DOI: 10.1002/chem.200601874

Anion Selectivity in Zwitterionic Amide-Functionalised Metal Salt Extractants

Stuart G. Galbraith,[a] Qiang Wang,[b] Li Li,[b] Alexander J. Blake,[b] Claire Wilson,[b] Simon R. Collinson,[b] Leonard F. Lindoy,[c] Paul G. Plieger,[d] Martin Schröder,*[b] and Peter A. Tasker*[a]

Abstract: Amide-functionalised salen ligands capable of extracting metal salts have been synthesised and characterised. Single-crystal X-ray structure determinations of complexes of $NiSO_4$, $[Ni(L)(SO_4)]$, confirm that the ionophores are in a zwitterionic form with Ni^{II} bound in the deprotonated salen moiety and the SO_4^{2-} ion associated with protonated pendant *N*′-amidopiperazine groups. Treatment of $[Ni(L)(SO_4)]$ with base removes the protons from the pendant amido–amine group resulting in loss of the SO_4^{2-} ion and formation of metal-only complexes of type $[Ni(L-2H)]$, which have been characterized by single-crystal X-ray diffraction. Three of the ligands with solubilities suitable for solvent extraction studies show loading and stripping pH-profiles that are suitable for the recovery of $CuSO_4$ or $CuCl_2$ from industrial leach solutions. The copper-only complexes, $[Cu(L-2H)]$, are selective for Cl^- over SO_4^{2-} in both solvent extraction and bulk liquid membrane transport experiments and were found to bind Cl^- in two steps via the formation of a 1:1:1 $[Cu(L-H)Cl]$ assembly, followed by a 1:1:2 $[Cu(L)Cl_2]$ assembly as the pH of the aqueous phase is lowered. The anion transport selectivity was evaluated for a number of other mono-charged anions and interestingly the ligands were found to display a preference for the Br^- ion. To probe the influence of the Hofmeister bias on the selectivity of anion complexation, single-phase potentiometric titration experiments were employed to investigate the binding of SO_4^{2-} and Cl^- by one of the copper only complexes, $[Cu(L-2H)]$ in 95%/5% MeOH/water. Under these conditions selectivity was reversed ($SO_4^{2-} > Cl^-$) confirming that the Hofmeister bias, which reflects the relative hydration energies of the anions, dominates the selectivity of anion extraction from aqueous media into $CHCl_3$.

Keywords: anions · copper · extractive metallurgy · hydrogen bonds · nickel · receptors · solvent extraction

Introduction

Cation-exchange reagents such as the phenolic oximes[1,2] are well suited to solvent extraction processes used for the recovery of base metals from their oxidic ores after leaching with sulfuric acid, and such processes now account for around 30% of the world's copper production.[3] Different types of hydrometallurgical flowsheets are needed for metal-recovery from sulfide ores in order to exploit a range of very efficient leaching processes that have been developed recently by the mining industry.[4] Extraction of a metal salt to achieve the unit operations of concentration and separation (Figure 1) has been suggested as an approach that will result in better materials balances, particularly from pregnant leach solutions, which contain high concentrations of metal salts.[2,5,6] Transport of a metal salt across a flowsheet by means of a water-immiscible solvent can be facilitated through the use of zwitterionic heterotopic ligands

[a] Dr. S. G. Galbraith, Prof. P. A. Tasker
School of Chemistry, University of Edinburgh
Edinburgh, EH9 3JJ (UK)
Fax: (+44) 131-650-6543

[b] Dr. Q. Wang, Dr. L. Li, Prof. A. J. Blake, Dr. C. Wilson, Dr. S. R. Collinson, Prof. M. Schröder
School of Chemistry, The University of Nottingham
University Park, Nottingham, NG7 2RD (UK)
Fax: (+44) 115-951-3563

[c] Prof. L. F. Lindoy
Centre for Heavy Metal Research, School of Chemistry F11
University of Sydney, N.S.W. (Australia)

[d] Dr. P. G. Plieger
Institute of Fundamental Sciences, Massey University
Private Bag 11 222, Palmerston North (New Zealand)

Supporting information for this article is available on the WWW under http://www.chemistry.org or from the author.

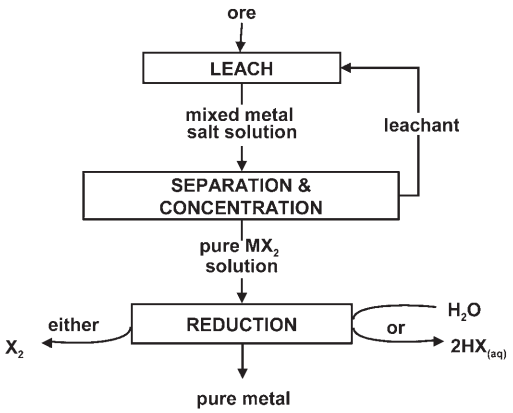


Figure 1. Recovery of a base metal by selective transport of a metal salt from a pregnant leach solution containing a complex mixture of cations and anions

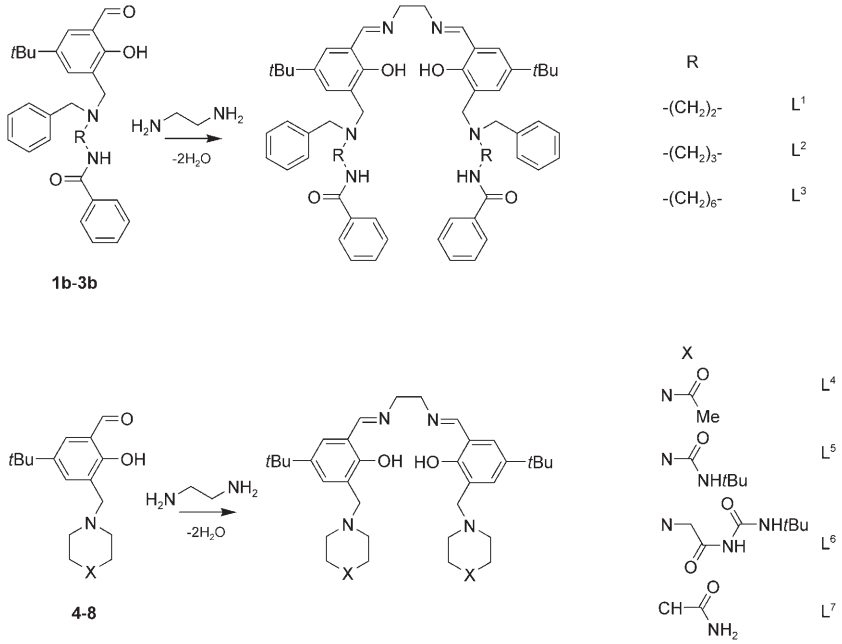
that have separate cation and anion binding sites; the zwitterionic nature of the reagent allows the metal and anion to be recovered separately by pH adjustment of the strip solution.[5,7] An efficient process requires the reagent to show high selectivity for both targeted metal cation and anion.[8] Ligand design to achieve selective complexation of metal cations is well understood[9] and many highly selective solvent extractants have been developed for use in extractive metallurgy.[2] In contrast, selective solvent extraction of anions, although of great potential commercial importance in extractive metallurgy especially for the recovery of precious metals as their chlorometallate complexes,[10] is much less well developed. The design of selective anion receptors is a rapidly expanding area,[11,12] and the simultaneous binding of both cationic and anionic moieties of metal salts by polytopic ligands with chemically distinct binding sites is currently a very active area of research.[12–23]

Typically, many anion receptors use several non-covalent interactions to achieve strong binding, and hydrogen-bonding donor sites are most commonly incorporated into synthetic receptors, because their directionality allows steric and conformational control of the hydrogen-bond donors to match the requirements of anions of different sizes and geometries. A striking example of such a naturally occurring system is the phosphate-binding protein (PBP), which uses twelve hydrogen bonds including seven from amide NH groups to bind a monohydrogen phosphate anion selectively.[24]

We report herein the incorporation of amide and urea groups into the zwitterionic ditopic ligand framework of bis-salicylaldimine (salen-type) ligands.[25–29] It was anticipated that the presence of hydrogen-bond donors in the target ionophores L^n ($n=1$–8; Scheme 1) would aid these derivatives to address the solvation spheres of complexed anions and hence influence the observed selectivity towards anion transport.

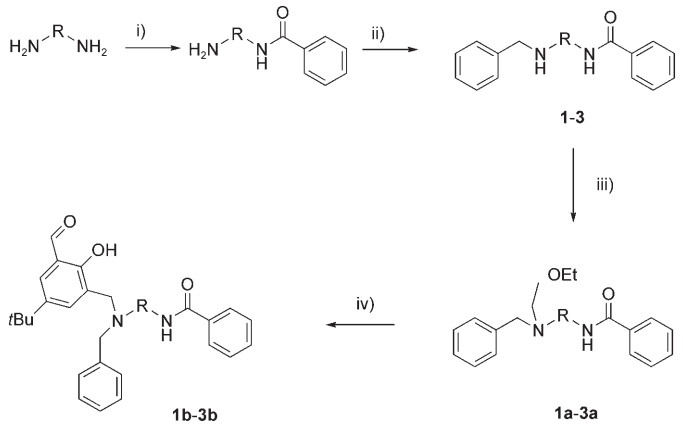
Results and Discussion

Synthesis of ligands and complexes: The ionophores L^n ($n=$ 1–8) were prepared from the appropriately substituted sali-



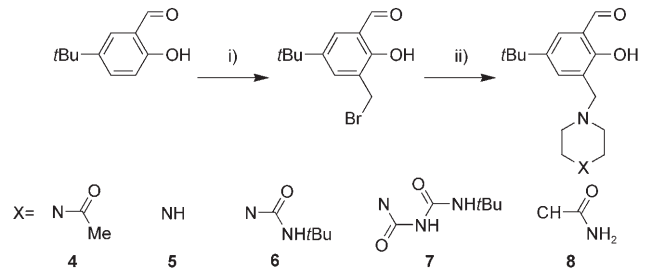
Scheme 1. Preparation of salen derivatives with pendant anion-complexing groups *ortho* to the phenolate donor atoms. Ligand L^8 has the same structure as L^7, but with mixed isomer/multibranched nonyl groups replacing the *tert*-butyl substituents.

cylaldehyde by condensation with 1,2-diaminoethane (Scheme 1). The secondary amines **1**–**3**, which are precursors for L^n ($n=1$–3), respectively, were obtained by mono-derivatisation of the appropriate diamine with benzoic anhydride by using a modification of a literature method (Scheme 2),[30] followed by reaction with benzaldehyde and reduction with $NaBH_4$. Compounds **1**–**3** were then treated with paraformaldehyde and 2-hydroxy-5-*tert*-butylbenzaldehyde in a two-step Mannich reaction[31] to give the corresponding salicylaldehydes in typically 30–40% yields. Initially a conventional Mannich reaction[31] between 5-*tert*-butyl-2-hydroxybenzaldehyde[32] and 1-acetylpiperazine was used to generate the aldehyde **4** in 69% yield as a precursor for



Scheme 2. Synthesis of **1–3** as the secondary amines precursors for the preparation of L^1–L^3. i) $(PhCO)_2O/CH_2Cl_2$; ii) PhCHO, $NaBH_4$; iii) paraformaldehyde, K_2CO_3, EtOH, 0 °C, 72 h; iv) 5-*tert*-butyl-2-hydroxybenzaldehyde, MeCN, reflux, 72 h.

L^4 (Scheme 3). A significantly improved yield for **4** (85 %) was obtained by reaction of 5-*tert*-butyl-3-bromomethyl-2-hydroxybenzaldehyde[33] (Scheme 3) with 1-acetylpiperazine;



Scheme 3. Synthesis of salicylaldehyde derivative precursors for L^4–L^7. i) reference [33]; ii) appropriate piperazine or piperidine, K_2CO_3 and KI in CH_3CN. Aldehyde **9** has the same structure as **8**, but with a mixed isomer nonyl group replacing the *tert*-butyl substituent.

similar methodologies were employed to obtain aldehydes **5–9** as precurors to L^n (n = 5–9).

All ionophores were characterised by ^1H and ^{13}C NMR spectroscopy, by FTIR spectroscopy, mass spectrometry and elemental analysis. Evidence for the complete formation of products was confirmed by the presence of characteristic resonances for the imine proton at δ = 8.2–8.5 ppm in the ^1H NMR spectrum and of the imine C centre at δ = 165–168 ppm in the ^{13}C NMR spectrum, coupled with the absence of resonances for aldehydic C and H centres. The presence of amide linkages in the products L^n (n = 1–3) was confirmed by a resonance for the NH proton at $\delta \approx 6.9$ ppm and a peak in the ^{13}C NMR spectra at $\delta \approx 167$ ppm corresponding to the carbonyl carbon (NH*C*O). In the case of L^6, the urea linkage was characterised by the presence of resonances for the NH protons at δ = 8.9 and 8.2 ppm, while for L^7 the presence of an amide group was confirmed by the presence of a resonance for the NH protons at $\delta \approx 6.7$ ppm. The structure of the urea-substituted ligand L^6 was confirmed by single-crystal X-ray diffraction and its structure is compared to that of its $NiSO_4$ complex below.

The neutral complexes [Cu(L^1−2H)], [Cu(L^2−2H)] and [Cu(L^3−2H)] were prepared by stirring a solution of the ligand in $CHCl_3$ with a solution of $Cu(OAc)_2$ in MeOH. The crude complex was washed with ammonia solution (pH 9) to remove any excess $Cu(OAc)_2$ and to ensure that the pendant amine groups were fully deprotonated. These complexes, their copper(II) salt derivatives [Cu(L)X] (L = L^1–L^3 and X = 2 Cl or SO_4) as well as the free ligands all showed sufficient solubility in $CHCl_3$ to allow solvent extraction experiments to be carried out. The latter were employed to probe the metal and anion binding properties of these ionophores and define the relative affinities of their complexes for different anions (see below). Metal salt complexes of piperidino- and piperazino-substituted ligands L^4–L^8 were much less soluble and consequently their coordination chemistry and structures were studied largely in the solid-state. Even the incorporation of multibranched/mixed isomer nonyl groups as in L^8 failed to solubilize the $CuSO_4$ complex sufficiently in $CHCl_3$ to allow comparisons to be made with L^1–L^3 in solvent extraction experiments.

Nickel(II) sulfate and copper(II) sulfate complexes [M(L)SO_4] (L = L^4–L^8) were readily isolated from the reaction of metal sulfate with the respective ligands in MeOH. Complex formation was confirmed in each case by elemental analysis and electrospray mass spectrometry. The diamagnetism of the nickel(II) complexes is confirmed from the sharpness of the peaks in their respective ^1H NMR spectra recorded in $CDCl_3$ and is in accordance with the expected square-planar geometry for the nickel(II) centres; this was confirmed also by single-crystal X-ray analysis (see below).

Complexation to nickel(II) leads to shifts of the ^1H NMR signals associated with the salen unit to higher field compared to those of the metal-free ligands. For example, for ligand L^6 the imine proton signal shifts from δ = 8.40 to 7.65 ppm upon reaction with nickel(II) sulfate. The spectra of [Ni(L^6)SO_4] and [Ni(L^6)$(BF_4)_2$] show differences that suggest that the urea protons within each pendant arm interact in different ways with the anions. Such interactions were later confirmed in the solid-state by single-crystal X-ray structures of the SO_4^{2-} complexes [Ni(L^5)SO_4)] and [Ni(L^6)SO_4)]. A resonance due to one of the pendant amido NH protons in L^6 is particularly sensitive to the nature of the anion present and shifts from δ = 9.06 ppm in the nickel(II) sulfate complex to δ = 8.63 ppm in the tetrafluoroborate complex. The other amido NH proton resonance shows a smaller shift from δ = 8.28 to 8.19 ppm in the same complexes. This is consistent with the observed solid-state structure for [Ni(L^6)(SO_4)] (see below), which reveals only one of the amide NH centres interacting with the anion, N4H···$(OSO_3)^{2-}$. In the solid-state, an additional intramolecular hydrogen bond between the remaining amido NH group and a carbonyl oxygen, N5H···O2, is observed.

Treatment of the metal sulfate complexes [M(L)SO_4] with KOH in MeOH afforded the metal-only forms [M(L−2H)].

These were isolated as solids and shown to be identical to the products prepared directly from the corresponding metal(II) acetates. The deprotonation of the pendant amino groups was followed by ^{1}H NMR spectroscopy in CD_3OD and $CDCl_3$. The SO_4^{2-}-free complex [Ni(L^7−2H)] shows well-resolved resonances for the pendant amide arm and methylene groups, which were found to have very similar chemical shifts to those of the free ligand. Such studies demonstrate that selective stripping/exchange of anions is possible with these polytopic complexing agents. The pH dependence of anion loading in solvent extraction experiments with [Cu(L−2H)] (L = L^1–L^3) will be now discussed.

Solvent extraction: New hydrometallurgical flowsheets for the recovery of metal ions from their sulfidic ores require the extraction and transport of metal salts. A practicable extractant needs to show selectivity for both the targeted metal cation and anion as downstream electrolytic reduction requires electrolytes of high purity. The anions most commonly found in the leach solutions produced in primary base-metal recovery are SO_4^{2-} and Cl^-, so achieving selectivity of SO_4^{2-} over Cl^- (or vice versa) is essential.

The selectivity of solvent extraction of metal cations into the organic phase by organic acid extractants is directly related to the $pH_{1/2}$, the pH associated with 50% loading of the extractant at a stated concentration and for a defined composition of aqueous feed. We have recently described a method for using the $pH_{1/2}$ to also evaluate anion extraction selectivities.[29] In these two-phase experiments the uptake of acids by the metal-only complexes [M(L−2H)] to form metal salt complexes is monitored over a range of pH in order to yield the $pH_{1/2}$ values for the anions [Eq. (1)].

$$[M(L-2H)]_{(org)} + 2\,HX = [M(L)X_2]_{(org)} \quad (1)$$

This gives information on the strength and selectivity of anion binding and if the metal concentrations in both the organic and aqueous phases are also recorded we can analyse the effect of pH on the stability of the metal complex and the strength of metal binding.

The results of such an experiment with the copper-only complex [Cu(L^2−2H)] and sulfuric acid are displayed in Figure 2. The loading of Cu^{2+} and SO_4^{2-} is ≈100% in the pH range 2–3 and both the metal and anion can be conveniently recovered by pH adjustment. This allows the metal salt to be efficiently loaded and recovered and is therefore an ideal profile for base-metal recovery from SO_4^{2-} feeds.[5,7]

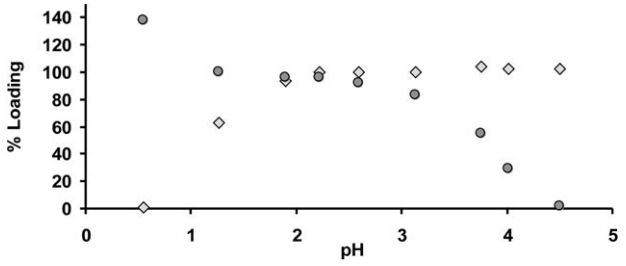


Figure 2. The pH dependence of H_2SO_4 uptake by [Cu(L^2−2H)] and the strength of copper-binding (circles and diamonds define S and Cu molar concentrations, respectively, as percentage of the molar concentration of L^2).

Leach solutions produced in base-metal recovery processes typically contain SO_4^{2-} and/or Cl^- ions. Consequently, we monitored the uptake of HCl by the copper complex [Cu(L^2−2H)] and compared this with the pH profile for SO_4^{2-} to evaluate the anion selectivity of the extractant (Figure 3).

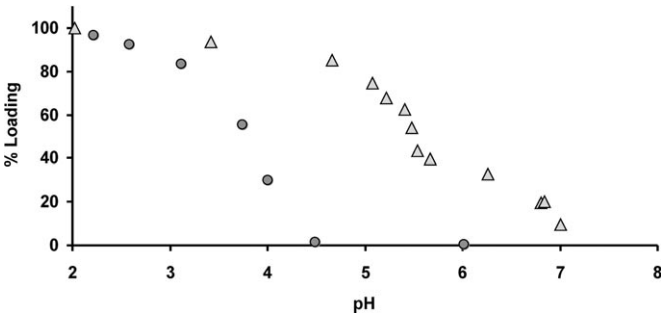


Figure 3. The pH dependence of H_2SO_4 (circles) and HCl (triangles) uptake by [Cu(L^2−2H)].

[Cu(L^2−2H)] was found to extract HCl at a higher pH than H_2SO_4, 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,[34,35] which predicts that charge-diffuse anions (such as mono-charged Cl^-) will in general be more favourably extracted into low polarity solvents than more hydrophilic anions such as SO_4^{2-}.

In Figure 3 a value of 100% for the extraction of Cl^- corresponds to formation of a 1:1:2 [Cu(L−2H)Cl_2] complex. In contrast, 100% extraction of SO_4^{2-} involves a 1:1:1 [Cu(L−2H)SO_4] complex and consequently different shaped pH-loading curves are expected. As the pH is lowered the loading of Cl^- is first observed at pH < 7, but the curve then flattens as the pH approaches 6, rising again sharply at pH < 5.5. This is consistent with a two-step process and the loading of the second Cl^- being less favourable.

It was hoped that the use of ligands with shorter (L^1) or longer (L^3) alkyl chains between the teriary amine and amide groups in the anion binding sites would provide an insight into how such systems might be tuned for anion selectivity. The uptake of H_2SO_4 and HCl by [Cu(L^3−2H)] and [Cu(L^1−2H)] is illustrated in Figures 4 and 5, respectively. [Cu(L^3−2H)], containing the 1,6-hexane-linked amide groups, is more selective for Cl^- over SO_4^{2-} than the 1,3-propane-linked analogue [Cu(L^2−2H)]; for [Cu(L^3−2H)] the $2\,Cl^-/SO_4^{2-}$ $\Delta pH_{1/2} = 2.3$ (Figure 4), which compares with $\Delta pH_{1/2} = 1.7$ for [Cu(L^2−2H)] (Figure 3). A two-step profile for Cl^--loading is observed for [Cu(L^3−2H)] between pH 6 and pH 7 (Figure 4). [The solvent extraction experiments

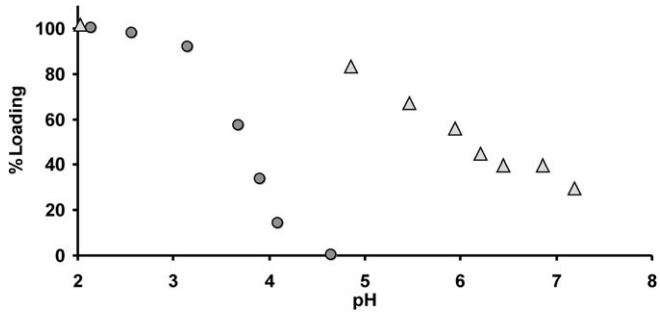


Figure 4. The pH dependence of H_2SO_4 (circles) and HCl (triangles) uptake by [Cu(L^3−2H)]

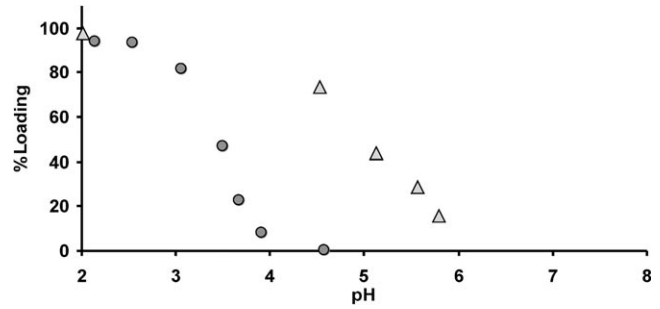


Figure 5. The pH dependence of H_2SO_4 (circles) and HCl (triangles) uptake by [Cu(L^1−2H)].

were not conducted above pH 7, because $CHCl_3$ becomes unstable in the presence of hydroxide.]

The copper-only complex [Cu(L^1−2H)] begins to load Cl^- at a lower pH (<6.0) than [Cu(L^3−2H)], but still shows selectivity for Cl^- over SO_4^{2-}. For [Cu(L^1−2H)] the $pH_{1/2}$ drops to 5.1 for Cl^- and 3.5 for SO_4^{2-}, which gives a value for $\Delta pH_{1/2}$ of 1.6. Although this value for $\Delta pH_{1/2}$ is not much lower than that recorded for [Cu(L^2−2H)] ($\Delta pH_{1/2}=1.7$), there is a significant reduction in the Cl^- to SO_4^{2-} selectivity as no clear two-step loading of Cl^- is observed with [Cu(L^1−2H)]. This result is important for Cl^--stripping from [Cu(L^1)Cl_2] as in contrast to the other two systems, all Cl^- in [Cu(L^1)Cl_2] can be removed by raising the pH above 6.0.

It appears that as the alkyl chain between the amine nitrogen and amide group is made more flexible {1,2-ethane in [Cu(L^1−2H)]→1,3-propane [Cu(L^2−2H)]→1,6-hexane [Cu(L^3−2H)]} the selectivity of the ligand for Cl^- over SO_4^{2-} increases. This may be a result of the longer arms facilitating the formation of more favourable binding environments by separating the two Cl^- binding sites and thus reducing electrostatic repulsion between these two bound anions. Conversely, an enhancement of SO_4^{2-} over Cl^- selectivity might be achieved by the development of a rigid and pre-organised anion binding site for SO_4^{2-}, which would consequently disfavour incorporation of two monoanions.

UV/Vis titrations: UV/Vis spectra were used to monitor the stoichiometry of anion binding by the copper-only complexes [Cu(L−2H)] (L=L^1–L^3). Of particular interest was the interaction of Cl^- ions with the complexes given that the solvent extraction experiments indicated potential formation of both 1:1 and 1:2 complex/anion species. The experiments involved incremental addition of 0–5 equivalents of H_2SO_4 or HCl in isopropanol to 0.05 mM solutions of [Cu(L−2H)] in the same solvent. The addition of H_2SO_4 to the complexes resulted in clear isosbestic points until greater than one equivalent of acid was added indicating that the initial complex formed had a [Cu(L−2H)]/H_2SO_4 ratio of 1:1 (Figure 6). Such behaviour was expected as this 1:1 complex

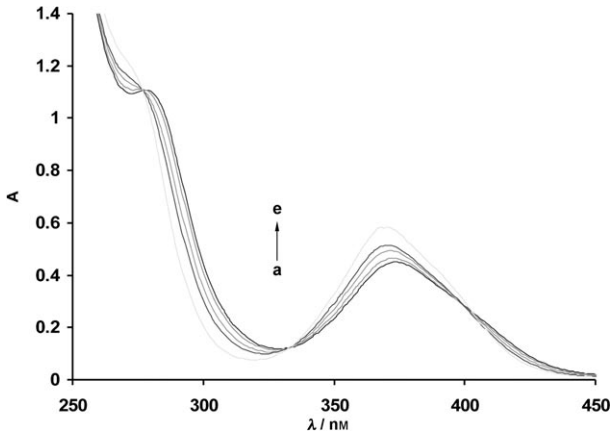


Figure 6. The absorption spectra of [Cu(L^1−2H)] (0.05 mM) upon the addition of H_2SO_4 in isopropanol at 20 °C; the number of equivalents of H_2SO_4 added are: a) 0; b) 0.2; c) 0.4; d) 0.6; e) 1.0.

appears to be the dominant form in the extraction experiments, except at very low pH at which there is a predominance of mono-charged HSO_4^- ions. Upon addition of more than one equivalent of acid the respective spectra did not pass through the existing isobestic points, indicating that new species were formed. It is interesting to note that the band at λ_{max} 374 nm observed for the complexes [Cu(L−2H)] shifted by 10 nm for [Cu(L^2)] and [Cu(L^3)] compared to only 3 nm for [Cu(L^1−2H)] on addition of one equivalent of H_2SO_4. This may indicate that a different anion binding mode might occur for the more flexible hosts.

Similar experiments to the above were performed with HCl and the results are consistent with the formation of an initial 1:1 species followed by a complex with a [Cu(L−2H)]/HCl ratio of 1:2. Thus, by the addition of one equivalent of acid, a clear isosbestic point was observed. This indicates that only the 1:1 complex is present and no 1:2 species has been formed at this stage. Upon the incremental addition of two equivalents of acid the intial isosbestic point is lost, but a new isosbestic point is generated reflecting formation of a 1:2 species from the already formed 1:1 complex. No further changes were observed in the spectra on the further addition of more than two equivalents of HCl. A plot of the formation of the 1:1 and 1:2 [Cu(L−2H)]/HCl species by addition of HCl to [Cu(L^2−2H)] is shown in Figure 7. These results are consistent with the two-step Cl^--loading observed in the solvent extraction experi-

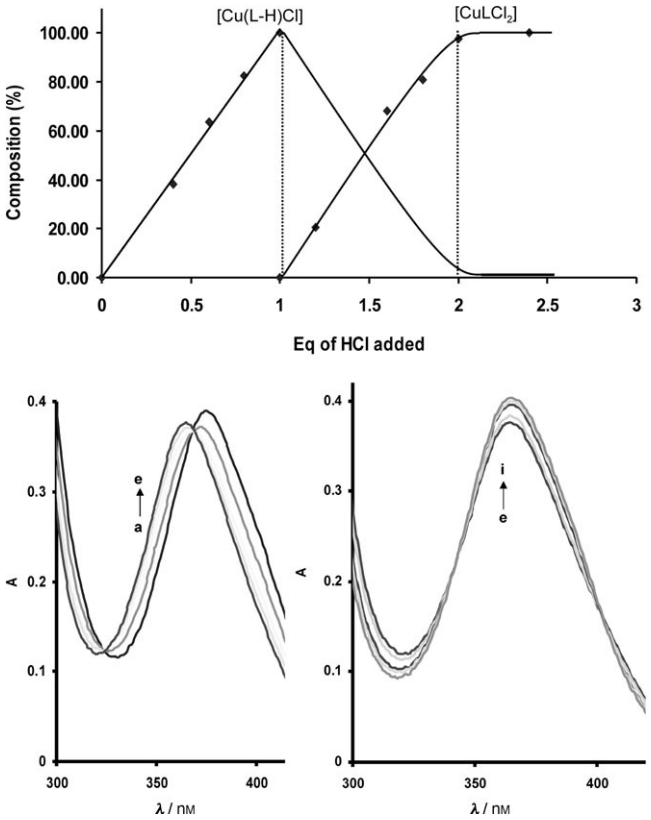


Figure 7. Plot of the formation of the 1:1 and 1:2 $[Cu(L^2-2H)]/HCl$ species in isopropanol at 20 °C. The % composition was calculated from the absorbances recorded at the peak formed at 365 nm in the absorption spectra of $[Cu(L^2-2H)]$ upon the addition of HCl in isopropanol; the number of equivalents of HCl added are: a) 0, b) 0.4, c) 0.6, d) 0.8, e) 1.0, f) 1.2, g) 1.6, h) 1.8, i) 2.0.

ments with $[Cu(L^2-2H)]$ (Figure 3), indicating the exclusive formation of a 1:1 complex followed by the subsequent formation of the 1:2 complex on further addition of acid under the conditions employed.

Membrane transport of anions: To gain further understanding of anion extraction and transport, the copper-only complexes $[Cu(L-2H)]$ ($L = L^1$–L^3) were used as the carriers in a $CHCl_3$ bulk liquid membrane (BLM) system. The initial experiments involved monitoring the rate of transport of SO_4^{2-} and Cl^- through the BLM from an acidic source phase (pH 1.8 ± 0.1) to a neutral receiving phase (pH 7.0) buffered with phosphate. It was assumed that transport occurs by means of a symport mechanism[36] in which anion(s) and protons are co-complexed and co-transported. These experiments are summarised in Table 1 and were performed by either using source phases containing only one anion or with mixed SO_4^{2-}/Cl^- ions.

Both complexes showed a slightly higher rate of SO_4^{2-} transport compared to Cl^- from source phases containing only a single anion type. This modest increase in rate can be rationalised by comparing the pH profiles obtained for SO_4^{2-} and Cl^- extraction (Figures 3 and 5). The $pH_{1/2}$ values are greater for Cl^- so it seems likely that SO_4^{2-} will be more

Table 1. Transport rates[a] of H_2SO_4 and 2 HCl (10^{-6} mol).

Source phase[b]	$[Cu(L^1-2H)]$	$[Cu(L^2-2H)]$
SO_4^{2-} only	39	33
Cl^- only[c]	37	27
SO_4^{2-}/Cl^- [c]	1.0/37	0.3/29

[a] Across a $CHCl_3$ BLM (50 mL), [carrier] = 1 mM, for 23 h based upon anion concentrations in the receiving phase {30 mL buffered at pH 7.0 ± 0.1 with NaH_2PO_4/Na_2HPO_4 (50 mM)}. Experimental uncertainty in the recorded rates is ±5%. [b] 10 mL of a 0.1 M solution of anion(s), pH 1.8 ± 0.1. [c] The reported values for Cl^- represent the moles of $(Cl^-)_2$ transported and is scaled in terms of charge balance.

efficiently stripped into the receiving phase at pH 7. This may compensate for the lower strength of binding shown by the extractants for SO_4^{2-} in the solvent extraction experiments. This is supported by the lower transport rates observed for $[Cu(L^2-2H)]$ compared to $[Cu(L^1-2H)]$, with the latter having lower SO_4^{2-} and Cl^- $pH_{1/2}$ values (Figures 3 and 5). When a mixed SO_4^{2-}/Cl^- source phase was used the transport rates for Cl^- were found to be similar to those obtained for a Cl^--only source phase and only a very small amount of SO_4^{2-} was transported. The indication that Cl^- anions are preferentially bound by the complexes in the BLM is consistent with the solvent extraction data presented earlier and the results indicate that solvent extraction pH profiles can be used to define the conditions required for efficient transport of anions in BLM studies of the present type.

To gain a wider appreciation of the extraction selectivity of the copper-only complexes $[Cu(L-2H)]$, mixed-anion-source-phase membrane-transport experiments were performed for a variety of anions including SO_4^{2-}, Cl^-, Br^-, NO_3^- and $H_2PO_4^-$. Comparative transport experiments were also performed by using dibenzylamine as a carrier so that the selectivity and efficiency of transport by the complexes could be compared to those of a simple protonatable amine with an environment about the nitrogen atom that is similar to that in the extractant ligands. These experiments were performed using a pH 5.2 citrate buffer solution as the receiving phase rather than phosphate buffer solution since phosphate was one of the anions present in the source phase.

The observed transport employing dibenzylamine as the carrier (Figure 8) followed the expected Hofmeister order[34,35] of hydrophobicity: $NO_3^- > Br^- > Cl^- > H_2PO_4^- > SO_4^{2-}$ and neither SO_4^{2-} nor $H_2PO_4^-$ were detected in the receiving phase. The amide-functionalised copper-only complexes were found to transport Br^- more efficiently than the other anions. This was particularly evident for $[Cu(L^1-2H)]$ for which the bromide flux was close to double that obtained for NO_3^-. This poorer transport of NO_3^- by $[Cu(L^1-2H)]$ relative to Br^- may perhaps reflect the larger size of the NO_3^- ion and the *cis* disposition of the anion-binding groups making it less favourable for these arms to accommodate two NO_3^- ions on one "edge" of the salen unit.

No SO_4^{2-} or $H_2PO_4^-$ ion transport occurred in the presence of Cl^-, Br^- or NO_3^-. To evaluate the selectivity order

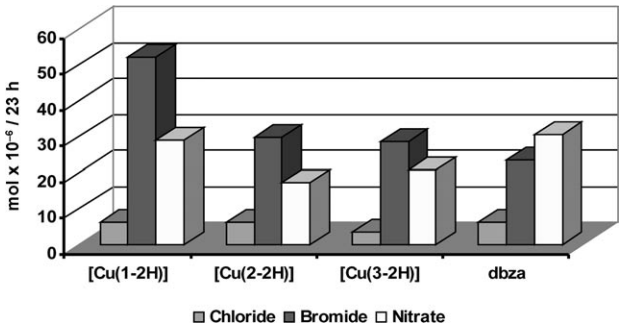


Figure 8. The transport rates of Cl^-, Br^-, and NO_3^- from a mixed anion source phase using [Cu(L−2H)] (L = L^1–L^3) and dibenzylamine (dbza) as carrier. [The concentration of dibenzylamine was 2 mM in the membrane-transport experiments, so that the results could be fairly compared to the dibasic ligands.]

for these former anions, membrane-transport experiments were run using a mixed $SO_4^{2-}/H_2PO_4^-$ aqueous source phase. The pH of the source phase was set at 3.3 to ensure that $H_2PO_4^-$ was the dominant phosphate species present (pK_{a1} for phosphoric acid = 2.12). [Cu(L^1−2H)] and [Cu(L^2−2H)] were tested and both showed complete selectivity for SO_4^{2-} over $H_2PO_4^-$ (Figure 9), providing another example of anti-Hofmeister behaviour.[34,35] Again, the *cis* disposi-

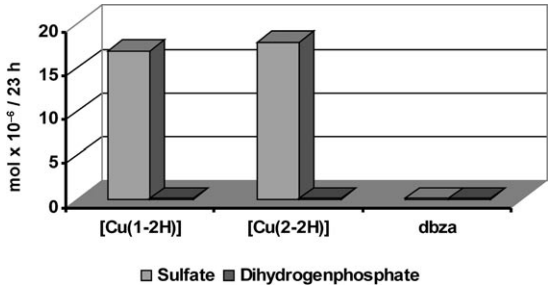


Figure 9. Transport rates of sulfate and dihydrogenphosphate from a mixed $SO_4^{2-}/H_2PO_4^-$ source phase through a $CHCl_3$ bulk liquid membrane using the copper complexes [Cu(L^1−2H)], [Cu(L^2−2H)] and dibenzylamine (dbza) as carrier. [The concentration of dibenzylamine was 2 mM in the membrane-transport experiments, so that the results could be fairly compared to the dibasic ligands.]

tion of the pendant anion-binding arms may be significant. Such an arrangement is presumably more favourable for accommodating a single dianion, (SO_4^{2-}) over two monoanions ($2\times H_2PO_4^-$).

Potentiometric titrations: The extent to which the observed anion discrimination in two-phase solvent extraction and three-phase BLM transport experiments reflects the differences in solvation energies was examined using potentiometric titrations in 95%/5% MeOH/water to probe anion binding corresponding to the equilibria in Equations (2) and (3). This was achieved indirectly by determining the stepwise protonation constants for the pendant amines in [Cu(L^1−2H)] [Eq. (4)].

$$[Cu(L^1-2H))] + H_2SO_4 = [Cu(L^1)SO_4] \quad (2)$$

$$[Cu(L^1-2H)] + 2\,HCl = [Cu(L^1)Cl_2] \quad (3)$$

$$[Cu(L^1-2H)] + 2\,H^+ = [Cu(L^1)]^{2+} \quad (4)$$

A conventional pH titration procedure in 95%/5% MeOH/water [I = 0.1 M $(C_2H_5)_4N^+ClO_4^-$] was employed both in the absence of added anion and in the presence (see Table 2) of Cl^- or SO_4^{2-} added as tetraalkylammonium salts.

Table 2. Protonation constants for [Cu(L^1−2H)] in 95%/5% MeOH/water; I = 0.1 M $(C_2H_5)_4N^+ClO_4^-$[a] in the presence of HSO_4^- and Cl^-.

Anion added[b]	[Anion][c]	Log K_1	Log K_2
–	–	8.96	7.02
HSO_4^-[d]	1×10^{-3}	9.11	7.28
Cl^-	2×10^{-3}	8.98	7.06

[a] K_1 and K_2 refer to the equilibria $[Cu(L^1-H)]^+ = [Cu(L^1-2H)] + H^+$ and $[Cu(L^1)]^{2+} = [Cu(L^1-H)]^+ + H^+$—they relate to the basicity of the pendant amine groups in the presence of the "conducting anion" ClO_4^- and with the addition of sulfate or chloride. All log K values are ±0.05. [b] HSO_4^- was added using tetrabutylammonium hydrogensulfate and tetrapropylammonium chloride was used for the addition of Cl^-. [c] Anion concentration. [d] Although hydrogen sulfate anion was added it is present as SO_4^{2-} anion before the protonation constants are calculated.

Addition of Cl^- was found to give no change within experimental error in the stepwise log K values relative to the absence of this anion. This is in accord with little or no interaction between Cl^- and the protonated amine sites under the somewhat polar conditions employed. In contrast, the addition of SO_4^{2-} resulted in a small, but significant increase in both log K_1 and log K_2 and is in keeping with inhibition of proton ionisation occurring through specific hydrogen-bond formation with the SO_4^{2-} ion. The increase is most noticeable for log K_2 and is consistent with formation of a 1:1 assembly involving SO_4^{2-} and $[Cu(L^1)]^{2+}$, which is more favourable than formation of a 2:1 assembly with Cl^- and $[Cu(L^1)]^{2+}$.

The above corresponds to the reverse of the selectivity observed in the solvent extraction and BLM experiments, but can be rationalised because the Hofmeister bias, which favours the extraction of charge-diffuse anions, is not a major factor in these single-phase experiments. The selectivity of SO_4^{2-} binding over Cl^- in a single phase (95%/5% MeOH/water) reflects the design features incorporated into ionophores L^1–L^8 to allow formation of 1:1:1 assemblies of SO_4^{2-}:L:Cu^{2+} by exploiting a chelating arrangement of the pendant anion complexing groups. Clearly, this preference is not sufficient to overcome the relative solvation energy terms involved in two-phase systems, reflecting the importance of the Hofmeister bias in developing successful recovery processes.[34] Also, formation of higher order assemblies in solution involving pendant arms in different molecules associating with the same anions cannot be ruled out. Such ar-

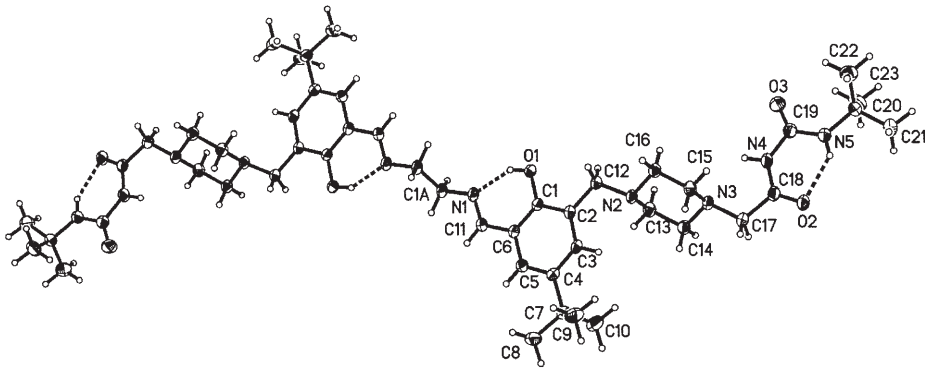


Figure 10. A view of the structure of L^6, showing the atom labelling scheme. Intramolecular hydrogen bonds are indicated by solid dashed lines. Displacement ellipsoids are drawn at the 50% probability level.

rangements predominate in the solid-state structures, which are now described.

Single-crystal X-ray structure determinations: In addition to providing information on the modes of binding of anions to the pendant amine groups in these ligands, single-crystal X-ray structure determinations were undertaken to indicate the extent to which incorporation of the Ni^{II} dication into the salen $N_2O_2^{2-}$ donor set controls the disposition of the functionalities at the respective anion binding sites. This is exemplified by a comparison of the structures of L^6 and two crystalline forms of $[Ni(L^6)SO_4]$.

The free ligand L^6 adopts an extended structure with the pendant benzylamino N centres, N2 and $N2^i$ ($i=3-x, -y, -z$) being separated by 16.64 Å. The molecule adopts an *anti* conformation at the central ethane link between the imino N atoms (Figure 10), the torsion angle N1-C1a-$C1a^i$-$N1^i$ ($i=3-x, -y, -z$) of 180° a consequence of the inversion centre between C1a and $C1a^i$. The two phenol groups form intramolecular hydrogen bonds to the imine N centres, O1–H1···N1, $d(O\cdots N)=2.6121(13)$ Å. There is a further intramolecular hydrogen bond between an NH group and the O centre of the urea in the pendant arm, N5–H5B···O2, $d(N\cdots O)=2.7253(14)$ Å. We have previously observed a similar intramolecular hydrogen bond forming a six-membered ring with this pendant arm when attached to an aza-thioether macrocycles.[13]

The single-crystal X-ray structures of two crystalline forms of the nickel sulfate complex of L^6, $[Ni(L^6)SO_4]\cdot1.75\,H_2O\cdot2.25\,MeOH$ and $[Ni(L^6)SO_4]\cdot7.5\,H_2O$ differing in their levels of solvation, were obtained. The latter has two crystallographically independent $[Ni(L^6)SO_4]$ units per unit cell. The incorporation of Ni^{II} into the salen unit leads to formation of very nearly planar $N_2O_2^{2-}$ donor sets (Figures 11 and 12) with the deviation of Ni^{II} from the plane defined by the $N_2O_2^{2-}$ donor sets being 0.036, 0.022, 0.363 and 0.10 Å for $[Ni(L^5)SO_4]\cdot8\,H_2O\cdot2\,MeOH$, $[Ni(L^6)SO_4]\cdot1.75\,H_2O\cdot2.25\,MeOH$, and for the two crystallographically independent molecules of $[Ni(L^6)SO_4]\cdot7.5\,H_2O$, respectively. The complexation of Ni^{II} brings the pendant amino/amido groups closer together, with the intramolecular separations of N2 and N2′ being 4.80, 6.12 and 5.97 Å in $[Ni(L^6)SO_4]\cdot1.75\,H_2O\cdot2.25\,MeOH$ and in the two crystallographically independent complexes of $[Ni(L^6)SO_4]\cdot7.5\,H_2O$.

The proximity of the anion-complexing groups in $[Ni(L^6)SO_4]\cdot1.75\,H_2O\cdot2.25\,MeOH$ allows the protonated piperazine hydrogen atoms to "chelate" a SO_4^{2-} ion, although in practice this ion is very exposed and is able to form further hydrogen bonds to the urea moiety of an adjacent complex as well as to a lattice molecule of MeOH; there are also weaker interactions with a poorly defined solvent region. The urea fragments in this structure form intramolecular NH···O bonds as is also observed in the structure of the free

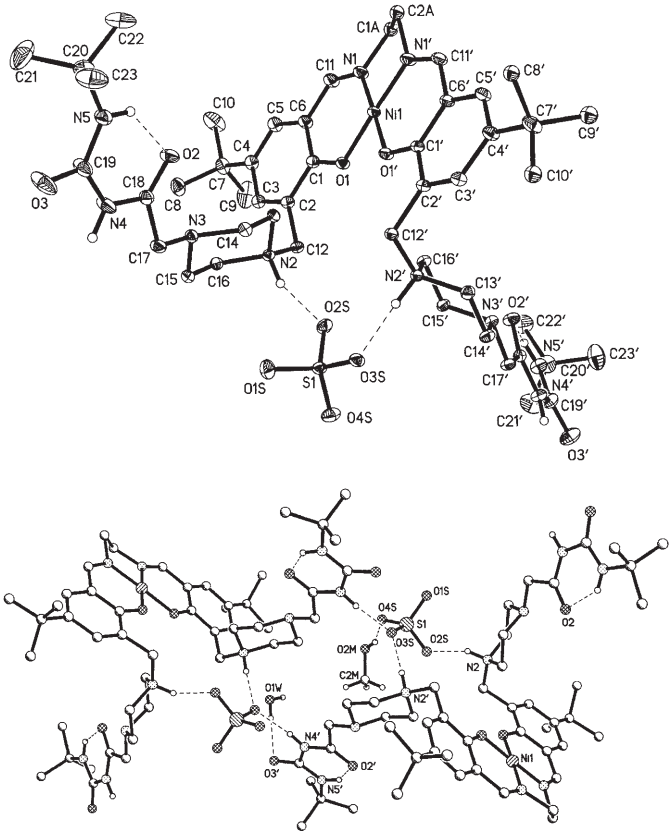


Figure 11. Top: The structure of $[Ni(L^6)SO_4]\cdot1.75\,H_2O\cdot2.25\,MeOH$, showing the atom labelling scheme and intramolecular hydrogen bonding. Minor disorder components for the ethane bridge and one *t*Bu group, all H atoms except NH and all solvent molecules have been omitted. Displacement ellipsoids are drawn at the 30% probability level. Bottom: Intermolecular hydrogen bonding involving the sulfate anions. General notes: The 1,2-diiminoethane links have an approximately *syn* conformation with an N-C-C-N torsion angles of 45.41 and 19.55° in the major and minor disorder components. The RMS deviation of the N_2O_2 donors and the Ni^{II} cation from their least-squares mean plane is 0.022 Å.

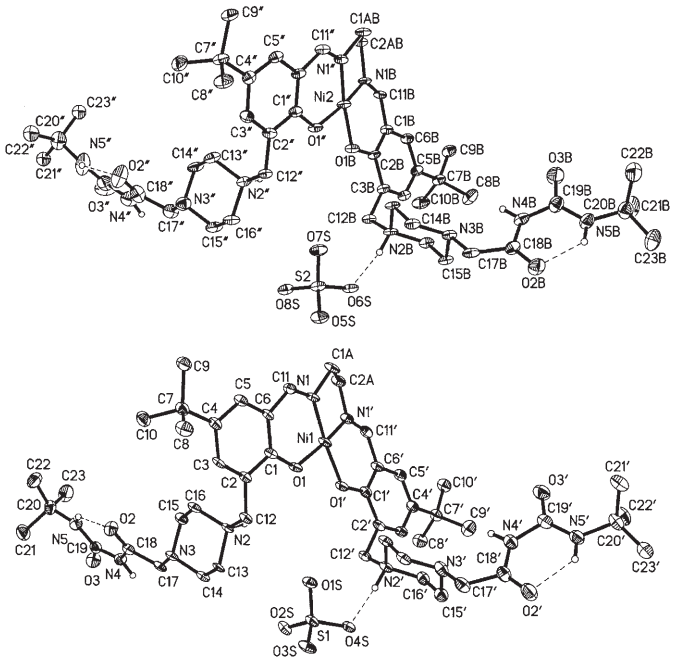


Figure 12. Views of the two independent $[Ni(L^6)SO_4]$ units in $[Ni(L^6)SO_4]\cdot 7.5\,H_2O$ showing the atom labelling schemes. Minor disorder components for the *t*Bu group, all H atoms except NH and all solvent molecules have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen bonds are indicated by dashed lines. General notes: The 1,2-diiminoethane links have approximately *syn* conformation with N-C-C-N torsion angles of −43.46 and −38.93° The RMS deviation of the N_2O_2 donors and the Ni^{II} cation from their least-squares mean planes in the two crystallographically independent complexes are 0.363 and 0.100 Å.

ligand. In addition, one of the urea groups forms two centrosymmetrically related intermolecular hydrogen bonds with an adjacent complex (see Supporting Information Table S1). Ignoring interactions with solvent molecules, the combined effect of the hydrogen-bonding interactions between the SO_4^{2-} ion and the complex cation is to generate a chain running parallel to the [0 1 1] direction. Supramolecular assemblies have also been found for metal sulfate complexes of salen ligands bearing just simple tertiary amine groups,[7,26,27,37] but the more prolific intermolecular hydrogen bonding in the SO_4^{2-} complexes of the amido-substituted ligand L^6 (and L^5, see below) is consistent with their very low solubility in non-polar water-immiscible solvents, and underlines a problem in designing receptors for solvent extractants for anions like SO_4^{2-} that have very high hydration energies.

Quite different interactions with SO_4^{2-} are observed in the other crystalline modification, $[Ni(L^6)SO_4]\cdot 7.5\,H_2O$ (Figures 12 and 13). The asymmetric unit contains two independent Ni^{II} complexes, two SO_4^{2-} ions and a total of fifteen lattice water molecules, giving a stoichiometry of $7.5\,H_2O$ per Ni^{II} centre. The structures of the Ni(salen) units are similar to each other as well as to that in $[Ni(L^6)SO_4]\cdot 1.75\,H_2O\cdot 2.25\,MeOH$. The hydrogen-bonding interactions differ for the two crystallographically independent

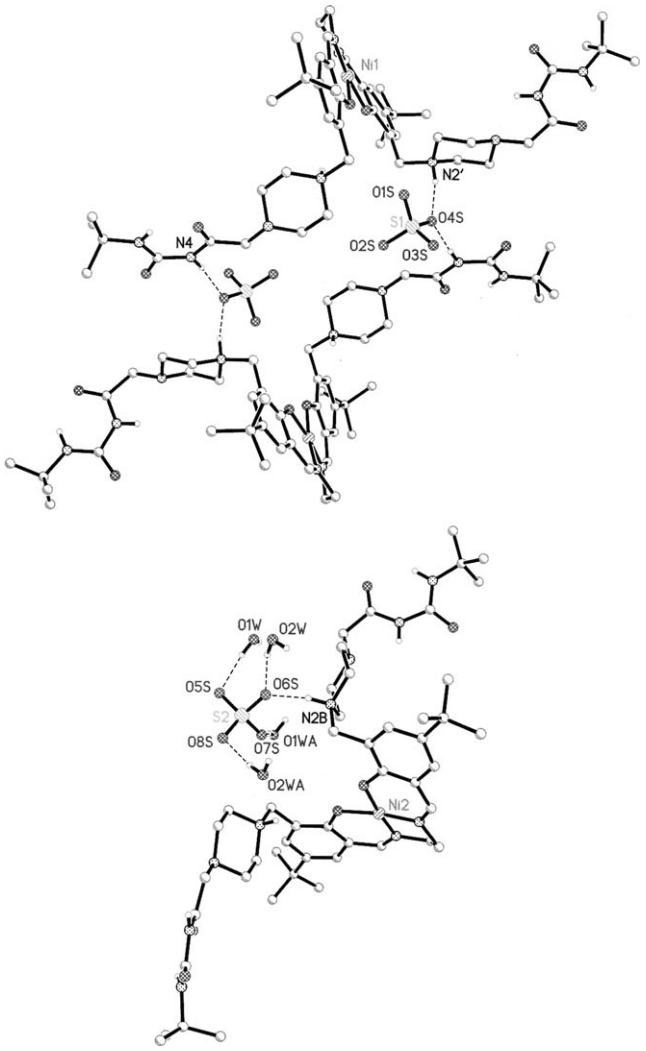


Figure 13. Views showing selected hydrogen-bonding interactions in $[Ni(L^6)SO_4]\cdot 7.5\,H_2O$. Hydrogen bonds are indicated by dashed lines.

complexes (see Supporting Information Table S2). The complex cation centred on Ni1 interacts with two separate but symmetry-equivalent SO_4^{2-} ions through one N(piperazinium)H···O and one N(urea)H···O hydrogen-bonding interaction. In this way each SO_4^{2-} interacts with two adjacent complexes to form a dimer containing two $[Ni(L^6)SO_4]$ units (Figure 13). The remaining piperazinium NH hydrogen bonds to a water molecule and there is further extensive hydrogen bonding involving many of the water molecules in the structure. The complex cation containing Ni2 interacts through a single N(piperazinium)H···O hydrogen bond with the SO_4^{2-} centred on S2. The three remaining SO_4^{2-} oxygen atoms are involved in hydrogen bonding with lattice water molecules. A ribbonlike motif is formed through a combination of these SO_4^{2-}–water interactions with the Ni2 centres lying on alternate sides of the ribbon.

The highly hydrated nickel sulfate complex of ligand L^5, $[Ni(L^5)SO_4]\cdot 8\,H_2O\cdot 2\,MeOH$, shows similar structural features (Figure 14) to those of the complexes of L^6. Three of

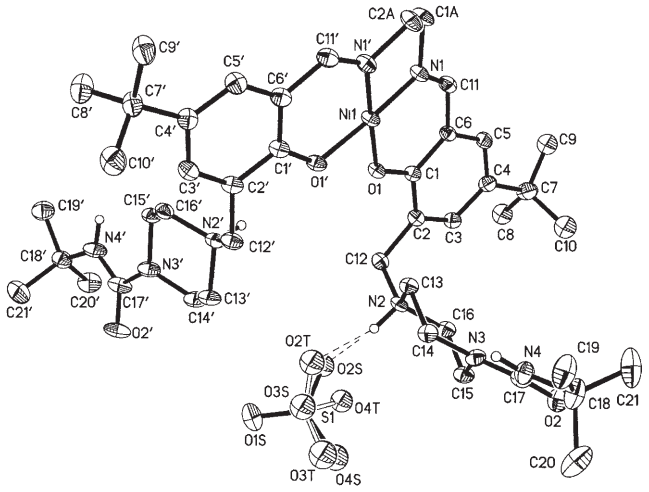


Figure 14. A view of the structure of $[Ni(L^5)SO_4]\cdot 8H_2O\cdot 2MeOH$, showing the atom labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Minor disorder components of *t*Bu groups, and all H atoms except NH, have been omitted for clarity. The two partially occupied orientations of the sulfate oxygen atoms are distinguished by solid and open bonds. Hydrogen bonds are indicated by dashed lines. General notes: The 1,2-diiminoethane link has an approximately *syn* conformation with N-C-C-N torsion angles of 39.0(6)°. The RMS deviation of the N_2O_2 donors and the Ni^{II} cation from their least-squares mean plane is 0.036 Å. The N2···N2′ contact distance is 5.24 Å.

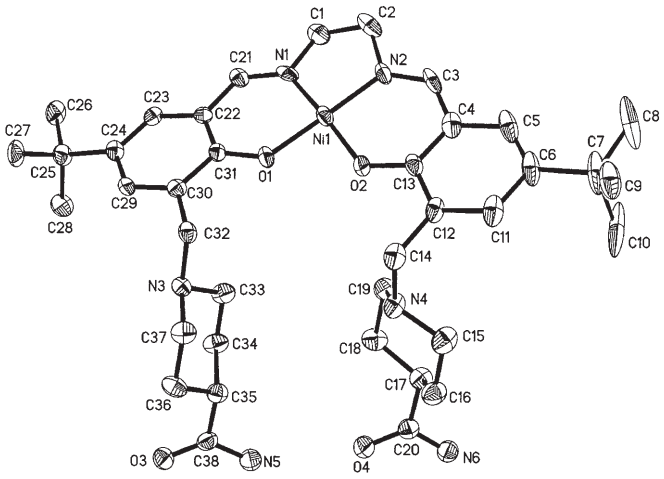


Figure 15. View of one of the three independent $[Ni(L^7-2H)]$ complexes showing the atom labelling scheme (the numbering for the other two complexes is analogous with the prefix 2 and 3 for the second and third, respectively). The displacement ellipsoids are drawn at 30% probability level and all hydrogens are omitted.

the four SO_4^{2-} oxygen atoms are disordered over two partially occupied sites; this results in two hydrogen-bonding interactions, one from N2–H2a to O2S (65% occupancy), the second to O2T (35% occupancy). All other oxygen atoms of the SO_4^{2-} and other hydrogen-bond donor and acceptor atoms, including the amide, phenolate and second piperazinium groups are involved in an extensive hydrogen-bonding network with the lattice water and methanol molecules (see Supporting Information Table S3).

As might be expected the coordination geometry of the Ni^{II} centres in these complexes is very similar (see Supporting Information Table S4). There are also no major differences from that observed in the nickel-only complex $[Ni(L^7-2H)]$, which contains three crystallographically independent neutral $[Ni(L^7-2H)]$ moieties (Figure 15). The incorporation of Ni^{II} into the salen unit again leads to formation of very nearly planar $N_2O_2^{2-}$ donor sets with the deviation of the Ni^{II} cation from the plane defined by the $N_2O_2^{2-}$ donor sets being 0.075, 0.083 and 0.020 Å for the three crystallographically independent molecules. Additionally, the complexation of Ni^{II} brings the pendant amino/amido groups closer together, the intramolecular separations of the benzylamines being 5.23, 5.13 and 5.51 Å in the three crystallographically independent complexes. The solid-state structure of $[Ni(L^7-2H)]$ is dominated by intermolecular hydrogen bonding between the pendant amides. Firstly, both the Ni1 and Ni2 complex moieties exhibit intramolecular hydrogen bonding between the carbonyl of one pendant arm and the amide NH_2 of the other pendant arm of the same ligand; secondly, intermolecular hydrogen bonding is observed between the amide groups of ligands bound to Ni1 and Ni2 (Figure 16) to form a dimeric structure. The complex units containing Ni3 link through intermolecular hydrogen bonds to form a ribbonlike structure. There is no intramolecular hydrogen bonding and the pendant piperazine arms lie on opposite sides of the square planar Ni^{II} centre. There are also hydrogen-bonding interactions between the amides on the Ni1 and those on the Ni3 fragments.

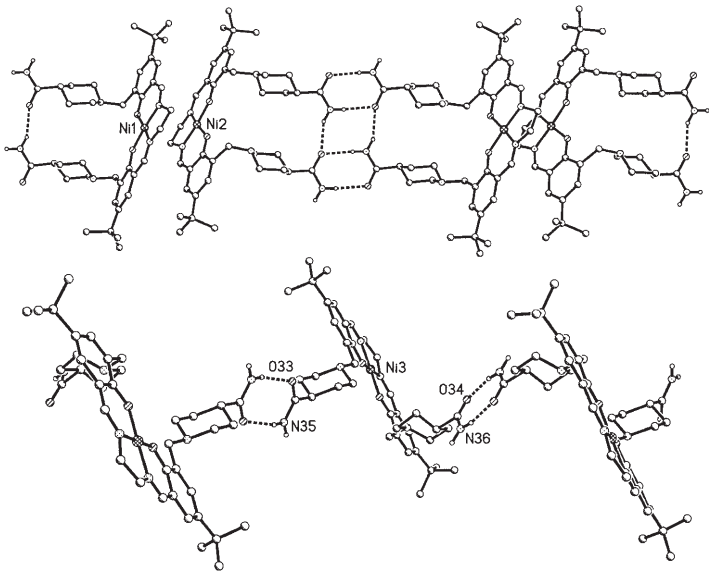


Figure 16. Hydrogen-bonding intermolecular interactions involving the Ni1 and Ni2 centres (top) and the Ni3 centres (bottom) in the crystal structure of $[Ni(L^7-2H)]$.

Conclusions

The intermolecular hydrogen bonding between the pendant amido groups in [Ni(L^7−2H)] illustrates a challenge which we face in designing solvent extractants for metal salts that will show high selectivity for the anion component. Whilst amido groups form effective hydrogen bonds to anions, their propensity for bonding to each other leads to the formation of high-molecular-weight assemblies in solution and will greatly reduce the solubilities of the unloaded extractants. The other feature of the X-ray structure determinations which is clear for all the SO_4^{2-} complexes is the propensity for this anion to retain a coordination sphere which contains water, consistent with the Hofmeister bias[34,35] (see solvent extraction experiments). Whilst there is no reason in principle why an extractant cannot incorporate hydrated SO_4^{2-} ions, it will make it more difficult to design ligands that show a high selectivity of anion complexation, because a much larger entity needs to be incorporated into the receptor and the plasticity and flexibility of the hydration spheres makes it more difficult to use the disposition of hydrogen-bond donors in the receptor to control selectivity. Transporting hydrated SO_4^{2-} ions into non-polar water-immiscible solvents will also be more difficult in terms of their incompatibility with these solvents.

In the context of extractive metallurgy the solvent extraction studies have shown that the ligands L^1–L^3 have almost ideal pH profiles for loading and stripping of copper(II) sulfate. The challenge in applying such ligands commercially is to ensure that high selectivity of transport of SO_4^{2-} over Cl^- can be achieved to deliver a pure electrolyte for copper production [Eq. (5)], because it is probable that most pregnant leach solutions will contain significant concentrations of Cl^- ion.

$$CuSO_4 + H_2O = Cu + H_2SO_4 + {}^1/_2O_2 \quad (5)$$

Whilst the incorporation of chelating amido/alkylammonium groups into the structures of L^1–L^3 to favour the binding of a single dianion over two monoanions leads to selective uptake of SO_4^{2-} over Cl^- in a single phase (95%/5% MeOH/water), it is not sufficient to overcome the Hofmeister bias in solvent extraction experiments using $CHCl_3$ as the water-immiscible solvent. These results provide a striking example of how important the relative solvation energies are to the development of selective anion extractants.

An alternative strategy is to exploit ligands similar to L^1–L^3 to transport metal chlorides in the flowsheet outlined in Figure 1, and then to use the chlorine liberated in electrowinning the metal to regenerate the leachant. This approach, recycling the chlorine to generate $FeCl_3$ [Eq. (6)] for oxidative leaching of sulfides [Eq. (7)] has been suggested for the CUPREX process and has the advantage of generating elemental sulfur as a by product of metal recovery rather than sulfuric acid.[2,38]

$$2\,FeCl_2 + Cl_2 \rightarrow 2\,FeCl_3 \quad (6)$$

$$2\,FeCl_3 + MS \rightarrow MCl_2 + 2\,FeCl_2 + S \quad (7)$$

Experimental Section

Nuclear magnetic resonance spectra were obtained on Bruker AC 200 and Bruker AC 250 instruments, FAB mass spectra on a Kratos MS 50 machine, FTIR spectra on a Perkin–Elmer Paragon 1000 spectrometer as oils on NaCl plates or as KBr discs and electronic absorption spectroscopy on a Perkin–Elmer λ-900 spectrometer. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis of copper and sulfur was recorded on a Thermo Jarrell Ash IRIS ICP-AES spectrometer. The measurement of pH was carried out on a Fisher Scientific AR 50 pH meter. Concentrations of Cl^- in the solvent extraction experiments were measured using a Cl^--selective Thermo Orion Ion Plus electrode. Anion concentrations in the membrane transport experiments were determined by using a Dionex DX-100 ion chromatograph. Unless stated to the contrary, commercial grade chemicals were obtained from Aldrich or Acros and were used without further purification.

Ligand synthesis: 2-Hydroxy-5-*tert*-butylbenzaldehyde was prepared by the methods of Levin or Lindoy and co-workers.[32,39] 3-Bromomethyl-2-hydroxy-5-*tert*-butylbenzaldehyde and its 5-nonyl homologue were made by the procedure described recently by Wang et al. (Scheme 3).[33] *N*-(3-Aminopropyl)benzamide, *N*-(2-aminoethyl)benzamide and *N*-(6-aminohexyl)benzamide were obtained using a modified version of the method of Jacobson and co-workers and is described for *N*-(3-aminopropyl)benzamide.[30] The procedures employed for the preparation of L^2 were also used for ligands L^1 and L^3.

***N*-(3-Aminopropyl)benzamide**: Benzoic anhydride (8.0 g, 0.035 mol) in CH_2Cl_2 (200 mL) was added dropwise to a stirred solution of 1,3-diaminopropane (13.1 g, 0.18 mol) in CH_2Cl_2 (400 mL) at −80 °C and stirred overnight. The solution was concentrated in vacuo to 100 mL and extracted with 5% HCl (2×50 mL). The two aqueous extracts were combined, basified with 10% NaOH solution and concentrated in vacuo to 200 mL, and the product extracted with CH_2Cl_2 (3×50 mL). The combined organic extracts were dried over $MgSO_4$, filtered and evaporated in vacuo to yield *N*-(3-*a*mino-propyl)benzamide as a colourless oil (4.92 g, 78% yield). ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ = 7.85–7.79 (m, 2H; Ar-*H*), 7.46–7.38 (m, 3H; Ar-*H*), 3.58 (q, J = 6 Hz, 2H; NHCH_2CH$_2$), 2.90 (t, J = 6.2 Hz, 2H; NH$_2$CH_2CH$_2$), 1.74 (quintet, J = 6.2 Hz, 2H; CH$_2$CH_2CH$_2$), 1.45 ppm (s, 2H; NH_2); ^{13}C NMR (60 MHz, $CDCl_3$, TMS): δ = 168.0 (*C*O), 135.4 (Ar *C*), 131.8 (Ar *C*H), 129.1 (Ar *C*H), 127.6 (Ar *C*H), 41.4 (CONHCH$_2$), 40.0 (NH$_2$CH$_2$), 32.0 ppm (CH$_2$CH$_2$CH$_2$); IR: $\tilde{\nu}$ = 3286 (s), 2936 (s), 2869 (s), 1635 (s), 1541 (s), 1490, 1435, 1309, 700 cm^{-1}; MS (FAB): m/z: 179 $[M]^+$.

***N*-(2-Aminoethyl)benzamide**: This compound was prepared by a similar procedure to that described for *N*-(3-*a*mino-propyl)benzamide from 1,2-diaminoethane. It was obtained as a colourless oil (69% yield). ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ = 7.98–7.94 (2H; m, Ar-*H*), 7.65–7.55 (3H; m, Ar-*H*), 3.58 (2H; t, J = 6.4 Hz, CONHCH_2), 2.99 ppm (2H; t, J = 6.4 Hz, NH$_2$CH_2); ^{13}C NMR (60 MHz, $CDCl_3$, TMS): δ = 170.0 (*C*O), 135.8 (Ar *C*), 132.8 (Ar *C*H), 129.6 (Ar *C*H), 128.4 (Ar *C*H), 43.7 (CONHCH$_2$), 42.1 ppm (NH$_2$CH$_2$); IR: $\tilde{\nu}$ = 3275 (s), 2940 (s), 2843 (s), 1642 (s), 1542 (s), 1488, 1314, 687 cm^{-1}; MS (FAB): m/z: 165 $[M]^+$.

***N*-(6-Aminohexyl)benzamide**: This compound was prepared by a similar procedure to that described for *N*-(3-*a*mino-propyl)benzamide from 1,6-diaminoethane. It was obtained as a colourless oil (77%). ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ = 7.79–7.75 (m, 2H; Ar-*H*), 7.51–7.41 (m, 3H; Ar-*H*), 6.25 (br, 1H; N*H*CO), 3.48 (q, J = 6.7 Hz, 2H; CONHCH_2), 2.70 (t, J = 6.7 Hz, 2H; NH$_2$CH_2), 1.67 (quintet, J = 7.0 Hz, 2H; CONHCH$_2$CH_2), 1.45 (m, 6H; NH$_2$CH$_2$CH_2CH_2CH_2), 1.19 ppm (t, J = 6.7 Hz, 2H; NH_2CH$_2$); ^{13}C NMR (60 MHz, $CDCl_3$, TMS): δ = 170.0 (*C*O), 136.0 (Ar *C*), 132.6 (Ar *C*H), 129.6 (Ar *C*H), 128.3 (Ar *C*H), 42.3 (CONHCH$_2$), 40.9 (NH$_2$CH$_2$), 33.2 (CONHCH$_2$CH$_2$), 30.5 (NH$_2$CH$_2$CH$_2$), 27.9 (CONHCH$_2$CH$_2$CH$_2$), 27.7 ppm (NH$_2$CH$_2$CH$_2$CH$_2$); IR: $\tilde{\nu}$ = 3286 (s), 2936 (s), 2869 (s), 1635 (s), 1541 (s), 1490, 1435, 1309,

704 cm^{-1}; MS (FAB): *m/z*: 221 $[M]^+$; elemental analysis calcd (%) for $C_{13}H_{20}N_2O$: C 70.9, H 9.2, N 12.7%; found: C 70.9, H 8.9, N 12.4.

***N*-(3-Benzylaminopropyl)benzamide (2)**: *N*-(3-Aminopropyl)benzamide (19.4 g, 0.109 mol) in EtOH (20 mL) was added dropwise to a stirred solution of benzaldehyde (11.6 g, 0.109 mol) in EtOH (200 mL). The reaction was refluxed for 1 h then cooled to room temperature. $NaBH_4$ (12.4 g, 0.327 mol) was added portion-wise to maintain a gentle effervescence. The reaction was refluxed for a further 1 h and cooled to room temperature. A solution of 10% NaOH (150 mL) was added, with caution, under N_2. The EtOH was removed in vacuo and CH_2Cl_2 (2× 150 mL) was then added to extract the product. The combined organic extracts were dried over $MgSO_4$, filtered and evaporated in vacuo to yield **2** as a viscous colourless oil (28.0 g, 96% yield). ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ=8.2 (br, 1H; N*H*CO), 7.79–7.70 (m, 2H; Ar-*H*), 7.46–7.29 (m, 8H; Ar-*H*), 3.8 (s, 2H; NHCH_2Ar), 3.58 (q, J= 6 Hz, 2H; CONHCH_2), 2.90 (t, J=5.7 Hz, 2H; $CH_2CH_2NHCH_2$), 1.79 ppm (quintet, J=5.9 Hz, 2H; $CH_2CH_2CH_2$); ^{13}C NMR (60 MHz, $CDCl_3$, TMS): δ=167.9 (*C*O), 139.8 (Ar *C*), 135.2 (Ar *C*), 131.8 (Ar *C*H), 129.2 (Ar *C*H), 129.1 (Ar *C*H), 129.0 (Ar *C*H), 127.9 (Ar *C*H), 127.6 (Ar *C*H), 54.7 (ArCH_2NH), 49.3 (CONHCH_2), 40.7 (CH_2NHCH_2CH_2), 28.6 ppm ($CH_2CH_2CH_2$); IR: $\tilde{\nu}$=3296 (s), 3060, 3028, 2931 (s), 1640 (s), 1539 (s), 1306 (s), 697 cm^{-1} (s); MS (FAB): *m/z*: 269 $[M]^+$; elemental analysis calcd (%) for $C_{17}H_{20}N_2O$: C 76.1, H 7.5, N 10.4; found: C 76.1, H 7.7, N 10.2.

***N*-(2-Benzylamino-ethyl)-benzamide (1)**: This compound was prepared by a similar procedure to that described for **2** from *N*-(2-aminoethyl)-benzamide. It was obtained as a sticky white solid (94% yield). ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ=7.80–7.76 (m, 2H; Ar-*H*), 7.50–7.42 (m, 8H; Ar-*H*), 6.95 (br, 1H; N*H*CO), 3.81 (s, 2H; NHCH_2Ar), 3.53 (q, J= 5.6 Hz, 2H; CONHCH_2), 2.87 (t, J=5.8 Hz, 2H; $CH_2CH_2NHCH_2$), 1.85 ppm (br, 1H; CH_2NHCH_2); ^{13}C NMR (60 MHz, $CDCl_3$, TMS): δ= 168.2 (*C*O), 140.7 (Ar *C*), 135.2 (Ar *C*), 132.0 (Ar *C*H), 129.4 (Ar *C*H), 129.1 (Ar *C*H), 128.7 (Ar *C*H), 127.7 (Ar *C*H), 127.6 (Ar *C*H), 54.1 (ArCH_2NH), 48.5 (CONHCH_2), 40.1 ppm (CH_2NHCH_2CH_2); IR: $\tilde{\nu}$= 3256 (s), 3062, 3027, 2926 (s), 1638 (s), 1537 (s), 1311 (s), 693 cm^{-1} (s); MS (FAB): *m/z*: 255 $[M]^+$; elemental analysis calcd (%) for $C_{16}H_{18}N_2O$: C 75.6, H 7.1, N 11.0; found: C 75.3, H 7.2, N 10.6.

***N*-(6-Benzylaminohexyl)benzamide (3)**: This compound was prepared by a similar procedure to that described for **2** from *N*-(6-aminohexyl)benzamide. It was obtained as a sticky white solid (98% yield). ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ=7.78–7.74 (m, 2H; Ar-*H*), 7.49–7.27 (m, 8H; Ar-*H*), 6.27 (br, 1H; N*H*CO), 3.78 (s, 2H; NHCH_2Ar), 3.42 (q, J= 6.7 Hz, 2H; CONHCH_2), 2.62 (t, J=7.1 Hz, 2H; $CH_2CH_2NHCH_2$), 1.62 (m, 5H; $CH_2NHCH_2CH_2CH_2CH_2CH_2$), 1.38 ppm (m, 4H; $NHCH_2CH_2CH_2CH_2CH_2$); ^{13}C NMR (60 MHz, $CDCl_3$, TMS): δ=168.2 (*C*O), 141 (Ar *C*), 135.5 (Ar *C*), 131.9 (Ar *C*H), 129.7 (Ar *C*H), 129.2 (Ar *C*H), 129.0 (Ar *C*H), 128.8 (Ar *C*H), 127.5 (Ar *C*H), 54.7 (ArCH_2NH), 49.9 (CONHCH_2), 40.6 (CH_2NHCH_2CH_2), 30.6 (CONHCH_2CH_2), 30.3 (NHCH_2CH_2), 27.6 (CONHC$H_2CH_2CH_2$), 27.5 ppm (CH_2NHC$H_2CH_2CH_2$); IR: $\tilde{\nu}$=3296 (s), 3060, 3028, 2931 (s), 1640 (s), 1539 (s), 1306 (s), 697 cm^{-1} (s); MS (FAB): *m/z*: 311 $[M]^+$; elemental analysis calcd (%) for $C_{20}H_{26}N_2O$: C 77.4, H 8.4, N 9.0; found: C 77.4, H 8.4, N 8.9.

***N*-[3-(Benzylethoxymethylamino)propyl]benzamide (2a)**: Compound **2** (28 g, 0.104 mol) in EtOH (10 mL) was added dropwise to a stirred suspension of paraformaldehyde (3.13 g, 0.104 mol) and K_2CO_3 (28.75 g, 0.208 mol) in EtOH (120 mL) at 0°C. The mixture was allowed to warm to room temperature and continually stirred for 72 h. The solution was filtered to remove the K_2CO_3 and the solvent was then evaporated in vacuo to yield compound **2a** as a colourless oil, which was used in the second step of the Mannich reaction without further purification (33.74 g, 99.4% yield). ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ=7.76–7.66 (m, 2H; Ar-*H*), 7.53–7.28 (m, Ar-*H*), 4.13 (s, 2H; NCH_2O), 3.78 (s, 2H; NCH_2Ar), 3.53 (m, 2H; CONHCH_2), 3.43 (m, 2H; OCH_2CH_3), 2.85 (t, J=6 Hz, 2H; CH_2CH_2N), 1.75 (quintet, J=6.1 Hz, 2H; $CH_2CH_2CH_2$), 1.15 ppm (t, J=6.1 Hz, 3H; CH_2CH_3); IR: $\tilde{\nu}$=3321 (s), 3061, 3028, 2929 (s), 2863 (s), 1640 (s), 1541 (s), 1375, 1064, 699 cm^{-1} (s); MS (FAB): *m/z*: 281 $[M-EtO]^+$.

***N*-[2-(Benzylethoxymethylamino)ethyl]benzamide (1a)**: This compound was prepared by a similar procedure to that described for **2a** from compound **1**. It was obtained as a colourless oil (98% yield). ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ=7.77–7.73 (m, 2H; Ar-*H*), 7.47–7.27 (m, 8H; Ar-*H*), 4.26 (s, 2H; NCH_2O), 3.92 (s, 2H; NCH_2Ar), 3.52 (m, 2H; OCH_2CH_3), 3.51 (m, 2H; CONHCH_2), 3.05 (t, J=5.5 Hz, 2H; CH_2CH_2N), 1.21 ppm (t, J=7 Hz, 3H; CH_2CH_3); ^{13}C NMR (60 MHz, $CDCl_3$, TMS): δ=167.8 (*C*O), 139.4 (Ar *C*), 135.3 (Ar *C*), 131.6 (Ar *C*H), 129.1 (Ar *C*H), 128.9 (Ar *C*H), 128.8 (Ar *C*H), 127.7 (Ar *C*H), 127.4 (Ar *C*H), 85.9 (NCH_2O), 63.8 (ArCH_2N), 55.7 (CH_3CH_2O), 51.5 (CONHCH_2), 37.5 (NCH_2CH_2), 15.7 ppm (CH_3CH_2); IR: $\tilde{\nu}$=3334 (s), 3062, 3026, 2934 (s), 2855 (s), 1639 (s), 1537 (s), 1383, 1062, 704 cm^{-1} (s); MS (FAB): *m/z*: 267 $[M-EtO]^+$.

***N*-[6-(Benzylethoxymethylamino)hexyl]benzamide (3a)**: This compound was prepared by a similar procedure to that described for **2a** from compound **3**. It was obtained as a colourless oil (37.1 g, 96% yield). ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ=7.74–7.70 (m, 2H; Ar-*H*), 7.46–7.24 (m, 8H; Ar-*H*), 4.09 (s, 2H; NCH_2O), 3.76 (s, 2H; NCH_2Ar), 3.39 (m, 2H; OCH_2CH_3), 3.37 (m, 2H; CONHCH_2), 2.63 (t, J=7.2 Hz, 2H; CH_2CH_2N), 1.52 (m, 4H; $CH_2NHCH_2CH_2CH_2CH_2CH_2$), 1.32 (m, 4H; $NHCH_2CH_2CH_2CH_2CH_2$), 1.15 ppm (t, J=7.1 Hz, 3H; CH_2CH_3); ^{13}C NMR (60 MHz, $CDCl_3$, TMS): δ=167.8 (*C*O), 140.2 (Ar *C*), 135.3 (Ar *C*), 131.7 (Ar *C*H), 129.2 (Ar *C*H), 129.1 (Ar *C*H), 129.0 (Ar *C*H), 128.8 (Ar *C*H), 127.5 (Ar *C*H), 85.0 (NCH_2O), 63.8 (ArCH_2N), 56.6 (CH_3CH_2O), 51.9 (CONHCH_2), 40.4 (NCH_2CH_2), 30.1 (CONHCH_2CH_2), 28.5 (NCH$_2$CH_2), 27.4 (CONHCH$_2$CH_2CH$_2$), 27.3 (NCH$_2$CH$_2$CH_2CH$_2$), 15.7 ppm (CH_3CH_2); IR: $\tilde{\nu}$=3321 (s), 3061, 3028, 2929 (s), 2863 (s), 1640 (s), 1541 (s), 1375, 1064, 699 cm^{-1} (s); MS (FAB): *m/z*: 323 $[M-EtO]^+$.

***N*-{3-[Benzyl(5-*tert*-butyl-3-formyl-2-hydroxybenzyl)amino]propyl}benzamide (2b)**: A solution of **2a** (33.7 g, 0.103 mol) and 5-*tert*-butyl-2-hydroxybenzaldehyde (18.4 g, 0.103 mol) in MeCN (400 mL) was refluxed under N_2 for 72 h. The reaction was cooled to room temperature and the solvent evaporated in vacuo to yield a dark brown oil which was purified by silica column chromatography (ethyl acetate/hexane 1:2) to yield **2b** as a yellow oil (18.2 g, 38% yield). ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ=10.15 (s, 1H; C*H*O), 7.58–7.25 (m, 12H; Ar-*H*), 6.42 (br, 1H; N*H*CO), 3.78 (s, 2H; NCH_2CCOH), 3.66 (s, 2H; NCH_2Ar), 3.49 (q, J= 6.2 Hz, 2H; CONHCH_2), 2.64 (t, J=6.5 Hz, 2H; CH_2CH_2N), 1.91 (quintet, J=6.3 Hz, 2H; $CH_2CH_2CH_2$), 1.27 ppm (9H; s, C(CH_3)$_3$); ^{13}C NMR (60 MHz, $CDCl_3$, TMS: δ=194.3 (*C*HO), 168.2 (NH*C*O), 159.2 (Ar *C*), 142.8 (Ar *C*), 138.3 (Ar *C*), 135.2 (Ar *C*), 134.8 (Ar *C*H), 131.9 (Ar *C*H), 130.0 (Ar *C*H), 129.2 (Ar *C*H), 129.0 (Ar *C*H), 128.2 (Ar *C*H), 127.5 (Ar *C*H), 127.0 (Ar *C*H), 125.5 (Ar *C*), 121.8 (Ar *C*), 59.1 (NCH_2CCOH), 55.2 (NCH_2Ar), 51.6 (CONHCH_2), 38.7 (CH_2NCH_2CH_2), 34.7 (*C*(CH_3)$_3$), 31.9 (C(*C*H$_3$)$_3$), 26.9 ppm ($CH_2CH_2CH_2$); IR: $\tilde{\nu}$=3326, 3062, 3027, 2961 (s), 1651 (s), 1538 (s), 1479 (s), 1216, 753 cm^{-1}; MS (FAB): *m/z*: 459 $[M]^+$; elemental analysis calcd (%) for $C_{29}H_{34}N_2O_3$: C 76.0, H 7.5, N 6.1; found: C 76.0, H 7.3, N, 6.1.

***N*-{2-[Benzyl(5-*tert*-butyl-3-formyl-2-hydroxybenzyl)amino]ethyl}benzamide (1b)**: This compound was prepared by a similar procedure to that described for **2b** from compound **1a**. It was obtained as a yellow oil (30%). ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ=9.99 (s, 1H; C*H*O), 7.74–7.22 (m, 12H; Ar-*H*), 6.90 (br, 1H; N*H*CO), 3.74 (s, 2H; NCH_2CCOH), 3.62 (s, 2H; NCH_2Ar), 3.58 (q, J=5.6 Hz, 2H; CONHCH_2), 2.75 (t, J= 5.8 Hz, 2H; CH_2CH_2N), 1.27 ppm (s, 9H; C(CH_3)$_3$); ^{13}C NMR (60 MHz, $CDCl_3$, TMS): δ=196.3 (*C*HO), 168.0 (NH*C*O), 159.0 (Ar *C*), 143.0 (Ar *C*), 138.9 (Ar *C*), 135.8 (Ar *C*H), 135.3 (Ar *C*), 132.0 (Ar *C*H), 129.7 (Ar *C*H), 129.1 (Ar *C*H), 129.0 (Ar *C*H), 128.4 (Ar *C*H), 128.1 (Ar *C*H), 127.5 (Ar *C*H), 126.3 (Ar *C*), 121.4 (Ar *C*), 59.1 (NCH_2CCOH), 54.4 (NCH_2Ar), 53.0 (CONHCH_2), 37.7 (CH_2NCH_2CH_2), 34.7 (*C*(CH_3)$_3$), 31.9 ppm (C(*C*H$_3$)$_3$); IR: $\tilde{\nu}$=3339, 3062, 3027, 2963 (s), 1649 (s), 1535 (s), 1480 (s), 1217, 754 cm^{-1}; MS (FAB): *m/z*: 445 $[M]^+$; elemental analysis calcd (%) for $C_{28}H_{32}N_2O_3 \cdot C_4H_8O_2$: C 72.2, H 7.6, N 5.3; found: C 72.0, H 7.1, N 5.3.

***N*-{6-[Benzyl(5-*tert*-butyl-3-formyl-2-hydroxybenzyl)amino]hexyl}benzamide (3b)**: This compound was prepared by a similar procedure to that described for **2b** from **3a**. It was obtained as a light yellow oil (36% yield). ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ=10.35 (s, 1H; C*H*O), 7.78–

7.28 (m, 12H; Ar-*H*), 6.28 (br, 1H; N*H*CO), 3.77 (s, 2H; NCH_2CCOH), 3.65 (s, 2H; NCH_2Ar), 3.40 (q, J=6.7 Hz, 2H; CONHCH_2), 2.52 (t, J=7.2 Hz, 2H; CH_2CH_2N), 1.58 (m, 4H; CH_2NHC$H_2C H_2CH_2CH_2CH_2$), 1.34 (m, 4H; NHC$H_2CH_2CH_2CH_2CH_2$), 1.30 ppm (s, 9H; C(CH_3)$_3$); ^{1}H NMR (60 MHz, $CDCl_3$, TMS): δ=192.6 (*C*HO), 168.1 (NH*C*O), 159.9 (Ar *C*), 142.5 (Ar *C*), 137.7 (Ar *C*), 135.4 (Ar *C*), 133.5 (Ar *C*H), 132.0 (Ar *C*H), 130.0 (Ar *C*H), 129.2 (Ar *C*H), 129.0 (Ar *C*H), 128.2 (Ar *C*H), 127.5 (Ar *C*H), 125.1 (Ar *C*H), 124.7 (Ar *C*), 122.7 (Ar *C*), 58.9 (N*C*H$_2$CCOH), 56.6 (N*C*H$_2$Ar), 53.9 (CONH*C*H$_2$), 40.6 (CH_2N*C*H$_2CH_2$), 34.7 (*C*(CH_3)$_3$), 32.0 (C(*C*H$_3$)$_3$), 30.2 (CONHCH$_2$*C*H$_2$), 27.5 (NCH$_2$*C*H$_2$), 27.3 (CONHCH$_2$*C*H$_2CH_2$), 27.0 ppm (NCH$_2$*C*H$_2CH_2$); IR: $\tilde{\nu}$=3335, 3062, 3029, 2930 (s), 1735, 1653 (s), 1539 (s), 1472 (s), 1242, 894 cm^{-1}; MS (FAB): m/z: 501 $[M]^+$; elemental analysis calcd (%) for $C_{32}H_{40}N_2O_3$: C 76.8, H 8.0, N 5.6; found: C 77.2, H 8.2, N 5.8.

Ligand L^2: 1,2-Diaminoethane (0.13 g, 0.0021 mol) in MeOH (50 mL) was added to a stirred solution of **2b** (1.93 g, 0.0042 mol) in $CHCl_3$ (50 mL). After stirring for 10 h the solvent was removed in vacuo to give a yellow oil which was dissolved in $CHCl_3$ (100 mL) and washed with water (2×50 mL). The resulting solution was dried with $MgSO_4$, filtered and evaporated in vacuo to yield L^2 as a yellow oil (1.93 g, 98% yield).[1] H NMR (250 MHz, $CDCl_3$, TMS): δ=8.30 (s, 2H; N=C*H*), 7.57–7.52 (m, 4H; Ar-*H*), 7.42–7.20 (m, 20H; Ar-*H*), 7.07 (br, 2H; N*H*CO), 3.72 (s, 4H; NCH_2CCOH), 3.70 (s, 4H; CH=NCH_2), 3.64 (s, 4H; NCH_2Ar), 3.50 (q, J=6.5 Hz, 4H; CONHCH_2), 2.60 (t, J=6 Hz, 4H; CH_2CH_2N), 1.81 (quintet, J=5.8 Hz, 4H; CH_2CH_2CH_2), 1.26 ppm (s, 18H; C(CH_3)$_3$); ^{13}C NMR (60 MHz, $CDCl_3$, TMS): δ=167.8 (*C*ONH), 167.3 (N=*C*H), 158.0 (Ar *C*), 141.5 (Ar *C*), 139.7 (Ar *C*), 135.4 (Ar *C*), 131.8 (Ar *C*H), 131.5 (Ar *C*H), 129.9 (Ar *C*H), 129.8 (Ar *C*H), 128.9 (Ar *C*H), 128.8 (Ar *C*H), 128.7 (Ar *C*H), 127.7 (Ar *C*H), 126.4 (Ar *C*), 118.4 (Ar *C*), 60.2 (N*C*H$_2$CCOH), 59.5 (CH=N*C*H$_2$), 53.2 (N*C*H$_2$Ar), 52.5 (CONH*C*H$_2$), 39.8 (CH_2N*C*H$_2CH_2$), 34.6 (*C*(CH_3)$_3$), 32.0 (C(*C*H$_3$)$_3$), 26.6 ppm (CH_2*C*H$_2CH_2$); IR: $\tilde{\nu}$=3325, 3060, 2952 (s), 1633 (s), 1538, 1273, 1026, 697 cm^{-1}; UV/Vis ($CHCl_3$): $\lambda_{max}(\varepsilon)$=261 (23342), 331 nm (8616 dm^{3}mol^{-1}cm^{-1}); FAB (MS): m/z: 941 $[M]^+$; elemental analysis calcd (%) for $C_{60}H_{72}N_6O_4{\cdot}2H_2O$: C 73.7, H 7.8, N 8.6; found: C 73.6, H 8.0, N 8.2.

Ligand L^1: This compound was prepared by a similar procedure to that described for L^2 from **1b** to give a yellow oil (95% yield). ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ=8.25 (s, 2H; N=C*H*), 7.76–7.72 (m, 4H; Ar-*H*), 7.41–7.10 (m, 20H; Ar-*H*), 3.80 (s, 4H; NCH_2CCOH), 3.76 (s, 4H; CH=NCH_2), 3.58 (s, 4H; NCH_2Ar), 3.57 (m, 4H; CONHCH_2), 2.69 (t, J=5.7 Hz, 4H; CH_2CH_2N), 1.22 ppm (s, 18H; C(CH_3)$_3$); ^{13}C NMR (60 MHz, $CDCl_3$, TMS): δ=167.7 (*C*ONH), 167.6 (N=*C*H), 158.2 (Ar *C*), 141.5 (Ar *C*), 140.1 (Ar *C*), 135.7 (Ar *C*), 132.1 (Ar *C*H), 131.5 (Ar *C*H), 129.5 (Ar *C*H), 128.9 (Ar *C*H), 128.8 (Ar *C*H), 127.8 (Ar *C*H), 127.7 (Ar *C*H), 127.6 (Ar *C*H), 126.3 (Ar *C*), 118.4 (Ar *C*), 60.2 (N*C*H$_2$CCOH), 58.9 (CH=N*C*H$_2$), 53.1 (N*C*H$_2$Ar), 52.4 (CONH*C*H$_2$), 37.5 (CH_2N*C*H$_2CH_2$), 34.5 (*C*(CH_3)$_3$), 32.0 ppm (C(*C*H$_3$)$_3$); IR: $\tilde{\nu}$=3358, 3062, 2962 (s), 1633 (s), 1479, 1277, 754 cm^{-1}; UV/Vis ($CHCl_3$): $\lambda_{max}(\varepsilon)$=263 (22800), 332 nm (8540 dm^{3}mol^{-1}cm^{-1}); MS (FAB): m/z: 913 $[M]^+$; elemental analysis calcd (%) for $C_{58}H_{68}N_6O_4{\cdot}1.5H_2O$: C 74.1, H 7.6, N 8.9; found: C 74.2, H 7.6, N 9.0.

Ligand L^3: This compound was prepared by a similar procedure to that described for L^2 from **3b** to give a light yellow oil (95%). ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ=8.36 (s, 2H; N=C*H*), 7.75–7.12 (m, 24H; Ar-*H*), 6.30 (br, 2H; N*H*CO), 3.88 (s, 4H; NCH_2CCOH), 3.65 (s, 4H; CH=NCH_2), 3.58 (s, 4H; NCH_2Ar), 3.35 (q, J=6.7 Hz, 4H; CONHCH_2), 2.44 (t, J=7 Hz, 4H; CH_2CH_2N), 1.53 (m, 8H; CH_2NHCH_2C$H_2CH_2CH_2$CH_2), 1.29 (m, 8H; NHCH$_2CH_2$CH_2CH_2CH_2), 1.27 ppm (s, 18H; C(CH_3)$_3$); ^{13}C NMR (60 MHz, $CDCl_3$, TMS): δ=168.1 (*C*ONH), 167.1 (N=*C*H), 157.5 (Ar *C*), 141.4 (Ar *C*), 140.7 (Ar *C*), 135.5 (Ar *C*), 131.9 (Ar *C*H), 130.7 (Ar *C*H), 129.3 (Ar *C*H), 129.1 (Ar *C*H), 128.7 (Ar *C*H), 127.5 (Ar *C*H), 127.3 (Ar *C*H), 127.1 (Ar *C*), 126.7 (Ar *C*H), 118.3 (Ar *C*), 60.6 (N*C*H$_2$CCOH), 59.2 (CH=N*C*H$_2$), 54.3 (N*C*H$_2$Ar), 52.3 (CONH*C*H$_2$), 40.6 (CH_2N*C*H$_2CH_2$), 34.6 (*C*(CH_3)$_3$), 32.1 (C(*C*H$_3$)$_3$), 30.2 (CONHCH$_2$*C*H$_2$), 27.7 (NCH$_2$*C*H$_2$), 27.6 (CONHCH$_2CH_2$*C*H$_2$), 27.5 ppm (NCH$_2CH_2$*C*H$_2$); IR: $\tilde{\nu}$=3330, 3062, 2935 (s), 1630 (s), 1540, 1216, 745 cm^{-1}; UV/Vis ($CHCl_3$): $\lambda_{max}(\varepsilon)$=264 (24300), 330 nm (9018 dm^{3}mol^{-1}cm^{-1}); MS (FAB): m/z: 1025 $[M]^+$; elemental analysis calcd. (%) for $C_{66}H_{84}N_6O_4{\cdot}H_2O$: C 76.0, H 8.3, N 8.1; found: C 76.2, H 8.4, N 8.2.

Ligands L^4–L^8, which contain piperazino and piperidino groups as pendant amines, were obtained by similar procedures from the parent aldehydes **4**–**9**.

5-*tert*-Butyl-2-hydroxy-3-(*N*′-acylpiperazinomethyl)benzaldehyde (4): 3-Bromomethyl-5-*tert*-butyl-2-hydroxybenzaldehyde (1.00 g, 3.69 mmol) and $KHCO_3$ (0.56 g, 5.60 mmol) were added to a solution of 1-acetylpiperazine (0.47 g, 3.69 mmol) in dry MeCN (40 mL). The mixture was heated to reflux under N_2 for 6 h and then allowed to cool to room temperature. The yellow solution was filtered and a yellow solid was obtained after removal of the solvent under reduced pressure. The solid was re-dissolved in CH_2Cl_2. The yellow solution was filtered, evaporated to dryness and the bright yellow solid was purified by chromatography upon silica gel (DCM:MeOH=95:5) as eluent and the first band was collected. Removal of solvent afforded **4** as off-white solid (1.0 g, 85% yield).

5-*tert*-Butyl-2-hydroxy-3-(piperazinomethyl)benzaldehyde (5): A solution of compound **4** (0.55 g, 1.72 mmol) in HCl (2 M, 15 mL) was heated under reflux for 2 days. After cooling to room temperature, the mixture was brought to pH≈7 with saturated Na_2CO_3, extracted with $CHCl_3$, dried over Na_2SO_4 and concentrated to yield 5-*tert*-butyl-2-hydroxy-3-(piperazinomethyl)benzaldehyde as a yellow solid (70% yield). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=10.18 (s, 1H; C*H*O), 7.54 (s, 1H; aromatic), 7.30 (s, 1H; aromatic), 3.65 (s, 2H; CH_2), 2.97 (s, 4H; CH_2), 2.57 (s, 4H; CH_2), 2.07 (s, 3H CH_3), 1.22 ppm (s, 9H; C(CH_3)$_3$); ^{13}C NMR (67.93 MHz, $CDCl_3$, TMS): δ=192.0, 159.3, 141.9, 133.1, 125.0, 122.8, 122.1, 60.6, 53.7, 45.9, 34.2, 31.4 ppm; MS (LR-ES): m/z: 277 $[M+H]^+$; elemental analysis cacld (%) for $C_{16}H_{24}N_2O_2{\cdot}0.15CH_2Cl_2$: C 67.09, H 8.47, N 9.69: found: C 67.11, H 8.43, N 9.30.

5-*tert*-Butyl-2-hydroxy-3-{*N*′-(*tert*-butylurea)piperazinomethyl}benzaldehyde (6): *tert*-Butyl isocyanate (0.112 g, 1.1 mM) was dissolved in dry CH_2Cl_2 (15 mL) and added to a solution of compound **5** (0.183 g, 0.66 mmol) in dry CH_2Cl_2 (25 mL), which was then stirred overnight at room temperature under N_2. After removal of the solvent under reduced pressure, the product was subjected to chromatography on silica gel (EtOAc/hexane 8:2) to give **6** as a white solid (65% yield). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=10.22 (s, 1H; C*H*O), 7.61 (s, 1H; aromatic), 7.43 (s, 1H; aromatic), 4.32 (s, 1H; N*H*), 3.73 (s, 2H; CH_2), 3.40 (s, 4H; CH_2), 2.57 (s, 4H; CH_2), 1.36 (s, 9H; C(CH_3)$_3$), 1.31 ppm (s, 9H; C-(CH_3)$_3$).

***N*′-(1-*tert*-Butyl-3-acylurea)piperazine**: A solution of 1-*tert*-butyl-3-(chloroacetyl)urea (1.03 g, 5.24 mmol) in dry CH_3CN (10 mL) was added into a stirred mixture of piperazine (2.73 g, 31.44 mmol), K_2CO_3 (1.10 g, 7.92 mmol) and KI (25 mg) in dry CH_3CN (20 mL). The resulting mixture was stirred at 80 °C under N_2 for 3 h. The solvent was removed under reduced pressure and the residue was dissolved in water before extraction with CH_2Cl_2, the extracts were dried over $MgSO_4$, and concentrated to afford the product as a while solid (62% yield). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=8.92 (brs, 1H; N*H*), 8.22 (brs, 1H; N*H*), 3.04 (s, 2H; CH_2), 2.95 (s, 4H; CH_2), 2.60 (s, 4H; CH_2), 1.40 ppm (s, 9H; C(CH_3)$_3$).

5-*tert*-Butyl-2-hydroxy-3-{*N*′-(1-*tert*-butyl-3-acylurea)piperazinomethyl}-benzaldehyde (7): A solution of *N*′-(1-*tert*-butyl-3-acylurea)piperazine (0.11 g, 0.45 mmol) in CH_3CN (10 mL) was added into a solution of 3-bromomethyl-5-*tert*-butylsalicyclaldehyde (0.13 g, 0.48 mmol), K_2CO_3 (0.13 g, 0.94 mmol) and KI (ca 0.005 g) in CH_3CN (20 mL). The resulting mixture was stirred at 80 °C under N_2 overnight. After filtration, the solvent was removed under reduced pressure and the residue was purified by using preparative TLC on silica gel (EtOAc/hexane 8:2) to give **7** as a yellow solid (63% yield). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ=10.24 (s, 1H; C*H*O), 8.85 (brs, 1H; NH), 8.21 (brs, 1H; N*H*), 7.62 (s, 1H; aromatic H), 7.38 (s, 1H; aromatic H), 3.74 (s, 2H; CH_2), 3.10(s, 2H; CH_2), 2.65 (brs, 8H; CH_2), 1.31 (s, 9H;C(CH_3)$_3$) 1.29 ppm (s, 9H;C(CH_3)$_3$); ^{13}C NMR (67.93 MHz, $CDCl_3$, TMS): δ=192.11, 171.57, 158.80, 151.19, 142.20, 133.74, 126.02, 123.06, 121.76, 58.87, 53.30, 52.52, 50.92, 34.42, 31.36, 28.87 ppm.

5-*tert*-Butyl-2-hydroxy-3-(*N*-isonipecotamidemethyl)benzaldehyde (8): Isonipecotamide (0.56 g, 4.43 mmol) was dissolved in dry MeCN (40 mL) and to it was added 3-bromomethyl-5-*tert*-butyl-2-hydroxy-benzaldehyde (1.20 g, 4.43 mmol) and $KHCO_3$ (0.69 g, 6.9 mmol). The mixture was heated to reflux under N_2 for 6 h and then cooled to room temperature. The yellow solution was filtered and a yellow solid obtained after removal of solvent under reduced pressure. The solid was re-dissolved in CH_2Cl_2, and the yellow solution was filtered. Removal of CH_2Cl_2 from the filtrate afforded the product as a yellow solid (98% yield). M.p. 150–153°C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 10.24$ ppm (s, 1H; C*H*O), 7.63 (d, $J = 2.49$ Hz, 1H; aromatic H), 7.53 (d, $J = 2.49$ Hz, 1H; aromatic H); 5.84 (br, 2H; NH_2), 3.84 (s, 2H; CH_2N), 3.18 (s, 1H), 3.14 (s, 1H), 2.37 (br, 3H), 1.98 (m, 4H), 1.32 ppm (s, 9H; CH_3); ^{13}C NMR (67.93 MHz, $CDCl_3$, TMS): $\delta = 193.0$ (CHO), 176.9 ($CONH_2$), 159.2, 142.3, 134.3, 126.4, 121.7, 58.8, 52.2, 41.3, 34.3, 31.4, 28.1 ppm; IR (KBr): $\tilde{\nu} = 1676$ cm^{-1} (CHO, vs); MS (ES$^+$): *m*/*z*: 319 $[M+1]^+$; elemental analysis calcd (%) for $C_{18}H_{26}N_2O_3 \cdot 0.45\,CH_2Cl_2$: C 62.14, H 7.60, N 7.86; found: C 62.21, H 7.63, N 7.60.

5-Nonyl-2-hydroxy-3-(*N*-isonipecotamidemethyl)benzaldehyde (9): Isonipecotamide (0.51 g, 4.01 mmol) and $KHCO_3$ (0.61 g, 6.10 mmol) were added to 3-bromomethyl-5-nonyl-salicylaldehyde (1.37 g, 4.01 mmol) in dry MeCN (30 mL) and $KHCO_3$ (0.61 g, 6.1 mmol). The mixture was heated at reflux for 6 h under N_2 atmosphere. A similar work up to that used for **8** afforded **9** as a yellow solid (88% yield). M.p. 85–88°C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 10.16$ (m, 1H; C*H*O), 7.53 (m, 1H; aromatic H), 7.26 (m, 1H; aromatic H), 6.13 (s, 1H; NH_2), 5.86 (s, 1H; NH_2), 3.75 (s, 2H; CH_2N), 3.04 (br, 2H; *C*H_2N), 2.24 (br, 1H; CH_2*CH*$CONH_2$), 1.91 (br, 4H; *C*H_2CHCONH$_2$), 0.76–1.66 ppm (m, 19H; nonyl-H); ^{13}C NMR (67.93 MHz, $CDCl_3$, TMS): $\delta = 193.8$, 176.8, 158.6, 158.5, 142.0, 139.3 (m), 135.8–136.4 (m), 121.0, 120.4, 57.3, 51.8, 51.3, 29.0–43.9 (m), 27.4–24.4 ppm (m); IR (KBr): $\tilde{\nu} = 1663$ cm^{-1} (CHO, vs); MS (ES$^+$): *m*/*z*: 389 $[M+1]^+$; elemental analysis calcd (%) for $C_{23}H_{36}N_2O_3 \cdot 0.75\,CH_2Cl_2$: C 63.19, H 8.31, N 6.21; found: C 63.13, H 8.39, N 6.32.

Ligand L^4: A solution of **4** (0.46 g, 1.44 mmol) with $MgSO_4$ (0.27, 2.25 mmol) and molecular sieves 4 Å (1 g) in dry CH_2Cl_2 (20 mL) was added into a solution of 1,2-diaminoethane (0.043 g, 0.72 mmol) in dry CH_2Cl_2 (3 mL). The resulting mixture was stirred at room temperature under N_2 overnight. After filtration, the mixture was recrystallized from $CHCl_3$/Et_2O to give a yellow powder (84% yield). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 8.41$(s, 2H; *HC*=N), 7.47 (s, 2H; aromatic), 7.19 (s, 2H; aromatic), 3.94 (s, 4H; CH_2N=), 3.64 (s, 8H; C*H*$_2$), 3.47 (s, 4H; C*H*$_2$), 2.51 (s, 8H C*H*$_2$), 2.09 (s, 6H; CH_3), 1.31 ppm (s, 18H; C(CH_3)$_3$); ^{13}C NMR (67.93 MHz, $CDCl_3$, TMS): $\delta = 169.0$, 166.8, 157.4, 157.0, 140.9, 131.3, 127.2, 124.1, 117.9, 59.9, 56.2, 53.2, 52.8, 46.4, 41.5, 34.0, 31.5, 21.5 ppm; IR: $\tilde{\nu} = 1636$ (C=N), 1462 cm^{-1} (C=O); MS (LR-ES$^+$): *m*/*z*: 661 $[M+H]^+$; elemental analysis calcd (%) for $C_{38}H_{56}N_6O_4$: C 69.06, H 8.54, N 12.72; found: C 69.14, H 8.47, N 12.69.

Ligand L^5: This compound was prepared by a similar procedure to that described for L^4 starting from **6** to give a bright yellow solid after recrystallization from $CHCl_3$/Et_2O (70% yield). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 8.41$(s, 2H; *HC*=N), 7.51 (s, 2H; aromatic), 7.14 (s, 2H; aromatic), 4.38 (s, 2H; NH), 3.94 (s, 4H; CH_2N=), 3.77 (s, 4H; CH_2), 3.37 (s, 8H; CH_2N), 2.52 (s, 8H; CH_2N), 1.35 (s, 18H; CH_3), 1.31 ppm (s, 18H; CH_3); ^{13}C NMR (67.93 MHz, $CDCl_3$, TMS): $\delta = 167.12$ (C=N), 157.71, 157.50, 141.17, 131.60, 127.49, 124.23, 118.17, 60.17, 58.62, 56.47, 52.99, 51.13, 44.01, 31.78, 29.80 ppm; IR: $\tilde{\nu} = 3417$ (NH, br), 1636 (C=N), 1534 cm^{-1} (C=O); MS (LR-ES$^+$): *m*/*z*: 776 $[M+H]^+$; elemental analysis calcd (%) for $C_{44}H_{70}N_8O_4$: C 68.18, H 9.10, N 14.46; found: C 68.28, H 9.19, N 14.44.

Ligand L^6: This compound was prepared by a similar procedure to that described for L^4 starting from **7** to give a yellow powder (34% yield). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 8.92$ (s, 2H; N*H*), 8.40 (s, 2H; *HC*=N), 8.23 (s, 2H; N*H*), 7.40 (s, 2H; aromatic H), 7.18 (s, 2H; aromatic H), 3.94 (s, 4H; CH_2N=), 3.64 (s, 4H; C*H*$_2$), 3.06 (s, 4H; C*H*$_2$), 2.60 (brs, 16H; C*H*$_2$), 1.39 (s, 18H; C(CH_3)$_3$) 1.30 ppm (s, 18H; C(CH_3)$_3$); ^{13}C NMR (67.93 MHz, $CDCl_3$, TMS): $\delta = 171.02$, 165.66 (C=N), 156.32, 150.19, 139.65, 130.18, 126.07, 122.99, 116.81, 60.56, 58.85, 52.43, 51.78, 50.2, 49.76, 32.89, 30.41, 27.79 ppm; IR: $\tilde{\nu} = 3444$ (NH, br), 1716 (C=O), 1633 (C=N), 1552 cm^{-1} (C=O); MS (LR-ES$^+$): *m*/*z*: 890 $[M+H]^+$; elemental analysis calcd (%) for $C_{48}H_{76}N_{10}O_6 \cdot CH_2Cl_2$: C 64.84, H 8.62, N, 15.75; found: C 64.28, H 8.91, N 15.94.

Ligand L^7: A solution of 1,2-diaminoethane (0.035 g, 0.59 mmol) in dry MeOH (10 mL) was added dropwise to a solution of **8** (0.37 g, 1.16 mmol) in dried MeOH (15 mL). The yellow solution was stirred at room temperature under N_2. After reaction for 24 h, the MeOH was removed under reduced pressure to afford the product as bright yellow solid (98% yield). M.p. 123–126°C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 8.41$ (s, 2H; C*H*=N), 7.42 (d, $J = 2.40$ Hz, 2H; aromatic H), 7.18 (d, $J = 2.44$ Hz, 2H; aromatic H), 5.69 (br, 2H; NH_2), 5.65 (br, 2H; NH_2), 3.93 (s, 4H; CH_2N=C), 3.63 (s, 4H; C*H*$_2$N), 3.05 (s, 2H; C*H*$_2$), 3.01 (s, 2H; C*H*$_2$), 2.15 (br, 4H; C*H*$_2$), 1.83 (m, 8H; C*H*$_2$), 1.30 ppm (s, 18H; CH_3); ^{13}C NMR (67.93 MHz, $CDCl_3$, TMS): $\delta = 177.9$ (*C*ONH_2), 166.4 (*C*=N), 157.2, 140.7, 131.0, 126.7, 117.8, 59.8, 56.3, 52.9, 42.6, 33.9, 31.4, 28.7 ppm; IR (KBr): $\tilde{\nu} = 1665$ ($CONH_2$, vs), 1632 cm^{-1} (C=N, vs); MS (ES$^+$): *m*/*z*: 661 $[M+H]^+$; elemental analysis calcd (%) for $C_{38}H_{56}N_6O_4 \cdot 2H_2O$: C 65.49, H 8.68, N 12.06; found: C 65.36, H 8.44, N 11.68.

Ligand L^8: This compound was prepared by a similar procedure to that described for L^7 starting from **9**. The isolated bright yellow solid was redissolved in CH_2Cl_2 and hexane added to precipitate the product which was dried in vacuo (80% yield). M.p. 103–106°C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 8.42$ (s, 2H; C*H*=N), 7.34 (m, 2H; aromatic H), 7.13 (m, 2H; aromatic H), 5.78 (br, 2H; NH_2), 5.70 (br, 2H; NH_2), 4.00 (s, 4H), 3.60 (s, 4H; C*H*$_2$N=C), 3.00, 2.98 (br, 2H each; C*H*$_2$N), 2.11 (m, 6H), 1.85 (m, 8H), 0.57–1.68 ppm (m, 38H; nonyl-H); ^{13}C NMR (67.93 MHz, $CDCl_3$, TMS): $\delta = 177.6$, 166.7, 157.0, 140.0, 137.8, 132.5 (m), 128.0 (m), 124.2 (m), 117.6, 59.9, 56.2, 53.0, 42.8, 40.1–31.0 (m), 28.9, 24.0–8.0 (m) ppm; IR (KBr): $\tilde{\nu} = 1632$ cm^{-1} (C=N, vs); MS (ES$^+$): *m*/*z*: 801 $[M]^+$; elemental analysis calcd (%) $C_{48}H_{76}N_6O_4 \cdot CH_2Cl_2 \cdot H_2O$: C 65.09, H 8.92, N 9.30; found: C 65.00, H 8.94, N 9.38.

General preparation of copper-only complexes [Cu(L^1−2H)], [Cu(L^2−2H)] and [Cu(L^3−2H)]: Solutions of the appropriate ligand (1.4 mmol) in $CHCl_3$ (30 mL) and $Cu(CH_3COO)_2 \cdot H_2O$ (0.28 g, 1.4 mmol) in MeOH (50 mL) were mixed and stirred overnight. The solvent was removed in vacuo to yield a black oil which was dissolved in $CHCl_3$ (60 mL) and washed with a pH 9 ammonia solution (2 × 30 mL). The resulting organic phase was dried with $MgSO_4$, filtered and then concentrated in vacuo to yield the metal complex which was used without further purification.

Data for [Cu(L^1−2H)]: Yield: 1.33 g, 97%; Cu-content by ICP-OES for a 0.001 M solution in butan-1-ol: elemental analysis calcd (ppm) for $C_{58}H_{66}N_6O_4Cu$: 78.9; found: 77.8; IR: $\tilde{\nu} = 3337$, 2962 (s), 1628 (s), 1539, 1444, 1216, 753 cm^{-1}; UV/Vis ($CHCl_3$): $\lambda_{max}(\varepsilon) = 280$ (23600), 381 (9862), 572 nm (430 dm^{3}mol^{-1}cm^{-1}); MS (FAB): *m*/*z*: 974 $[M]^+$.

Data for [Cu(L^2−2H)]: Yield: 1.37 g, 98%; Cu-content by ICP-OES for a 0.002 M solution in butan-1-ol: elemental analysis calcd (ppm) for $C_{60}H_{70}N_6O_4Cu$: 157.9; found: 157.0; IR: $\tilde{\nu} = 3310$, 2958 (s), 1624 (s), 1536, 1442, 1261, 697 cm^{-1}; UV/Vis ($CHCl_3$): $\lambda_{max}(\varepsilon) = 278$ (24460), 381 (11672), 573 nm (400 dm^{3}mol^{-1}cm^{-1}); MS (FAB): *m*/*z*: 1003 $[M]^+$.

Data for [Cu(L^3−2H)]: Yield: 1.45 g, 95%; Cu-content by ICP-OES for a 0.001 M solution in butan-1-ol: elemental analysis calcd (ppm) for $C_{66}H_{82}N_6O_4Cu$: 78.9; found: 79.7; IR: $\tilde{\nu} = 3313$, 2933 (s), 1626 (s), 1538, 1443, 754 cm^{-1}; UV/Vis ($CHCl_3$): $\lambda_{max}(\varepsilon) = 281$ (25800), 382 (10514), 565 nm (450 dm^{3}mol^{-1}cm^{-1}); MS (FAB): *m*/*z*: 1086 $[M]^+$.

Nickel(II) and copper(II) complexes of L^4–L^8: A solution of the appropriate ligand (0.3 mmol) in MeOH (5 mL) was added to a stired solution of the appropriate nickel(II)/copper(II) salt (0.3 mmol) in MeOH (5 mL). Colour changes due to complexation were rapid and after 12 h water (5 mL) was added before the solutions were left to evaporate. The powders obtained were collected by filtration and dried in vacuo.

Data for [Ni(L^4)SO$_4$]: Red microcrystalline solid, which was recrystallised by vapour diffusion of hexane into a solution of the complex in $CHCl_3$ (53% yield). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 7.72$ (s, 2H; *HC*=N), 7.30 (s, 2H; aromatic), 7.25 (s, 2H; aromatic), 4.30 (s, 4H; CH_2),

3.94 (s, 8H; CH_2), 3.52 (s, 4H; CH_2), 3.04 (s, 8H; CH_2), 2.02 (s, 6H; CH_3), 1.26 ppm (s, 18H; $C(CH_3)_3$); IR: $\tilde{\nu}$ = 1626 (C=N), 1562 cm^{-1} (C=O); MS (LR-ES$^+$): *m/z*: 718 $[Ni(L^4-2H)]^+$, 360 $[Ni(L^4)]^{2+}$; elemental analysis calcd (%) for $C_{38}H_{58}N_6O_8NiS{\cdot}CHCl_3$: C 50.10, H 6.14, N 8.99; found: C 49.49, H 6.63, N 8.85.

Data for [Ni(L^5)SO$_4$]: Red microcrystalline solid (87% yield); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 7.58 (s, 2H; *HC*=N), 7.42 (s, 2H; aromatic), 7.07 (s, 2H; aromatic), 3.72 (brs, 4H; CH_2), 3.52 (brs, 8H; CH_2), 2.58 (s, 4H; CH_2), 1.75 (s, 8H; CH_2), 1.34 (s, 18H; $C(CH_3)_3$), 1.28 ppm (s, 18H; $C(CH_3)_3$); IR: $\tilde{\nu}$ = 3452 (NH, br), 1624 (C=N), 1545 cm^{-1} (C=O); MS (LR-ES$^+$): *m/z*: 831 $[Ni(L^5-H)]^+$, 416 $[Ni(L^5)]^{2+}$; elemental analysis calcd (%) for $C_{44}H_{70}N_8O_8NiS$: C 56.83, H 7.59, N 12.05; found: C 56.86, H 7.87, N 12.10.

Data for [Ni(L^6)SO$_4$]: Orange solid (90% yield); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 9.03 (s, 2H; N*H*), 8.28 (s, 2H; N*H*), 7.65 (s, 2H; *HC*=N), 7.32 (s, 2H; aromatic H), 7.24 (s, 2H; aromatic H), 4.34 (s, 4H; CH_2), 3.58 (s, 4H; CH_2), 3.50(s, 4H; CH_2), 3.27 (s, 8H; CH_2), 2.83 (brs, 8H; CH_2), 1.35 (s, 18H; $C(CH_3)_3$), 1.31 ppm (s, 18H; $C(CH_3)_3$); IR: $\tilde{\nu}$ = 3452 (NH, br), 1706 (C=O), 1629 (C=N), 1557 cm^{-1} (C=O); MS (LR-ES$^+$): *m/z*: 946 $[Ni(L^6)]^+$, 473 $[Ni(L^6)]^{2+}$; elemental analysis calcd (%) for $C_{48}H_{76}N_{10}O_{10}NiS$: C 55.22, H 7.34, N 13.42; found: C 55.08, H 7.44, N 13.34.

Data for [Ni(L^6)(BF$_4$)$_2$]: Orange solid (82% yield); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 8.63 (s, 2H; N*H*), 8.19 (s, 2H; N*H*), 7.67 (s, 2H; *HC*=N), 7.45 (s, 2H; aromatic H), 7.31 (s, 2H; aromatic H), 4.35 (s, 4H; CH_2), 3.52 (s, 8H; CH_2), 3.18 (s, 8H; CH_2), 2.96 (brs, 8H; CH_2), 1.37 (s, 18H; $C(CH_3)_3$) 1.32 ppm (s, 18H; $C(CH_3)_3$); IR: $\tilde{\nu}$ = 3452 (NH, br), 1711 (C=O), 1624 (C=N), 1552 cm^{-1} (C=O); MS (LR-ES$^+$): *m/z*: 946 $[Ni(L^6)]^+$, 473 $[Ni(L^6)]^{2+}$; elemental analysis calcd (%) for $Ni_1B_2F_8C_{48}H_{76}N_{10}O_6$: C 51.41, H 6.83, N 12.49; found: C 51.50, H 6.73, N 12.51.

Data for [Ni(L^7)SO$_4$]: Orange-yellow solid (85% yield); ^{1}H NMR (300 MHz, CD_3OD, TMS): δ = 7.90 ppm (s, 2H; C*H*=N), 7.50 (d, *J* = 2.41 Hz, 2H; Ph-H), 7.41 (d, *J* = 2.35 Hz, 2H; Ph-H), 4.28 (s, 4H; C=NCH_2), 3.48 (s, 4H; CH_2N), 2.81 (br, 4H; CH_2), 2.44 (br, 4H; CH_2), 2.16 (br, 6H; CH_2, $CHCONH_2$), 1.52 (br, 4H; CH_2), 1.32 (s, 18H; CH_3); IR: $\tilde{\nu}$ = 1664 ($CONH_2$), 1625(C=N), 1121 and 619 cm^{-1} (SO_4): MS (ES$^+$): *m/z*: 717 $[Ni(L^7-2H)]^+$, 815 $[M+H]^+$; elemental analysis calcd (%) for $C_{38}H_{56}N_6NiO_8S{\cdot}CH_3OH{\cdot}4H_2O$: C 50.93, H 7.45, N 9.14; found: C 51.02, H 7.19, N 9.41.

Data for [Cu(L^7)SO$_4$]: A black solid (80% yield); $\tilde{\nu}$ = 1664 ($CONH_2$), 1636 (C=N), 621 cm^{-1} (SO_4); MS (ES$^+$): *m/z*: 722 $[Cu(L^7)]^+$, 820 $[M+H]^+$; elemental analysis calcd (%) for $C_{38}H_{56}N_6CuO_8S{\cdot}CH_3OH{\cdot}4.5H_2O$: C 50.17, H 7.45, N 9.00; found: C 50.12, H 7.05, N 9.17.

Data for [Ni(L^6−2H)]: This was prepared by a similar procedure but using the nickel(II) acetate salt to give an orange solid (95% yield). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 8.96 (s, 2H; N*H*), 8.24 (s, 2H; N*H*), 7.54 (s, 2H; *HC*=N), 7.32 (s, 2H; aromatic H), 6.98 (s, 2H; aromatic H), 3.66 (s, 4H; CH_2), 3.39 (s, 4H; CH_2), 3.09 (s, 4H; CH_2), 2.64 (s, 16H; CH_2), 2.16 (brs, 6H; $CH_3CO_2^-$), 1.38 (s, 18H; $C(CH_3)_3$) 1.27 ppm (s, 18H; $C(CH_3)_3$); IR: $\tilde{\nu}$ = 3444 (NH, br), 1710 (C=O), 1613 (C=N), 1547 cm^{-1} (C=O); MS (LR-ES$^+$): *m/z*: 946 $[Ni(L^6-2H)]^+$, 473 $[Ni(L^6-2H)]^{2+}$; elemental analysis calcd (%) for $C_{48}H_{74}N_{10}O_6Ni$: C 60.95, H 7.89, N 14.81; found: C 61.05, H 7.75, N 14.83.

Metal-only complexes of L^7 and L^8: These complexes were prepared as follows for SO_4^{2-}-loading studies, but the solubilities of their SO_4^{2-} complexes in $CHCl_3$ were too low to allow results to be compared with those of L^1–L^3.

Complex [Ni(L^7−2H)]: A solution of KOH (0.011 g, 0.196 mmol) in dry MeOH (3 mL) was added to [Ni(L^7)SO$_4$] (0.061 g, 0.075 mmol) in dry MeOH (8 mL). The mixture was stirred at room temperature for 4.5 h, and the yellow precipitate was collected, washed with small amounts of MeOH and Et_2O and extracted into $CHCl_3$. Evaporation gave the product as a yellow solid which was dried in vacuo (65% yield). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 7.54 (s, 2H; N=C*H*), 7.39 (d, *J* = 2.24 Hz, 2H; aromatic H), 6.98 (d, *J* = 2.31 Hz, 2H; aromatic H), 5.81 (br, 4H; NH_2), 3.63 (s, 4H; C=NCH_2), 3.37 (s, 4H; NCH_2Ph), 3.01 (d, *J* = 11.2 Hz, 4H; isonipecotamide protons), 2.16 (m, 6H; CH_2, isonipecotamide protons), 1.77 (m, 8H; CH_2, isonipecotamide protons), 1.24 ppm (s, 18H; CH_3); ^{1}H NMR (300 MHz, CD_3OD, TMS): δ = 7.77 (s, 2H; N=C*H*), 7.42 (d, *J* = 2.24 Hz, 2H; aromatic H), 7.13 (d, *J* = 2.31 Hz, 2H; aromatic H), 3.65 (s, 4H; C=NCH_2), 3.43 (s, 4H; NCH_2Ph), 3.03, 3.29 (s, 2H each, isonipecotamide protons), 2.21 (m, 6H), 1.79 (m, 8H), 1.27 ppm (s, 18H; CH_3); IR: $\tilde{\nu}$ = 1666 ($CONH_2$), 1619 cm^{-1} (C=N); MS (ES$^+$): *m/z*: 717 $[M]^+$; elemental analysis calcd (%) for $C_{38}H_{54}N_6NiO_4{\cdot}0.3CHCl_3{\cdot}CH_3OH$: C 60.20, H 7.44, N 10.72; found: C 60.09, H 7.44, N 10.75.

Complex [Cu(L^7−2H)]: This complex was prepared by a procedure similar to that used for [Ni(L^7−2H)] from [Cu(L^7)SO$_4$]. It was obtained as a very dark red powder (90% yield). IR (KBr): $\tilde{\nu}$ = 1664 ($CONH_2$), 1629 cm^{-1} (C=N); MS (ES$^+$): *m/z*: 722 $[M]^+$; elemental analysis calcd (%) for $C_{38}H_{54}N_6CuO_4{\cdot}1.25CHCl_3{\cdot}CH_3OH$: C 53.50, H 6.61, N 9.30; found: C 53.54, H 6.68, N 9.66.

Complex [Ni(L^8−2H)]: This complex was prepared by a procedure similar to that used for [Ni(L^7−2H)] from [Ni(L^8)SO$_4$]. It was obtained as an orange solid (94% yield). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 7.55 (s, 2H; N=C*H*), 6.83, 6.91, 7.24, 7.28 (br, 1H each; Ph-*H*), 6.33 (br, 2H; NH_2), 5.90 (br, 2H; NH_2), 3.59 (s, 4H; C=NCH_2), 3.38 (s, 4H; NCH_2Ph), 2.85, 2.02, 2.19, 2.98 (br, 16H; CH_2 isonipecotamide group), 0.60–1.65 ppm (m, 38H; nonyl); IR: $\tilde{\nu}$ = 1670 (CO, s), 1618 cm^{-1} (C=N, vs); MS (ES$^+$): *m/z*: 857 $[M]^+$, 429 $[M+H]^{2+}$; elemental analysis calcd (%) for $C_{48}H_{74}N_6NiO_4{\cdot}0.8CHCl_3{\cdot}CH_3OH$: C 60.70, H 8.06, N 8.53; found C 60.72, H 8.00, N 8.24.

Complex [Cu(L^8−2H)]: This complex was prepared by a procedure similar to that used for [Ni(L^7−2H)] from [Cu(L^8)SO$_4$]. It was obtained as a dark red solid (90% yield). $\tilde{\nu}$ = 1664 (CO, s), 1624 cm^{-1} (C=N, vs); MS (ES$^+$): *m/z*: 432 $[M+2H]^{2+}$, 862 $[M]^+$.

Solvent extraction of SO_4^{2-} or Cl^- by the copper-only complexes [Cu(L^1−2H)]: Aqueous solutions of H_2SO_4/Na_2SO_4 and HCl/NaCl (0.8 M) were prepared with pH values in the range 0–7. An aliqout of each aqueous solution (10 mL) was intimately mixed with a 0.01 M solution of the copper-only complex in $CHCl_3$ (10 mL), at 20 °C, for 16 h to ensure equilibration. The organic layers were separated and 2 mL aliquots were removed from each for copper and sulfur or Cl^- analysis. The metal and sulfur content of the organic phase was analysed by ICP-OES and the Cl^- content was determined using a chloride selective electrode.

UV/Vis titrations: Titration experiments followed by UV/Vis spectroscopy were performed using 0.05 mM solutions of the copper-only complexes containing various concentrations (0–5 equiv) of HCl or H_2SO_4 in isopropanol and recording the resultant spectra.

Membrane transport of anions: [Cu(L^1−2H)], [Cu(L^2−2H)] and [Cu(L^3−2H)] (1 mM) were used as carriers for the transport of anions across a $CHCl_3$ (50 mL) bulk liquid membrane. Details of the cell design have been reported previously.[40] It was assumed that transport occurs by means of a symport mechanism[36] in which the anion(s) and protons are co-complexed and co-transported. The source phase consisted of 10 mL of a 0.1 M solution of anion(s) at pH 1.8 ± 0.1 except for the transport experiment employing a $SO_4^{2-}/H_2PO_4^-$ mixture, which had a pH of 3.3 ± 0.1. The receiving phase (30 mL) was either a pH 5.2 ± 0.1 citric acid/sodium citrate 0.01 M buffer solution or a pH 7.0 ± 0.1 NaH_2PO_4/Na_2HPO_4 50 mM buffer solution. All three phases in the transport cell were stirred at 25 °C, for 23 h, and the rate of transport was determined by analysing the anion concentration(s) in the receiving phase by using a Dionex DX-100 ion chromatograph. Experimental uncertainty in the recorded rates is ± 5%.

Potentiometric titrations: The protonation constants for the di-basic copper-only complex of ligand [Cu(L^1−2H))] in the absence and presence of added Cl^- (2 mM) or SO_4^{2-} (1 mM) were determined by using a conventional potentiometric (pH) titration procedure. HSO_4^- was added as its tetrabutylammonium hydrogen sulfate salt and Cl^- as its tetrapropylammonium chloride salt to the respective solutions to be titrated. All measurements were performed in 95% methanol at 25 ± 0.1 °C (*I* = 0.1; $[Et_4N]ClO_4$). The concentration of [Cu(L^1−2H)] for all experiments was 1 mM. Analytical grade methanol was fractionated and distilled over magnesium before use. The potentiometric titration apparatus consisted of a

water-jacketed titration vessel and a water-jacketed calomel reference electrode, connected by a salt bridge. A Philips glass electrode (GA-110) was used for all pH measurements. $[Et_4N]ClO_4$ (0.1 M), used as the background electrolyte, was also employed in the salt bridge, while the calomel reference electrode contained $[Et_4N]ClO_4$ (0.09 M) and $[Et_4N]Cl$ (0.01 M) in 95% methanol. Methanol-saturated N_2 was bubbled through the solution in the measuring cell and tetraethylammonium hydroxide solution was introduced into the cell by using a Metrohm Dosimat 665 automatic titration apparatus under PC control. A Corning model 130 Research pH meter was employed for the pH determinations. The data sets obtained from these experiments were processed by using a local version of MINIQUAD.[41] Precipitation occurred at high pH (>10), but in each case sufficient data had been obtained by this stage to allow the determination of the two protonation constants. All protonation constants are the mean of at least three individual determinations.

X-ray structure determinations

Data collection and processing: Single-crystal diffraction data for L^6, $[Ni(L^5)SO_4]$ and $[Ni(L^7-2H)]$ were collected on a either a Bruker SMART1000 CCD or APEX area detector diffractometer,[42] equipped with an Oxford Cryosystem open-flow nitrogen cryostat,[43] using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Data for both complexes of $[Ni(L^6)SO_4]$ reported herein were collected on Station 9.8 at the Daresbury SRS, using synchrotron radiation ($\lambda = 0.6902$ Å). Integrated intensities, corrected for Lorentz and polarization effects, were obtained using the Bruker SAINT package,[44] as were the cell parameters. Data were corrected for absorption using a multi-scan method.

Structure solution and refinement: The crystal structures were solved by direct methods except for that of $[Ni(L^7-2H)]$ which was solved by heavy atom methods and all structures were refined on F^2 using SHELXL-97.[46] All ordered non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed in geometrically calculated positions, except NH and OH atoms, which were located from difference Fourier maps and subsequently included as part of a riding model, except those of the H_2O in Ni(5) for which the positional parameters were refined. Disorder was present in a number of *t*Bu groups and solvent molecules in all structures of the complexes. Details of the modelling are given in the deposited CIFs.

Crystal data for L^6: Formula: $C_{48}H_{76}N_{10}O_6$, $M_r = 889.19$, monoclinic, space group $P2_1/n$ (non-standard setting of $P2_1/c$, no. 14), $a = 6.3692(9)$, $b = 21.174(3)$, $c = 19.273(3)$ Å, $\beta = 92.211(3)$, $V = 2597.2(10)$ Å^3, $\rho_{cald} = 1.137$ g cm^{-3}, $Z = 2$, $T = 150(2)$ K, $\mu(Mo_{K\alpha}) = 0.076$ mm^{-1}, reflections collected = 16237, unique reflections, $(R_{int}) = 5888$ (0.036), $R_1 = 0.041$ $[F > 4\sigma(F)]$, $wR_2 = 0.110$ for all data; crystal colour: yellow; shape: tablet; size: $0.33 \times 0.25 \times 0.09$ mm^3.

Crystal data for $[Ni(L^5)SO_4]\cdot 8H_2O\cdot 2MeOH$: Formula $C_{46}H_{94}N_8NiO_{18}S$, $Ni[C_{44}H_{70}O_4N_8]SO_4\cdot 8H_2O\cdot 2CH_3OH$, $M_r = 1138.06$, triclinic, space group $P\bar{1}$, $a = 13.349(2)$, $b = 14.247(2)$, $c = 15.576(2)$ Å, $\alpha = 92.161(2)$, $\beta = 96.629(2)$, $\gamma = 93.931(2)°$, $V = 2932.5(7)$ Å^3, $\rho_{cald} = 1.289$ g cm^{-3}, $Z = 2$, $T = 150(2)$ K, $\mu(Mo_{K\alpha}) = 0.439$ mm^{-1}, reflections collected = 26664, unique reflections $(R_{int}) = 13107$ (0.030), $R_1 = 0.065$ $[F > 4\sigma(F)]$, $wR_2 = 0.188$ for all data; crystal colour: orange; shape: needle; size: $0.63 \times 0.13 \times 0.11$ mm^3.

Crystal data for $[Ni(L^6)SO_4]\cdot 1.75H_2O\cdot 2.25MeOH$: Formula: $C_{50.25}H_{88.5}N_{10}NiO_{14}S$, $M_r = 1147.58$, triclinic, space group $P\bar{1}$, $a = 14.5518(4)$, $b = 14.5716(4)$, $c = 15.3812(5)$ Å, $\alpha = 71.5760(4)$, $\beta = 76.0602(4)$, $\gamma = 83.9082(4)°$, $V = 3001.6(2)$ Å^3, $\rho_{cald} = 1.270$ g cm^{-3}, $Z = 2$, $T = 150(2)$ K, $\mu(0.6902) = 0.426$ mm^{-1}, reflections collected = 33650, unique reflections $(R_{int}) = 17445$ (0.023), $R_1 = 0.053$ $[F > 4\sigma(F)]$, $wR_2 = 0.158$ for all data; crystal colour: red; shape: plate; size: $0.13 \times 0.13 \times 0.02$ mm^3.

Crystal data for $[Ni(L^6)SO_4]\cdot 7.5H_2O$: Formula: $C_{48}H_{91}N_{10}NiO_{17.5}S$, $M_r = 1179.08$, triclinic, space group $P\bar{1}$, $a = 10.733(2)$, $b = 19.913(4)$, $c = 29.059(6)$ Å, $\alpha = 75.732(3)$, $\beta = 87.738(3)$, $\gamma = 81.260(3)°$, $V = 5949(2)$ Å^3, $\rho_{cald} = 1.310$ g cm^{-3}, $Z = 2$, $T = 150(2)$ K, $\mu(0.6902) = 0.435$ mm^{-1}, reflections collected = 50235, unique reflections $(R_{int}) = 24152$ (0.110), $R_1 = 0.084$ $[F > 4\sigma(F)]$, $wR_2 = 0.225$; crystal colour: red; shape: lath; size: $0.255 \times 0.057 \times 0.014$ mm^3.

Crystal data for $[Ni(L^7-2H)]\cdot 0.42CHCl_3\cdot 0.167Et_2O$: Formula: $C_{39.08}H_{56.08}Cl_{1.25}N_6NiO_{4.17}$, $M_r = 779.67$; triclinic, space group $P\bar{1}$, $a = 19.037(2)$, $b = 19.768(2)$, $c = 22.353(3)$ Å, $\alpha = 65.593(2)$, $\beta = 64.947(2)$, $\gamma = 73.545(2)$, $V = 6879.5(14)$ Å^3, $\rho_{cald} = 1.129$ g cm^{-3}, $Z = 6$, $T = 150(2)$ K, $\mu(Mo_{K\alpha}) = 0.537$ mm^{-1}, reflections collected = 61701, unique reflections $(R_{int}) = 30905$ (0.069), $R_1 = 0.087$ $[F > 4\sigma(F)]$, $wR_2 = 0.251$ for all data; crystal colour: orange; shape: sphenoid; size: $0.82 \times 0.26 \times 0.12$ mm^3.

CCDC-623271–623275 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We thank the EPSRC (UK), the University of Nottingham, and the Australian Research Council for support, and the National Mass Spectrometry Service at the University of Wales, Swansea (UK) for mass spectra. L.L. acknowledges receipt of a research fellowship from the Royal Society/Sino-British Trust, and S.G.G. for an Outgoing Research Fellowship from the Royal Society. We thank CCLRC for the award of the beam time on Station 9.8 and Dr. John E. Warren for his assistance. M.S. gratefully acknowledges receipt of a Royal Society Wolfson Merit Award and of a Royal Society Leverhulme Trust Senior Research Fellowship.

[1] J. Szymanowski, *Hydroxyoximes and Copper Hydrometallurgy*, CRC, London, **1993**.
[2] P. A. Tasker, P. G. Plieger, L. C. West in *Comprehensive Coordination Chemistry II* (Ed.: J. A. McCleverty, T. B. Meyer), Elsevier, Oxford, **2004**.
[3] G. A. Kordosky, *Proc. Int. Solvent Extr. Conf.* **2002**, 853.
[4] D. Dreisinger, *Hydrometallurgy* **2006**, *83*, 10.
[5] S. G. Galbraith, D. K. Henderson, H. A. Miller, P. G. Plieger, P. A. Tasker, K. J. Smith, L. C. West, *Hydrometallurgy 2003* (Ed.: C. A. Young), Warrendale, Pennsylvannia, **2003**, p. 941.
[6] D. M. Gunn, H. A. Miller, R. M. Swart, G. W. Seward, P. A. Tasker, L. C. West, D. J. White, *Proc. Int. Solvent Extr. Conf.* **2002**, 280.
[7] N. Akkus, J. C. Campbell, J. Davidson, D. K. Henderson, H. A. Miller, A. Parkin, S. Parsons, P. G. Plieger, R. M. Swart, P. A. Tasker, L. C. West, *Dalton Trans.* **2003**, 1932.
[8] S. G. Galbraith, P. A. Tasker, *Supramol. Chem.* **2005**, *17*, 191.
[9] L. F. Lindoy, *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, Cambridge (UK), **1989**.
[10] F. L. Bernardis, R. A. Grant, D. C. Sherrington, *React. Funct. Polym.* **2005**, *65*, 205.
[11] P. D. Beer, P. A. Gale, *Angew. Chem.* **2001**, *113*, 502; *Angew. Chem. Int. Ed.* **2001**, *40*, 486.
[12] P. A. Gale, *Coord. Chem. Rev.* **2003**, *240*, 191; K. Wichmann, B. Antonioli, T. Söhnel, M. Wenzel, K. Gloe, K. Gloe, J. R. Price, L. F. Lindoy, A. J. Blake and M. Schröder, *Coord. Chem. Rev.* **2006**, *250*, 2987.
[13] J. B. Love, J. M. Vere, M. W. Glenny, A. J. Blake, M. Schröder, *Chem. Commun.* **2001**, 2678; L. G. A. van de Water, W. L. Driessen, M. W. Glenny, J. Reedijk, M. Schröder, *React. Funct. Polym.* **2002**, *51*, 33; M. W. Glenny, A. J. Blake, C. Wilson, M. Schröder, *Dalton Trans.* **2003**, 1941; M. W. Glenny, L. G. A. van de Water, W. L. Driessen, J. Reedijk, A. J. Blake, M. Schröder, *Dalton Trans.* **2004**, 1953; M. W. Glenny, L. G. A. van de Water, J. M. Vere, A. J. Blake, W. L. Driessen, J. Reedijk, M. Schröder, *Polyhedron* **2006**, *25*, 599; M. W. Glenny, M. Lacombe, J. B. Love, A. J. Blake, L. F. Lindoy, R. C. Luckay, K. Gloe, B. Antonioli, C. Wilson, M. Schröder, *New J. Chem.* **2006**, *30*, 1755.
[14] R. Custelcean, L. H. Delmau, B. A. Moyer, J. L. Sessler, W.-S. Cho, D. Gross, G. W. Bates, S. J. Brooks, M. E. Light, P. A. Gale, *Angew. Chem.* **2005**, *117*, 2593; *Angew. Chem. Int. Ed.* **2005**, *44*, 2537.
[15] G. Cafeo, G. Gattuso, F. H. Kohnke, A. Notti, S. Occhipinti, S. Pappalardo, M. F. Parisi, *Angew. Chem.* **2002**, *114*, 2226; *Angew. Chem. Int. Ed.* **2002**, *41*, 2122.

[16] M. J. Deetz, M. Shang, B. D. Smith, *J. Am. Chem. Soc.* **2000**, *122*, 6201.
[17] A. J. Evans, P. D. Beer, *Dalton Trans.* **2003**, 4451.
[18] W. W. H. Wallace, D. Curiel, S-W. Lai, M. G. B. Drew, P. D. Beer, *Dalton Trans.* **2005**, 774.
[19] M. D. Lankshear, A. R. Cowley, P. D. Beer, *Chem. Commun.* **2006**, 612.
[20] A. Channa, J. W. Steed, *Dalton Trans.* **2005**, 2455.
[21] P. K. Panda, C. H. Lee, *J. Org. Chem.* **2005**, *70*, 3148.
[22] C. M. Pask, K. D. Camm, N. J. Bullen, M. J. Carr, W. Clegg, C. A. Kilner, M. A. Halcrow, *Dalton Trans.* **2006**, 662.
[23] H. Miyaji, S. R. Collinson, I. Prokeš, J. H. R. Tucker, *Chem. Commun.* **2003**, 64; F. Otón, A. Tarraga, M. D. Velasco, P. Molina, *Dalton Trans.* **2005**, 1159.
[24] H. Luecke, F. A. Quiocho, *Nature* **1990**, *347*, 402.
[25] D. J. White, N. Laing, H. Miller, S. Parsons, S. Coles, P. A. Tasker, *Chem. Commun.* **1999**, 2077.
[26] H. A. Miller, N. Laing, S. Parsons, A. Parkin, P. A. Tasker, D. J. White, *J. Chem. Soc. Dalton Trans.* **2000**, 3773.
[27] P. G. Plieger, P. A. Tasker, S. G. Galbraith, *Dalton Trans.* **2004**, 313.
[28] S. G. Galbraith, P. G. Plieger, P. A. Tasker, *Chem. Commun.* **2002**, 2662.
[29] S. G. Galbraith, L. F. Lindoy, P. A. Tasker, P. G. Plieger, *Dalton Trans.* **2006**, 1134.
[30] A. R. Jacobson, A. N. Makris, L. M. Sayre, *J. Org. Chem.* **1987**, *52*, 2592.
[31] H. Adams, N. A. Bailey, D. E. Fenton, G. Papageorgiou, *J. Chem. Soc. Dalton Trans.* **1995**, 1883.
[32] L. F. Lindoy, G. V. Meehan, N. Svenstrup, *Synthesis* **1998**, 1029.
[33] Q. Wang, C. Wilson, A. J. Blake, S. R. Collinson, P. A. Tasker, M. Schröder, *Tetrahedron Lett.* **2006**, *47*, 8983.
[34] T. G. Levitskaia, M. Marquez, J. L. Sessler, J. A. Shriver, T. Vercouter, B. A. Moyer, *Chem. Commun.* **2003**, 2248.
[35] F. Hofmeister, *Arch. Exp. Pathol. Pharmakol.* **1888**, *24*, 247.
[36] J. L. Sessler, D. A. Ford, M. J. Cyr, H. Furuta, *J. Chem. Soc. Chem. Commun.* **1991**, 1733.
[37] V. Gasperov, S. G. Galbraith, L. F. Lindoy, B. R. Rumbel, B. W. Skelton, P. A. Tasker, A. H. White, *Dalton Trans.* **2005**, 139.
[38] R. F. Dalton, G. Diaz, R. Price, A. D. Zunkel, *JOM* **1991**, *43*, 51.
[39] R. Aldred, R. Johnston, D. Levin, J. Neilan, *J. Chem. Soc. Perkin Trans. 1* **1994**, 1823.
[40] P. S. K. Chia, L. F. Lindoy, G. W. Walker, G. W. Everett, *Pure Appl. Chem.* **1993**, *65*, 521.
[41] P. Gans, A. Sabatini, A. Vacca, *Inorg. Chim. Acta* **1976**, *18*, 237.
[42] Bruker, SMART Area-Detector Software Package. Version 5.054, Bruker AXS, Inc, Madison, Wisconsin (USA), **1998**.
[43] J. Cosier, A. M. Glazer, *J. Appl. Crystallogr.* **1986**, *19*, 105.
[44] Bruker, SAINT frame integration software, Version 6.02a, Bruker AXS, Inc, Madison, Wisconsin (USA), **2000**.
[45] SADABS, Bruker AXS, Madison, Wisconsin (USA), **1996–2004**.
[46] G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Göttingen (Germany), **1997**.

Received: December 23, 2006
Published online: May 3, 2007

