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Review

Co-extraction of cations and anions in base metal recovery☆

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Abstract

Solvent extraction is used increasingly in extractive hydrometallurgy. Conventionally, for base metal recovery, metal cations are transferred selectively to a water-immiscible phase using ligands as ion-exchangers which release an equivalent number of cations, usually protons, back to the aqueous feed solution. This review focuses on a new type of extractant, polytopic zwitterionic ligands, which transfers metal *salts* into a water-immiscible phase. The systems discussed have metal-coordinating sites based on salicylaldimines or salicylaldoximes and the anion-binding sites are provided by pendant alkyl ammonium groups which sometimes also contain amido moieties to enhance the anion-uptake. These new reagents provide an alternative strategy for the *concentration* and *separation* of the metal values which eliminates the necessity of proton transfer, thus opening new flowsheets with good materials balances. In many cases anion- and cation-loading prove to be co-operative processes.

Keywords: Extractive metallurgy; Salicylaldimines; Salicylaldoximes; Metal salt extraction; Cation binding; Anion binding; Ditopic ligands; Copper extraction; Nickel extraction

1. Introduction

The last three decades have seen a significant increase in the use of solvent extraction for the recovery of base metals. This can be attributed in part to the earlier development by the nuclear industry of robust continuous processes using mixer settlers [6]. In a typical flowsheet (Fig. 1), the metal values in an ore are leached into an aqueous solution and the desired metal is then transferred to a water-immiscible solvent to achieve the unit operations of *concentration* and *separation*. Stripping back to give a pure electrolyte allows the metal to be recovered by electroreduction.

The transfer of a metal value from the pregnant leach solution to the water-immiscible solvent can be effected by a number of

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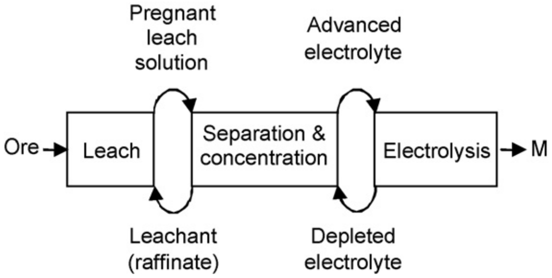


Fig. 1. The basic flowsheet for extractive hydrometallurgy which allows complexing agents to achieve the operations of *separation* and *concentration*.

different mechanisms, which depend on whether the extractant operates on the inner or outer coordination sphere of the metal ion and how the loading/stripping equilibria are controlled. In order to obtain effective separation and maintain high electrolyte purity for the electrowinning process, metal extractants must show very high selectivity for the metal of interest.

1.1. Conventional solvent extractants for metal recovery

Cation exchange reagents generate neutral, organic-soluble metal complexes $[ML_n]$ by providing anionic donors (L^-) to the inner coordination sphere. In most cases the anion is generated from an acidic ligand (LH) and the loading-stripping equilibrium is pH-dependent,

$$n\mathrm{LH}_{(\mathrm{org})} + \mathrm{M}^{n+} \leftrightarrows \mathrm{ML}_{n(\mathrm{org})} + n\mathrm{H}^+$$

Flowsheets using such reagents transfer protons across the circuit in the opposite direction to the desired metal cation and can give a very good materials balance if leaching consumes acid and electroreduction generates acid, as in the recovery of copper from oxidic ores which is shown in Fig. 2. Such processes currently account for nearly a third of the world's copper production [7].

Anion exchange reagents complex metal anions and transfer them into water-immiscible solvents, usually as contact ion-pairs, for example the extraction of $\mathrm{FeCl_4}^-$ from an aqueous solution using tetraalkylammonium salts (1) or by trialkylamines (2),

$$\mathrm{FeCl_4}^- + [\mathrm{R_4N}]\mathrm{Cl}_{(\mathrm{org})} \leftrightarrows [\mathrm{R_4N}][\mathrm{FeCl_4}]_{(\mathrm{org})} + \mathrm{Cl}^- \qquad (1)$$

$$\mathrm{R_3N}_{(\mathrm{org})} + \mathrm{H}^+ + \mathrm{FeCl_4}^- \leftrightarrows [\mathrm{R_3NH}][\mathrm{FeCl_4}]_{(\mathrm{org})} \qquad (2)$$

The electrostatic attraction between the anion and trialkylammonium ion is assumed to be complemented by hydrogen-bonding in extractions from acidic chloride solutions [6]. Trialkylammonium reagents are used in commercial processes to recover kinetically inert precious metals as their chlorometallate complexes from acidic media [8] but few details of the reagents used have been published. Selective transfer of the desired metal value remains a challenge in designing this type of reagent.

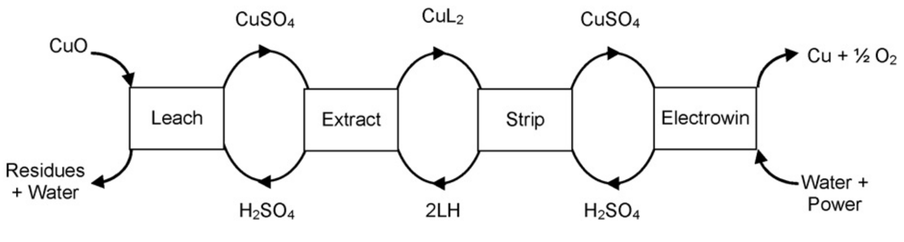
Solvating reagents are neutral molecules which confer organic solubility to metal salts by binding to either the inner or outer coordination sphere of the metal cation [6]. In one of the best defined examples,

$$\mathrm{UO_2}^{2+} + 2\mathrm{NO_3}^- + 2\mathrm{TPB}_{(\mathrm{org})} \leftrightarrows [\mathrm{UO_2(NO_3)_2(TBP)_2}]_{(\mathrm{org})}$$

both the solvating reagent, tributyl phosphate (TPB), and attendant nitrate anion participate in inner sphere coordination. Positioning the equilibrium to favour either loading or so stripping of the metal cation can be controlled by manipulating the concentration of the coordinating anion in the aqueous phase.

1.2. Polytopic solvent extractants for metal salts

Attendant anions in the pregnant leach solution are not transported in conventional *ion exchange* processes. Reagents which transfer a metal *salt* across a circuit may give improved materials balances in circuits where the leaching step does not re-use the exchanged ion [6]. Some examples of ditopic receptors which transport alkali [9–11] and uranyl [12] salts have been reported. This review focuses on extractants which transport metal *salts* by complexing the metal cation and attendant anion(s) in separate binding sites. Such *polytopic* ligands (Fig. 3) also have the potential advantages over the conventional reagents discussed above



$\mathrm{CuO + H_2SO_4}$	$\rightleftharpoons$	$\mathrm{CuSO_4 + H_2O}$	Leach
$\mathrm{CuSO_4 + 2LH_{(org)}}$	$\rightleftharpoons$	$\mathrm{CuL_{2\,(org)} + H_2SO_4}$	Extraction
$\mathrm{CuL_{2(org)} + H_2SO_4}$	$\rightleftharpoons$	$\mathrm{CuSO_4 + 2LH_{\,(org)}}$	Strip
$\mathrm{CuSO_4 + H_2O}$	$\rightleftharpoons$	$\mathrm{Cu + ½\,O_2 + H_2SO_4}$	Electrowin
CuO	$\rightleftharpoons$	$\mathrm{Cu + ½\,O_2}$	Overall

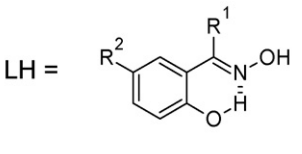


Fig. 2. Steps and materials balance for copper production using phenolic oximes as cation exchange solvent [3].

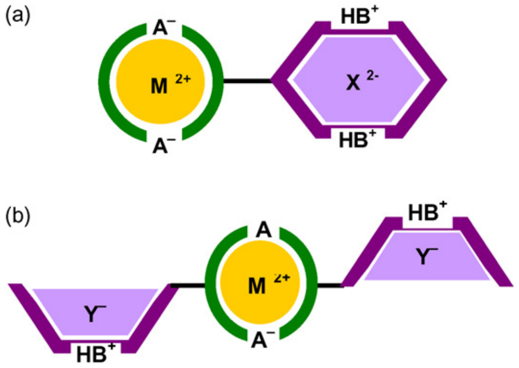


Fig. 3. Ditopic (a) and tritopic (b) systems giving neutral complexes with M(II)X and M(II)Y_2 salts where the cation and anion(s) are bound in zwitterionic forms of the ligands.

because they could open up flowsheets in which the cation and anion are separately stripped from the reagent. If the polytopic ligands are designed with zwitterionic cation- and anion-binding sites then changes in pH can be used to strip the metal and attendant anion(s) in the recovery process.

Whilst the loading of a metal salt into a polytopic ligand (Fig. 3) apparently involves independent cation- and anion-binding processes, in practice these are usually interdependent. The co-operativity of cation/anion binding and how this can be exploited to enhance the strength and selectivity of loading of metal salts is one of the themes considered below in the design of solvent extractants to meet the requirements of the *concentration* and *separation* operations of particular flowsheets.

1.3. Leaching and recovery of base metals from sulfidic ores

Polytopic reagents of greatest interest for base metal recovery are those which can selectively extract sulfates or chlorides from pregnant leach solutions. The major primary sources of base metals are sulfidic ores which can be oxidatively leached to generate sulfate streams,

$$\mathrm{MS} + 2\mathrm{O_2} \rightarrow \mathrm{MSO_4}$$

and several processes for high pressure oxidative leaching have been developed recently [13]. In many cases the resulting pregnant leach solution also contains some chloride ions which are added to accelerate leaching or are present in saline bore waters used in the processes [14]. In other cases, for example when oxidative ferric chloride leaching is used [6], chloride ion predominates in the pregnant leach solution,

$$\mathrm{MS} + 2\mathrm{FeCl_{3(org)}} \leftrightarrows \mathrm{MCl_2} + \mathrm{S_{(s)}} + 2\mathrm{FeCl_2}$$

Because chloro-complexes of many base metals have high thermodynamic stability, *solvating* extractants can be used to generate neutral complexes in water-immiscible solvents.

$$\mathrm{M^{2+}} + \mathrm{L_{(org)}} + 2\mathrm{Cl^-} \leftrightarrows [\mathrm{MLCl_2}]_{(org)}$$

However, it is often not easy to reverse this equilibrium to recover the metal chloride and recycle the ligand [6], and consequently transporting chloride ions into a polytopic reagent in a water-immiscible solvent without direct bonding to the metal's inner coordination sphere offers an easier mechanism for stripping.

Sulfate is a much poorer ligand for base metal cations and there are no commercially available *solvating* regents which allow formation of organic-soluble [$\mathrm{MLSO_4}$] species with the sulfate in the metal's inner coordination sphere [6].

In both chloride and sulfate process streams the base metals are usually in their divalent form. The examples described below focus on the recovery of Ni(II) and Cu(II).

2. The design of polytopic solvent extractants for transition metal salts

The rational development of new polytopic solvent extractants for transition metal sulfates or chlorides can draw on the principles for the design of anion receptors, a rapidly expanding area of research [15–20] Most of the work on the measurement of the relative strengths of anion-binding by different receptors has involved complex formation in a single phase solvent system. Nevertheless, the information these measurements provide is very useful for the development of highly selective extractants for use in two phase systems. The design of multidentate ligands to achieve high selectivity of complexation of cations is now well understood [21] and consequently the major challenges in extraction of metal salts lie in achieving high selectivity of anion transport.

2.1. Factors influencing the strength of anion-uptake

The strength and selectivity of extraction of anions into a water-immiscible medium depends on a number factors [22]. The Hofmeister bias [23] predicts that where substantial dehydration of the anion accompanies phase-transfer then those anions which have the highest hydration free energies are those which are least effectively transferred from an aqueous solution. In the context of chloride or sulfate feed streams for base metal recovery, this results in it being significantly more difficult to extract metal sulfates (see below).

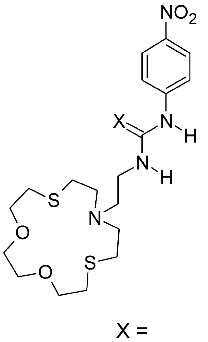
Appropriate combinations of electrostatic and secondary bonding interactions, particularly H-bonding, can be used to enhance the enthalpies of host-anion binding and control of the geometrical disposition of cationic groups and hydrogen-bond donors in an anion receptor can lead to high selectivity of anion-binding [15–19].

2.2. Co-operativity of anion and cation uptake

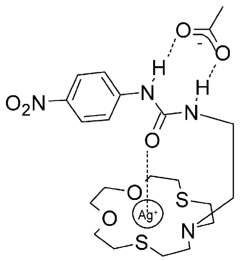
A number of elegant studies of the binding of transition metal salts by polytopic ligands in the solution state have been reported recently [24–38] and several illustrate co-operativity of cation/anion binding [25–28,31,38–42] Silver(I) complexes of thioether macrocycles which have a pendant urea or thiourea units show enhanced binding of oxoanions. The Ag(I)-enhancement of binding by 10^3–10^6 is thought to arise from the coordination of the oxygen or sulfur atom in the urea/thiourea in **1** to the silver atom which increases the H-bond donor capability of the NH groups, for example to an acetate ion as in **2**. It is also possible that the anion may bind to the silver atom and also form a bifurcated H-bond with the urea, for example as in **3**.

An extensive range of aza-thioester macrocycles containing a single methylene linker between a macrocycle N-atom and an amide or acetylurea group has been reported [43]. The nature of the anion has been shown to have a major effect on solution speciation and on the efficiency of extraction of silver, for example the loading of silver(I) by **4** [43] varies in the order of $ClO_4^- \approx BF_4^- > NO_3^-$. This would be predicted from the relative hydration energies of the anions and thus follows the Hofmeister bias [23] (see above).

The urea-functionalized phenanthroline ligand **5** was designed so that in a tetrahedral 2:1 complex of the phenanthroline units with a Cu(I) ion the pendant urea groups could chelate an anion. $[Cu(\mathbf{5})_2]^+$ shows a selectivity for $H_2PO_4^-$ over $CH_3CO_2^-$ in a low polarity solvent to give $[Cu(\mathbf{5})_2(H_2PO_4)]$, but in higher polarity media the complex can open up to give 1:2 *exo* complexes with acetate $[Cu(\mathbf{5}\ldots OCCH_3)_2]^-$ [26].



X =
1a O
1b S



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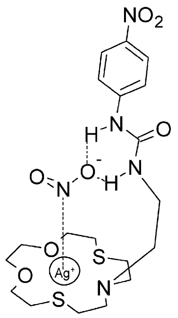

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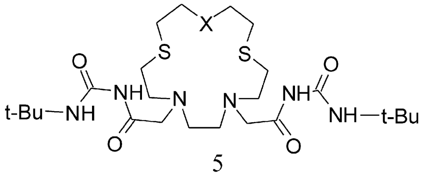
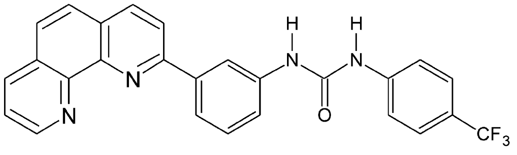


5
4, X = O or S



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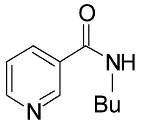
Control of the disposition of pendant amide or urea moieties on the pyridine and quinoline ligands **6** and **7** [44,45] in kinetically inert Pt(II) complexes, $[Pt(L)_4]^{2+}$, allows these to bind strongly to anions. Complexes with tetraoxoanions such as sulfate, $[PtL_4\ldots SO_4]^0$, or rhenate, $[PtL_4\ldots ReO_4]^+$, are thought to have all four hydrogen bonding sites oriented on the same side of the Pt(II) coordination plane whilst monoanions such as halides or PF_6^- form 1:2 complexes $[PtL_4\ldots X_2]^0$ in which the anions are on opposite sides of the coordination plane each being bound by two pendant amido or urea units.



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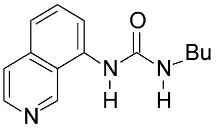

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The binding of anions to ligands with urea groups attached *meta* and *para* to the pyridine nitrogen atom has been shown to vary greatly when complexed to Ag(I) ions [27,42]. In these cases it is hard to predict or determine what disposition of the urea groups in solution results from the coordination of the pyridino N-atoms to Ag(I) centres, but some very interesting solid state assemblies have been observed.

In terms of enhancing the binding of anions it is clear from these studies that two important roles of the attendant cation are to template the functional groups which bond to the anion, pre-organizing these to provide a good fit for a particular anion, and also to provide additional binding sites for the anion via its own inner or outer coordination sphere.

3. Zwitterionic extractants for base metal recovery

Relatively few of the polytopic ligands for metal salts which have been described in the literature have been designed to function in metal recovery processes. An important issue for successful commercial use of such reagents is their cost and recyclability. Even though most flowsheets ensure that reagents are recycled there is always some loss, and even when losses are small very expensive reagents translate to high capital costs in plants [1].

As suggested earlier, reagents for extractive metallurgy that provide separate cation and anion binding sites are advantageous because the anion and cation can be stripped selectively. If the binding sites are part of a zwitterionic form of the reagent then loading and stripping can be controlled by varying the pH of the aqueous phase in contact with the reagent (Fig. 4). Path A illustrates how the metal is recovered from the metal salt complex which is formed by contacting the free ligand with the pregnant leach solution. The metal can be selectively stripped from the metal salt complex by decreasing the pH, leaving the ligand salt. The free ligand can then be recovered via path A by contacting the ligand salt with a basic aqueous phase. Path B illustrates how the anion can be exchanged by removing the anion X^{2-} with base then contacting the resulting metal-only complex with H_2Y to obtain the metal salt MY_2.

3.1. Selectivity of anion binding in zwitterionic extractants

We have developed a simple procedure for quantifying the selectivity of anion extraction in two-phase systems by extractants which operate in the zwitterionic forms shown in Fig. 4. Solutions of metal-only complexes, [M(L-2H)], in water-immiscible solvents can be titrated with acids,

$$[M(L–2H)]_{org} + H_2X \rightleftarrows [MLX_2]_{(org)}$$

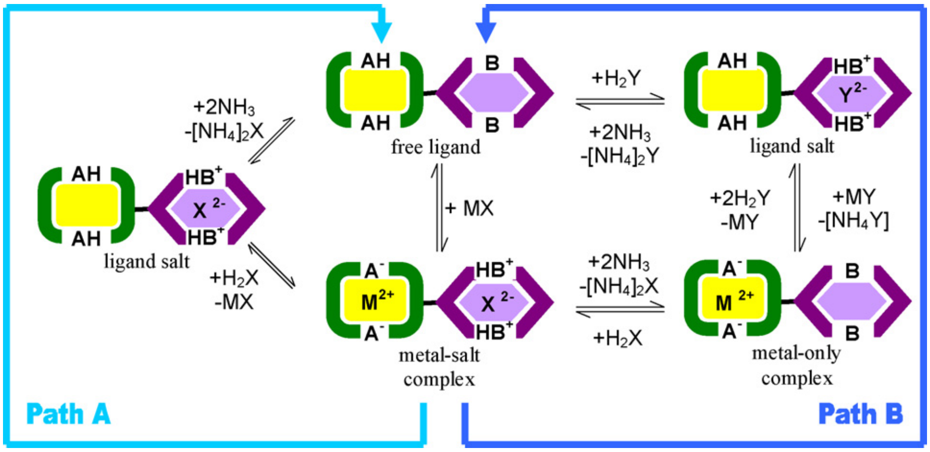


Fig. 4. The pH dependent interconversions of the ditopic ligand, its salts and its 'metal-only' and 'metal-salt' complexes.

The apparent basicity of the pendant amine arms is greater when the anion is more strongly bound and the $pH_{1/2}$ (i.e. the pH associated with 50% loading) is higher (Fig. 5). The difference between $pH_{1/2}$ values from titrations with different acids provides a direct measure of the selectivity of extraction of the acids' conjugate anions. For base metal recovery, streams usually contain either sulfate and/or chloride salts depending on the leaching technology employed (see above). Consequently high selectivity of anion transport of sulfate over chloride or vice versa is essential to generate a pure electrolyte for electrowinning in the flowsheet outlined in Fig. 1.

3.2. Zwitterionic extractants based on salicylaldimines

We have used simple derivatives of salicylaldimine ligands (Fig. 7) to develop zwitterionic reagents for extractive metallurgy. Pendant amine groups can be protonated to provide the anion-binding site(s) whilst the deprotonated salicylaldiminato units create a conventional binding site for a metal cation. The solid state structure (Fig. 6) of a nickel(II) sulfate complex of a 'salen-type' ligand demonstrates that the pendant morpholinium groups 'chelate' the sulfate ion in the [$NiLSO_4$] assembly. A combination of electrostatic forces and bifurcated H-bonds hold the sulfate anion between the morpholinium nitrogen atoms.

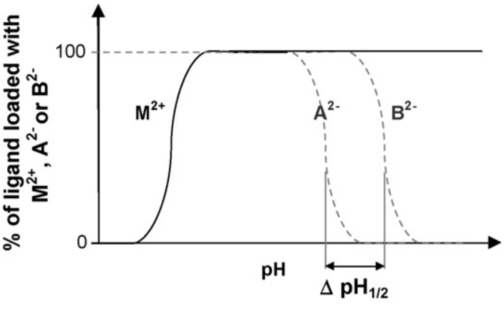


Fig. 5. The pH profiles for loading of a divalent cation, M^{2+}, and two different anions, A^{2-} or B^{2-} onto ligands with protonatable pendant groups which form anion-binding sites.

The structure in Fig. 6 illustrates a key feature of the coordination chemistry of these systems, the cooperativity of cation and anion binding. The free 'salen' ligands have extended structures in the solid state usually with a 180° torsion angle between the N–C–C–N in the central ethane unit [2,4,5]. As a result, the separation between the pendant amine N-atoms is ∼16 Å. Incorporation of the Ni^{2+} to generate a planar $N_2O_2{}^{2-}$ donor set 'templates' the morpholinium groups to chelate a dianion. The importance of approximating the pendant anion-binding groups has been demonstrated by solvent extraction experiments. Some of the pH dependent equilibria are shown in Fig. 7 [46]. 'Metal only' complexes, [M(**8**-2H)], are formed at high pH and sulfate and bisulfate salts of the ligand, [(**8** + 2H)SO_4] and [(**8** + 2H)$(HSO_4)_2$], are formed at low pH.

The pH-dependence of sulfate loading by the *o*-phenylene-bridged ligand **8a** and its 'copper only' complex [Cu(**8a**-2H)] are compared in Fig. 8. The uptake of sulfate by the free ligand is typical of salen-type systems like **8**, with very little transfer of sulfate from the aqueous phase being observed at pH > 2.0. When the pH is decreased below 2.0, the sulfate-loading rises rapidly, approaching 200% at pH < 0.5. This is attributed to the

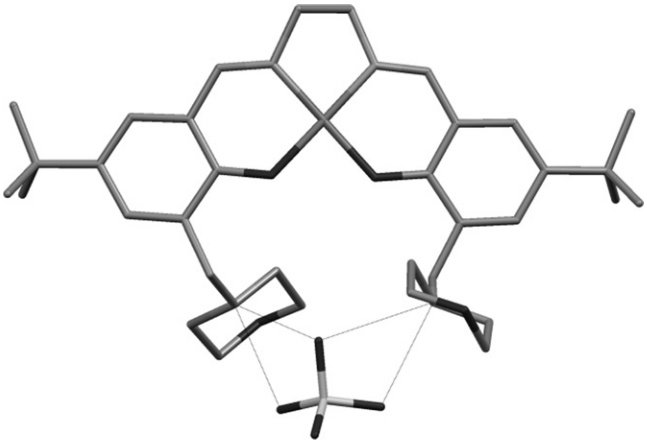
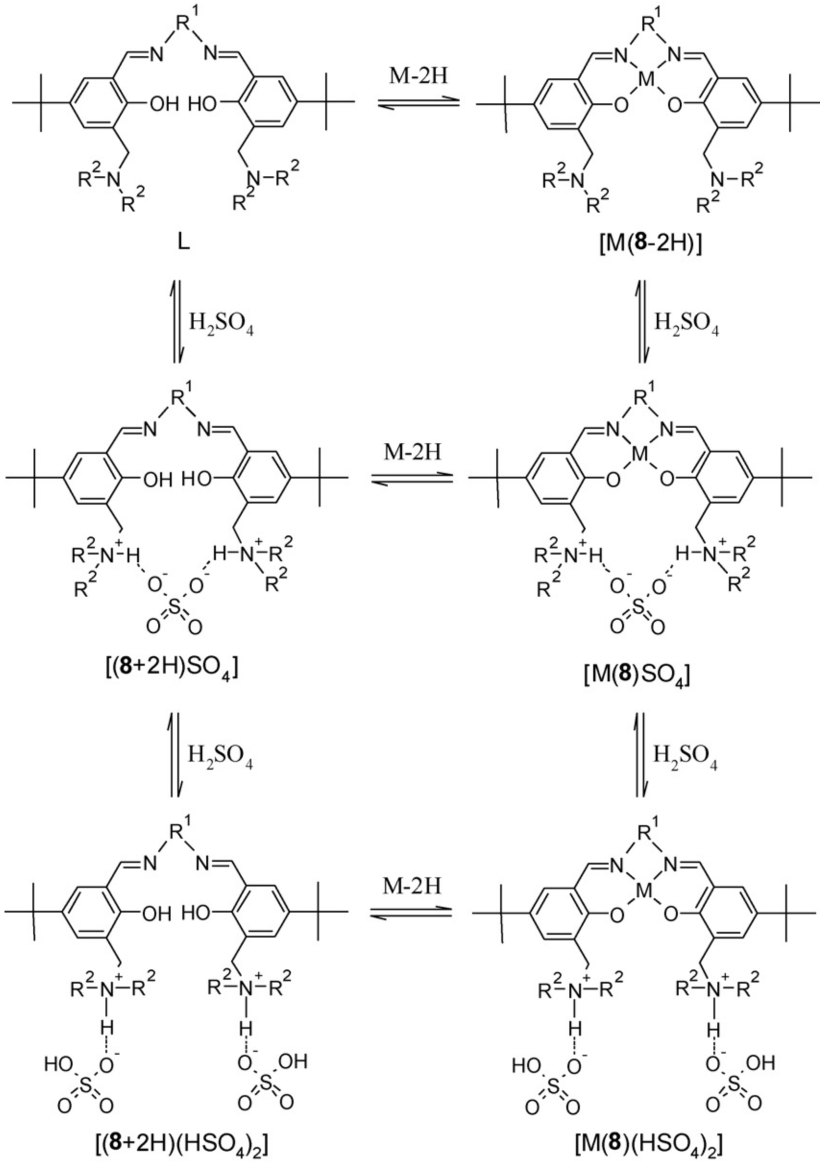


Fig. 6. Crystal structure of the [Ni(**8**)SO_4] complex in which the salen ligand bears pendant morpholinomethyl groups [38–40].



	R^1	R^2
8a	*o*-C_6H_4	*n* - C_6H_{13}
8b	$(CH_2)_2$	*piperidine*
8c	± *trans* - 1,2-cyclohexyl	*n* - C_6H_{13}
8d	2, 2’ - biphenyl	*n* - C_6H_{13}

Fig. 7. Equilibria of ditopic salen-based ligands, metal and sulfate with changing pH, M = Cu^{2+}.

extraction of two HSO_4^- anions per ligand which predominate in the aqueous phase at pH < 2.0. The copper complex [Cu(**8a**-2H)], loads sulfate at significantly higher pH values and the 1:1:1 complex [Cu(**8a**)SO_4] predominates in the pH range 1.5–3.5. In this region, the copper complex shows a marked selectivity for SO_4^{2-} over HSO_4^-. This, along with the increase in apparent basicity of the di-*n*-hexylamino methyl groups in the copper complex, is consistent with the copper ion templating the pendant amine groups to provide a good fit for the dianionic form of sulfate.

In the context of an efficient hydrometallurgical circuit, it is essential to have metal loading and stripping into the salen donor set in conveniently accessible pH-ranges. The ethane-bridged ligand, **8b**, shows Cu^{2+} loading and stripping and SO_4^- loading and stripping in almost an ideal pH-range for recovery of $CuSO_4$ from aqueous feed solutions which have been adjusted to pH ≈ 3.0 in order to remove Fe(III) from solution (Fig. 9) [5,47].

Incorporating additional hydrogen bonding groups in the form of amido or urea units in the pendant arms of the salen-

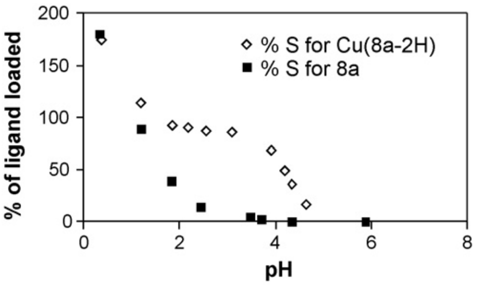


Fig. 8. The uptake of H_2SO_4 by 0.0100 M chloroform solutions of either **8a** or [Cu(**8a**-2H)] from an equal volume of H_2SO_4/Na_2SO_4 solutions [total SO_4^{2-} concentration was 0.800 mol dm^{-3}].

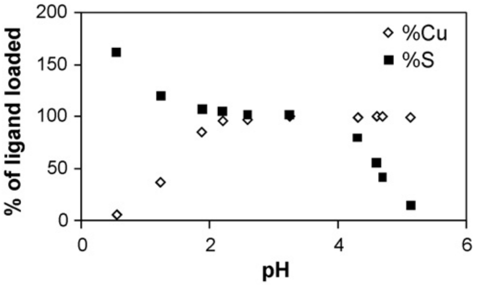


Fig. 9. The pH-dependence of Cu^{2+} and SO_4^{2-} loading of **8b**.

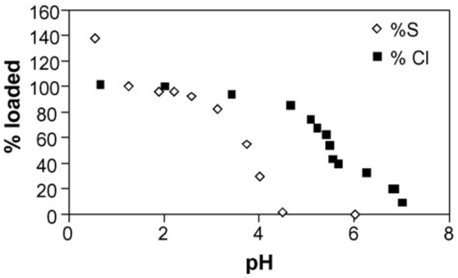


Fig. 11. The pH-dependence of chloride and sulfate loading of a chloroform solution of [Cu(**9b**-2H)].

type extractants (Fig. 10) provides the possibility of tuning the selectivity of anion binding [5,48].

[Cu(**9b**-2H)] was found to extract HCl at a higher pH than H_2SO_4 (Fig. 11), indicating that it is selective for binding Cl^- over SO_4^{2-} [$pH_{1/2}$ values: 5.5 ± 0.1 (Cl^-) and 3.8 ± 0.1 (SO_4^{2-})]. Such Cl^-/SO_4^{2-} selectivity is consistent with the Hofmeister bias [5] which recognizes that charge-diffuse anions such as Cl^- will be more readily extracted into low polarity solvents than more hydrophilic anions such as SO_4^{2-}. The selectivity for chloride over sulfate is also found in bulk liquid membrane experiments using [Cu(**9b**-2H)] as a carrier in chloroform. In contrast, this selectivity is reversed when binding is studied [5,48] by potentiometric titrations in a single phase containing water (95% MeOH). Under these circumstances it is likely the sulfate ion retains a level of hydration and the *cis*-disposition of the anion-binding groups favours the chelation of the dianion SO_4^{2-} over two monoanions.

The pH-profile for chloride loading (Fig. 11) is consistent with a two stage process and UV–vis spectra suggest that there is some interaction between the chloride ions and the copper centre. A much weaker interaction is indicated for the poorly coordinating sulfate ion.

The competition or co-operation between the metal cation and the anion-binding sites for the anion(s) when extracting metal salts is an issue of considerable practical significance in designing a flowsheet. Tritopic systems of the type shown schematically in Fig. 3, are formed by simple derivatives of the commercial phenolic oxime reagents. As these reagents usually adopt a *trans*-square planar geometry (Fig. 12) in complexes with base metal dications [3] the pendant arms are positioned to allow an interaction with the axial sites of the metal. They are very effective in extractants for copper, nickel or zinc salts [49], but the nature of the extracted species is very dependent on the affinity of the anion for the complexed metal ion and the latter's preference for particular coordination geometries. Weakly coordinating anions such as nitrate approach the axial sites of the

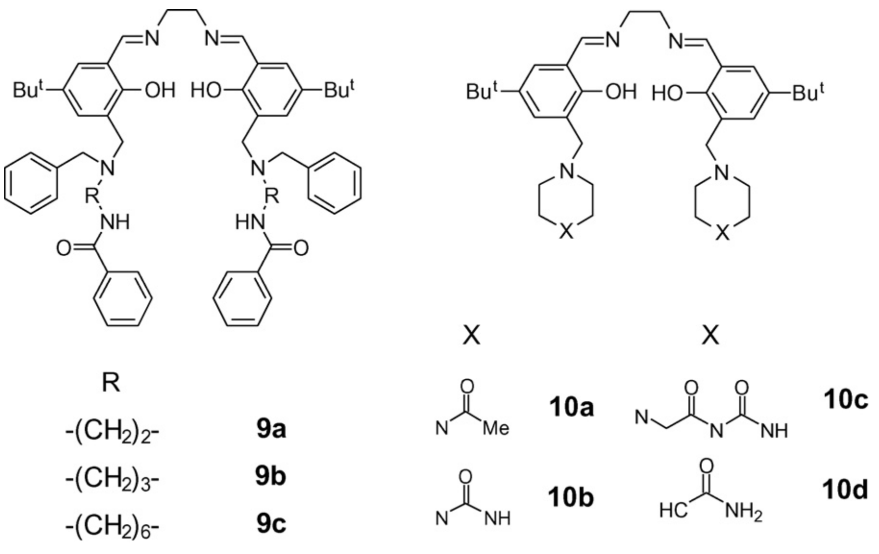


Fig. 10. *Salen* derivatives with pendant anion-complexing groups *ortho* to the phenolate donor atoms.

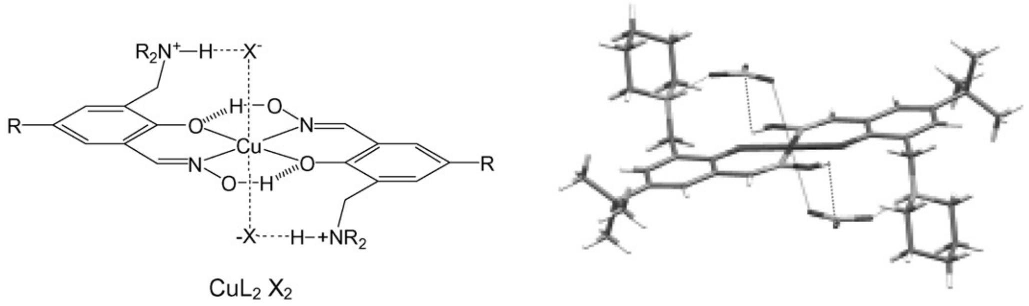


Fig. 12. General structure of charge-neutral 1:2 complexes, $[CuL_2X_2]$, of CuX_2 salts with salicylaldoxime ligands bearing 3-dialkylamino substituents and the X-ray structure of the $Cu(NO_3)_2$ complex of 3-(piperidinium-*N*-methyl)-5-*t*-butylsalicylaldoximate showing the attachment of the nitrates via secondary bonds to the piperidinium NH and to the copper(II) ion [3].

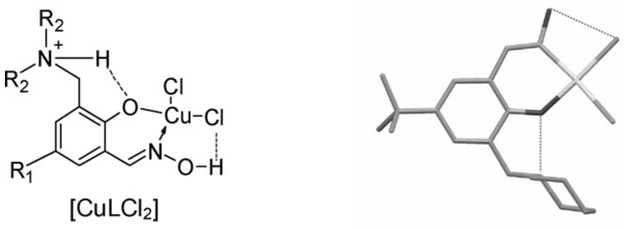


Fig. 13. The proposed structure of a charge-neutral 1:1 complex, $[CuLCl_2]$, of $CuCl_2$ with a salicylaldoxime ligands bearing 3-dialkylaminomethyl substituents and the X-ray structure of the $CuCl_2$ complex of 3-(piperidinium-*N*-methyl)-5-*t*-butylsalicylaldoximate showing interactions of the piperidinium group with the Cu-coordination sphere.

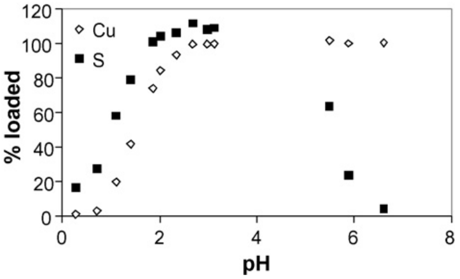


Fig. 15. The Cu^{2+} and $SO_4{}^-$ loading observed when $[Cu_2(\mathbf{12}\text{-}2H)_2]$ in chloroform solution is contacted with an aqueous solution containing an excess of Na_2SO_4 at different pH.

N_2O_2-plane in copper(II) complexes to generate a tetragonally distorted octahedron. The zwitterionic nature of the salicylaldoxime ensures that the assembly (Fig. 12) is charge-neutral.

A charge-neutral complex can also be formed by copper(II) chloride, in this case with chloride ions strongly bound in approximately planar four-coordinate complexes. These $CuNOCl_2{}^-$ units have intramolecular H-bonds to the protonated pendant amines (Fig. 13) and dimerize via weak Cu–O interactions generating a hydrophobic exterior. The formation of the 1:1 complex provides a very efficient mechanism for extraction of $CuCl_2$ in terms of mass transport efficiency but the incorporation of the chloride in the inner sphere of the copper removes the option for separate cation and anion stripping.

The target of loading both a metal dication and a *sulfate* counterion into a polytopic solvent extractant which could be used commercially remains elusive but, given the importance to the development of hydrometallurgical flowsheets, is worthy of further study. One approach is to abandon the concept of providing completely separated binding sites for the cation and anion and to allow some interaction between the sulfate and the inner or outer coordination sphere of the metal cation. The 2,2′-biphenylene bridge in the salen-type ligand **11** sets the two salicylaldiminato units approximately perpendicular to each other (Fig. 14) and provides a cavity for the sulfate to act as a bidentate ligand for the complexed nickel ion whilst still interacting favourably with the pendant piperidinium units in the zwitterionic form of the ligand [2]. Unfortunately this ligand is very susceptible to hydrolysis on acid-stripping.

Co-operativity of sulfate and copper extraction is particularly marked with **12** which provides a tridentate dianionic O···N···O donor motif to form $[Cu_2(\mathbf{12}\text{-}2H)_2]$. The uptake of H_2SO_4 by the copper-only complex, $[Cu_2(\mathbf{12}\text{-}2H)_2]$, is shown in Fig. 15. The stoichiometry at pH ≈ 3 corresponds to formation a neutral 2:2:1 assembly of the Cu(II), a monoanionic form of

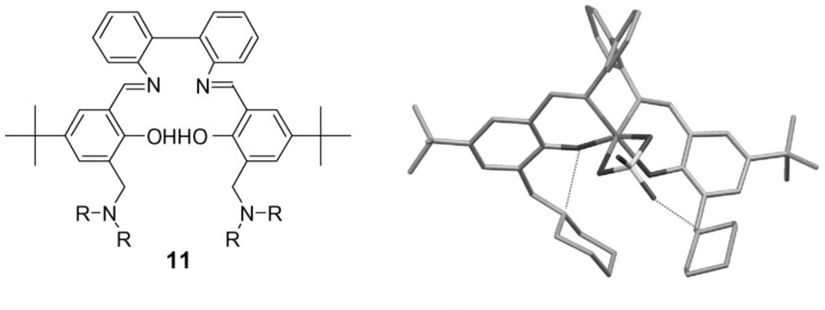
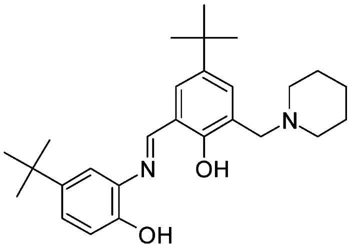


Fig. 14. Biphenylene bridged salen-type extractant **11** and the X-ray structure for $[Ni(\mathbf{11})SO_4]$ showing interactions between the Ni and sulfate as well as interactions between the piperidinium nitrogen and sulfate oxygen [2].

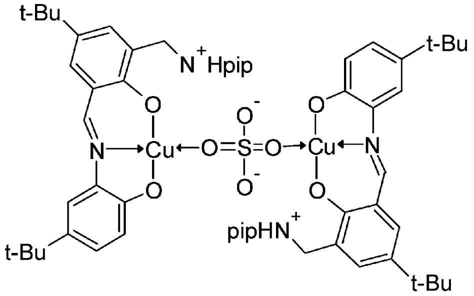
the ligand and a sulfate dianion [Cu_2(**12**-H)$_2$(SO_4)] [50].



12

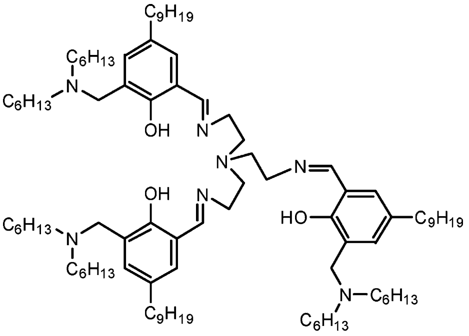
The central location of sulfate in the structure is consistent with the observation that transfer of sulfate to the organic phase is totally dependent on the presence of copper in the assembly. The loss of both copper and sulfate from the organic phase at low pH is accompanied by some hydrolysis of the ligand.

3.3. Criteria for technocommercial success



[Cu_2(**12**-H)$_2$(SO_4)]

The requirement for high selectivity of both cation- and anion-loading and for high chemical stability of the reagents under the conditions needed both for loading and stripping have already been mentioned. In addition, the kinetics of loading and stripping must be favourable as typically contact times of less than 5 min in a mixer settler are required to ensure a reasonable throughput in a plant. This is seldom a problem for the loading and stripping of Cu(II) in the salicylaldimine ligands discussed above, but can present a problem for Ni(II), especially when the stripping of planar low-spin complexes is required [51].



13

The poor solubility of complexes of metal salts in the very low polarity solvents used in extractive hydrometallurgy can present problems in terms of mass transport efficiency. The kerosene-soluble reagent, **13** (HNT), gives 98% recovery of nickel with 2-extract and 1-strip stages from a feed solution developed in the Bulong project in Western Australia [14] and is much more effective than conventional cation exchange reagents [52].

However, the very high molecular weight of the reagent **13** which results from it needing 3 multi-branched nonyl groups and 12 *n*-hexyl substituents to impart solubility in kerosenes, ensures that the mass transport efficiency (mass of metal transferred per load/strip cycle per unit mass of reagent) is very low.[1] The high viscosity of hydrocarbon solutions of reagents having such high molecular weights also presents problems in operating mixers efficiently.

4. Conclusions

The polytopic ligands described above are capable of extracting base metal chlorides or sulfates from an aqueous leach solution, providing the basis for *concentration* and *separation* to generate electrolytes with a suitable concentration and purity to generate metals by electroreduction.

All the reagents described in this review have the metal cation-binding component and the anion-binding component tethered in the same ligand superstructure and in several cases the uptake of a metal cation templates the binding site(s) for the anion(s), promoting their uptake in the water-immiscible phase. In principle the cation- and anion-binding components can be separate molecules [23,53] and a blend used for solvent extraction of metal salts, but this approach has not been explored in this review.

One of the major benefits of the new polytopic reagents is that loading of the metal salts will not create a major change in pH of the aqueous feed solution because they form metal salt complexes with zwitterionic forms of the ligands. This in turn means that interstage neutralization is not required to obtain high loadings of metal salts.

The co-extraction of a metal cation and its attendant anion(s) by a reagent in its zwitterionic form means that removal of a metal *salt* from an aqueous stream is essentially a "subtractive" process. This provides an advantage over conventional *ion-exchange* solvent extractants in processes aimed at purifying dilute streams before they are discharged because these always introduce another species into the effluent stream.

Acknowledgements

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[1] The trificated system gives high spin Ni(II) complexes and the loading and the stripping of nickel proceeds much faster than for the low spin complexes formed by the quadridentate salen-type extractants.

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