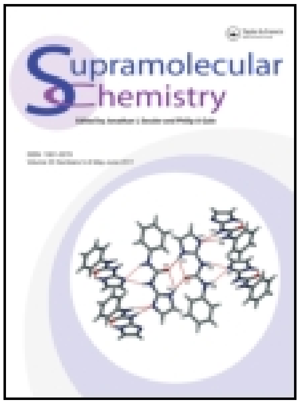

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A dual host approach to $NiSO_4$ extraction

Gareth W. Bates[a], James E. Davidson[b], Ross S. Forgan[b], Philip A. Gale[a]*, David K. Henderson[b], Michael G. King[c], Mark E. Light[a], Stephen J. Moore[a], Peter A. Tasker[b] and Christine C. Tong[a]

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This paper reports the synthesis of sulphate extractants, *N*,*N*′-bis-(2-dibutylamino-ethyl)-isophthalamide (**1**), pyridine-2,6-dicarboxylic acid bis-[(2-dibutylamino-ethyl)-amide] (**2**) and 3,4-diphenyl-1*H*-pyrrole-2,5-dicarboxylic acid bis-[(2-dibutylamino-ethyl)-amide] (**3**), and demonstrates that, in combination with a commercially available oxime extractant 2-hydroxy-5-nonyl benzaldehyde oxime (**P50**), these dual host systems are better extractants for nickel(II) sulphate than the metal salt extractant, 5-nonyl-3-dihexylaminomethyl-2-hydroxy-benzaldehyde oxime (**4**).

Keywords: anion binding; extraction; hydrometallurgy; hydrogen bonding

Introduction

Base metals are important commodities in the modern world and recently their demand and consumption have increased significantly. In particular, nickel, which is used mainly ($>70\%$) in the production of stainless steel and alloys, has seen demand outstrip supply mostly due to the rising demand for steel, particularly in China (*1*, *2*). As a consequence of this, major new projects and sources of nickel ores are required. Recent examples of such projects are the Bulong (*3*) operation in Western Australia, which produces nickel and cobalt from a lateritic ore and the Koniambo site in New Caledonia which, when up to full production in 2013, will aim to produce *ca*. 60,000 tons of nickel per year (*4*).

Metallurgy is the extraction, purification and modification of metals from their ores for a more useful purpose. Currently, industry predominantly uses pyrometallurgical smelting techniques in order to obtain metals; however, these processes require large amounts of energy and produce large volumes of pollutant and toxic gas emissions (*5*). Hydrometallurgy involves the extraction of metals from an aqueous solution of their ores (*5*). Hydrometallurgical extraction/separation techniques include selective crystallisation, selective reduction and adsorption of ions onto solid matrices (*5*). An area of increasing interest is extractive hydrometallurgy wherein the metal of value is typically leached into an acidic aqueous solution and subsequently transferred to a hydrophobic organic solvent, thus separating and concentrating the metal of value. A typical flowsheet for this process is illustrated in Figure 1 (*5*–*7*). This technique allows the metal of interest to be recovered from more complex and/or low-grade ore stocks. Other advantages are that the process usually requires less energy in comparison to pyrometallurgical techniques and the ore processing can be carried out close to mine sites thus removing high ore transport costs (*8*).

Liquid–liquid solvent extraction is becoming increasingly useful in extractive hydrometallurgy and involves the use of chemical processes, such as the formation of metal complexes, to selectively extract the metal of value from an aqueous medium into an immiscible organic phase (in practice high-boiling-point hydrocarbons, such as kerosene, are used in large-scale solvent extraction processes). This process affects the unit operations of separation and concentration as part of a four-step flowsheet (Figure 2) involving leaching, extraction, stripping and electrowinning (*9*). Leaching involves the dissolution of the metal from the ore to generate an aqueous pregnant leach solution (PLS) using a range of reactants, depending on the chemical composition of the ore (*9*). Selective extraction of the metal of value involves the transport of metal cation, metal salts or metallate anions into a non-polar organic phase *via* complexation by a hydrophobic ligand (*9*). The organic solubility of the complex is crucial for the success and overall efficiency of the extraction process. As a result, the complex ideally is charge neutral and the ligand contains hydrophobic groups, such as large and usually branched alkyl chains. The stripping stage involves the removal of the metal of value from the organic phase and the hydrophobic ligand, transferring it back to an aqueous solution from which the metal is recovered by reduction of the pure metal salt,

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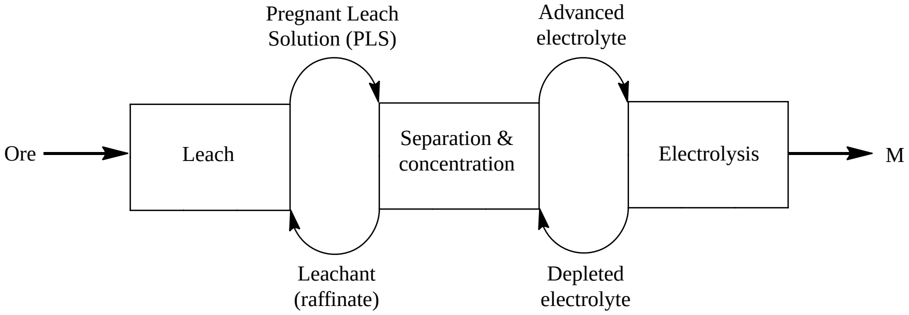


Figure 1. The basic flowsheet for extractive hydrometallurgy.

usually by electrolysis. The organic phase containing the regenerated hydrophobic ligand is recycled.

One of the most successful processes of this type involves the extraction of copper from oxidic ores using phenolic oxime ligands (Figure 3) to transport the copper from the PLS (*9*).

An area of increasing interest is the extraction of metals from sulphidic ores (*1*). In hydrometallurgical processes, these ores have low solubility and therefore cannot be effectively leached with dilute sulphuric acid under ambient conditions. The ores can be converted into their metal oxides by roasting in the presence of air (Scheme 1). The roasting process produces SO_2, which is a major pollutant gas that has to be recovered through the generation of sulphuric acid. This is capital intensive and the production of sulphuric acid on mining sites is not always economically viable (*5*, *8*).

New microbial leaching and high-pressure acid leaching techniques involve conversion of the sulphidic ore to the sulphate producing a PLS that can be used for the liquid–liquid solvent extraction of the metal of value (*7*, *10*). These leaching techniques are economically more viable compared to the roasting technique as they avoid the generation of SO_2. However, if the sulphate PLS is extracted with the commercial phenolic oxime ligand system, then during the extraction step, sulphuric acid builds up in the system (Scheme 2). This does not occur in the process for oxidic ores as the sulphuric acid is recycled for the leaching step. The buildup of sulphuric acid significantly reduces the extraction efficiency of the process as the decreasing pH hinders the complexation of the metal ion to the ligand in the aqueous phase.

One way to overcome this problem is to use a ligand system that can extract both the metal cation and attendant sulfate anion(s) into the organic phase. Tasker and co-workers have approached this problem by synthesising a number of zwitterionic ditopic receptors in which the acid-binding site is covalently attached to a salen-based metal-binding site (*11*, *12*). The system was designed so that upon the coordination of the metal ion the two phenolic protons would be displaced and protonate the tertiary amine groups attached to the salen scaffold, which would then bind the sulphate anion thus removing the excess sulphuric acid generated in the extraction of the metal (Scheme 3).

This approach has been extended to tripodal systems (*13*) and to oxime-based metal salt extractants (Scheme 4) which show significantly increased resistance to hydrolysis and in some instances increased extraction efficiencies (*14*, *15*).

Such zwitterionic ditopic receptors have proven to be useful for the extraction of copper(II) sulphate and the introduction of hydrogen bonding groups to the pendent arms of the receptor has been shown to improve the sulphate selectivity (*16*) of the ditopic systems. However, increasing the functionalisation of the ditopic receptors to improve the affinity and selectivity of the receptors for sulphate inevitably requires more complex synthesis and ligands, which in turn increases the cost of manufacture and decreases the mass transport efficiency (the mass of extractant required per unit mass of metal recovered).

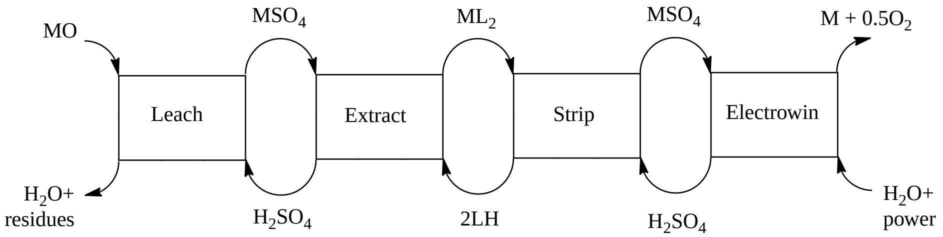


Figure 2. A flowsheet for the liquid–liquid solvent extraction of metals from their oxidic ores (*9*).

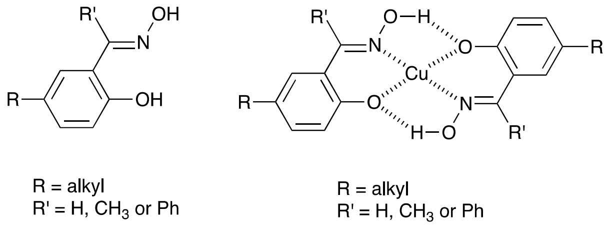


Figure 3. Commercial phenolic oxime copper extractants (*9*).

$$
\begin{array}{lcll}
MS + {}^{3}/_{4}\,O_2 & \rightleftharpoons & MO + SO_2 & \text{Roast} \\
SO_2 + {}^{1}/_{2}\,O_2 & \rightleftharpoons & SO_3 & \multirow{2}{*}{$\left.\right\}$ \text{SO}_2 \text{ recovery by acid generation}} \\
SO_3 + H_2O & \rightleftharpoons & H_2SO_4 & \\
MO + H_2SO_4 & \rightleftharpoons & MSO_4 + H_2O & \text{leaching} \\
\hline
\mathbf{MS + 2O_2} & \rightleftharpoons & \mathbf{MSO_4} & \textbf{Net}
\end{array}
$$

Scheme 1. The materials balance for the recovery of SO_2 by acid generation.

One approach to reduce manufacturing cost is to use simple small molecules to extract sulphuric acid from the PLS independently from the extraction of the metal ion, a strategy that has been successfully applied in the co-extraction of Cs^+ and NO_3^- ions (*17*). A major advantage of this 'dual host' approach compared to the ditopic ligand approach is that it is much easier to achieve selectivity for the metal cation and the sulphate anion with individual components, whereas in the case of the ditopic receptor selectivity for both the metal cation and the sulphate anion need to be included in a single extractive ligand. A number of groups have previously synthesised receptors that exhibit selectivity towards sulphate and hydrogen sulphate anions (*18*). Recently, Sessler, Moyer and co-workers (*19*) have described the use of a cyclo[8]pyrrole in the extraction of sulphate anions in the presence of nitrate. Tripodal tris-urea functionalised tren-based receptors have been reported by Custelcean and co-workers (*20*) as functioning as selective crystallisation agents for SO_4^{2-}. This class of sulphate receptor has also been studied by other groups (*21*). Additionally, Custelcean, Hay and co-workers (*22*) have developed self-assembling urea containing cage systems to arrange six urea groups around sulphate. Gale and co-workers (*23*) have reported that amido-indole and carbazole-functionalised diindolylureas are selective for sulphate. Macrocyclic sulphate receptors include Bowman–James' (*24*) cyclic tetraamide/amine system that forms sandwich complexes with SO_4^{2-} and Kubik's (*25*) bis-cyclic peptide-based molecular oyster. We have prepared simple anion extractants, which, alongside known anion, cation and metal salt extractants (Figure 4), were tested in the extraction of nickel sulphate.

Results and discussion

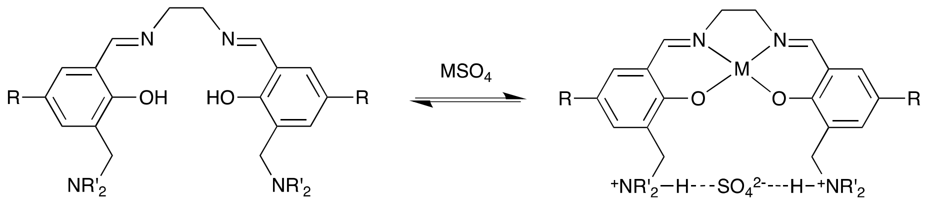
N,*N'*-bis-(2-dibutylamino-ethyl)-isophthalamide (**1**) and pyridine-2,6-dicarboxylic acid bis-[(2-dibutylamino-ethyl)-amide] (**2**) were prepared by reaction of *N*,*N*-di-*n*-butylethylenediamine with isophthaloyl dichloride and pyridine 2,6-diacetyldichloride in 80% and 82% yield, respectively. 3,4-Diphenyl-1*H*-pyrrole-2,5-dicarboxylic acid bis-[(2-dibutylamino-ethyl)-amide] (**3**) was prepared in 67% overall yield from 3,4-diphenyl-1*H*-pyrrole-2,5-dicarboxylic acid (*26*) *via* the acid chloride.

X-ray quality crystals of **3** were obtained *via* slow evaporation of a methanol solution. The crystal structure revealed that a hydrogen-bonded dimer was formed in the solid state by interactions between the pyrrole NH group and a carbonyl group with a N2···O1′ distance of 2.9872(16) Å (Figure 5).

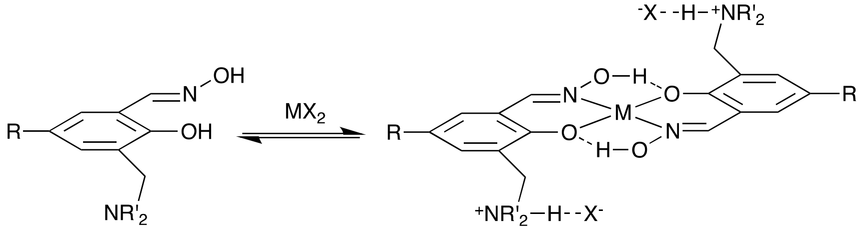
5-Nonyl-3-dihexylaminomethyl-2-hydroxy-benzaldehyde oxime (**4**) was prepared by the oximation of 5-nonyl-3-dihexylaminomethyl-2-hydroxybenzaldehyde

$$
\begin{array}{lcll}
MS + 2O_2 & \rightleftharpoons & MSO_{4\,(aq)} & \text{Leaching} \\
MSO_{4\,(aq)} + 2LH_{\,(org)} & \rightleftharpoons & ML_{2\,(org)} + H_2SO_{4\,(org)} & \text{Extraction} \\
ML_{2\,(org)} + H_2SO_{4\,(aq)} & \rightleftharpoons & MSO_{4\,(aq)} + 2LH_{\,(org)} & \text{Stripping} \\
MSO_{4\,(aq)} + H_2O & \rightleftharpoons & M + {}^{1}/_{2}\,O_2 + H_2SO_{4\,(aq)} & \text{Electrowinning} \\
\hline
\mathbf{MS + {}^{3}/_{2}\,O_2 + H_2O} & \rightleftharpoons & \mathbf{M + H_2SO_4} & \textbf{Net}
\end{array}
$$

Scheme 2. Material balance of phenolic oxime extraction of metals from sulphidic ores showing the generation of sulphuric acid during the extraction step.



Scheme 3. Expected binding of metal sulphates with salen-based zwitterionic receptors.



Scheme 4. Oxime-based metal salt extractants showing generic coordination of a mono-anion to the protonatable pendant amine arms.

(*13*) in 93% yield. The nickel complex of an analogue of this ligand, 5-*t*-butyl-3-piperidinomethyl-2-hydroxy-benzaldehyde oxime (**5**) (*14*), was prepared and single crystals, suitable for X-ray diffraction, were grown by slow evaporation from hexane. The structure (Figure 6) has a square planar nickel centre on a point of inversion. The oximic protons show bifurcated hydrogen bonding to both the phenolic oxygen (O23···O1A 2.564 Å) and the nitrogen on the piperidine ring (O23···N62 2.831 Å). More significantly due to the preferred hydrogen bonding arrangement of the oxime, the anion-binding sites are arranged on opposite sides, above and below the plane of the molecule. This will clearly be disadvantageous for the binding of di-anions such as SO_4^{2-}, however, the related copper complex has been demonstrated to be an efficient extractant for a range of mono-anions (*15*).

Extraction results

Compounds **1**, **2** and **3** were investigated as sulphuric acid extractants both on their own and as part of a dual host system, in the presence of Ni(**P50**-H)$_2$. A simple tertiary

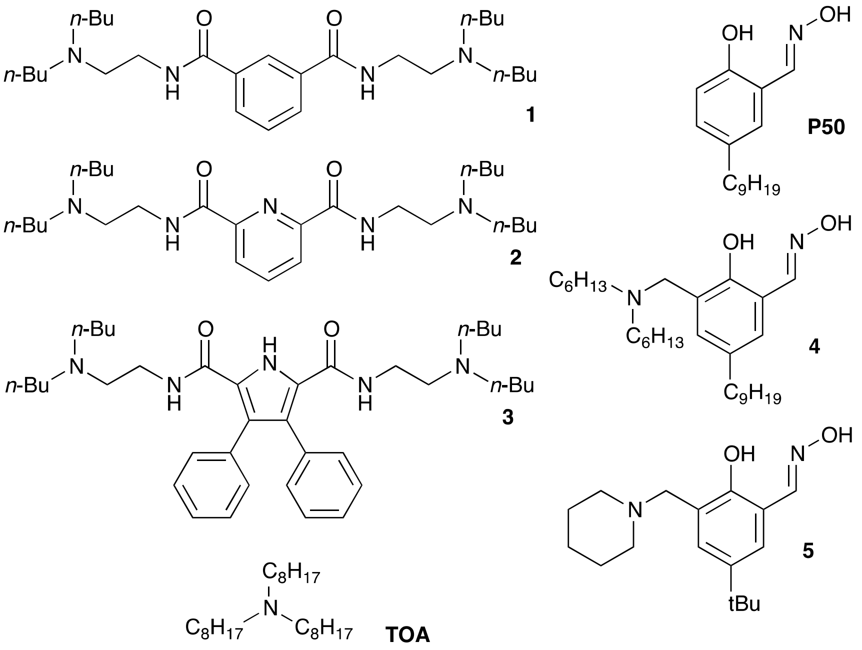


Figure 4. Anion, cation and metal salt extractants studied.

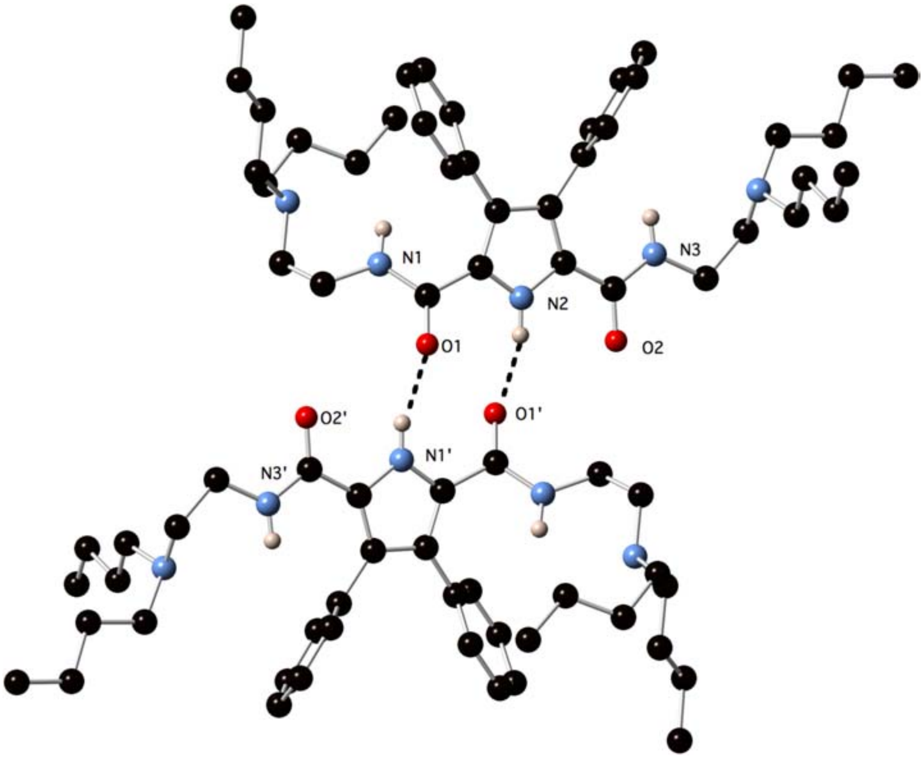


Figure 5. X-ray crystal structure of **3** showing the formation of the hydrogen-bonded dimer.

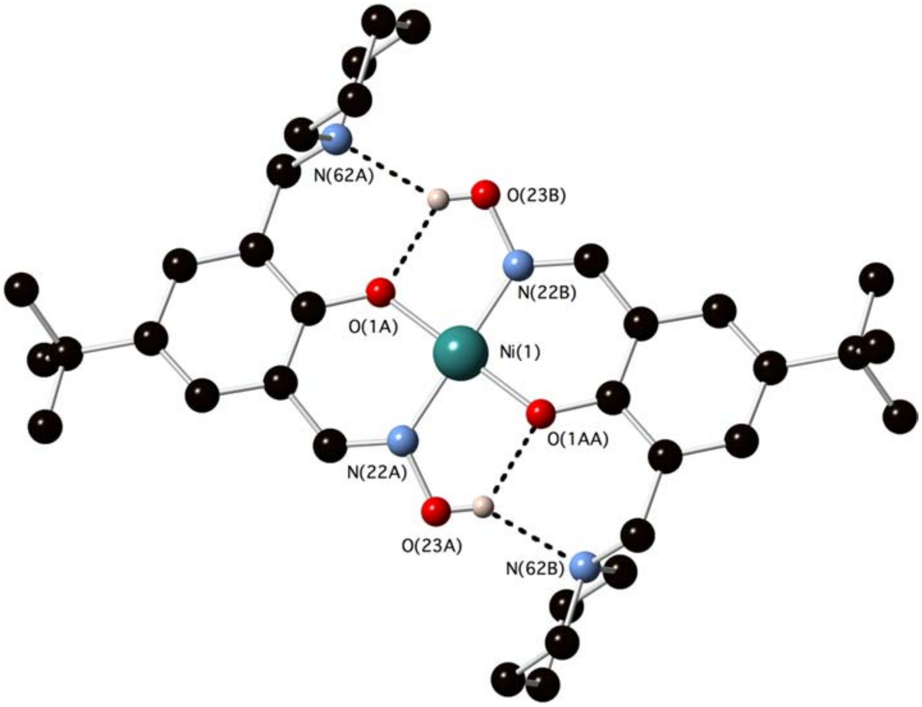


Figure 6. Structure of Ni(**5**-H)$_2$ (*30*) showing the bifurcated hydrogen bonding of the oximic proton and the arrangement of the piperidino anion-binding arms.

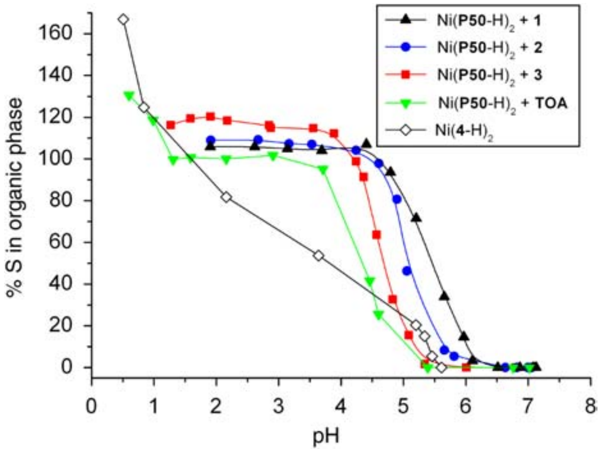


Figure 7. Quantity of sulphur in the organic phase as a percentage of the amount of extractant at equilibrium at different pH values in the in the system at equilibrium in the presence of Ni(**P50**-H)$_2$. The lines are added as visual aids and do not represent fitted data.

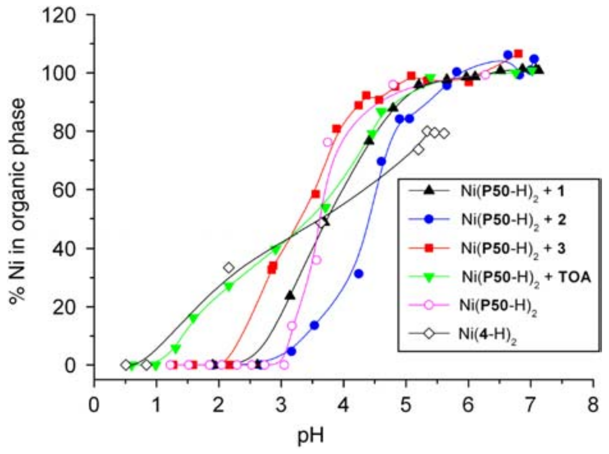


Figure 8. Quantity of nickel in the organic phase as a percentage of the amount of extractant in the system at equilibrium. The lines are added as visual aids and do not represent fitted data.

amine, tri-*n*-octylamine (**TOA**), was included for comparison as this is often used as a model for the commercial ion pair extractant alamine 336 (*27*). The dual host systems were also compared with the metal salt extractant **4**.

pH profiles for sulphate loading were determined by taking chloroform solutions containing 0.01 M of either **1**, **2**, **3** or **TOA** (0.02 M) and contacting the organic solutions with 0.8 M aqueous sulphate solutions at different pH values and recording the % sulphur uptake into the organic phase. Dual host experiments were carried out in the same manner but in the presence of 0.01 M Ni(**P50**-H)$_2$. pH profiles for Ni-content in the organic phase obtained from this procedure represent the stripping of the nickel from the ligand.

For the sulphate receptors the extraction strength order was found to be **1** > **2** > **3** > **TOA** (Figure 7 and Table 1). While this order does not change with the presence of Ni(**P50**-H)$_2$ in the system, there is a slight increase in $pH_{\frac{1}{2}}$ (S) for all ligands except **3** (see Supplementary Information for graphs, available online). The results show that the incorporation of hydrogen bonding groups into the ligand systems enhances sulphate extraction when compared to **TOA**. Unfavourable interactions of the anion in the binding cavity with the lone pair on the pyridine ring may be the reason why **1** is superior to **2**. The weaker performance of **3** is more difficult to explain but may be due to the slightly different geometry of the amide arms created by the pyrrole ring (*cf.* pyridine and benzene) not allowing creation of the optimum anion-binding cavity size for sulphate.

The metal salt complex, Ni(**4**-H)$_2$ shows no selectivity for sulphate versus hydrogen sulphate as expected from the unfavourable arrangement of the anion-binding sites. All other ligands show a plateau indicative of sulphate selectivity (*12*). The increase in sulphur loading beyond 100% at pH <1 shown by some of the systems is due to extraction of HSO_4^- as this species dominates at low pH. Equally, the drop in sulphur extraction exhibited by both **1** and **2** at low pH in the absence of Ni(**P50**-H)$_2$ (see Supplementary Information for graphs, available online) can be attributed to the increased solubility of the HSO_4^- complex in the aqueous phase and has been observed previously (*28*).

The $pH_{\frac{1}{2}}$ (Ni) of **P50** varies by approximately 1 pH unit over the series of sulphate extractants **3** < **TOA** < **1** < **2** (Figure 8 and Table 1). For comparison, when measured on its own, Ni(**P50**-H)$_2$ has a $pH_{\frac{1}{2}}$ of 3.7. This shows that while the presence of **1** has little or no effect on the nickel loading of **P50**, **2** significantly decreases (0.7 pH units) and **3** increases (0.4 pH units) extraction strength. **TOA** shows a slight increase in extraction strength (0.2 pH units). Although **4** begins to extract nickel at lower pH than the **P50** systems, it has a $pH_{\frac{1}{2}}$ value of 3.75 and the extraction curve is very shallow and maximum loading (80%) is only reached above pH 5. Interestingly, the Ni(**P50**-H)$_2$ + **TOA** system initially follows the same trend but displays greater

Table 1. $pH_{\frac{1}{2}}$ values estimated from the % uptake versus equilibrium pH plots.

Extractant	$pH_{\frac{1}{2}}$ Ni loading	$pH_{\frac{1}{2}}$ S loading (with Ni)	$pH_{\frac{1}{2}}$ S loading (without Ni)
3 + Ni(**P50**-H)$_2$	3.30	4.75	4.9
2 + Ni(**P50**-H)$_2$	4.40	5.20	5.0
1 + Ni(**P50**-H)$_2$	3.75	5.50	5.4
TOA	3.50	4.40	4.1
Ni(**4**-H)$_2$	3.75	3.70	–
Ni(**P50**)$_2$	3.70	–	–

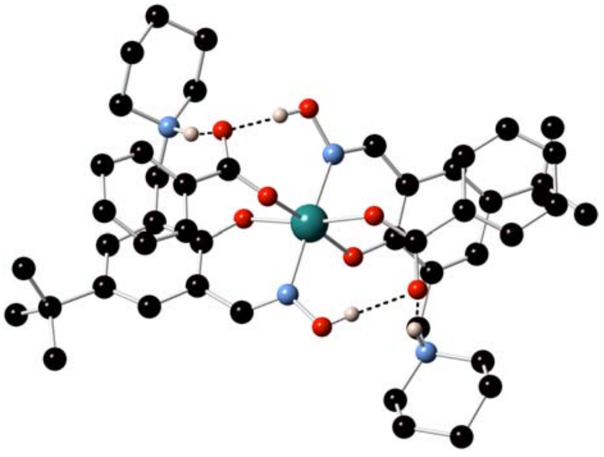


Figure 9. Structure of [Ni(**5**)$_2$(benzoate)$_2$] showing the octahedral coordination sphere of the nickel.

extraction above pH 3, again reaching maximum (100%) above pH 5.

Significant synergistic effects have been observed in carboxylic acid/oxime mixtures of versatic acid 10 with LIX$^{®}$84-IC (*2*) and LIX$^{®}$63 (*29*). However, in these cases, the effect is probably due to direct coordination (*31*) of the carboxylic acid forming an octahedral complex in a similar manner to that seen in [Ni(**5**)$_2$(benzoate)$_2$] (*32*) (Figure 9) and in oxime/diamine systems (*33*).

Conclusions

We have shown that for sulphate binding, the ligands **1**, **2** and **3** that contain hydrogen bonding functionality outperform simple trialkylamines such as **TOA**. As part of a dual host system, they show significant influence on the nickel extraction strength of **P50** oxime. The reason behind these synergistic effects is not clear and will require further investigation to elucidate. The dual host systems also perform better than the metal salt reagent **4** as nickel sulphate extractants. However, none of the systems investigated show sufficiently strong extraction to be applicable in industrial circuits.

Experimental

General

Proton and ^{13}C NMR were obtained using either a Bruker AC250 (UoE) spectrometer or a DPX400 (UoS) spectrometer and the chemical shifts reported in ppm. The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet and m = multiplet. Fast atom bombardment (FAB)-MS was recorded using a Kratos MS50TC spectrometer with a 3-nitrobenzyl alcohol or thioglycerol matrix. Low-resolution mass spectra (electrospray mass spectrometry) were recorded on a Micromass Platform single quadrupole spectrometer. Analytical data were obtained on a CE-440 Elemental Analyser by the University of Edinburgh Microanalytical service or were performed by Medac Ltd (Chobham, Surrey, United Kingdom). Inductively coupled plasma-optical emission spectrometer (ICP-OES) analysis was carried out using a Perkin-Elmer Optima 5300DV spectrometer. The measurement of pH was carried out using a Fisher Scientific AR50 pH meter fitted with a CW711 pH probe. 5-Nonyl-3-dihexylaminomethyl-2-hydroxybenzaldehyde (*13*) and 5-*t*-butyl-3-piperidinomethyl-2-hydroxybenzaldehyde oxime (**5**) (*14*) were prepared as previously reported. 2-Hydroxy-5-nonylbenzaldehyde oxime (**P50**) was gratefully received from Cytec Industries (Stamford, CT, USA). Thionyl chloride was distilled from 10% (w/w) triphenyl phosphate and stored under nitrogen. All other solvents and reagents were purchased from commercial sources and used without further purification unless otherwise stated.

Crystal data for **3** and Ni(**5**-H)$_2$ and [Ni(**5**)$_2$(benzoate)$_2$] are given in the electrospray ionization (ESI).

Preparation of compounds

N,N′*-bis-(2-dibutylamino-ethyl)-isophthalamide (**1**)*

Isophthaloyl dichloride (2.00 g, 9.9 mmol) in dichloromethane (50 ml) was added dropwise to a stirred solution of *N*,*N*-dibutylethylenediamine (3.45 g, 20 mmol) and triethylamine (5 ml) in dichloromethane (50 ml) with a catalytic amount of dimethylaminopyridine (DMAP) and the reaction mixture was stirred for 24 h. Water (100 ml) was added and the organic layer separated, dried with MgSO$_4$, filtered and concentrated *in vacuo*. The resulting oil was purified *via* a flash column chromatography (SiO$_2$, dichloromethane (DCM)/1% MeOH) to give the product as a viscous yellow oil. Yield: 82%, 3.85 g; ESI-MS $m/z = 475.5$ $[M + H]^+$. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.88 (t, 2H), 125–1.35 (m, 8H), 1.38–1.46 (m, 8H), 2.45 (t, 8H), 2.63 (t, 4H), 3.48 (q, 4H), 6.97 (s, 2H); 7.49 (t, 1H), 8.33 (dd, 7.8 Hz, 2H), 8.23 (t, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 14.4, 21.1, 29.6, 37.9, 52.9, 54.0, 125.8, 129.2, 129.9, 135.6, 166.8. Elemental anal. Calcd for $C_{28}H_{50}N_4O_2$: C, 70.84; H, 10.62; N, 11.80%. Found: C, 70.77; H, 10.53; N, 11.79%.

*Pyridine-2,6-dicarboxylic acid bis-[(2-dibutylamino-ethyl)-amide] (**2**)*

Pyridine 2,6-diacetyldichloride (2.00 g, 9.8 mmol) in dichloromethane (50 ml) was added dropwise to a stirred solution of *N*,*N*-dibutylethylenediamine (3.45 g, 20 mmol) and triethylamine (5 ml) in dichloromethane (50 ml) with a catalytic amount of DMAP and the reaction mixture stirred for 24 h. Water (100 ml) was added and the organic layer separated, dried with $MgSO_4$, filtered and concentrated *in vacuo*. The resulting oil was purified *via* a flash column chromatography (SiO_2, DCM/1% MeOH) to give the product as a viscous orange oil. Yield: 80%, 3.73 g; ESI-MS $m/z = 476.5$ $[M + H]^+$. ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, 12H), 1.26–1.35 (m, 8H), 1.41–1.49 (m, 8H), 2.49 (t, 8H), 2.67 (t, 4H), 3.56 (q, 4H), 8.00 (t, 1H), 8.33 (d, 2H), 8.43 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.4, 20.1, 29.6, 37.8, 53.8, 54.5, 125.1, 139.2, 149.4, 164.0. Elemental anal. Calcd for $C_{27}H_{49}N_5O_2$: C, 68.17; H, 10.38; N, 14.71%. Found: C, 68.15; H, 10.32; N, 14.70%.

*3,4-Diphenyl-1H-pyrrole-2,5-dicarboxylic acid bis-[(2-dibutylamino-ethyl)-amide] (**3**)*

3,4-Diphenyl-1*H*-pyrrole-2-carboxylic acid[124] (1.75 g; 5.7 mmol) was refluxed in thionyl chloride (40 ml) for 3 h. The thionyl chloride was evaporated and the resultant solid was dissolved in dichloromethane (50 ml). This was then added dropwise to a stirring solution of *N,N*-dibutylethylenediamine (2 g, 12 mmol) and triethylamine (5 ml) in dichloromethane (50 ml) with a catalytic amount of DMAP. The reaction mixture was stirred for 48 h. Water (100 ml) was added to the reaction mixture and the organic layer was separated, dried with $MgSO_4$, filtered and concentrated *in vacuo*. The product was then recrystallised from acetonitrile to give the product as a white powder. Yield 67%, 2.21 g; ESI-MS $m/z = 616.7$ $[M + H]^+$. ^1H NMR (400 MHz, $CDCl_3$): δ 0.84 (bt, 12H), 1.13 (m, 16H), 2.17 (m, 8H), 2.33 (bt, 4H), 3.28 (br, 4H), 6.09 (bt, 2H), 7.11–7.14 (m, 4H), 7.20–7.24 (m, 6H), 10.23 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 20.1, 29.2, 37.6, 52.9, 53.8, 124.1, 126.2, 128.0, 128.9, 131.1, 133.8, 160.8; Elemental anal. Calcd for $C_{38}H_{57}N_5O_2$: C, 74.11; H, 9.33; N, 11.37%. Found: C, 74.04; H, 9.43; N, 11.36%.

*5-Nonyl-3-dihexylaminomethyl-2-hydroxy-benzaldehyde oxime (**4**)*

5-Nonyl-3-dihexylaminomethyl-2-hydroxybenzaldehyde (25 g, 60.2 mmol) was dissolved in toluene (50 ml) in a 250 ml 3-necked RB flask and the solution warmed to 45°C. Hydroxylamine sulphate (6.36 g, 38.8 mmol) was dissolved in water (30 ml) and warmed to 45°C before adding to the reaction flask. Sodium carbonate (4.11 g, 38.8 mmol) in water (30 ml) was added slowly to the reaction mixture with stirring. The reaction was stirred overnight (17 h) at 45°C before cooling to room temperature. The organic phase was separated and washed with sulphuric acid solution (50 ml) followed by water (2 × 50 ml). The organic was dried over $MgSO_4$ and the solvent was removed under vacuum at 70°C. Yield: 93%, 24 g; FAB-MS $m/z = 461$ $[M + H]^+$. ^1H NMR (250 MHz, $CDCl_3$): δ 0.51–1.60 (41H, m, AlkH), 2.50 (4H, t, $2 \times NCH_2CH_2$), 3.79 (2H, s, $ArCH_2N$), 6.76 (1H, m, ArH), 7.19 (1H, m, ArH), δ 8.30 (1H, s, CHN). Elemental anal. Calcd for $C_{29}H_{52}N_2O_2$: C, 75.60; H, 11.38; N, 6.08%. Found: C, 74.10; H, 11.18; N, 5.95%. Discrepancy in carbon analysis may be due to the presence of a small amount of the sulphate salt of **4** in the analysis sample: Calcd for $C_{29}H_{52}N_2O_2(H)_{0.2}(SO_4)_{0.1}$: C 74.02; H, 11.18; N, 5.95%. Found: C, 74.10; H, 11.18; N, 5.95%.

*[Ni(**4**-H)$_2$]*

A solution of **4** (5 g, 10.9 mmol) in methanol (60 ml) was added to a solution of nickel acetate tetrahydrate (1.37 g, 5.5 mmol) in methanol (60 ml) and stirred overnight. The solvent was removed *in vacuo* to give a dark green viscous oil. This was dissolved in dichloromethane (100 ml) and washed with a pH 9 ammonia solution (2 × 50 ml). The organic layer was separated, dried with magnesium sulphate, filtered and the solvent was removed *in vacuo* to give the product as a sticky green solid. Yield: 80%, 4.3 g; FAB-MS $m/z = 980$ $[M + H]^+$.

*[Ni(**5**-H)$_2$]*

A solution of **5** (1.03 g, 3.6 mmol) in methanol (60 ml) was added to a solution of nickel acetate tetrahydrate (0.45 g, 1.8 mmol) in methanol (60 ml) and stirred overnight. The solvent was removed *in vacuo* and the residue dissolved in dichloromethane (100 ml) and washed with a pH 9 ammonia solution (2 × 50 ml). The organic layer was separated, dried with magnesium sulphate, filtered and the solvent was removed *in vacuo* to give the product as a green crystalline solid which was recrystallised from hexane. Yield: 37%, 0.41 g; FAB-MS $m/z = 637$ $[M + H]^+$. ^1H NMR (250 MHz, $CDCl_3$): δ 1.15 (s, 9H, $C(CH_3)_3$), 1.45 (m, 2H, CH_2), 1.50 (m, 4H, $2 \times CH_2$), 2.15 (m, 4H, $2 \times CH_2$), 3.22 (s, 2H, $ArCH_2N$), 6.90 (s, 1H, ArH), 6.95 (s, 1H, ArH), 7.78 (s, 1H, ArCHN). ^{13}C NMR (63 MHz, $CDCl_3$): δ 24.0, 25.0, 31.5, 33.5, 54.0, 58.0, 125.5, 131.5, 153.5. Elemental anal. Calcd for $C_{34}H_{50}N_4O_4Ni$: C, 64.05; H, 7.85; N, 8.79%. Found: C, 64.10; H, 7.80; N, 8.50%.

*[Ni(**P50**-H)$_2$]*

A solution of **P50** (5.0 g, 19 mmol) in methanol (60 ml) was added to a solution of nickel acetate tetrahydrate (2.4 g, 9.5 mmol) in methanol (100 ml) and stirred overnight. The solvent was removed *in vacuo* to give a dark green viscous oil. This was dissolved in dichloromethane (100 ml) and washed with a pH 9 ammonia solution (2 × 50 ml). The organic layer was separated, dried with magnesium sulphate, filtered and the solvent was removed in vacuo to give the product as a sticky green solid. Yield: 88%, 4.9 g; FAB-MS $m/z = 584$ $[M + H]^+$.

$[Ni(\mathbf{5})_2(benzoate)_2]$

Sodium benzoate (125 mg, 0.86 mmol) and **5** (250 mg, 0.86 mmol) were added to a solution of nickel nitrate hexahydrate (127 mg, 0.43 mmol) in methanol (75 ml) and stirred overnight. The solvent was removed *in vacuo* to leave a green powder. Yield: 350 mg. X-ray quality crystals were grown in low yield by layering of a chloroform solution with hexane.

Extraction studies

General procedure (sulphate extraction)

Stock solutions of 0.01 M ligand (0.02 M in the case of TOA) were prepared in chloroform. Five millilitre portions of the stock solutions were contacted with 5 ml of 0.8 M aqueous sulphate solutions over a range of pH values and stirred for 24 h. The aqueous and organic phases were separated and the equilibrium pH of the aqueous phase determined. Aliquots (0.5 ml) of the organic phase were removed, evaporated to dryness *in vacuo* and the residue redissolved in butan-1-ol for sulphur determination by ICP-OES. From this plots of percentage sulphur loading versus pH were generated.

*Metal salt **4***

Procedure as above but using 0.01 M $[Ni(\mathbf{4}\text{-}H)_2]$. Butan-1-ol solutions analysed for both nickel and sulphur contents by ICP-OES. From this plots of percentage nickel and sulphur loading versus pH were generated.

Dual host

Procedure as above but with the addition of 0.01 M $[Ni(\mathbf{P50}\text{-}H)_2]$ to the ligand stock solutions. Butan-1-ol solutions analysed for both nickel and sulphur contents by ICP-OES. From this plots of percentage nickel and sulphur loading versus pH were generated.

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