Polyacidic multiloading metal extractants†

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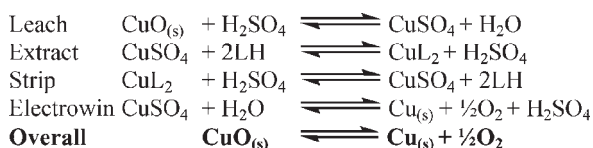
Novel polynucleating, di- and tri-acidic ligands have been designed to increase the molar and mass transport efficiencies for the recovery of base metals by solvent extraction.

Solvent extraction provides highly efficient *concentration* and *separation* operations in extractive hydrometallurgy.[1] Major new plants to recover zinc have opened recently[2] and *ca.* 20% of the global production of copper is achieved using phenolic oxime extractants[3] (*e.g.* L^1H, Fig. 1) in an acid leach–solvent extraction–electrowinning flowsheet (Scheme 1). The latter gives an excellent materials balance for recovery from oxidic ores because the leach, extractant and electrolyte solutions are recycled, and the process can be adapted to work efficiently with wide variation of compositions of pregnant leach solutions.[1,4]

| Leach	$CuO_{(s)}$	$+ H_2SO_4$	$\rightleftharpoons$	$CuSO_4 + H_2O$
Extract	$CuSO_4$	$+ 2LH$	$\rightleftharpoons$	$CuL_2 + H_2SO_4$
Strip	CuL_2	$+ H_2SO_4$	$\rightleftharpoons$	$CuSO_4 + 2LH$
Electrowin	$CuSO_4 + H_2O$		$\rightleftharpoons$	$Cu_{(s)} + \frac{1}{2}O_2 + H_2SO_4$
Overall	$CuO_{(s)}$		$\rightleftharpoons$	$Cu_{(s)} + \frac{1}{2}O_2$

Scheme 1 Materials balance for the recovery of copper from oxidic ores.

Whilst the flowsheet outlined in Scheme 1 is very efficient in terms of the overall materials balance, there is scope to improve the throughput by increasing the transport efficiency in the solvent extraction step. The mass of copper transferred to the water-immiscible solvent in the extraction stage is limited by the 1 : 2 stoichiometry required to generate a neutral, organic soluble, complex from the monoanionic phenolic oxime reagents. We recognized that the molar ratio of copper to extractant could be improved if polynucleating ligands capable of existing as di- or tri-anions after deprotonation were designed. Some systems developed to achieve this are shown in Fig. 1. A key design feature is that the anionic donor atoms, X^- or W^- in Fig. 1, are able to bridge two Cu(II) atoms in planar complexes.

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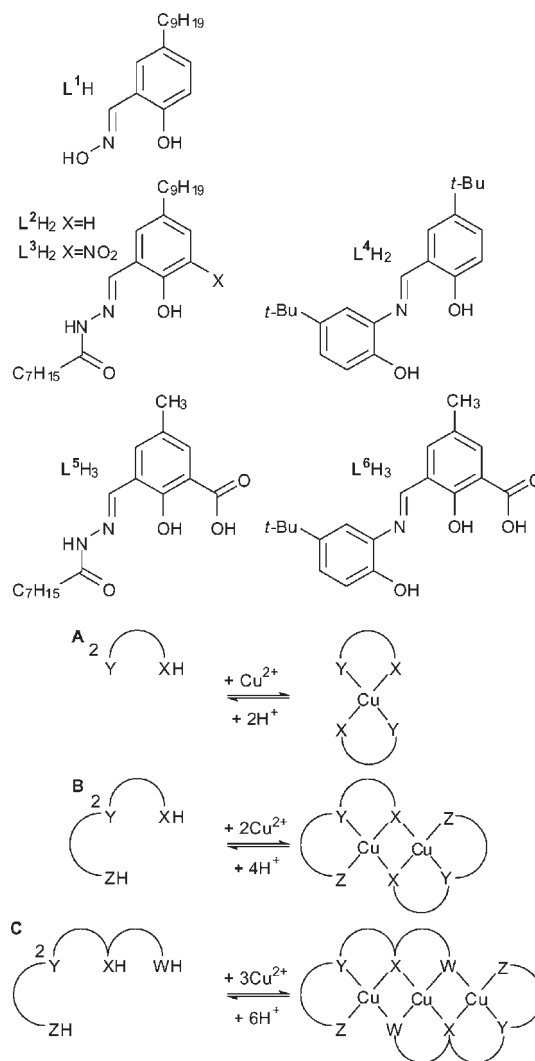
Fig. 1 Functionalization of the conventional type of extractant L^1H to generate di- and tri-acidic reagents L^2H_2–L^6H_3 which can form di- and tri-nuclear Cu(II) complexes (**B** and **C**).

Studies of the pH-dependence of Cu(II) extraction into chloroform solutions using the ligands (Fig. 2) show that the metal to ligand stoichiometry can be increased from 1 : 2 to 2 : 2 or 3 : 2, corresponding to 100, 200 and 300% Cu-loading for ligands L^1H, L^2H_2 to L^4H_2 or L^5H_3, respectively. The loading curves (Fig. 2) for L^3H_2 and L^5H_3 show plateaux which indicate that stepwise loading is possible, *e.g.* in
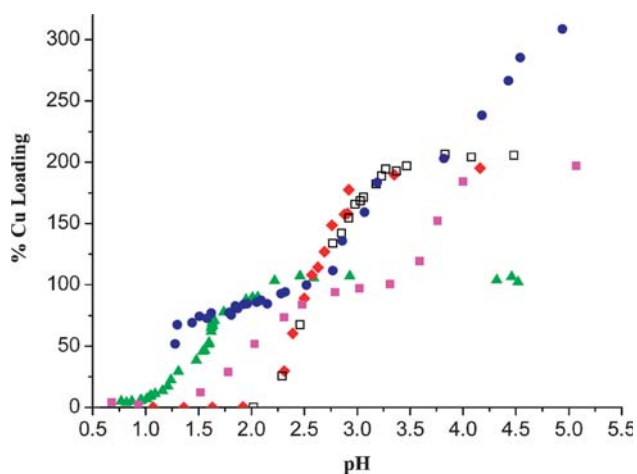
Fig. 2 Cu-loading by CHCl$_3$ solutions of L^1H (▲), L^2H_2 (♦), L^3H_2 (■), L^4H_2 (□) and L^5H_3 (●) as a function of pH. Loadings of 100, 200 and 300% correspond to Cu : 2L, 2Cu : 2L and 3Cu : 2L molar ratios.

addition to forming species with a stoichiometry consistent with the desired trinuclear complex, [Cu$_3$(L^5)$_2$], at pH > 5 the ligand L^{5}H$_3$ also forms species corresponding to mono- or dinuclear complexes, [Cu(L^{5}H$_2$)$_2$] and [Cu$_2$(L^{5}H)$_2$], at pH values of *ca.* 2.2 or 3.8, respectively.

The Cu-uptake by chloroform solutions of L$^{2-4}$H$_2$ can be followed by monitoring X-band EPR spectra. The intensity of the signal increases (**A** in Fig. 3) until the Cu-loading corresponds to a metal to ligand stoichiometry of 1 : 2. Further loading is accompanied by a decrease in signal intensity (**B** in
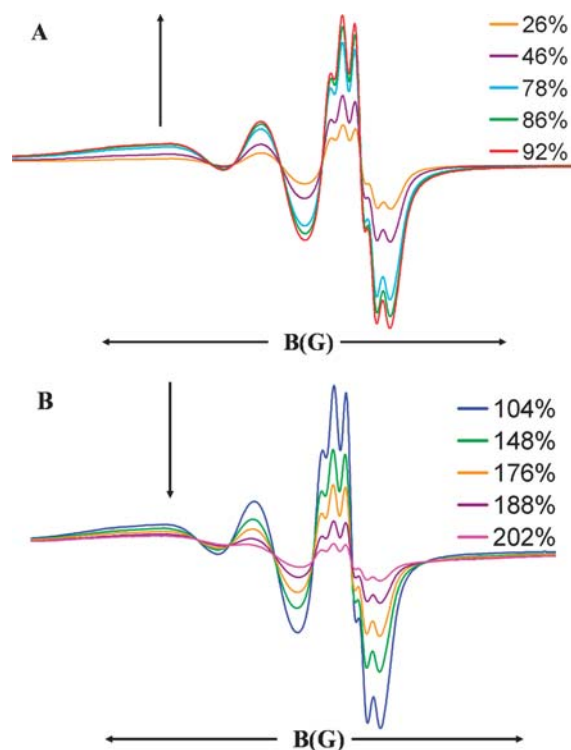

Fig. 3 EPR spectra of CHCl$_3$ solutions of L^{2}H$_2$ as Cu-loading increases from 0–100% (curves **A**) and from 100–200% (curves **B**).
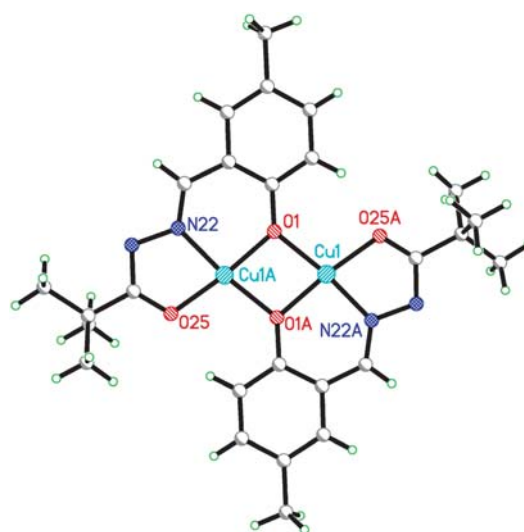
Fig. 4 Dinuclear copper complex of a structural analogue of L^{2}H$_2$.

Fig. 3) and at 2 : 2 stoichiometry there is almost no signal. Antiferromagnetic coupling between the two copper centres in the dinuclear complexes could account for these changes. There is some ambiguity as to the structure of the dinuclear complexes, and in particular which of the oxygen atoms in L$^{2-4}$H$_2$ or L$^{5-6}$H$_3$ form bridges between the two Cu atoms. An analogue of L^{2}H$_2$, with *t*-Bu and Me groups replacing the heptyl and nonyl substituents, gives a complex (Fig. 4)‡ which is similar to several reported in the CSD[5] in which the phenolate oxygen atom of the salicylaldimine component bridges the two copper centres. In contrast, in the dinuclear complex (Fig. 5)‡ formed by L^{6}H$_3$, it is another type of phenolate oxygen atom which forms the bridges and much more irregular NO$_3$$^{2-}$ donor sets are presented to the copper atoms by the ligands.

Whilst the new di- and tri-acidic extractants increase the *molar* transport efficiency two or three fold, it is the *mass* transport which is of greater practical significance. Based on the molecular weights shown in Table 1, it can be seen that
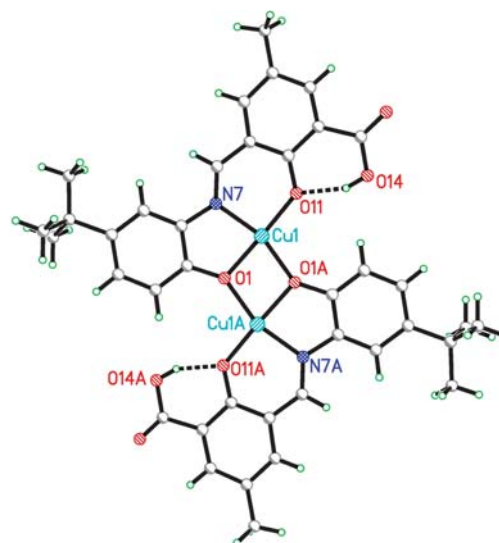
Fig. 5 Crystal structure of dinuclear copper complex of L^{6}H$_3$.

Table 1 Comparison of the mass transport efficiencies $L^{2-4}H_2$, and L^5H_3 with the commercial extractant, 5-nonylsalicylaldoxime (L^1H)

Reagent	M_r	Stoichiometry (Cu : L)	Cu Transport g per kg reagent	Cu Transport Relative to L^1H
L^1H	263	1 : 2	121	1.00
L^2H_2	388	2 : 2	164	1.36
L^3H_2	433	2 : 2	147	1.21
L^4H_2	325	2 : 2	195	1.62
L^5H_3	320	3 : 2	298	2.47

between 1.36 to 2.47 fold improvements relative to the commercial extractant 5-nonylsalicylaldoxime (L^1H) result from using the reagents L^2H_2 to L^5H_3.

Exploiting the improved transport efficiency of these new reagents will only be possible if they have high solubility in the hydrocarbon solvents used industrially and are stable to hydrolysis and show selectivity for Cu-loading in the low pH ranges used in commercial circuits. Nevertheless, the work described in this communication has shown that substantial increases in mass transport efficiency are possible by designing multi-loading extractants which incorporate into the ligand super structure several acidic groups which can function in a metal–metal bridging mode.

Notes and references

‡ **Crystal data** for [Cu$_2$L$_2$]·2CHCl$_3$ (Fig. 4):
Data were collected on a 3 circle Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) equipped with an Oxford Cryosystems low temperature device operating at 150 K. The crystal was indexed using the Bruker Smart software[6] and found to be triclinic with a = 5.9794(3), b = 9.9352(5), c = 15.3792(9) Å, and α = 98.853(4), β = 94.933(4), γ = 103.343(4)°. From initial indexing a data collection strategy was refined which aimed to collect fully complete data to a resolution of 53° in 2θ in as short a time as possible. In total 8149 reflections were collected and from these the space group was determined to be $P\bar{1}$. Absorption correction was performed using a multi-scan method by applying the SADABS[7] program to the data. The data were merged according to the crystal system in SHELX[8] which gave 3052 unique reflections with a merging R-factor of 0.0442. The initial solution was determined by direct methods with the SHELXS[8] program. All heavy atoms were refined anisotropically and hydrogen atoms were placed geometrically and allowed to ride on their host atom. Full matrix least squares refinement was carried out against F^2 producing a final conventional R-factor of 0.0957 based on 2750 reflections.

Crystal data for [Cu$_2$(L^{6}H)$_2$] (Fig. 5):
Data were collected on a 3 circle Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and equipped with an Oxford Cryosystems low temperature device operating at 150 K. The crystal was indexed using the Cell_now indexing program[9] and found to be triclinic with a = 6.8829(7), b = 9.6493(10), c = 12.3771(12) Å and α = 88.498(6), β = 83.850(6), γ = 83.339(6)°. The crystal was also twinned and the twin law obtained after global cell refinement was (−0.99434 −0.00064 −0.02085), (0.00755 −0.99936 −0.01644), (−0.43677 −0.05385 0.99478). From initial indexing a data collection strategy was refined which aimed to collect fully complete data to a resolution of 53° in 2θ in as short a time as possible. In total 3802 reflections were collected and from these the space group was determined to be $P\bar{1}$. Absorption correction was performed using a multi-scan method by applying the TWINABS[10] program to the data. The initial solution was determined by direct methods with the SHELXS[8] program. All heavy atoms were refined anisotropically and hydrogen atoms were placed geometrically and allowed to ride on their host atom. Full matrix least squares refinement was carried out against F^2 producing a final conventional R-factor of 0.0865 based on 3091 reflections.

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