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 recently2 and ca. 20% of the global production of copper is achieved using phenolic oxime extractants3 (e.g. L1H, 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

![Scheme 1 Materials balance for the recovery of copper from oxidic ores.](image)

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.

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 L1H, L2H2 to L4H2 or L5H3, respectively. The loading curves (Fig. 2) for L3H2 and L5H3 show plateaux which indicate that stepwise loading is possible, e.g. in

![Fig. 1 Functionalization of the conventional type of extractant L1H to generate di- and tri-acidic reagents L2H2–L6H3 which can form di- and tri-nuclear Cu(II) complexes (B and C).](image)
addition to forming species with a stoichiometry consistent with the desired trinuclear complex, \([\text{Cu}_3(L^5H_3)_2]\), at pH \(\approx 4\) the ligand \(L^5H_3\) also forms species corresponding to mono- or dinuclear complexes, \([\text{Cu}(L^5H_2)_2]\) and \([\text{Cu}_2(L^5H)_2]\), at pH values of ca. 2.2 or 3.8, respectively.

The Cu-uptake by chloroform solutions of \(L^2–4H_2\) 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) 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 \(L^2–4H_2\) or \(L^5–6H_3\) form bridges between the two Cu atoms. An analogue of \(L^2H_2\), 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 \(L^6H_3\), it is another type of phenolate oxygen atom which forms the bridges and much more irregular \(\text{NO}_3^2\) 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...
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^4H_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 superstructure several acidic groups which can function in a metal-metal bridging mode.

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Notes and references

1 Crystal data for [Cu_2(L^2H)_3] (Fig. 4): Data were collected on a 3 circle Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo-K\textsubscript{α} radiation (\(\lambda = 0.71073 \text{ Å}\)) and equipped with an Oxford Cryosystems low temperature device operating at 150 K. The crystal was indexed using the Cell_NOW indexing program\(^7\) and found to be triclinic with \(a = 6.852(4), b = 9.649(10), c = 12.377(12)\) Å and \(\alpha = 88.493(4), \beta = 94.933(4), \gamma = 103.343(4)\). From initial indexing a data collection strategy was refined which aimed to collect fully complete data to a resolution of 53 \(^{\circ}\) in 20 in as short a time as possible. In total 8149 reflections were collected and from these the space group was determined to be \(P\). 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.

Crystal data for [Cu_2(L^1H)_3] (Fig. 5): Data were collected on a 3 circle Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo-K\textsubscript{α} radiation (\(\lambda = 0.71073 \text{ Å}\)) and equipped with an Oxford Cryosystems low temperature device operating at 150 K. The crystal was indexed using the Cell NOW indexing program\(^7\) and found to be triclinic with \(a = 6.852(4), b = 9.649(10), c = 12.377(12)\) Å and \(\alpha = 88.493(4), \beta = 94.933(4), \gamma = 103.343(4)\). From initial indexing a data collection strategy was refined which aimed to collect fully complete data to a resolution of 53 \(^{\circ}\) in 20 in as short a time as possible. In total 8149 reflections were collected and from these the space group was determined to be \(P\). 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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