

## Cation and Anion Selectivity of Zwitterionic Salicylaldoxime Metal Salt Extractants

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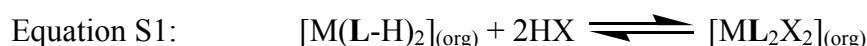
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### Supplementary Information

#### Anion Selectivity by Solvent Extraction

The solvent extraction experiments described in this section were carried out under identical conditions, by contacting a 0.01 M chloroform solution of the metal-only complex  $[M(L1-H)_2]$  with a 0.8 M aqueous solution of the appropriate anion, which was made up using HX and NaX (where X<sup>-</sup> is the anion) with the anion concentration being kept constant. Varying the anion concentration in the aqueous phase of an extraction has been demonstrated<sup>S1</sup> to have a great effect on distribution coefficients and so keeping the concentration constant throughout the experiments is paramount if comparisons are to be made and anion selectivities inferred.

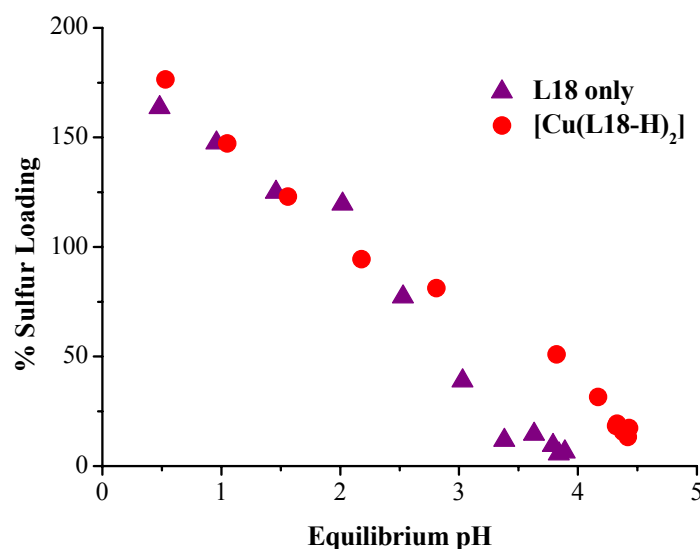
By measuring the anion content of the organic phase and plotting the percentage loading values against the equilibrium pH of the aqueous phase, it is possible to determine the anion loading S-curve. The percentages are calculated by assuming the extraction equilibrium is as follows:



where 2HX is either 2HCl or H<sub>2</sub>SO<sub>4</sub>. To compare selectivities the pH<sub>0.5</sub> value is measured, which is the pH of the aqueous phase at which 50% of the theoretical maximum loading of the anion is in the organic phase. As the anion binding site must

be protonated to extract an anion, the *higher* the  $\text{pH}_{0.5}$  for anion loading the stronger the binding.

Attempts to examine the binding motif for  $\text{CuSO}_4$  *via* X-ray crystallographic studies were unsuccessful, so solvent extraction experiments were carried out to determine the influence of copper on anion binding, by contacting **L1** with sulfate in the absence of copper under identical conditions.



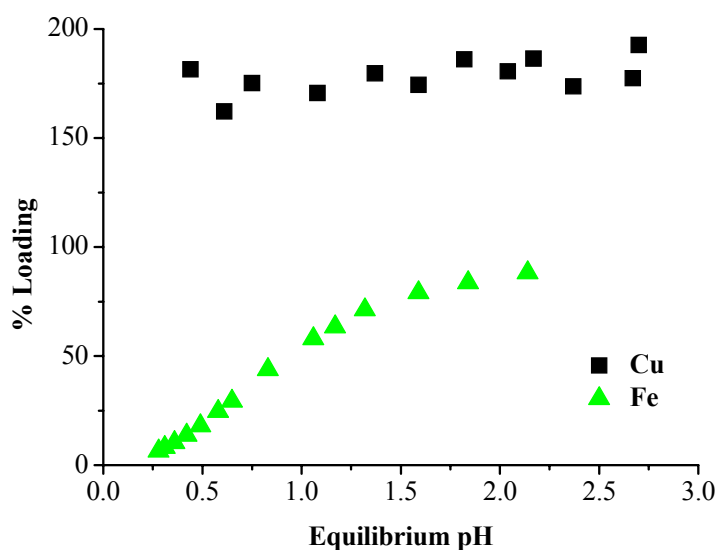
**Figure S1:** Loading of sulfate by in the organic phase when a 0.01 M chloroform solution of  $[\text{Cu}(\text{L1}-\text{H})_2]$  (red circles) or **L1** (purple triangles) is contacted with 0.8 M aqueous sulfate solutions of various pH values. 100% sulfate loading is based on formation of the tritopic assembly  $[\text{Cu}(\text{L1})_2\text{SO}_4]$  or the ion pair  $[(\text{L1}+\text{H})_2\text{SO}_4]$ .

Figure S1 shows that sulfate loading by **L1** is enhanced when copper is present, *i.e.*, the copper(II) complex of **L1** binds sulfate more strongly than the free ligand. The  $\text{pH}_{0.5}$  for sulfate loading by **L1** only is  $\sim 2.8$ , compared to the value of 3.8 for  $[\text{Cu}(\text{L1}-\text{H})_2]$ , indicating possible synergistic  $\text{CuSO}_4$  binding. This phenomenon has been observed previously in the uptake of  $\text{CuSO}_4$  by the substituted salen ligands described in the main text,<sup>S2,S3</sup> and is attributed to the preorganisation of the anion binding site for sulfate when copper is bound. This is unlikely to be the case for **L1** as it binds copper in a *trans* configuration, and in the crystal structure of  $[\text{Cu}(\text{L2}-\text{H})_2]$  the piperidino nitrogen atoms N62A and N62B are separated by 8.703(3) Å. A more likely explanation is that there is an interaction between the copper(II) centre and the

sulfate anion, expected to be similar to the apical Cu...O interactions seen in the crystal structures of [Cu(L2)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>], [Cu(L2)<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub>] and [Cu(L2)<sub>2</sub>(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>]. At lower pH values sulfur loading exceeds 100%, and this is due to the extraction of the bisulfate anion, HSO<sub>4</sub><sup>-</sup>, which is prevalent in copper sulfate solutions at pH < 2.<sup>S4</sup>

### Cation Selectivity with Excess Chloride Ion

As Cu<sup>II</sup>/Fe<sup>III</sup> selectivity is the most commercially significant and as these metal cations have the lowest pH<sub>0.5</sub> values for extraction by L1, S-curves with an excess of chloride (0.8 M) were determined for these two metal ions only. A 0.01 M solution of L1 in chloroform was mixed with an aqueous feed with a concentration of 0.01 M of the appropriate metal cation, but with a chloride concentration of 0.8 M, and pH adjusted by HCl/NaCl.

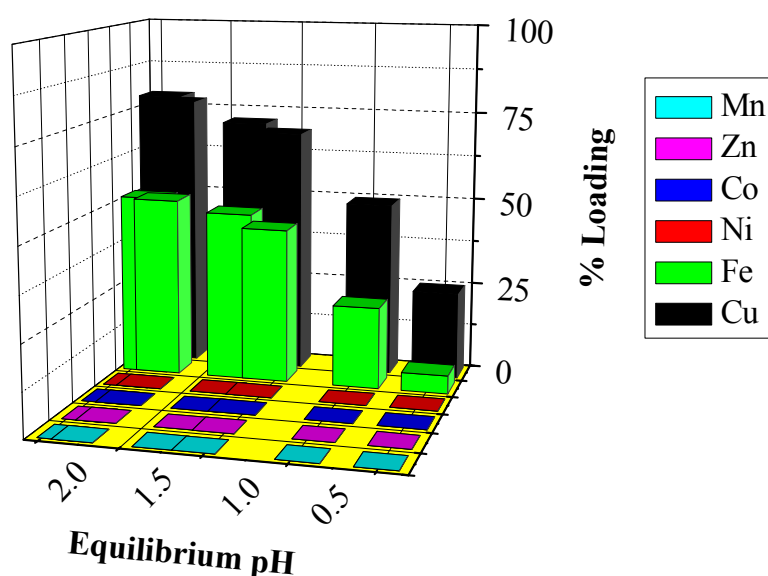


**Figure S2:** pH-profiles for loading of Cu<sup>II</sup> (black) and Fe<sup>III</sup> (green) by 0.01 M chloroform solutions of L1 from equal volumes of aqueous solutions with metal concentrations of 0.01 M and chloride concentrations of 0.8 M. 100% metal loading based on formation of [M(L1)<sub>2</sub>Cl<sub>2</sub>] tritopic assemblies.

The S-curves for copper and iron loading (Figure S2) from chloride media show an improvement when the chloride anion is in excess. Copper loading has previously been shown to increase when chloride concentration increases due to the formation of [CuLCl<sub>2</sub>] complexes.<sup>S1</sup> Iron loading reaches approximately 90% at pH ~ 2 and the

$\text{pH}_{0.5}$  for  $\text{Fe}^{\text{III}}$  loading is 0.9, compared to the value of 1.3 measured previously with equimolar amounts of chloride present. This again indicates that a cooperative binding mechanism exists in the extraction of  $\text{Fe}^{\text{III}}$  and  $\text{Cl}^-$ .

Comparing the S-curves suggests that **L1** may be selective for  $\text{Cu}^{\text{II}}$  over  $\text{Fe}^{\text{III}}$  when extracting from concentrated chloride media. This was investigated by contacting a 0.01 M chloroform solution of **L1** with a mixed metal feed (each metal has a concentration of 0.01 M) with 0.8 M chloride concentration. The results are displayed in Figure S3, and show that **L1** is not selective for  $\text{CuCl}_2$ .

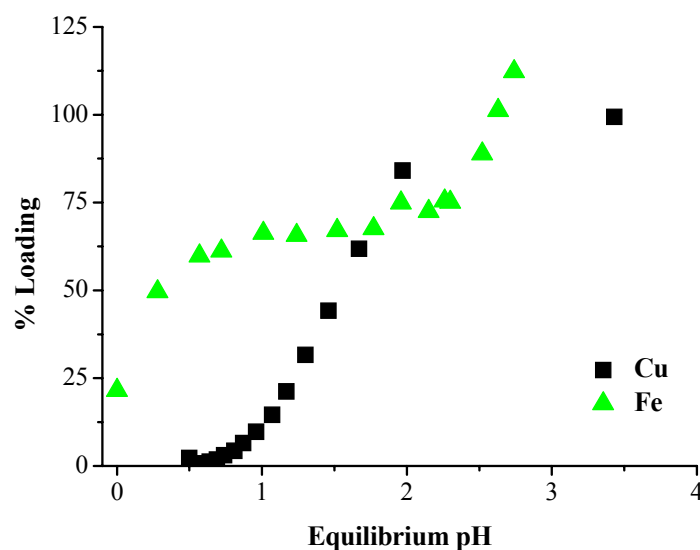


**Figure S3:** Loading of base metals by 0.01 M chloroform solutions of **L1** from equal volumes of an aqueous solution containing each metal chloride shown at a concentration of 0.01 M, with chloride concentration adjusted to 0.8 M with NaCl/HCl. 100% metal loading based on formation of  $[\text{M}(\text{L1})_2\text{Cl}_2]$  tritopic assemblies.

Significant quantities of  $\text{Fe}^{\text{III}}$  are extracted alongside  $\text{Cu}^{\text{II}}$ , which means that **L1** will not be a suitable extractant for  $\text{CuCl}_2$  from a high  $[\text{Cl}^-]$  feed unless this selectivity issue is addressed. This will involve elucidation of  $\text{FeCl}_3$  binding by **L1** and any possible mechanisms of co-extraction.

### Cation Selectivity with Excess Sulfate Ion

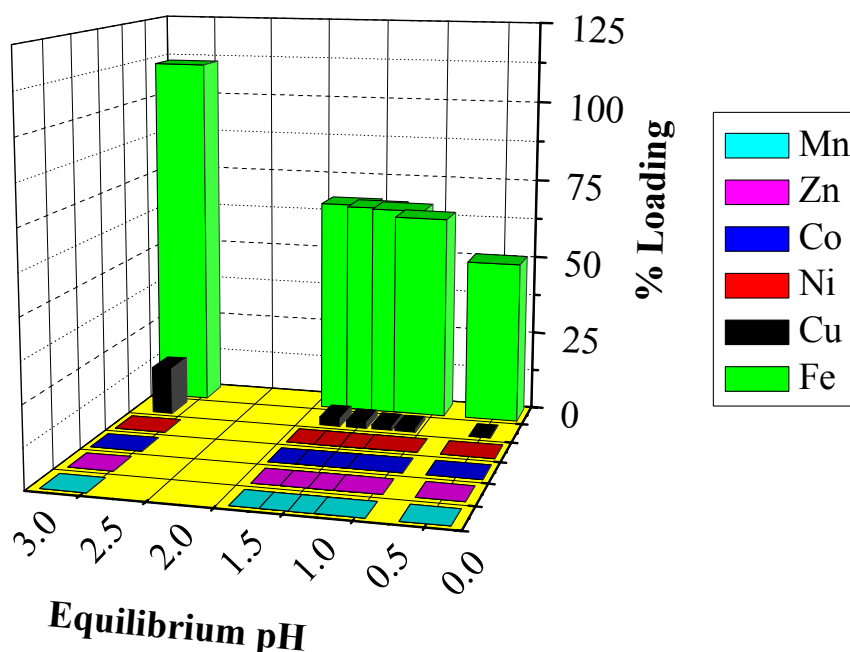
To determine the cation selectivity of **L1** in the presence of an excess of sulfate, a 0.01 M solution of **L1** in chloroform was mixed with an aqueous feed with a concentration of 0.01 M of the appropriate metal cation, but with a sulfate concentration of 0.8 M. The pH was varied by addition of Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> and careful control of the total sulfate concentration was ensured throughout. The S-curves can be seen in Figure S4.



**Figure S4:** pH-profiles for loading of Cu<sup>II</sup> (black) and Fe<sup>III</sup> (green) by 0.01 M chloroform solutions of **L1** from equal volumes of aqueous solutions with metal concentrations of 0.01 M and sulfate concentrations of 0.8 M. 100% metal loading based on formation of [M(L1)<sub>2</sub>SO<sub>4</sub>] tritopic assemblies.

The effect of the increased sulfate concentration is to increase slightly the selectivity of **L1** for Fe<sup>III</sup>: the pH<sub>0.5</sub> for Fe<sup>III</sup> loading of 0.3 is slightly lower for feeds with no added sulfate, whilst the pH<sub>0.5</sub> for Cu<sup>II</sup> loading of 1.5 is slightly increased. Previous examples have observed an increase in pH<sub>0.5</sub> for Cu<sup>II</sup> loading by unsubstituted phenolic oxime extractants when sulfate concentration in the aqueous phase is increased,<sup>S5</sup> but the *decrease* in pH<sub>0.5</sub> for Fe<sup>III</sup> loading indicates that the metal salt complex being formed involves some kind of cooperative interaction between the Fe<sup>III</sup> cation and SO<sub>4</sub><sup>2-</sup> anion. The other notable effect of increasing sulfate concentration is that a plateau at the loading stoichiometry of 3Fe<sup>III</sup>:1**L1** persists to higher pH, indicating that the complex formed involves a favourable interaction with the sulfate anion.

As the increase in sulfate concentration appears to favour  $\text{Fe}^{\text{III}}$  extraction and disfavour  $\text{Cu}^{\text{II}}$  extraction, it was expected that, when extracting from a mixed metal feed, **L1** would favour  $\text{Fe}^{\text{III}}$  uptake. This is confirmed by the data in Figure S5 which shows that  $\text{Fe}^{\text{III}}$  is extracted preferentially, with  $\text{Cu}^{\text{II}}$  extraction only occurring at pH values high enough for iron to be partially precipitated from the feed.



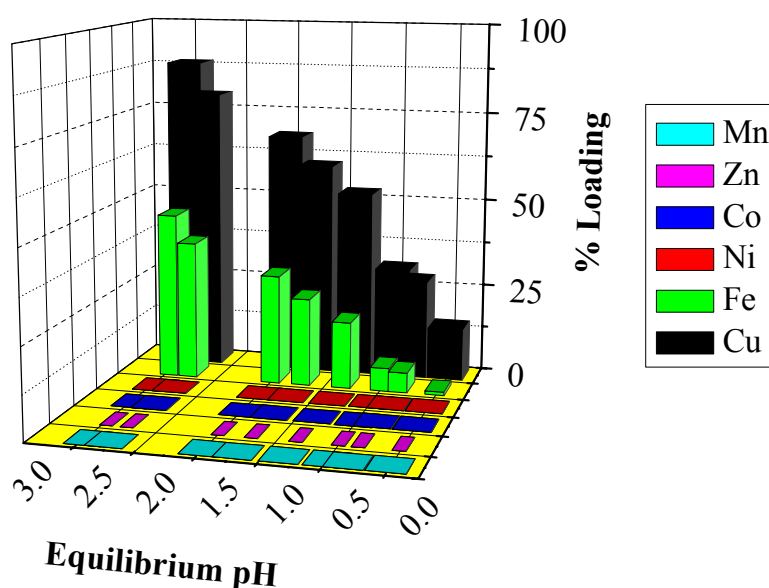
**Figure S5:** Loading of base metals by 0.01 M chloroform solutions of **L1** from equal volumes of an aqueous solution containing each metal sulfate shown at a concentration of 0.01 M, with sulfate concentration adjusted to 0.8 M by addition of  $\text{Na}_2\text{SO}_4/\text{H}_2\text{SO}_4$ . 100% metal loading based on formation of  $[\text{M}(\text{L1})_2\text{SO}_4]$  tritopic assemblies.

### Metal Loading by **L1** from Excess Mixed-Anion Media

A final experiment was carried out in an attempt to partially recreate industrial extraction conditions, using a mixed metal feed containing an excess of both chloride and sulfate, each at a concentration of 0.4 M giving a total ionic strength of 0.8 M. To ensure equal concentrations of chloride and sulfate anions in the feed solution, pH

was adjusted by HCl/NaCl and H<sub>2</sub>SO<sub>4</sub>/Na<sub>2</sub>SO<sub>4</sub> solutions. Metal loadings are displayed in Figure S6.

Again it is clear that L1 is not selective for either Cu<sup>II</sup> or Fe<sup>III</sup>, but extracts a mixture of both metals. Cu<sup>II</sup> is favoured slightly, with loadings of approximately double that of Fe<sup>III</sup> over the pH range, but it seems the selectivity problem will persist while Fe<sup>III</sup> is present in the aqueous phase.



**Figure S6:** Loading of base metals by 0.01 M chloroform solutions of L1 from equal volumes of an aqueous solution containing each metal shown at a concentration of 0.01 M, with chloride concentration adjusted to 0.4 M with NaCl/HCl and sulfate concentration adjusted to 0.4 M by addition of Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub>, giving a total ionic strength of 0.8 M. 100% metal loading based on formation of the tritopic assemblies [M(L1)<sub>2</sub>Cl<sub>2</sub>] and [M(L1)<sub>2</sub>SO<sub>4</sub>].

## References

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