ORIGINAL ARTICLE

Anion-selective receptors based on dinuclear copper(II) and nickel(II) cage complexes of bis-salicylaldimines

John Yu-Chih Chang · Simon Parsons · Paul G. Plieger · Peter A. Tasker

Abstract The selectivity, anion uptake and exchangeability of anion-binding by metal *salt* extractants of the form $[M_2L_2]^{4+}$ have been assessed by the method of anion exchange chromatography in biphasic systems. The order of sulfate-, nitrate-, and chloride-uptake into the solid copper(II) complex as of the dioxime pro-ligand *N,N'*-dimethyl-*N,N'*-hexamethylenedi(3-hydroxyiminomethyl-2-hydroxy-5-*tert*-butylbenzylamine ($\mathbf{L^1}$) is 56, 42, and 16%, respectively, consistent with the relative magnitudes of formation constants for the inclusion complexes, $[A{\subset}Cu_2L^1{}_2]^{n+}$ where A = anion, found in UV–vis titration studies in a single phase. X-ray structural determination of the bis-benzylimine pro-ligand, *N,N'*-dimethyl-*N,N'*-hexamethylenedi-(3-benzyliminomehyl-2-hydroxy-5-*tert*-butylbenzylamine), nickel(II) sulfato complex $[SO_4{\subset}Ni_2L^2{}_2]SO_4$ reveals the nickel atoms to have a significant tetrahedral distortion, providing more favourable sulfate-alkylammonium interactions within the cage.

Keywords Zwitterionic complexes · Anion selectivity · Nickel · Copper

Introduction

Selective transport of anions is an essential requirement in hydrometallurgical flowsheets which involve the extraction

J. Y.-C. Chang · S. Parsons · P. A. Tasker
School of Chemistry, University of Edinburgh, EH9 3JJ
Edinburgh, UK

P. G. Plieger (✉)
Institute of Fundamental Sciences, Massey University,
Palmerston North, New Zealand
e-mail: p.g.plieger@massey.ac.nz

of metal *salts* because downstream electrowinning of the metal usually requires electrolytes of high purity in order to control overpotentials at cathodes and to ensure that single reactions occur at anodes [1]. The most common oxidative acid leaching processes for base metal ores generate sulfate or chloride salts [2], and frequently these contain a mixture of these anions. Chloride solutions are generally more corrosive and generate elemental chlorine when electrowinning the metal. As a consequence, solvent extraction of the desired metal selectively as its sulfate rather than chloride to achieve the unit operations of concentration and separation in a flowsheet is preferred on the grounds of cost and safety.

Ditopic pro-ligands (**1** in Fig. 1), offer the possibility of independently tuning the selectivity of the sulfate- and the metal cation-binding sites in a solvent extractant [1]. If these binding sites are created in a zwitterionic form of the extractant (**3** in Fig. 1), adjustment of the pH of the aqueous phase can be used to control the loading and stripping of the metal cation and sulfate anion and it is possible to form "metal-only" and "sulfate-only" loaded forms of the extractant (**2** and **3**) [3].

The feasibility of this approach was demonstrated [4, 5] using "salen" ligands ($\mathbf{L^0}$, Scheme 1) although such imine systems proved to be insufficiently stable to hydrolysis on acid-stripping and did not show high enough sulfate/chloride selectivity to be used in the recovery of nickel from feed streams typical of those involved in commercial operations [6].

Results and discussion

In this paper we consider anion-uptake by metal complexes of the bis-oxime extractant $\mathbf{L^1}$ and its imine analogues, $\mathbf{L^2}$
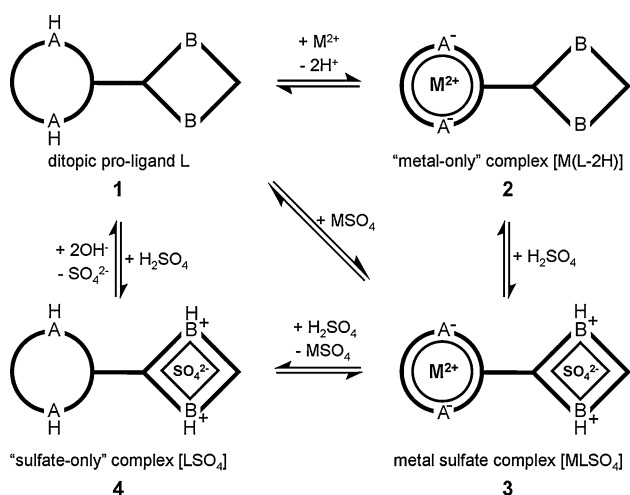
Fig. 1 Formation of "metal-only", metal sulfate and "sulfate-only" assemblies of ditopic pro-ligands which use a zwitterionic form of the pro-ligand to bind the metal sulfate
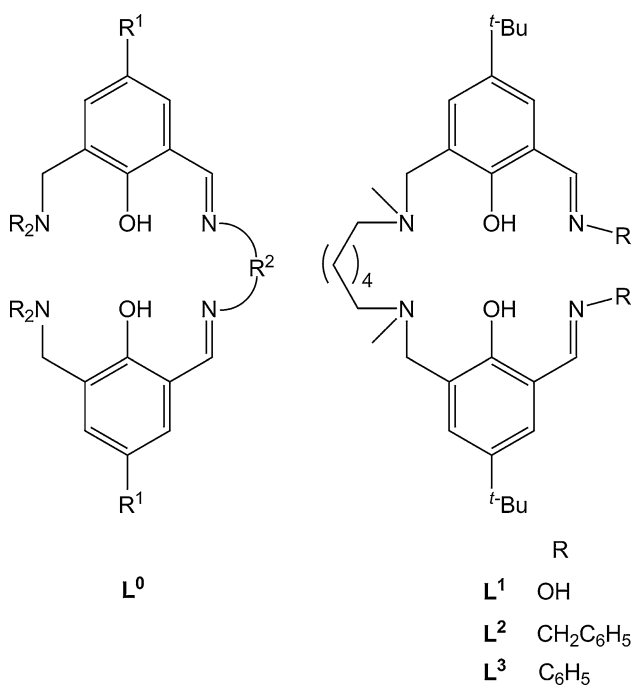
Scheme 1 Mononucleating bis-salicylaldimine ligands L^0 used to demonstrate [4, 5, 7] transport of metal sulfates as $[ML^0SO_4]$ in solvent extraction experiments and the dinucleating systems, L^1–L^3, giving $[SO_4 \subset Cu_2L_2](SO_4)$, described in this work

and L^3. Oxime extractants have been shown to be very stable towards hydrolysis in hydrocarbon solvents [8] and are currently used in hydrometallurgical processes that account for between 20 and 30% of the world's copper production [9, 10]. The phenolic oxime motif in salicyl-aldoxime ligands favours the formation of pseudo-macro-cyclic planar complexes with strong hydrogen bonds between the oximic OH groups and the phenolate oxygen

atoms [11], and this provides a driving force for L^1 to form helical 2:2 Cu(II) complexes which can encapsulate anions (Fig. 2) [12–14].

Reaction of the "metal-only" form of the complex (5 in Fig. 2) with acids results in protonation of the amine nitrogen atoms in the straps and leads to encapsulation of an anion as in 6. The selectivity of anions in such receptors is of considerable current interest [15–17]. Specific binding can be accomplished with highly pre-organised molecules such as indolocarbazole oligomers [18]. Whilst macrocy-clic or macrobicyclic ligands [19–27] are likely to give high selectivity of anion uptake, complex formation involving such rigid receptors is often slow, and flexible open chain ligands [28–35] or metallocyclic supramole-cules [8, 36, 37] may be more suited to industrial processes. The latter potentially have an additional advantage; the host structure is formed in situ and benefits from increased strength and selectively of anion uptake by formation of metal-anion bonds [38, 39].

Selective solvent extraction of sulfate over chloride pre-sents a major challenge because the higher hydration energy of the former disfavours transport into low polarity water-immiscible solvents and is an example of the Hofmeister bias [40]. Preliminary work involving analysis by electrospray mass spectrometry of chloroform solutions of $[Cu_2(L^1\text{-}2H)_2]$ after contact with an aqueous mixed sulfate/chloride solution has suggested [13] that the approximately tetrahedral
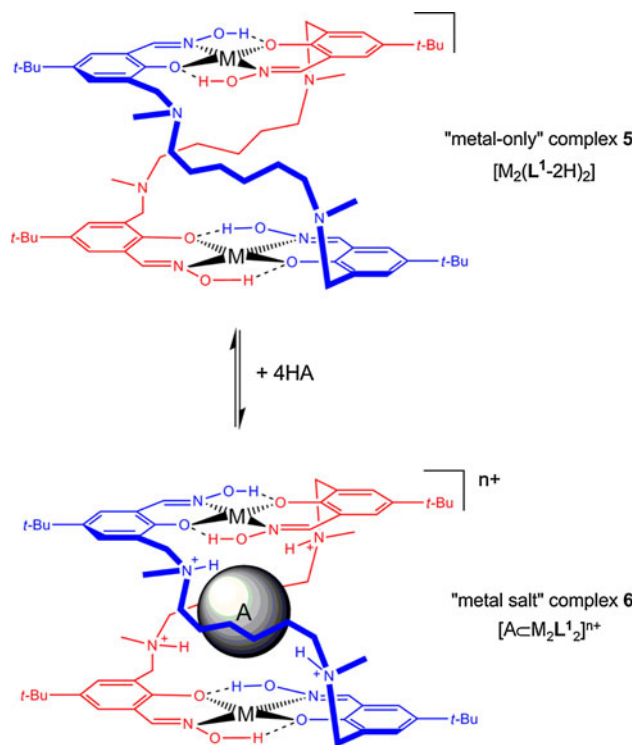

Fig. 2 Anion uptake on protonation of the tertiary amine groups in the straps of the "metal only" complexes, $[M_2(L\text{-}2H)_2]$

disposition of the alkylammonium N–H groups in the copper sulfate complexes of L^1 provides a strong binding site for sulfate and a strong preference for uptake of sulfate over chloride. The favoured binding of oxoanions over halides is supported by titration experiments followed by UV–Vis spectroscopy in a single phase (isopropanol/1,2-dichloroethane) which gave formation constants for anion binding to form $[A \subset Cu_2 L_2]^{n+}$ in the order $H_2PO_4^- \geq SO_4^{2-} \geq NO_3^- > I^- > Br^-$ [13]. Competition studies have been used to assess the preferences of anion-uptake by contacting a suspension of L^1 in methanol with an aqueous solution containing the anions of interest (a 1:1:2:2 molar ratio of L^1 to $CuSO_4$ to NaCl to $NaNO_3$ or a 1:1:2 molar ratio of L^1 to $CuSO_4$ to K_2HPO_4). Crystal structures obtained from the product mixture all revealed sulfate as the captured anion within the helicate [13]. In the work reported in this paper we have used anion exchange chromatography to determine the composition of the methanolic mother liquor after removing the insoluble copper complexes of L^1 formed from a 1:1:2:2 molar ratio of L^1 to $CuSO_4$ to NaCl to $NaNO_3$. Determination of the sulfate, nitrate and chloride concentrations in the mother liquor provides a quantitative measurement of the anion content of the copper complexes by difference. The order of sulfate-, nitrate-, and chloride-uptake into the solid complex removed by filtration (55.9, 42.3, and 15.9%, respectively, see Fig. 3) is consistent with the relative magnitudes of formation constants for the inclusion complexes, $[A \subset Cu_2 L_2]^{n+}$, found in the UV–Vis titration study in a single phase (see above).

The total number of moles of sulfate removed from solution (1.48×10^{-8}) after formation of the insoluble dinuclear copper complex is half that of the total number of moles of nitrate and chloride (3.01×10^{-8}).[1] This ratio and the X-ray structure determinations of $[SO_4 \subset Cu_2(L^1)_2](NO_3)_2$, and $[SO_4 \subset Cu_2(L^1)_2]Cl_2$ isolated from reactions containing sulfate with nitrate or chloride respectively, gives a strong indication that $[SO_4 \subset Cu_2 L_2](NO_3)_2$, $[SO_4 \subset Cu_2 L_2](NO_3)Cl$ or $[SO_4 \subset Cu_2 L_2]Cl_2$ are the predominant products in the reaction of a 1:1:2:2 molar ratio of L^1 to $CuSO_4$ to NaCl to $NaNO_3$. The preference for sulfate over other anions in the cavity extends to phosphate; the complex $[SO_4 \subset Cu_2(L^1)_2](H_2PO_4)_2$, characterised by X-ray structure determination, is formed exclusively from L^1 on reaction with $CuSO_4$ in the presence of phosphate. [13] The origins of this selectivity are

considered in the discussion of structures of the complexes of L^1 below.

Exchange of anions in the cavity of $[A \subset Cu_2 L_2]^{n+}$, is rapid. When a sample of $[SO_4 \subset Cu_2 L_2](SO_4)$ in 10% methanol was injected directly onto an anion exchange chromatography column and eluted with the standard carbonate solution,[2] a single sharp sulfate peak is obtained with a concentration corresponding to both the encapsulated and counterion sulfate.

As the effective uptake of divalent metal cations and sulfate by self-assembling systems such as L^1 is most immediately applicable to the recovery of nickel from sulfate streams [6], we have also considered formation of complexes of nickel salts with the dioxime L^1 and the related di-imines L^2 and L^3. These ligands appear to give nickel-only and nickel sulfate complexes with dinuclear structures similar to those of their copper analogues, but it proved more difficult to isolate single crystals for X-ray structure determination. An exception is the complex of the dibenzylimine pro-ligand L^2, $[SO_4 \subset Ni_2(L^2)_2]SO_4$, the structure of which is shown in Fig. 4 (refer to Table 1 for the structural parameters).

The complex exhibits a 2:2 nickel to ligand helical assembly common to the copper complexes of the bisoxime ligand, L^1. The nickel atoms are 6.874(2) Å apart at the ends of the helix with twist angles (O1A-Ni·Ni2-O1C, and O1D-Ni1·Ni2-O1B) of 128.35(12) and 128.30(14)° between their trans-$N_2O_2^{2-}$ donor sets. The nickel atoms have slightly different coordination environments. Ni1 can be considered to be five coordinate, forming a bond to one of the sulfate anion oxygens (O2S) of 2.328(4) Å. Ni2 shows a much weaker interaction with the encapsulated sulfate (O4S·Ni2 2.662 (5) Å). The $N_2O_2^{2-}$ donor sets show significant tetrahedral distortions from planarity (see Table 2). The equilibrium between square planar and tetrahedral complexes with a range of β-ketoiminato ligands has been studied extensively by Holm and co-workers in the 1960's [41–44]. They showed planar geometry is the preferred coordination geometry for nickel(II) complexes of N-alkyl-salicylaldiminato ligands [43, 45]. Cluster analysis of structures in the Cambridge Crystallographic Database [46] and recently determined crystal structures [47–50] reveal that for simple mononuclear bis-salicylaldiminato nickel(II) complexes, distortion towards tetrahedral geometry is only observed when the imino nitrogen atom carries a very bulky group (see also Table 2). Consequently it is surprising that in $[SO_4 \subset Ni_2(L^2)_2]^{2+}$ both Ni atoms have a significant tetrahedral distortion. It appears that these distortions from planarity allow the phenolate donor atoms to be displaced towards the cavity which in

---

Fig. 3 Sulfate, nitrate and chloride concentrations in methanol before and after reaction of a 1:1:2:2 molar ratio of L^1 to $CuSO_4$ to NaCl to $NaNO_3$ followed by removal of insoluble copper complexes. Anion uptake and representation information deduced from ion chromatography are illustrated in the % bar and pie graph, respectively
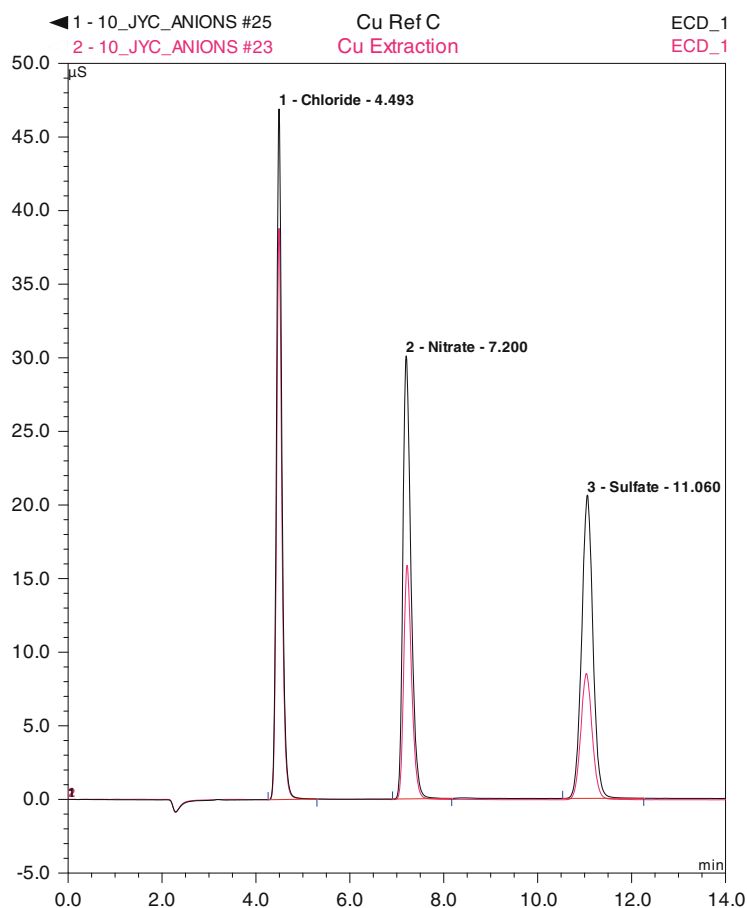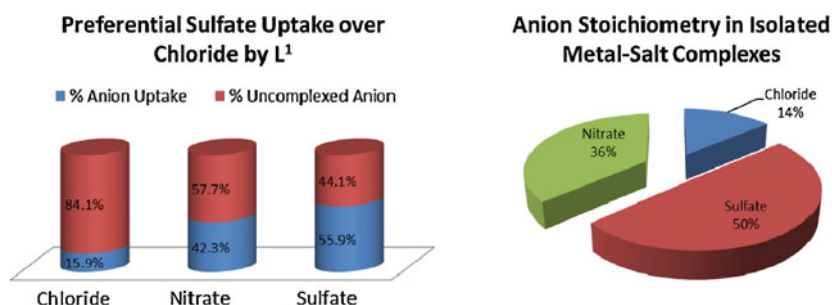
Anion content before extraction (black line):

No.	Ret.Time min	Peak Name	Height μS	Area μS*min	Rel.Area %	Conc. mg L^{-1}	Peak Overlap?
1	4.49	Chloride	46.914	6.334	34.99	74.192	No
2	7.20	Nitrate	30.093	6.018	33.25	127.969	No
3	11.06	Sulfate	20.607	5.749	31.76	101.806	No
Total:				97.614	18.102	100.00	303.968	

Anion content after extraction (grey line):

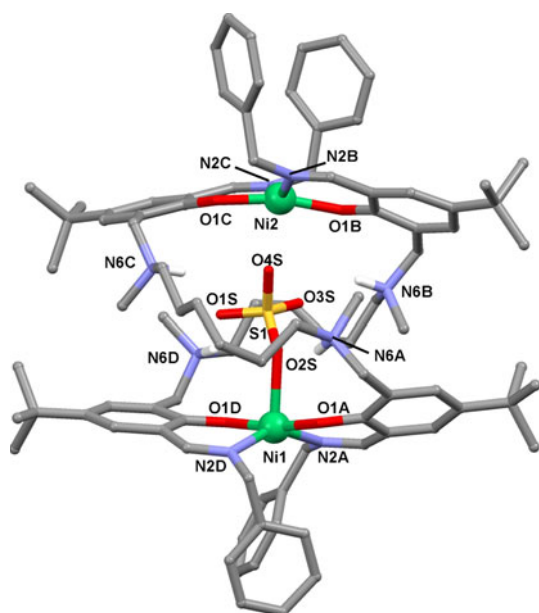| No.	Ret.Time min	Peak Name	Height μS	Area μS*min	Rel.Area %	Conc. mg L^{-1}	Peak Overlap?
1	4.49	Chloride	38.796	5.177	48.19	62.384	No
2	7.22	Nitrate	15.912	3.133	29.16	73.898	No
3	11.04	Sulfate	8.567	2.433	22.65	44.940	No
Total:				63.274	10.744	100.00	181.221	

Fig. 4 Solid state structure of $[SO_4 \subset Ni_2L^2_2]^{2+}$ showing the atom numbering scheme. The lower occupancy atoms in disordered benzyl and t-butyl groups and C–H hydrogen atoms have been omitted for clarity

Table 1 Crystal and experimental data

Molecular formula	$C_{92} H_{124} N_8 Ni_2 O_{14} S_2$
Formula wt.	1715.53
Crystal system	Triclinic
Space group	P
Z	2
a (Å)	16.149 (3)
b (Å)	16.355 (3)
c (Å)	21.617 (4)
α	83.86 (3)
β	68.57 (3)
γ	71.56 (3)
V (Å³)	5042 (2)
D_x (g/cm³)	1.130
Crystal size (mm)	0.06 × 0.06 × 0.03
Crystal color	Red-brown
2θ range	$1.90 \leq \theta \leq 29.4°$
μ_{exp} (mm⁻¹)	0.472
Reflection independent	27071
Refln obs.(I > 2σ(I))	14262
R_1 ($F^2 > 2\sigma$ (F^2))	0.0925
wR_2 (F^2)	0.2864
S	0.94
Residual electron density (e Å⁻³)	1.63 and −1.01

turn allows the alkylammonium N–H groups to approach the sulfate ion more closely. The shortest contact from each of the four nitrogen atoms are: N6A·O2S 2.847(5),

Table 2 Ni-donor bond lengths and angles in $[SO_4 \subset Ni_2(L^2)_2]^{2+}$ compared with those in mononuclear complexes[a] of bis-salicyladoximates, $[Ni(L^n-H)_2]$, with their CCDC codes

Bond	Dist. (Å)	Angle	(°)
Ni1–O1A	1.912 (3)	O1A–Ni1–O1D	171.80 (13)
Ni1–O1D	1.898 (3)	N2A–Ni1–N2D	145.93 (17)
Ni1–N2A	2.055 (4)		
Ni1–N2D	2.014 (4)		
Ni1–O2S	2.328 (4)		
Ni2–O1B	1.890 (3)	O1B–Ni2–O1C	167.80 (14)
Ni2–O1C	1.902 (3)	N2B–Ni2–N2C	149.81 (17)
Ni2–N2B	2.019 (4)		
Ni2–N2C	2.022 (4)		
Ni2 O4S	2.662 (5)		
Planar $[Ni(L^4-H)_2]$ (RISRAN)[a]			
Ni1–O1	1.817 (2)	O1–Ni1–O1	180 (1)
Ni1–N1	1.926 (3)	N1–Ni1–N1	180 (1)
Planar $[Ni(L^5-H)_2]$ (FOWGOO)[a]			
Ni1–O1	1.8294 (12)	O1–Ni1–O1	180.00 (8)
Ni1–N1	1.9242 (14)	N1–Ni1–N1	180.00 (7)
Planar $[Ni(L^6-H)_2]$ (ODIZIL)[a]			
Ni1–O1	1.823 (4)	O1–Ni1–O2	176.8 (2)
Ni1–O2	1.823 (4)	N1–Ni1–N2	176.1 (2)
Ni1–N1	1.936(4)		
Ni1–N2	1.935 (4)		
Pseudo-tetrahedral $[Ni(L^7-H)_2]$ (HAWGAO)[a]			
Ni1–O1	1.905 (2)	O1–Ni1–O1	141.4 (2)
Ni1–N1	2.013 (3)	N1–Ni1–N1	116.3 (2)

[a] L^4: bis(2-(benzyliminomethyl)-4-chlorophenolato-$\kappa^2 N$,O)-nickel(II), L^5: bis(2-[(E)-benzyliminomethyl]-4-methylphenolato- $\kappa^2 N$,O)-nickel (II), L^6: bis(N-(R)-1-Naphthylethyl-3,5-dichlorosalicylideneaminato)-nickel(II), L^7: bis(R-N-phenylethyl-3,5-dichlorosalicylideneaminato)-nickel(II)

N6B·O3S 2.783(5), N6C·O1S 2.883(4) and N6D·O1S 2.789(4) Å. The comparable distances in the analogous Cu(II) complexes containing sulfate of L^1 fall in the range 2.537–2.894 Å.

Conclusions

The cavities in dinuclear complexes, $[M_2L^2_2]^{4+}$, of the di-oxime and di-imine ligands L^1 and L^2 provide very effective binding sites for sulfate with a combination of electrostatic forces, strong N–H and weak C–H hydrogen bonding interactions and the formation of coordinate bonds to the metal ions contributing to the more favourable encapsulation of this anion than halides or nitrate or phosphate. Whilst this high selectivity for the inclusion of sulfate into the cavity of the assemblies to form $[SO_4 \subset M_2L_2]^{2+}$ is a very useful feature in the development

of reagents to transport base metal sulfates in hydromet-allurgical circuits, the net dicationic charge on the sulfato complex means that counter anions are needed to generate species which can be extracted into the low polarity, water-immiscible, solvents used in commercial solvent extraction processes. Unfortunately in processing mixed sulfate/chloride feed solutions the high hydration energy of sulfate disfavours its uptake as the counter anion and consequently co-extraction of sulfate and chloride in assemblies such as $[SO_4 \subset M_2 L_2]Cl_2$ will result.

Experimental

Standard solutions containing seven anions (F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, and SO_4^{2-}) obtained from Dionex (P/N 057590) were used to prepare standards for calibration. The CO_3^-/HCO_3^{2-} eluent was prepared from a concentrate supplied by Dionex (P/N 063965). Milli-Q water was used in the preparation of all stock, standard and eluent solutions. Analytical grade methanol was obtained from Fisher Scientific and was used without further purification.

Ion chromatography analysis was performed on a Dionex ICS-1100 system running a 45 µM CO_3^-/14 µM HCO_3^{2-} eluent. Detection and determination of the concentrations of ions used the suppressed conductivity method. The system is equipped with a DS6 conductivity cell, an ASRS 300 suppressor unit, a thermal compartment housing a Dionex IonPac AG22 (4 × 50 mm) guard column and a Dionex IonPac AS22 (4 × 250 mm) analytical column. 25 µL samples were injected. The flowrate was set at 1.2 mL/min and the column temperature maintained at 30 °C throughout. Chromeleon 6.8 software package supplied by Dionex was used for data collection and processing.

N,N'-dimethyl-*N,N'*-hexamethylenedi-(3-benzyliminomehyl-2-hydroxy-5-*tert*-butylbenzylamine), **L**²

Benzylamine (0.832 g, 7.8 mmol) in acetonitrile (20 mL) was added dropwise to *N,N'*-dimethyl-*N,N'*-hexamethy-lenedi-(3-formyl-2-hydroxy-5-*tert*-butylbenzyl-amine) [51] (2.00 g, 3.8 mmol) in acetonitrile (200 mL). The mixture was stirred overnight and the clear yellow solution was then dried over anhydrous $MgSO_4$ and reduced to dryness in vacuo. The residue was extracted with pentane and dried under high vacuum to give **L**² as a yellow oil (1.744 g, 65%). ¹H NMR δ (360 MHz, CDCl₃) 1.28 (4H, m, NCH₂CH₂*CH₂*), 1.29 (18H, s, C(CH₃)₃), 1.53 (4H, m,

NCH₂*CH₂*CH₂), 2.23 (6H, s, N*CH₃*), 2.38 (4H, t, $J = 7.6$ Hz, N*CH₂*CH₂CH₂), 3.55 (4H, s, Ph*CH₂*NCH₃), 4.77 (4H, s, Ph*CH₂*NCH), 7.36 – 7.24 (10H, benzyl), 7.21, 7.38 (2H, d, $J = 2.4$ Hz, phenyl), 8.47 (2H, s, PhCH₂N*CH*), 13.35 (2H, bs, *OH*). MS(FAB +) m/z 703 [M + H]⁺.

N,N'-Dimethyl-*N,N'*-hexamethylenedi-(3-phenyliminomethyl-2-hydroxy-5-*tert*-butylbenzylamine), **L**³

N,N'-dimethyl-*N,N'*-hexamethylenedi(3-formyl-2-hydroxy-5-*tert*-butylbenzyl-amine) [51] (2.00 g, 3.8 mmol) in acetonitrile (200 mL) was added to aniline (0.710 g, 7.6 mmol) in acetonitrile (20 mL). The mixture was stirred for 4 d and the clear yellow solution was then dried over anhydrous $MgSO_4$ and reduced to dryness in vacuo. The residue was extracted with pentane and dried under high vacuum to give **L**³ as a yellow oil (2.563 g, 100%). ¹H NMR δ (360 MHz, CDCl₃) 1.32 (4H, m, NCH₂CH₂*CH₂*), 1.33 (18H, s, C(CH₃)₃), 1.58 (4H, m, NCH₂*CH₂*CH₂), 2.27 (6H, s, N*CH₃*), 2.44 (4H, t, $J = 7.5$ Hz, N*CH₂*CH₂CH₂), 3.62 (4H, s, Ph*CH₂*NCH₃), 7.21-7.27 (4H, m, aniline), 7.25 (2H, d, $J = 2.2$ Hz, phenol), 7.35–7.40 (6H, m, aniline), 7.37 (2H, d, $J = 2.2$ Hz, phenol), 8.69 (2H, s, PhN*CH*), 12.55 (2H, bs, *OH*). MS(FAB +) m/z 675 [M + H]⁺.

$[Ni_2(L^1\text{-}2H)_2]$

A solution of the ligand **L**¹ (0.205 g, 0.37 mmol) and $Ni(OAc)_2 \cdot 4H_2O$ (0.090 g, 0.36 mmol) in methanol (40 mL) was refluxed over 4 d. The volume of the clear green solution obtained was reduced, filtered and then loaded onto a Sephadex SP-LH20 gel filtration column (2 × 30 cm). The column was eluted with methanol and the first major green band was collected. Evaporation to dryness gave the product as a green crystalline solid (98.1 mg, 44%). MS(ESI+) m/z 1222.32 [M + H]+. Anal. Calcd for $Ni_2C_{64}H_{96}N_8O_8 \cdot CH_3OH$ (1254.92): C 62.21, H 8.03, N 8.93. Found: C 62.60, H 8.32, N 8.98%.

$[SO_4 \subset Ni_2L^1{}_2](SO_4)$

To a suspension of **L**¹ (0.096 g, 0.17 mmol) in methanol (30 mL) was added $NiSO_4 \cdot 7H_2O$ (0.069 g, 0.25 mmol). The mixture was refluxed overnight after which the resulting green solution was reduced in volume to about 2 mL and columned on a Sephadex SP-LH20 column using methanol as the eluent. The major green band was collected and reduced to dryness to give a green powder (0.105 g, 86.0%). MS(ESI+) 1417.55 [M+]⁺.

X-ray crystallographic data

Crystals of $[SO_4 \subset Ni_2 L^2{}_2]$ suitable for X-ray analysis were grown by the slow diffusion of iso-propyl ether into a ethanolic solution containing the complex.

Data was collected at Daresbury station 9.8 using synchrotron radiation of 0.686 Å in the range 1.94–29.4°. Integrated intensities were obtained with SAINT+ [52]. Structure solution and refinement was performed with the SHELX-package [52]. The structures were solved by direct methods. One of the benzyl groups is positionally disorder over two sites in the ratio 73:27. There exists rotational disorder on a number of t-butyl groups in the structure (76:24 and 63:37). Diffuse solvent regions in the structure were treated in the manner described by van der Sluis and Spek [53], resulting in the removal of 156 e$^-$ per cell corresponding to one iso-propyl and 0.5 ethanol molecules per formula unit.

References

1. Tasker, P.A., Plieger, P.G., West, L.C.: Metal complexes for hydrometallurgy and extraction. In: McCleverty, J.A., Meyer, T.B. (eds.) Comprehensive Coordination Chemistry II, vol. 5, pp. 759–808. Elsevier, Oxford (2004)
2. McDonald, R.G., Whittington, B.I.: Atmospheric acid leaching of nickel laterites review Part 1. Sulfuric acid technologies. Hydrometallurgy **91**, 35–55 (2008)
3. Galbraith, S.G., L.F. Lindoy, P.A. Tasker, Plieger, P.G.: Simple procedures for assessing and exploiting the selectivity of anion extraction and transport. Dalton Trans. 1134–1136 (2006)
4. Galbraith, S.G., Henderson, D.K., Miller, H.A. Plieger, P.G., Tasker, P.A., Smith, K.J., West, L.C.: Development of extractants to transport metal salts in base metal recovery processes. Hydrometallurgy. In:Young, C. (ed.) Proceedings of 5th international symposium honoring Professor Ian M. Ritchie, Aug. 24–27. University of British Columbia, Vancouver, **1**, pp. 941–954 (2003)
5. Akkus, N., Campbell, J.C., Davidson, J., Henderson, D.K., Miller, H.A., Parkin, A., Parsons, S., Plieger, P.G., Swart, R.M., Tasker, P.A., West, L.C.: Exploiting supramolecular chemistry in metal recovery: novel zwitterionic extractants for nickel(II) salts. Dalton Trans. 1932–1940 (2003)
6. Soldenhoff, K., Hayward, N., Wilkins, D.: Direct solvent extraction of cobalt and nickel from laterite-acid pressure leach liquors. EPD Congr. 1998, Proc. Sess. Symp. 153–165 (1998)
7. Gunn, D.M., Miller, H.A., Swart, R.M., Tasker, P.A., West, L.C., White, D.J.: New types of extractant to transport metal sulfates in base metal recovery processes. Int. Solvent Extr. Conf. 280–290 (2002)
8. Forgan, R.S., Davidson, J.E., Fabbiani, F.P.A., Galbraith, S.G., Henderson, D.K., Moggach, S.A., Parsons, S., Tasker, P.A., White, F.J.: Cation and anion selectivity of zwitterionic salicylaldoxime metal salt extractants. Dalton Trans. **39**, 1763–1770 (2010)
9. Kordosky, G.A.: Copper recovery using leach/solvent extraction/electrowinning technology: forty years of innovation, 2.2 million tons of copper annually. Int. Solvent Extr. Conf. 853–862 (2002)
10. Mackey, P.J.: Rich heritage of copper production in Canada. CIM Magazine **2**, 35–42 (2007)
11. Forgan, R.S., Roach, B.D., Wood, P.A., White, F.J., Campbell, J., Henderson, D.K., Kamenetzky, E., McAllister, F.E., Parsons, S., Pidcock, E., Richardson, P., Swart, R.M., Tasker, P.A.: Using the outer coordination sphere to tune the strength of metal extractants. Inorg. Chem. **50**, 4515–4522 (2011)
12. Wenzel, M., Jameson, G.B., Ferguson, L.A., Knapp, Q.W., Forgan, R.S., White, F.J., Parsons, S., Tasker, P.A., Plieger, P.G.: Anion-induced contraction of helical receptors. Chem. Commun **28**(24), 3606–3608 (2009)
13. Wenzel, M., Knapp, Q.W., Plieger, P.G.: A bis-salicylaldoximato-copper(II) receptor for selective sulfate uptake. Chem. Commun. **47**, 499–501 (2011)
14. Plieger, P.G., Parsons, S., Parkin, A., Tasker, P.A.: Transport of metal salts; encapsulation of anions in dinuclear Cu(II) complexes $[Cu_2L_2SO_4]SO_4$ and $[Cu_2L_2BF_4](BF_4)_3$, where L = 2,2′-[1,6-hexanediylbis[(methylimino)methylene]]bis[4-tert-butyl-6-(phenylazomethinyl)phenol]. J. Chem. Soc. Dalton Trans. 3928–3930 (2002)
15. Mercer, D.J., Loeb, S.J.: Metal-based anion receptors: an application of second-sphere coordination. Chem. Soc. Rev. **39**, 3612–3620 (2010)
16. Kang, S.-O., Llinares, J.M., Day, V.W., Bowman-James, K.: Cryptand-like anion receptors. Chem. Soc. Rev. **39**, 3980–4003 (2010)
17. Hay, B.P.: De novo structure-based design of anion receptors. Chem. Soc. Rev. **39**, 3700–3708 (2010)
18. Kim, J.I., Juwarker, H., Liu, X., Lah, M.S., Jeong, K.S.: Selective sulfate binding induces helical folding of an indolocarbazole oligomer in solution and solid state. Chem. Commun. **46**, 764–766 (2010)
19. Moyer, B.A., Delmau, L.H., Fowler, C.J., Ruas, A., Bostick, D.A., Sessler, J.L., Katayev, E., Pantos, G.D., Llinares, J.M., Hossain, A., Kang, S.O., Bowman-James, K.: Supramolecular chemistry of environmentally relevant anions. Adv. Inorg. Chem. **59**, 175–204 (2007)
20. Eller, L.R., Stepien, M., Fowler, C.J., Lee, J.T., Sessler, J.L., Moyer, B.A.: Octamethyl-octaundecylcyclo[8]pyrrole: a promising sulfate anion extractant. J. Am. Chem. Soc. **129**, 11020–11021 (2007)
21. Bowman-James, K.: Alfred Werner revisited: the coordination chemistry of anions. Acc. Chem. Res. **38**, 671–678 (2005)
22. Ilioudis, C.A., Steed, J.W.: Organic macrocyclic polyamine-based receptors for anions. J. Supramol. Chem. **1**, 165–187 (2003)
23. Choi, K., Hamilton, A.D.: Macrocyclic anion receptors based on directed hydrogen bonding interactions. Coord. Chem. Rev. **240**, 101–110 (2003)
24. Amendola, V., Fabbrizzi, L., Mangano, C., Pallavicini, P., Poggi, A., Taglietti, A.: Anion recognition by dimetallic cryptates. Coord. Chem. Rev. **219–221**, 821–837 (2001)
25. Gale, P.A.: Anion and ion-pair receptor chemistry: highlights from 2000 and 2001. Coord. Chem. Rev. **240**, 191–221 (2003)
26. Gale, P.A., Quesada, R.: Anion coordination and anion-templated assembly: highlights from 2002 to 2004. Coord. Chem. Rev. **250**, 3219–3244 (2006)
27. Mateus, P., Delgado, R., Brandao, P., Felix, V.: Polyaza cryptand receptor selective for dihydrogen phosphate. J. Org. Chem. **74**, 8638–8646 (2009)
28. Wichmann, K., Antonioli, B., Soehnel, T., Wenzel, M., Gloe, K., Gloe, K., Price, J.R., Lindoy, L.F., Blake, A.J., Schroeder, M.: Polyamine-based anion receptors: extraction and structural studies. Coord. Chem. Rev. **250**, 2987–3003 (2006)
29. Hennrich, G., Anslyn, E.V.: 1,3,5–2,4,6-functionalized, facially segregated benzenes-exploitation of sterically predisposed systems in supramolecular chemistry. Chem. Eur. J. **8**, 2218–2224 (2002)
30. Filby, M.H., Steed, J.W.: A modular approach to organic, coordination complex and polymer based podand hosts for anions. Coord. Chem. Rev. **250**, 3200–3218 (2006)
31. Wu, B., Liang, J., Yang, J., Jia, C., Yang, X.J., Zhang, H., Tang, N., Janiak, C.: Sulfate ion encapsulation in caged supramolecular

structures assembled by second-sphere coordination. Chem. Commun. **15**, 1762–1764 (2008)

32. Ravikumar, I., Lakshminarayanan, P.S., Arunachalam, M., Suresh, E., Ghosh, P.: Anion complexation of a pentafluorophenyl-substituted tripodal urea receptor in solution and the solid state: selectivity toward phosphate. Dalton Trans. 4160–4168 (2009)
33. Zhuge, F., Wu, B., Liang, J., Yang, J., Liu, Y., Jia, C., Janiak, C., Tang, N., Yang, X.-J.: Full- or half-encapsulation of sulfate anion by a tris(3-pyridylurea) receptor: effect of the secondary coordination sphere. Inorg. Chem. **48**, 10249–10256 (2009)
34. Custelcean, R., Remy, P.: Selective crystallization of urea-functionalized capsules with tunable anion-binding cavities. Cryst. Growth Des. **9**, 1985–1989 (2009)
35. Warr, R.J., Westra, A.N., Bell, K.J., Chartres, J., Ellis, R., Tong, C., Simmance, T.G., Gadzhieva, A., Blake, A.J., Tasker, P.A., Schroder, M.: Selective extraction and transport of the [PtCl$_6$]$^{2-}$ anion through outer-sphere coordination chemistry. Chem. Eur. J. **15**, 4836–4850 (2009)
36. Kumar, A., Sun, S–.S., Lees, A.J.: Directed assembly metallocyclic supramolecular systems for molecular recognition and chemical sensing. Coord. Chem. Rev. **252**, 922–939 (2008)
37. Steed, J.W.: Coordination and organometallic compounds as anion receptors and sensors. Chem. Soc. Rev. **38**, 506–519 (2009)
38. Mahoney Joseph, M., Nawaratna Gayathri, U., Beatty Alicia, M., Duggan Peter, J., Smith Bradley, D.: Transport of alkali halides through a liquid organic membrane containing a ditopic salt-binding receptor. Inorg Chem. **43**, 5902–5907 (2004)
39. Mahoney Joseph, M., Beatty Alicia, M., Smith Bradley, D.: Selective solid-liquid extraction of lithium halide salts using a ditopic macrobicyclic receptor. Inorg. Chem. **43**, 7617–7621 (2004)
40. Moyer, B.A., Bonnesen, P.V., Custelcean, R., Delmau, L.H., Hay, B.P.: Strategies for using host–guest chemistry in the extractive separations of ionic guests. Kem. Ind. **54**, 65–87 (2005)
41. Holm, R.H., Swaminathan, K.: Nickel(II) complexes. IV. Bis(N-sec-alkylsalicylaldimine) complexes: conformational equilibriums in solution. Inorg. Chem. **2**, 181–186 (1963)
42. Holm, R.H., Swaminathan, K.: Nickel(II) complexes III. Bis-(N-arylsalicylaldimine) complexes. Inorg. Chem. **1**, 599–607 (1962)

43. Holm, R.H.: Nickel (II) complexes. II. The solution magnetism of bis(N-methylsalicylaldimine)nickel (II) and related complexes. J. Am. Chem. Soc. **83**, 4683–4690 (1961)
44. Holm, R.H., McKinney, T.M.: Magnetic observations of some substituted Ni(II) salicylaldimine complexes. J. Am. Chem. Soc. **82**, 5506–5507 (1960)
45. Holm, R.H.: Applications of isotropic shifts to the investigation of structures and structural equilibriums of metal complexes. Accounts Chem. Res. **2**, 307–316 (1969)
46. Parkin, A., Barr, G., Collins, A., Dong, W., Gilmore, C.J., Tasker, P.A., Wilson, C.C.: Using cluster analysis to study transition-metal geometries: four-coordinate complexes with two salicylaldiminato or related ligands. Acta Crystallogr. B: Struct. Sci. **B63**, 612–620 (2007)
47. Akitsu, T.: Photofunctional supramolecular solution systems of chiral Schiff base nickel(II), copper(II), and zinc(II) complexes and photochromic azobenzenes. Polyhedron **26**, 2527–2535 (2007)
48. Akitsu, T., Einaga, Y.: Synthesis, crystal structures and electronic properties of Schiff base nickel(II) complexes: towards solvato-chromism induced by a photochromic solute. Polyhedron. **24**, 1869–1877 (2005)
49. Li, Z.-X., Zhang, X.-L., Pu, X.-H.: Bis[2-(benzyliminomethyl)-4-chlorophenolato-k2 N, O]nickel(II). Acta Crystallogr. E Struct. Rep. Online **E64**, m202/1–m202/7 (2008)
50. Chen, S.Z., Xia, D.G.: Bis{2-[(E)-benzyliminomethyl]-4-methylphenolato-k2 N, O}nickel(II). Acta Crystallogr. E Struct. Rep. Online. **E65**, m923 (2009)
51. Plieger, P.G., Tasker, P.A., Galbraith, S.G.: Zwitterionic macrocyclic metal sulfate extractants containing 3-dialkylamino-methylsalicylaldimine units. Dalton Trans. 313–318 (2004)
52. Sheldrick, G.M.: SHELXTL, 5.1. Bruker AXS, Madison (1998)
53. Van der Sluis, P., Spek, A.L.: BYPASS: an effective method for the refinement of crystal structures containing disordered solvent regions. Acta Crystallogr. A: Found. Crystallogr. **A46**, 194–201 (1990)