

Transport of metal salts by zwitterionic ligands; simple but highly efficient salicylaldoxime extractants†

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Attaching dialkylaminomethyl arms to commercial phenolic oxime copper extractants yields reagents which transport base metal salts very efficiently by forming neutral 1 : 1 or 1 : 2 complexes with zwitterionic forms of the ligands.

Ligands capable of binding both a metal cation and its attendant anion(s) show the potential to perform the unit operations of *concentration* and *separation* in extractive hydrometallurgical circuits.^{1,2} Substituted, salen-like salicylaldoximes are effective metal salt extractants, with the *cis* arrangement of the cation binding groups forming a preorganised, doubly protonated anion binding site particularly suited to sulfate.³ However, the ease of acid hydrolysis of the imine functionality seen in related reagents⁴ may restrict their application in commercial operations which commonly use sulfuric acid concentrations of up to 150 g l⁻¹ to strip the metal.⁵ Conventional phenolic oxime cation exchange extractants account for approximately a fifth of the world's annual production of copper⁶ and have half lives of over 2.5 years in kerosenes in contact with acid solutions.³ Consequently we have developed a new class of metal salt extractants based on the salicylaldoxime scaffold, and report here some remarkable benefits in using these reagents for metal recovery from chloride streams.

5-*tert*-Butyl-2-hydroxy-3-dihexylaminomethylbenzaldehyde oxime (**L1**) and 5-*tert*-butyl-2-hydroxy-3-piperidin-1-ylmethylbenzaldehyde oxime (**L2**)† are salicylaldoximes bearing pendant dialkylaminomethyl arms, which are protonatable to form anion binding sites. As salicylaldoximes bind base metal cations in a *trans* arrangement⁷ these sites are expected to be well separated, forming a tritopic binding motif which may favour the transport of monoanions (Fig. 1).

The pendant dihexylaminomethyl arm of **L1** imparts good solubility of both the ligand and its complexes in water-immiscible solvents, allowing the extraction of copper and zinc salts to be studied (Table 1).

In both cases cation loading is greater from chloride media. Uptake is above 100%, implying that the expected tritopic

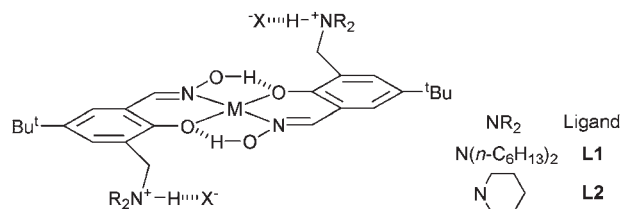


Fig. 1 Expected tritopic metal salt binding motif of **L1** and **L2**.

binding motif (Fig. 1) does not apply and that metal salt binding involves a 1 : 1 stoichiometry:



This unexpectedly high efficiency of metal salt uptake greatly improves mass transfer over that shown by conventional phenolic oxime reagents and deviates from the expected binding model. Formation of 1 : 1 assemblies was confirmed by X-ray structure determination of Cu^{II} and Zn^{II} chloride complexes of **L2**, the piperidinomethyl-substituted analogue of **L1**. [Cu(**L2**)Cl₂] \ddagger contains a zwitterionic form of the ligand with a phenolate oxygen atom and a piperidinium nitrogen atom (Fig. 2). This ensures that the overall assembly is charge neutral and allows the oximic O–H and the piperidinium N–H groups to form hydrogen bonds to chloride ions and the phenolate oxygen atom, which are in the inner coordination sphere of the Cu^{II} ion. This intracomplex H-bonding provides an explanation for the favourable formation of the 1 : 1 complex and, together with the close Cu1A...O1B contacts, generates an assembly with polar functionality located centrally and a hydrophobic exterior.

Similar features are present in the zinc chloride complex, which has the dinuclear structure [Zn₂(**L2**)₂Cl₄] \ddagger shown in Fig. 3. In this case the phenolate groups form similarly strong

Table 1 Cation and anion loadings (%)^a from aqueous 1 M solutions of metal chlorides or sulfates by a 0.01 M solution of **L1** in CHCl₃

Metal	% Loading from aqueous media			
	Chloride		Sulfate	
	M	Cl	M	SO ₄
Cu	184	160	100	91
Zn	138	143	10	18

^a Based on the formation of 1 : 2 metal salt to ligand ratios as in Fig. 1.

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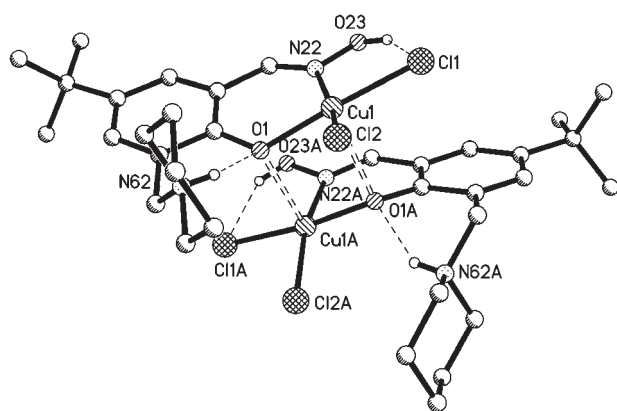
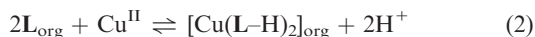


Fig. 2 Assembly of two $[\text{Cu}(\text{L}2)\text{Cl}_2]$ units in the solid state, with $\text{Cu1A}\cdots\text{O1B} = 2.507(2)$ Å. Intracomplex H-bonding contacts; $\text{N62}\cdots\text{O1} = 2.754(3)$ Å, $\text{N62}\cdots\text{Cl2} = 3.560(3)$ Å and $\text{O23}\cdots\text{Cl1} = 2.925(3)$ Å.

bonds to both metal atoms, and the oximic N and two chloride ligands complete the distorted trigonal bipyramidal $\text{NO}_2\text{Cl}_2^{3-}$ coordination sphere.

The favourable loadings of metal chlorides which are possible with the new type of extractant could underpin the development of very efficient processes for metal recovery from chloride feeds, for which a number of new leaching processes have recently been developed.¶ Whilst many of these have the advantage of generating elemental sulfur rather than sulfate as a by-product from the processing of sulfidic ores (see for example the oxidative ferric chloride leaching of copper in Scheme 1) the very high chloride and proton activities of these feeds² limits the efficiency of conventional phenolic oximes which operate in a pH-dependent process (2):



L1 has the advantage that it functions in a zwitterionic form, with no release of protons to the aqueous phase on extraction (eqn (1)) and therefore no pH adjustment is needed to achieve high loadings. Also, as a consequence of functioning in a zwitterionic form, it can be easily acid-stripped (Table 2) resulting in high mass transport efficiencies.¶

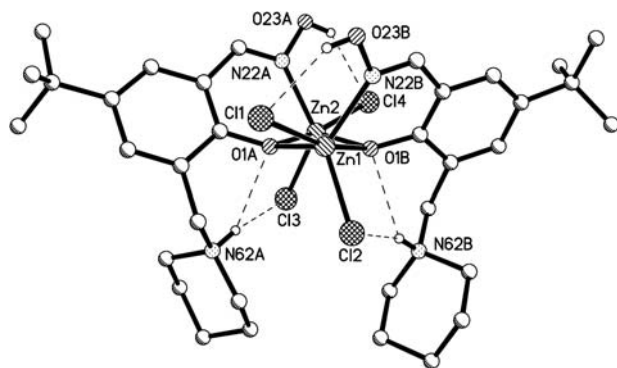
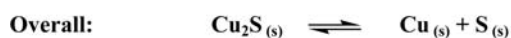
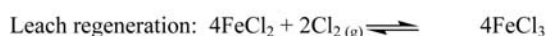
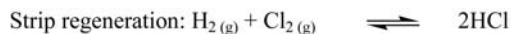
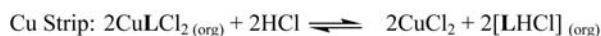


Fig. 3 The dinuclear complex $[\text{Zn}_2(\text{L}2)_2\text{Cl}_4]$, $\text{Zn1}-\text{O1A} = 2.031(2)$ Å, $\text{Zn1}-\text{O1B} = 2.109(2)$ Å, $\text{Zn2}-\text{O1A} = 2.078(2)$ Å and $\text{Zn2}-\text{O1B} = 2.021(3)$ Å. All chloride atoms form intramolecular H-bonds in the inner coordination spheres; $\text{Cl1}\cdots\text{O23B} = 2.987(3)$ Å, $\text{Cl2}\cdots\text{N62B} = 3.446(2)$ Å, $\text{Cl3}\cdots\text{N62A} = 3.379(3)$ Å and $\text{Cl4}\cdots\text{O23A} = 3.003(2)$ Å.



Scheme 1 Flowsheet for the processing of sulfidic copper ores, combining CUPREXTM technology⁸ and the chloralkali process with a metal salt extractant such as **L1**.

As the chloride anions are extracted within the inner coordination sphere of the Cu^{II} cation, high chloride concentration in the aqueous feed is expected to favour copper loading by **L1**. This is confirmed by solvent extraction (ESI†) with maximum copper loading values of $\sim 180\%$ observed with aqueous chloride concentrations above 0.8 M. These observations suggest **L1** could operate as a conventional cation exchange reagent for copper extraction from chloride feeds to which conventional phenolic oxime reagents are not suited.⁴

Stability of **L1** and **L2** to acid hydrolysis under extraction conditions is imperative for commercial application. Both show little degradation when contacted with aqueous sulfate solutions of $\text{pH} < 1$, while a structurally related “salen” extractant hydrolysed completely (ESI†). Most importantly in terms of material balances in metal recovery, the leaching and solvent extraction steps to effect concentration and separation could be coupled with well established technology, the CUPREX⁸ and chloralkali processes, to effect reduction to generate conductivity-grade copper and to regenerate all reagents used in the flowsheet (Scheme 1). In this case **L1** operates as a metal salt reagent, and the overall material balance effectively involves the splitting of copper(i) sulfide ore into its component elements with the consumption of electrical power. Attempts to replicate the unexpected binding motif for CuCl_2 and ZnCl_2 with other salts were unsuccessful, and in most cases tritopic complexes of the type shown in

Table 2 Dependence of Cu-stripping^a and molar transport efficiency^b on the concentration of the HCl strip solution

% Cu in loaded organic	%Cu in stripped organic ([HCl]/g l ⁻¹)	Molar transport efficiency
183	16 (55)	1.67
185	17 (110)	1.68
185	15 (165)	1.70
184	8 (220)	1.76

^a Based on formation of 1 : 2 CuCl_2 to **L1** complex as in Fig. 1. ^b Moles of Cu transported by 2 moles of **L1** after 1 load/strip cycle.

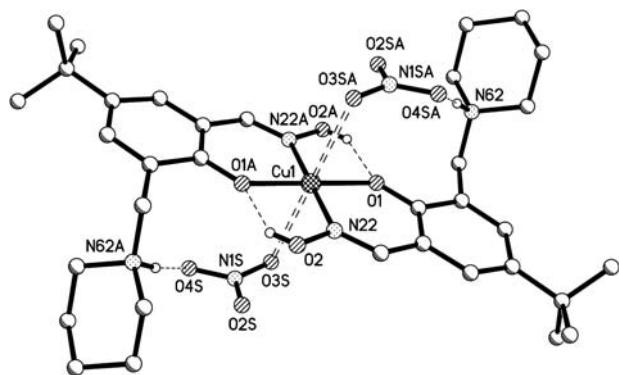


Fig. 4 The solid state structure of $[\text{Cu}(\text{L2})_2(\text{NO}_3)_2]$, showing the interaction of the nitrate anion with the piperidinium N–H group, $\text{N62A} \cdots \text{O4S} = 2.842(2) \text{ \AA}$, and the Cu^{II} cation, $\text{Cu1} \cdots \text{O3S} = 2.722(2) \text{ \AA}$.

Fig. 1 were obtained. $[\text{Cu}(\text{L2})_2(\text{NO}_3)_2]$ is typical, and shows the characteristic 14-membered *pseudomacrocyclic* H-bonding arrangement of bis-salicylaldoximate copper(II) species⁷ (Fig. 4). Protonation of the piperidine moieties has generated two equivalent anion loading sites occupied by the nitrate anions, which are bound by a combination of electrostatic and H-bond interactions. One oxygen atom of each nitrate anion is located above and below the CuO_2N_2 coordination plane.

As the favoured formation of 1 : 1 L : MCl_2 assemblies with copper and zinc and their solubility in water-immiscible solvents appears to be very dependent on the new ligands addressing the chloride ions in the outer coordination sphere, it might be expected that **L1** and its analogues will be selective for chloride over other anions. Preliminary results suggest that this is the case. Cation selectivity is also essential for commercial success,³ and detailed studies of these properties and other important features such as hydrolytic stability and solubility are in progress.⁹

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Notes and references

‡ **L1** and **L2** were prepared (ESI[†]) in high yields and purity by oximation¹⁰ of their precursor aldehydes, which have been synthesised previously.¹¹

§ Synthesis of complexes: $[\text{Cu}(\text{L2})\text{Cl}_2]$. **L2** (29.0 mg, 0.1 mmol) in CHCl_3 (10 ml) and CuCl_2 (1.34 g, 10 mmol) in water (10 ml) were stirred together for 16 h, the phases separated and the organic phase evaporated to give a purple solid (39.1 mg, 91%). Crystals of $[\text{Cu}(\text{L2})\text{Cl}_2]$ were grown by slow diffusion of Et_2O into a MeOH solution. $\text{C}_{17}\text{H}_{26}\text{Cl}_2\text{CuN}_2\text{O}_2$, $M_r = 424.85$, orthorhombic, space group, *Pbcn*, $a = 16.542(2)$, $b = 24.736(3)$, $c = 10.4427(13) \text{ \AA}$,

$V = 4272.9(9) \text{ \AA}^3$, $Z = 6$, $T = 150(2) \text{ K}$, 27 848 reflections collected, 4372 independent reflections [$R(\text{int}) = 0.0749$], $R(F) = 0.0545$, $wR_2 = 0.1319$, CCDC 612042 (Found: C, 47.4; H, 6.4; N, 5.8. $\text{C}_{17}\text{H}_{26}\text{Cl}_2\text{CuN}_2\text{O}_2 \cdot \text{CH}_3\text{OH}$ requires C, 47.3; H, 6.6; N, 6.1%). MS (FAB, NOBA) m/z 390 ($[\text{M} - \text{Cl}]^+$ 90%).

$[\text{Zn}_2(\text{L2})_2\text{Cl}_4]$. **L2** (29.0 mg, 0.1 mmol) in CHCl_3 (10 ml) and ZnCl_2 (1.36 g, 10 mmol) in water (10 ml) were stirred together for 16 h, the phases separated and the organic phase slowly evaporated to give colourless crystals of $[\text{Zn}_2(\text{L2})_2\text{Cl}_4] \cdot 4\text{CHCl}_3$. $\text{C}_{34}\text{H}_{52}\text{N}_4\text{O}_4\text{Zn}_2 \cdot 4\text{CHCl}_3$, $M_r = 1330.81$, triclinic, space group, *P1*, $a = 14.1922(16)$, $b = 15.2573(17)$, $c = 15.8100(17) \text{ \AA}$, $\alpha = 90.166(2)$, $\beta = 107.680(2)$, $\gamma = 117.492(2)^\circ$, $V = 2851.6(5) \text{ \AA}^3$, $Z = 2$, $T = 150(2) \text{ K}$, 25 571 reflections collected, 13 277 independent reflections [$R(\text{int}) = 0.0195$], $R(F) = 0.045$, $wR_2 = 0.1165$, CSD 660775. The crystals were sensitive to solvent loss, and after exposure to air gave an off white solid which analysed as $[\text{Zn}_2(\text{L2})_2\text{Cl}_4] \cdot 2\text{CHCl}_3$ (13.1 mg, 24%) (Found: C, 39.9; H, 5.1; N, 5.3. $\text{C}_{34}\text{H}_{52}\text{Cl}_4\text{N}_4\text{O}_4\text{Zn}_2 \cdot 2\text{CHCl}_3$ requires C, 39.6; H, 5.0; N, 5.1%). MS (FAB, NOBA) m/z 818 ($[\text{M} - \text{Cl}]^+$ 25%) 781 ($[\text{M} - 2\text{Cl}]^+$ 74%).

$[\text{Cu}(\text{L2})_2(\text{NO}_3)_2]$. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (23.3 mg, 0.096 mmol) and **L2** (52.0 mg, 0.179 mmol) were mixed in methanol (20 ml) for 16 h and the solvent removed *in vacuo* to give a brown solid (71.8 mg, 99%). Crystals suitable for analysis by X-ray diffraction were grown by diffusion of diethyl ether into a methanol solution. $\text{C}_{34}\text{H}_{52}\text{CuN}_6\text{O}_{10}$, $M_r = 768.37$, monoclinic, space group, *P2₁/n*, $a = 11.8940(6)$, $b = 11.1620(6)$, $c = 14.8410(7) \text{ \AA}$, $\beta = 112.682(3)^\circ$, $V = 1817.92(16) \text{ \AA}^3$, $Z = 2$, $T = 150(2) \text{ K}$, 29 119 reflections collected, 5192 independent reflections [$R(\text{int}) = 0.049$], $R(F) = 0.0409$, $wR_2 = 0.1119$, CSD 683051 (Found: C, 53.6; H, 6.9; N, 10.3. $\text{C}_{34}\text{H}_{52}\text{CuN}_6\text{O}_{10} \cdot 0.5\text{C}_4\text{H}_{10}\text{O}$ requires C, 53.7; H, 7.1; N, 10.4%). MS (FAB, NOBA) m/z 707 ($[\text{M} - \text{NO}_3]^+$, 18%).

¶ 16 papers discussing chloride hydrometallurgy were presented at the recent 6th Copper/Cobre Conference, Toronto, August 2007, proceedings available at www.metsoc.org

|| The mass of copper transported by 1 kg of ligand.⁵ Under the conditions in Table 2, **L1** has an *observed* mass transport efficiency of 143 g kg^{-1} per cycle when stripped with 220 g l^{-1} HCl, *cf.* a *theoretical* maximum of 121 g kg^{-1} calculated for the commercial reagent P50 (5-nonyl-2-hydroxybenzaldehyde oxime).

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