COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Cooperative sulfate binding by metal salt extractants containing 3-dialkylaminomethylsalicylaldimine units

Stuart G. Galbraith, Paul G. Plieger and Peter A. Tasker*

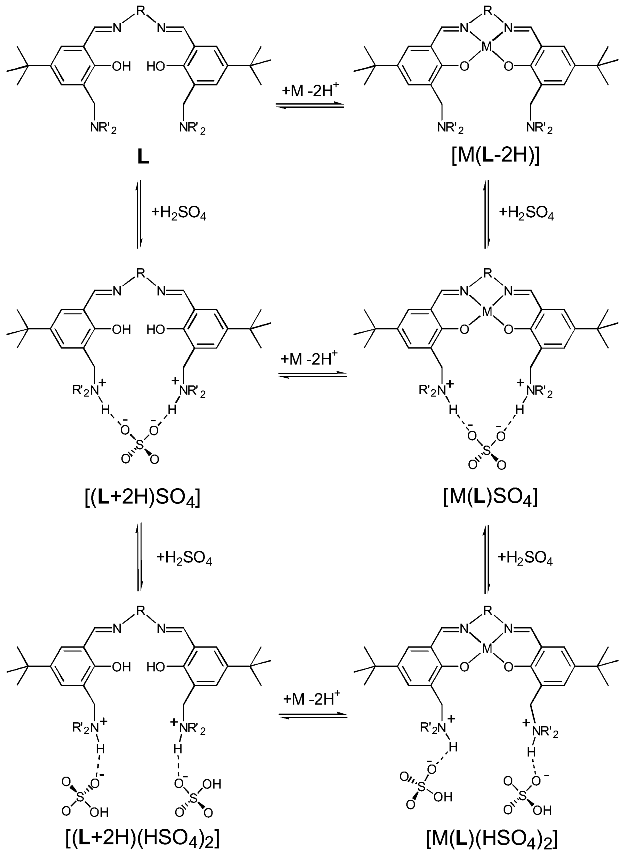
Department of Chemistry, The University of Edinburgh, Joseph Black Building, Kings Buildings, West Mains Road, Edinburgh, UK EH9 3JJ. E-mail: p.a.tasker@ed.ac.uk

Received (in Cambridge, UK) 30th August 2002, Accepted 1st October 2002
First published as an Advance Article on the web 14th October 2002

The pH-dependence of simultaneous metal- and sulfate-loading of simple salen derivatives demonstrates the feasibility of their application as extractants for recovery of base metals from the leaching of sulfidic ores. The efficacy of the ligands depends on the templating of the sulfate binding site by the attendant metal ion.

We have recently demonstrated the viability of using simple, inexpensive salen-derivatives **L** to extract both metal cations and their attendent anions from aqueous solutions.[1–4] Appending appropriate tertiary amine groups to the salen framework allows the metal salt to be transported in a zwitterionic form of the ligand (as in [M(**L**)SO$_4$] Scheme 1). In a solvent-extraction based process this leaves the pH of the aqueous 'feed' unchanged and removes the need for inter-stage neutralisation in a metal recovery circuit.[5]

The predominant anion in pregnant leach solutions from new hydrometallurgical processes to treat sulfidic ores is sulfate.[6,7] Commercial extraction is undertaken at low pH (<3) where there is a predominance of HSO_4^- over SO_4^{2-}. An extractant capable of selectively removing SO_4^{2-} from the aqueous feed solution is a key requirement to obtain good materials balances and a high purity electrolyte for the reduction step. To date, there are only a few systems tailored to bind SO_4^{2-}; the most successful are guanidinium-based ligands[8,9] that have shown selectivity for SO_4^{2-} over HPO_4^-.



Scheme 1 Some of the equilibria associated with metal- and sulfate-loading of the ditopic Schiff base ligands **L**. R′ = *n*-C$_6$H$_{13}$ for the CHCl$_3$/H$_2$O solvent extraction studies reported here, and R = –(CH$_2$)$_2$–, 2,2′-biphenyl, (±)-*trans*-1,2-cyclohexyl, *o*-C$_6$H$_4$ for **1**, **2**, **3**, **4**, respectively.

Direct addition of Ni(II) or Cu(II) sulfate to the ditopic ligands **L** in methanol yields the metal sulfate complexes [M(**L**)SO$_4$] which have been described previously.[3] The availibility of the 'metal-only' [M(**L** − 2H)] complexes from reaction with metal(II) acetates[3] has allowed us to study the uptake of sulfuric acid by these complexes in solvent extraction experiments, *e.g.*

$$[\mathrm{M}(\mathbf{L}-2\mathrm{H})]_{(\mathrm{org})} + \mathrm{H_2SO_{4(aq)}} \rightleftharpoons [\mathrm{M}(\mathbf{L})\mathrm{SO_4}]_{(\mathrm{org})} \qquad (1)$$

as a function of pH, and to determine how this depends on preorganisation of the ligands. Good chloroform solubility of both free ligands and complexes is shown by systems **1**–**4** with pendant di-*n*-hexylaminomethyl groups which are readily prepared by adaption of methods reported previously.† [3]

The sulfate uptake by the *o*-phenylene-bridged ligand **4** and its copper complex [Cu(**4** − 2H)] are compared in Fig. 1. The uptake by the free ligand is typical, with curves for **1**–**4** being almost superimposable.‡ Very little transfer of sulfate to the organic phase is observed at pH $>$ 2.0. As the pH is dropped below this value the uptake increases rapidly, approaching 200% at pH <0.5, which can be attributed to the extraction of two mono-charged HSO_4^- anions which are present[10] in the aqueous phase in an excess at pH $<$ 1. The SO_4^{2-} ion is present in a similar excess at pH $>$ 3. No loading was seen in this region.

In contrast, the 'copper-only' complex [Cu(**4** − 2H)] loads sulfate at pH values below 4.5, and the loading curve suggests that the 1:1:1 complex [Cu(**4**)SO$_4$] predominates in the pH range 1.5–3.5. This increase in apparent basicity of the pendant di-*n*-hexylaminomethyl groups in the copper complex favouring protonation and transport of sulfate is consistent with

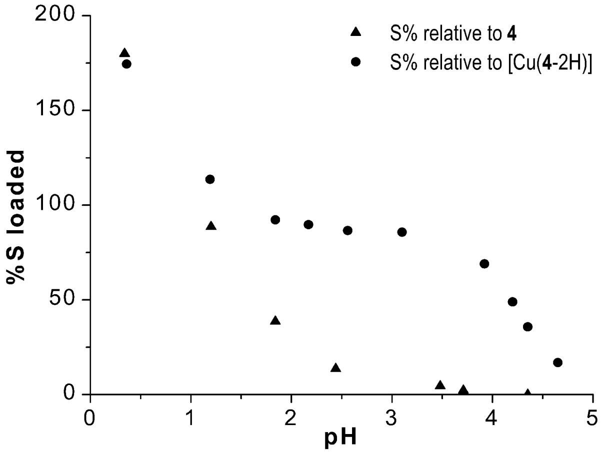


Fig. 1 The pH dependence of H$_2$SO$_4$ uptake by ligand **4** and [Cu(**4** − 2H)].

DOI: 10.1039/b208457k

the copper ion templating the pendant tertiary amine groups to assemble a good sulfate-binding site which is dicationic with two H-bond donors and a hydrophobic exterior.

An important feature of this loading behaviour is that the copper complex of **4** is effectively selective for SO_4^{2-} over HSO_4^-; in contact with an aqueous sulfate solution at pH = 1.92 where the $SO_4^{2-}:HSO_4^-$ ratio is 1:1 the organic phase contains only the 1:1:1 complex $[\mathrm{Cu}(\mathbf{4})\mathrm{SO_4}]$.§ [10]

The pH dependence of sulfate-loading by the ditopic ligands **L** in $CHCl_3$ is close to ideal for base metal recovery from sulfate feeds (Fig. 2). At pH ≈ 3.3, > 90% loading of MSO_4 is possible without pH adjustment.

$$\mathbf{L}_{(\mathrm{org})} + \mathrm{MSO}_{4(\mathrm{aq})} \rightleftharpoons [\mathrm{M}(\mathbf{L})\mathrm{SO}_4]_{(\mathrm{org})} \tag{2}$$

A very efficient materials balance for a circuit will result if the $pH_{½}$ for the formation of the salen complex,

$$\mathbf{L}_{(\mathrm{org})} + \mathrm{MSO}_{4(\mathrm{aq})} \rightleftharpoons [\mathrm{M}(\mathbf{L} - 2\mathrm{H})]_{(\mathrm{org})} + \mathrm{H_2SO}_{4(\mathrm{aq})} \tag{3}$$

were *ca.* 2.0 (as shown in Fig. 2). Acid stripping at pH $\leqslant$ 1.5,

$$[\mathrm{M}(\mathbf{L})\mathrm{SO}_4]_{(\mathrm{org})} + \mathrm{H_2SO}_{4(\mathrm{aq})} \rightleftharpoons [\mathrm{MSO}_4]_{(\mathrm{aq})} + [(\mathbf{L} + 2\mathrm{H})(\mathrm{SO}_4)]_{(\mathrm{org})}, \tag{4}$$

ligand regeneration with base to pH ≈ 3.0,

$$[(\mathbf{L} + 2\mathrm{H})(\mathrm{SO}_4)]_{(\mathrm{org})} + 2\ \mathrm{NH}_{3(\mathrm{aq})} \rightleftharpoons \mathbf{L}_{(\mathrm{org})} + [\mathrm{NH_4}]_2\mathrm{SO}_{4(\mathrm{aq})}, \tag{5}$$

and electrolytic recovery of the metal,

$$\mathrm{MSO_4} + \mathrm{H_2O} \rightleftharpoons \mathrm{M} + \mathrm{H_2SO_4} + 0.5\ \mathrm{O_2}, \tag{6}$$

regenerates the acid for stripping and gives a materials balance.

$$\mathrm{MSO_4} + \mathrm{H_2O} + 2\ \mathrm{NH_3} \rightleftharpoons \mathrm{M} + [\mathrm{NH_4}]_2\mathrm{SO_4} + 0.5\ \mathrm{O_2} \tag{7}$$

Any commercially viable extractant must show high stability towards hydrolysis or oxidation under operating conditions. The free ligands **1–4** were almost completely hydrolysed when $CHCl_3$ solutions were contacted with H_2SO_4 at pH ≤1 for 16 h, but at pH ≈ 3.0 the ligands were largely intact. This implies that at very low pH the transfer of sulfate to the chloroform phase involves the HSO_4^- salt of the protonated 5-*tert*-butyl-3-dihexylaminomethyl-2-hydroxybenzaldehyde, rather than $[(\mathbf{L} + 2\mathrm{H})(\mathrm{HSO_4})_2]$ as indicated in Scheme 1.

Development of more hydrophobic hydrocarbon soluble analogues of **1–4** with enhanced hydrolytic stability is in hand.¶ The favourable 'strength' of sulfate extraction and selectivity for SO_4^{2-} over HSO_4^- demonstrated in this paper provides the basis for very efficient recovery of base metals from sulfidic ores. The 'subtractive' removal of both the metal and its attendent sulfate anion could also open up an effective approach to treating acid mine drainage streams and other effluents prior to discharge.

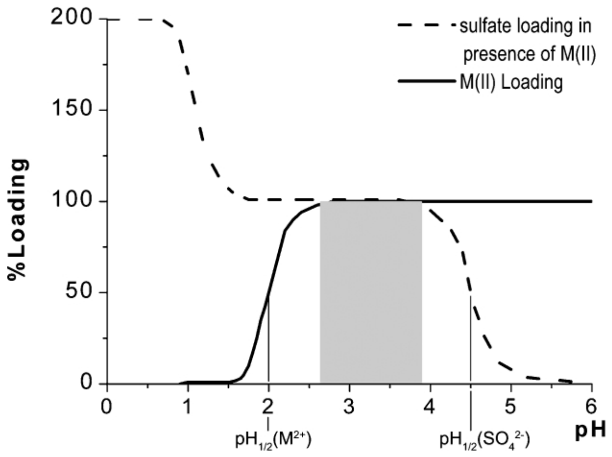


Fig. 2 Idealised pH profile for the loading and stripping of Cu(II) and SO_4

We thank Mr J. Millar and Mr W. Kerr for obtaining NMR spectra, Mr A. Taylor and Mr H. Mackenzie for mass spectra. We gratefully acknowledge the Christina Miller Bequest and the EPSRC (GRM/R21653) for support and Mr R Swart (Avecia plc) and Dr B Harris (Hatch Ltd) for helpful discussons.

Notes and references

† *Example* preparation of ligand **4**: to a stirred solution of 5-*tert*-butyl-3-dihexylaminomethyl-2-hydroxybenzaldehyde (3 g, 0.0080 mol) in ethanol (30 ml) was added a solution of phenylene-1,2-diamine (0.43 g, 0.0040 mol) in ethanol (25 ml). The orange solution was stirred overnight and then concentrated *in vacuo* to yield an orange oil. The product was then dissolved in dichloromethane (50 ml) and extracted with water (3 × 25 ml). The organic fraction was dried with $MgSO_4$, filtered and then evaporated *in vacuo* to yield **4** as a viscous orange oil (3.2 g, 98%). This was used without further purification. Calc. for $C_{54}H_{86}N_4O_2$: C, 78.78; H, 10.53; N, 6.81; Found: C, 78.30; H, 10.54; N, 6.92%. δ_{H} ($CDCl_3$, 250 MHz): 0.89 (t, 12H, *J* 6.6 Hz, $\mathrm{N(CH_2)_5C}\mathit{H}_3$), 1.29 (m, 24H, $\mathrm{NCH_2CH_2(C}\mathit{H}_2)_3\mathrm{CH_3}$), 1.33 (m, 18H, $\mathrm{(CH_3)_3C}$), 1.53 (m, 8H, $\mathrm{NCH_2C}\mathit{H}_2$), 2.54 (t, 8H, *J* 6.8 Hz, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2}$), 3.73 (s, 4H, Ar-$\mathrm{C}\mathit{H}_2\mathrm{N}$), 6.78 (m, 2H, Ar-*H*), 7.08 (m, 2H, Ar-*H*), 7.46 (m, 2H, Ar-*H*), 7.64 (d, 2H, Ar-*H*), 8.83 (s, 2H, N=CH). δ_{C} ($CDCl_3$): 14.4 ($\mathrm{N(CH_2)_5}\mathit{C}\mathrm{H_3}$), 22.9 ($\mathrm{N(CH_2)_4}\mathit{C}\mathrm{H_2CH_3}$), 26.6 ($\mathrm{N(CH_2)_3}\mathit{C}\mathrm{H_2CH_2CH_3}$), 27.1 ($\mathrm{N(CH_2)_2}\mathit{C}\mathrm{H_2(CH_2)_2CH_3}$), 31.9 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 32.2 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_2}$), 34.4 ($\mathit{C}\mathrm{(CH_3)_3}$), 53.9 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2}$), 54.4 ($\mathrm{ArC}\mathit{C}\mathrm{H_2N}$), 115.8 (Ar-*C*), 118.4 (Ar-*C*), 119.8 (Ar-*C*H), 125.4 (Ar-*C*H), 127.1 (Ar-*C*H), 130.3 (Ar-*C*H), 141.4 (Ar-*C*), 141.7 (Ar-*C*), 157.8 (Ar-*C*), 161.1 (N=CH). $\nu_{\mathrm{max}}/\mathrm{cm}^{-1}$ 2954s (C–H), 1619s (N=CH), 1205s (C–N), 822m, 748s. MS (FAB, NOBA): *m/z* 823 (MH^+, 56.9%).

‡ 10 ml aliquots of H_2SO_4/Na_2SO_4 with pH values in the range 0–6 and a constant SO_4^{2-} concentration (0.8 mol dm^{-3}) were intimately mixed for 16 h with $CHCl_3$ solutions of metal-only complexes (10 ml, 0.01 M). The organic layer was separated, a 2 ml aliquot removed, evaporated *in vacuo*, and then redissolved in butan-1-ol (10 ml). Analysis for M and S was performed on a Thermo Jarrell Ash IRIS ICP-AES spectrometer. Extraction experiments on the free ligands used the same procedure with 10 ml of a 0.01 M ligand solution in $CHCl_3$ and the degree of hydrolysis was determined by comparison of the intensities of the azomethine and aldehyde ^1H NMR signals.

§ On the basis of analytical data it is not possible to distinguish this from the complex $[\mathrm{Cu}(\mathbf{4} - \mathrm{H})\mathrm{HSO_4}]$. However, this is of no consequence to the materials balances, the ligand still effectively transports $CuSO_4$.

¶ Marked improvements in hydrolytic stability are observed when imine extractants are used in hydrocarbon solvents, *e.g.* 5-nonyl-derivatives of salicylaldoxime show long lifetimes when used in kerosene as extractants from acidic media.[11]

1 P. A. Tasker and D. J. White, *UK Pat.*, 9907485.8, 1999.
2 H. Miller and P. A. Tasker, *UK Pat.*, 0105768.6, 2002.
3 H. A. Miller, N. Laing, S. Parsons, A. Parkin, P. A. Tasker and D. J. White, *J. Chem. Soc., Dalton Trans.*, 2000, 3773.
4 D. J. White, N. Laing, H. Miller, S. Parsons, S. Coles and P. A. Tasker, *Chem. Commun.*, 1999, 2077.
5 D. M. Gunn, H. A. Miller, R. M. Swart, P. A. Tasker, L. C. West and D. J. White, *Proceedings of the International Solvent Extraction Conference*, 2002, p. 280.
6 K. Soldenhoff, N. Hayward and D. Wilkins, EPD Congress 1998, *Proceedings of Sessions and Symposia held at the TMS Annual Meeting*, San Antonio, Feb. 16–19, 1998, p. 1153.
7 E. C. Chou, P. M. Rooke, A. R. Williams and J. T. Hanks, EPD Congress 2000, *Proceedings of Sessions and Symposia held during the TMS Annual Meeting*, Nashville, TN, United States, Mar. 12–16, 2000, p. 469.
8 H. Stephan, K. Gloe, P. Schiessl and F. P. Schmidtchen, *Supramol. Chem.*, 1995, **5**, 273.
9 F. P. Schmidtchen and M. Berger, *Chem. Rev.*, 1997, **97**, 1609.
10 P. W. Atkins, *The Elements of Physical Chemistry*, 1st edn., 1996, p. 176.
11 J. Szymanowski, *Hydroxyoximes and Copper Hydrometallurgy*, CRC Press, Boca Raton, FL, 1993.