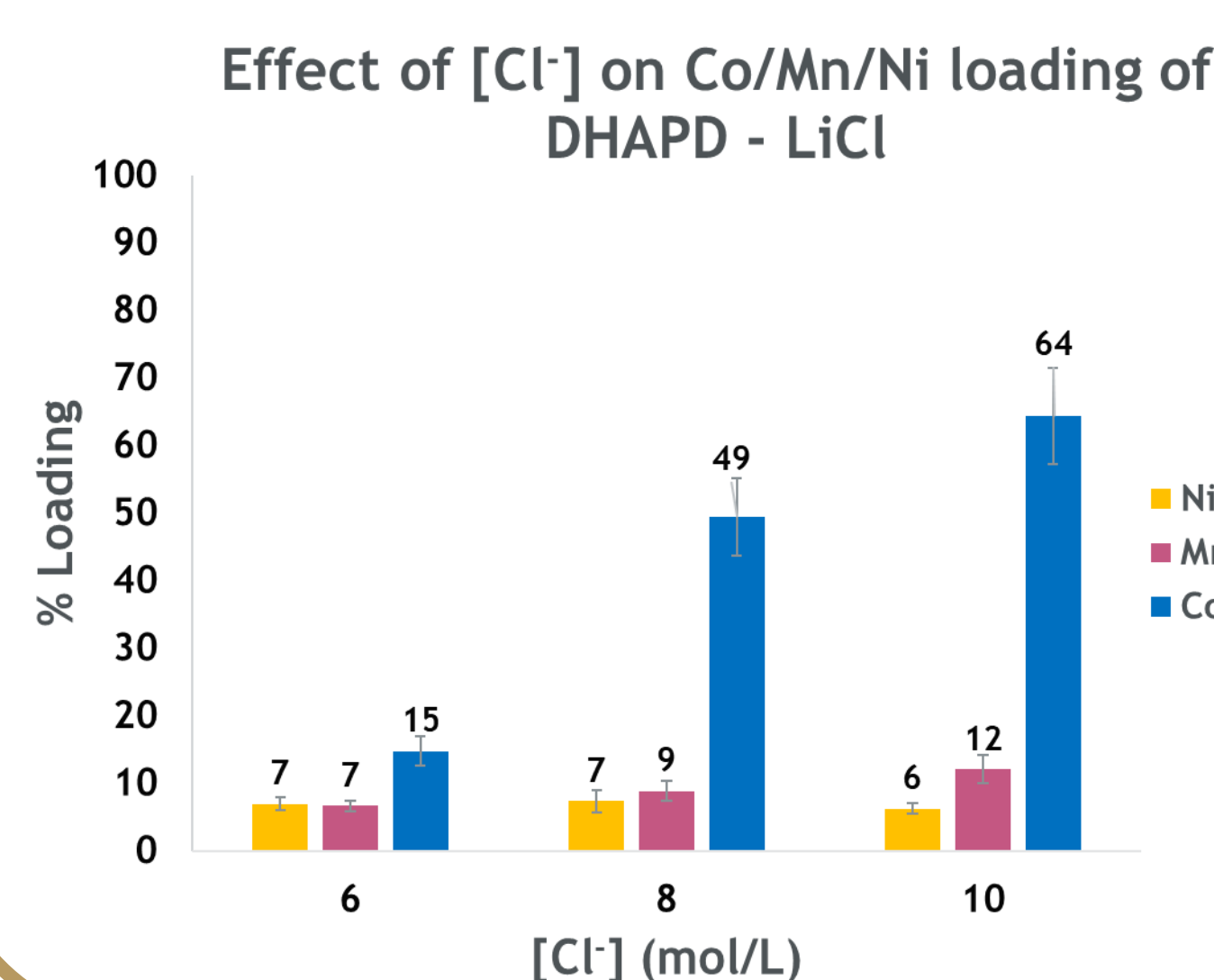
Metalate anion extraction



Ligand synthesis

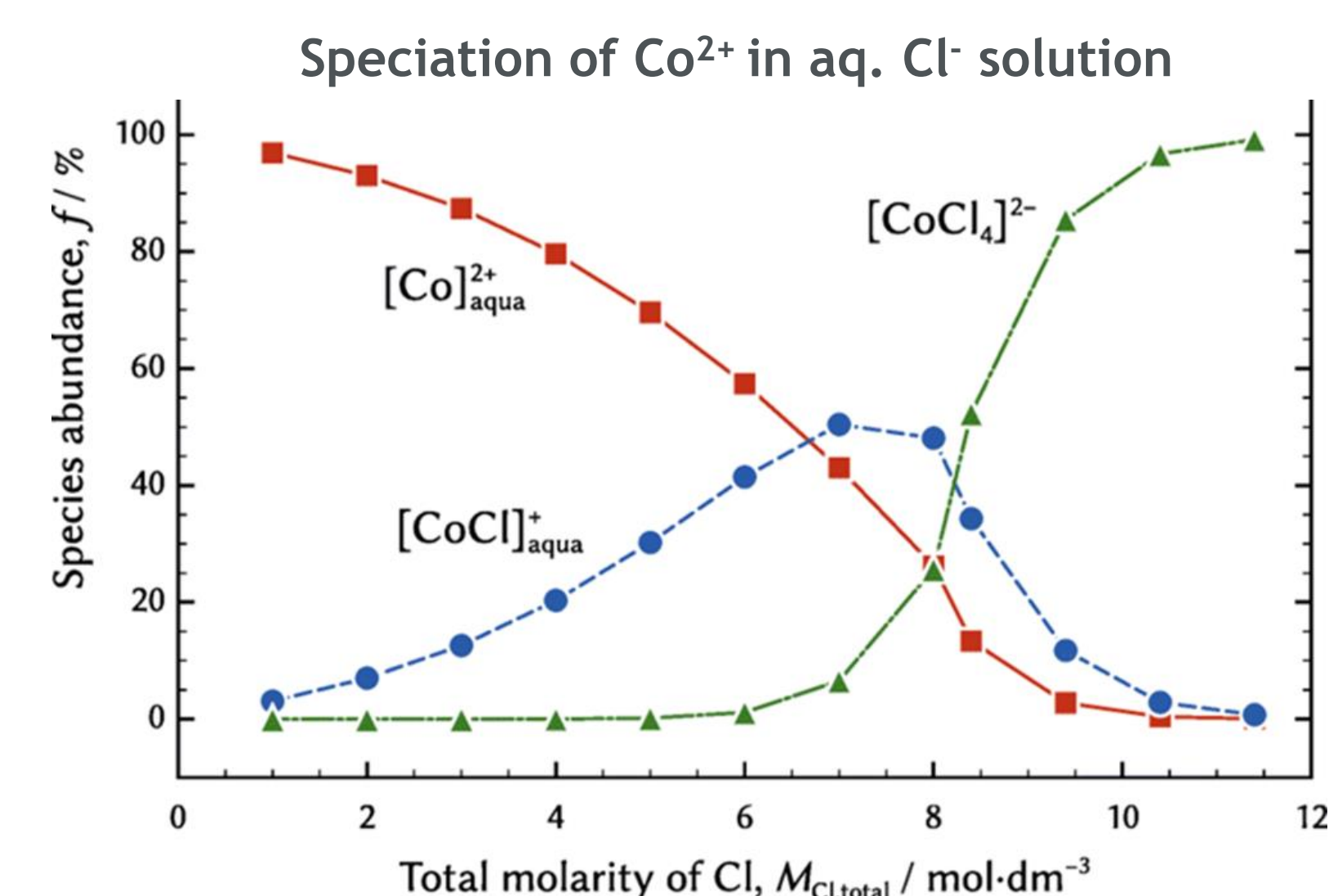


Chloride Concentration

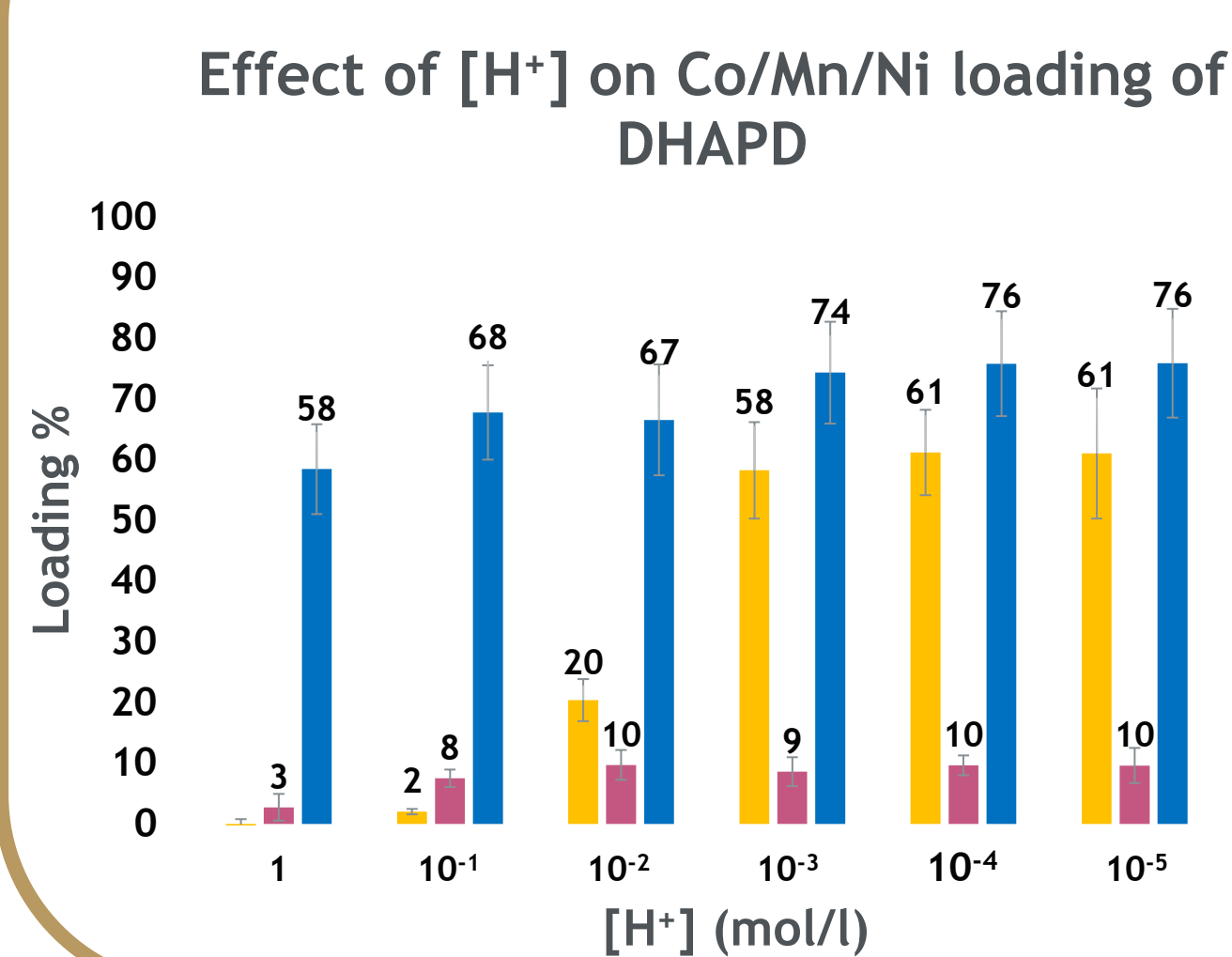


Why high [salt]?

- Cobalt speciation - Cl^-
- Salting out effect
 - High charge density ions have high hydration enthalpy which effectively reduces the hydration of the $[\text{CoCl}_4]^{2-}$ ions thus enhancing phase transfer
- Li^+ versus Ca^{2+} - Only 1 Ca^{2+} for every 2 Cl^- & formation of CaCl^+



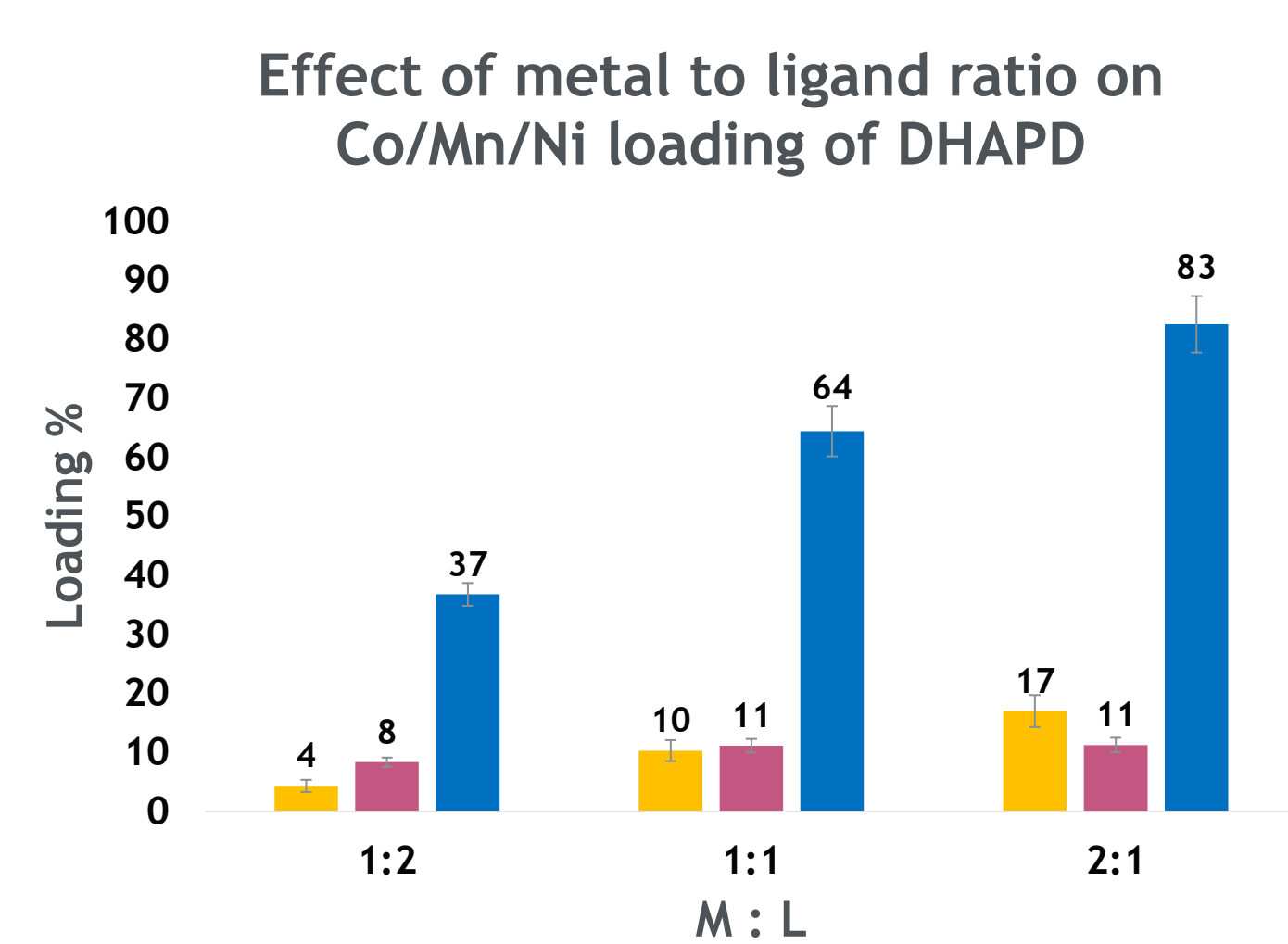
Acid concentration



- High selectivity for Co at low pH
- Extraction of Ni at higher pH
 - Inner-sphere coordination
- Low extraction of Mn

Metal to ligand ratio

- Improvement on extraction is greater when metal is in excess compared to ligand in excess



Conclusions & Future work

- An amide functionalised diamino macrocycle was synthesised and tested as a solvent extraction ligand for recovery of Co from Ni & Mn
- The ligand is selective for Co at high Cl^- concentration and low pH
- The cation of the chloride salt plays a major role in enhancing extraction through the salting out effect
- Higher metal to ligand ratios significantly enhances extraction
- Stripping of the metal from the organic phase is not presented here but is easily achieved by aqueous solution of 0.1M HCl

- This work forms part of a larger project that will investigate the role of the following parameters on the extraction percentage and selectivity.
 - Size of the macrocycle
 - Length and branching of the alkyl chains on the amide groups
 - The non-aqueous solvent
- The stripping of the metal and reusability of the ligands will be investigated
- Straight chain derivatives will be synthesised and compared to the macrocyclic ligands

References & acknowledgments

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