

Solvent extraction of metal sulfates by zwitterionic forms of ditopic ligands

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Ditopic ligands have been designed and synthesized for the solvent extraction and membrane transport of transition metal salts for application in metal separation and purification processes. Tetradentate salicylaldimine ligands of the H₂salen type bearing pendant tertiary amine groups undergo a zwitterionic transformation when binding metal salts, forming overall neutral assemblies which can be transferred into non-polar, water-immiscible solvents. A comparison of the solid state structures of copper(II) sulfate and neutral copper-only complexes demonstrates how incorporation of the metal ion into the salen²⁻ unit preorganises the anion binding site to accommodate the sulfate group. The extraction/recovery characteristics of copper and sulfate are reported for a ligand which has been modified to lower the strength of copper-binding and thus facilitate copper-recovery and ligand-recycling. An X-ray structure determination of this 2,2'-biphenylene-bridged ligand indicates a predisposition towards the provision of a non-planar N₂O₂²⁻ donor-set. This is exemplified by its *cis*-octahedral nickel(II) sulfate complex in which the sulfate acts as a bidentate ligand. Competitive metal ion transport experiments show the selectivity of this ligand for copper(II) transport over a range of other metals including nickel(II) and zinc(II). The pH profiles for loading of Cu²⁺ (pH_{1/2} 2.0, *i.e.* pH at 50 percent extraction) and of SO₄²⁻ (pH_{1/2} 9.7) into the ligand zwitterion in chloroform have been determined and this has allowed the demonstration of a protocol for loading of CuSO₄, stripping of copper and sulfate separately and recycling of the extractant. Such a protocol provides proof-of-concept for application of these ditopic ligands in metal recovery from sulfide leaching or from acid mine drainage streams.

Introduction

Traditional ion-exchange agents¹ used in solvent extraction processes to separate metal ions and recover metals from aqueous solution are well suited for use in circuits for processing oxidic and related 'transition' ores.² They provide excellent material balances in such processes because the acid consumed in leaching the oxide is regenerated by the solvent extraction step. There are a number of situations where release of acid into the aqueous raffinate from solvent extraction presents problems in circuit design, for example, in recovery from ores where the leaching step does not consume acid or when recovering metals sequentially from acid mine-drainage streams where interstage neutralisation will be required.

These problems could be overcome using reagents which would transport the desired metal as its *sulfate salt* across a leach/solvent extraction/electrowin circuit as shown in Fig. 1. Neutralisation of acid will then only be required to control the pH of the electrolyte at the back end of the circuit.

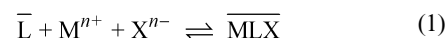
We have recently reported³ the development of ligands which bind transition metal *salts* and are designed to be part of metal recovery processes which require the transport of a metal cation and its attendant anion. The prototype ligands are based upon tetradentate H₂salen-type molecules bearing tertiary amine groups (morpholine or piperidine groups, see Fig. 2), *ortho* to the phenolic OH-groups.

The binding sites in these prototype ligands (Fig. 2) have been elucidated by X-ray structure determination of a series of free ligands, "nickel-only" complexes and nickel salt complexes (Scheme 1).³ Incorporation of the planar Ni²⁺ into the salen binding site has been shown to predispose the morpholinium groups for incorporation of SO₄²⁻. It has also been shown that titration of the "metal-only" complexes with rigid diacids

such as terephthalic acid leads to unusual assemblies with intermolecular dicarboxylate bridges between the pendant ammonium groups of the metal complexes.³

The key to the performance of these ditopic ligands is that the metal salt is bound to the *zwitterionic* form of the ligand generated by transfer of the phenolic protons from the metal binding site to the pendant amine groups, thus creating a dipositive cavity wherein the anion is bound by a combination of electrostatic interactions and favourable hydrogen bonding (Scheme 1).

This zwitterionic transformation allows the formation of neutral assemblies, which can then be transported into a water-immiscible liquid in solvent extraction processes, eqn. (1).



Another important feature of these *zwitterionic* ligands is their ditopic nature. In principle, the separation of metal- and anion-binding sites (Scheme 2) should permit the sequential stripping of the cation and anion as shown, recycling the ligand and generating a concentrated metal sulfate solution for electrowinning. If ammonia were used in the sulfate-stripping step, ammonium sulfate is generated as a saleable product. We report here a proof-of-concept study which establishes that copper could be recovered from sulfate-media using the loading/stripping protocol outlined in Scheme 2.

Experimental

Instrumentation

Nuclear magnetic resonance spectra were obtained on Bruker AC 200 and Bruker AC 250 instruments. FAB mass spectro-

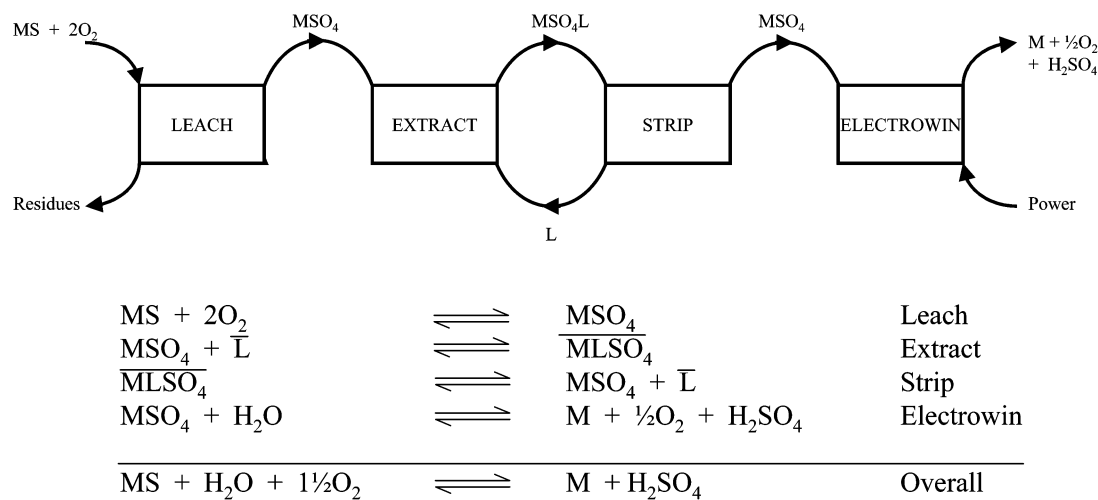
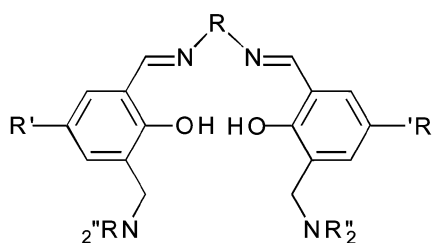


Fig. 1 A flowsheet and materials balance for recovery of metals from sulfidic ores using pressure leaching, solvent extraction of metal sulfate and electrowinning.



	R	R'	NR'' ₂
1	—(CH ₂) ₂ —	Bu ^t	morpholine
2	± <i>trans</i> -1,2-cyclohexyl	Bu ^t	morpholine
3	<i>o</i> -C ₆ H ₄	C ₉ H ₁₉	morpholine
4	—(CH ₂) ₂ —	Bu ^t	piperidine
5	biphenyl	Bu ^t	piperidine
6	biphenyl	C ₉ H ₁₉	piperidine
7	—(CH ₂) ₂ —	CH ₃	morpholine

Fig. 2 Ligand structures.

metry was performed on a Kratos MS 50 machine and EI mass spectrometry data were obtained on a Kratos Profile instrument. FTIR spectra were recorded on a Perkin-Elmer Paragon 1000 spectrometer as dichloromethane films on NaCl plates or as KBr discs. Electronic absorption spectroscopy was performed on a Unicam UV2 spectrometer. Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis was performed on a Thermo Jarrell Ash IRIS ICP-OES spectrometer. The measurement of pH was carried out using a ORION 410A pH meter. Atomic absorption spectroscopy was performed on a Varian Spectra AA-800 spectrometer.

Solvent and reagent pre-treatment

Unless stated to the contrary, commercial grade chemicals obtained from Aldrich or Acros companies were used without further purification.

Ligand synthesis

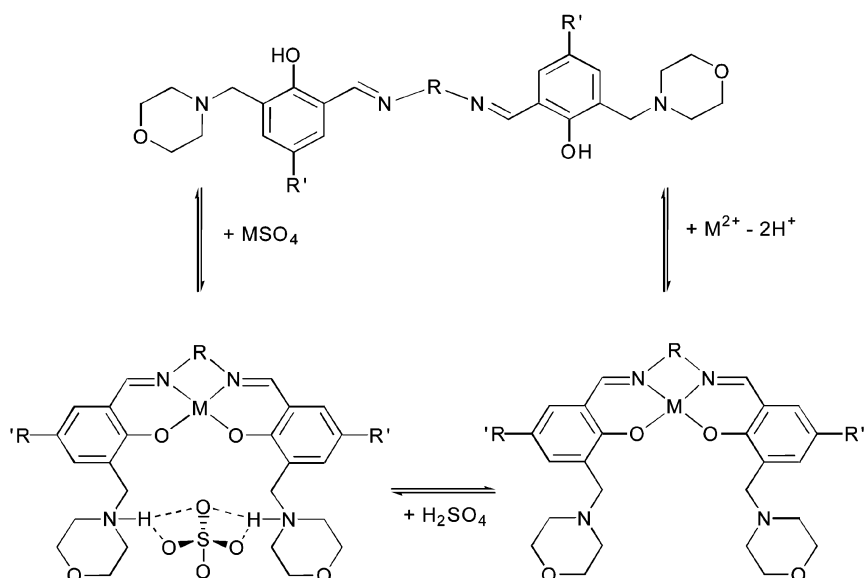
Ligands **1**, **2** and **3** were prepared as described previously.³ The 2-hydroxy-5-alkylbenzaldehydes and ethoxy-*N*-piperidinylmethane were prepared by the methods described by Levin and co-workers⁴ and Fenton and co-workers.⁵ 2,2'-Diaminobiphenyl was prepared from 2,2'-dinitrobiphenyl by a literature method.⁶ The salicylaldehydes substituted with pendant piperidinyl groups were prepared by an adaptation of the method of Fenton and co-workers;⁵ details of their synthesis follow.

2-Hydroxy-3-(piperidin-4-ylmethyl)-5-*tert*-butylbenzaldehyde.

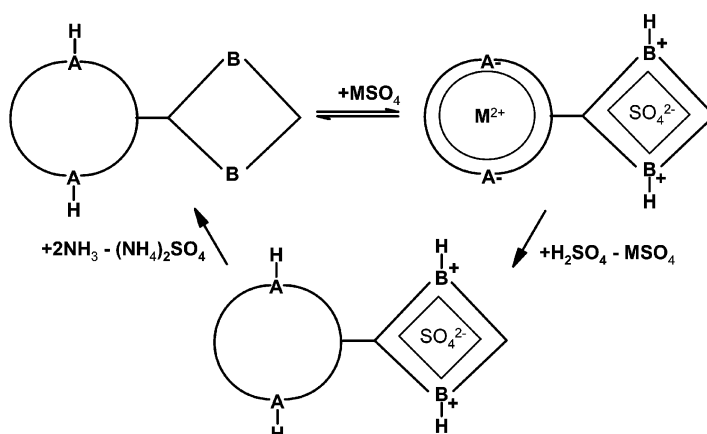
A mixture of 5-*tert*-butylbenzaldehyde (14.8 g, 0.1 mol) and ethoxy-*N*-piperidinylmethane (15.74 g, 0.11 mol) in acetonitrile (150 cm³) was heated to reflux under a dinitrogen atmosphere for 72 h. After cooling the solution to room temperature, the solvent was removed *in vacuo* to yield a viscous light green oil which formed a waxy solid upon standing (27.0 g, 98%). Found: C, 74.23; H, 9.08; N, 5.44. Calc. for C₁₇H₂₅NO₂: C, 74.14; H, 9.15; N, 5.09%. δ_H (CDCl₃, 200 MHz): 1.26 (s, 9H, C(CH₃)₃), 1.51 (m, 2H, NCH₂CH₂CH₂), 1.64 (m, 4H, NCH₂CH₂CH₂), 2.52 (m, 4H, NCH₂CH₂CH₂), 3.69 (s, 2H, Ar-CH₂N), 7.22 (d, 1H, *J* 2.1 Hz, Ar-*H*), 7.63 (d, 1H, *J* 2.1 Hz, Ar-*H*), 10.40 (s, 1H, CHO). δ_C (CDCl₃): 24 (NCH₂CH₂CH₂), 26 (NCH₂CH₂CH₂), 31 (CH₃), 34 (C(CH₃)₃), 54 (NCH₂CH₂CH₂), 61 (CCH₂N), 122.6 (Ar C), 122.2 (Ar C), 123 (Ar CH), 132 (Ar CH), 141 (Ar C), 159 (Ar C), 190 (CHN). MS (FAB, thioglycerol) *m/z* 346 (MH⁺, 100%).

2-Hydroxy-3-(piperidin-4-ylmethyl)-5-nonylbenzaldehyde.

A mixture of 5-nonylbenzaldehyde (12.46 g, 0.05 mol) and ethoxy-*N*-piperidinylmethane (7.85 g, 0.055 mol) in acetonitrile (200 cm³) was heated to reflux under a dinitrogen atmosphere for 120 h. After cooling the solution to room temperature, the solvent was removed *in vacuo* to yield a viscous light green oil. The product was dissolved in CH₂Cl₂ (150 cm³) and extracted with water (3 × 60 cm³). The organic fraction was evaporated *in vacuo* and dried under vacuum (17.2 g, 99%). Found: C, 77.08; H, 10.11; N, 4.27. Calc. for C₂₂H₃₅NO₂: C, 76.48; H, 10.21; N, 4.05%. δ_H (CDCl₃, 200 MHz): 0.4–1.4 (m, 19H, C₉H₁₉, mixed isomer chain), 1.50 (m, 2H, NCH₂CH₂CH₂), 1.63 (m, 4H, NCH₂CH₂CH₂), 2.50 (m, 4H, NCH₂CH₂CH₂), 3.68 (s, 2H, Ar-CH₂N), 7.16 (m, 1H, Ar-*H*), 7.53 (d, 1H, Ar-*H*), 10.74 (s, 1H, CHO). δ_C (CDCl₃): 24 (NCH₂CH₂CH₂), 26 (NCH₂CH₂CH₂), 8–52 (C₉, mixed isomer chain), 54 (NCH₂CH₂CH₂), 61 (CCH₂N), 122 (Ar C), 122 (Ar C), 133 (Ar CH), 138 (Ar CH), 140 (Ar C), 160 (Ar C), 191 (CHN). EIMS *m/z* 726 (MH⁺, 100%).



Scheme 1 Formation of metal sulfate and “metal only” complexes from ditopic salenH₂ ligands.



Scheme 2 Schematic representation of ditopic ligands for metal sulfates with diacid/dibasic sites to enable the hydrometallurgical unit operations of concentration and separation.

Ligand 4. To a stirred solution of 2-hydroxy-3-(piperidin-4-ylmethyl)-5-*tert*-butylbenzaldehyde (2 g, 7.27 mmol) in diethyl ether (20 cm³) was added a solution of ethylenediamine (0.218 g, 3.63 mmol) in ethanol (20 cm³). The yellow solution was stirred overnight and concentrated *in vacuo* to yield a yellow solid, which was recrystallised from hexane/diisopropyl ether (1.83 g, 88%); mp 99–101 °C. Found: C, 75.39; H, 9.42; N, 9.65. Calc. for C₃₆H₅₄N₄O₂: C, 75.22; H, 9.47; N, 9.75%. ¹H NMR (CDCl₃, 360 MHz): δ 1.28 (s, 9H, C(CH₃)₃), 1.43 (d, ³J_{HH} 5.3 Hz, 2H, NCH₂CH₂CH₂), 1.58 (t, ³J_{HH} 5.3 Hz, 4H, NCH₂CH₂CH₂), 2.45 (s, 4H, NCH₂CH₂CH₂), 3.57 (s, 2H, Ar-CH₂N), 7.19 (d, ³J_{HH} 2.5 Hz, 1H, Ar-H), 7.36 (d, ³J_{HH} 2.5 Hz, 1H, Ar-H) 8.40 (s, 1H, N=CH). ¹³C NMR (CDCl₃): δ 24.78 (NCH₂CH₂CH₂), 26.41 (NCH₂CH₂CH₂), 31.86 (CH₃), 34.34 (C(CH₃)₃), 54.85 (NCH₂CH₂CH₂), 56.93 (CCH₂N), 118.08 (Ar C), 126.10 (Ar CH), 126.44 (Ar CH), 128.63 (Ar CH), 130.72 (Ar CH), 131.04 (Ar CH), 162.08 (CHN). λ_{max}/nm (ε/dm³ mol⁻¹ cm⁻¹) 230 (36400), 266 (50000), 324 (18200). MS (FAB, NOBA) *m/z* 576 (MH⁺ 50%).

Ligand 5. To a stirred solution of 2-hydroxy-3-(piperidin-4-ylmethyl)-5-*tert*-butylbenzaldehyde (1.908 g, 6.93 mmol) in diethyl ether (20 cm³) was added a solution of 2,2'-diaminobiphenyl (0.638 g, 3.46 mmol) in acetone (20 cm³). The yellow solution was stirred overnight and concentrated *in vacuo* to yield a pale yellow powder, which was recrystallised from acet-

one (1.407 g, 58%); mp 198–201 °C. Found: C, 78.96; H, 8.40; N, 7.90. Calc. for C₄₆H₅₈N₄O₂: C, 79.04; H, 8.36; N, 8.02%. ¹H NMR (CDCl₃, 200 MHz): δ 1.24 (s, 9H, C(CH₃)₃), 1.42 (d, ³J_{HH} 4.4 Hz, 2H, NCH₂CH₂CH₂), 1.58 (t, ³J_{HH} 4.4 Hz, 4H, NCH₂CH₂CH₂), 2.41 (s, 4H, NCH₂CH₂CH₂), 3.51 (s, 2H, Ar-CH₂N), 7.10–7.44 (m, 6H, Ar-H), 8.50 (s, 1H, N=CH). ¹³C NMR (CDCl₃, 200 MHz): δ 24.19 (NCH₂CH₂CH₂), 25.88 (NCH₂CH₂CH₂), 31.28 (CH₃), 33.76 (C(CH₃)₃), 54.03 (NCH₂CH₂CH₂), 56.93 (CCH₂N), 118.08 (Ar C), 118.6 (Ar C), 124.3 (Ar C), 126.10 (Ar CH), 126.44 (Ar CH), 128.63 (Ar CH), 130.72 (Ar CH), 131.04 (Ar CH), 134.5 (Ar C), 140.46 (Ar C), 147.9 (Ar C), 153.8 (Ar C), 162.08 (CHN). λ_{max}/nm (ε/dm³ mol⁻¹ cm⁻¹) 229 (39300), 276 (29600), 349 (17400). MS (FAB, NOBA) *m/z* 699 (MH⁺ 75%).

Ligand 6. This compound was obtained from 2-hydroxy-3-(piperidin-4-ylmethyl)-5-nonylbenzaldehyde as a bright orange solid using the procedure for the preparation of **5** in 95% yield after water-soluble impurities were removed from the crude product by extraction with water. Found: C, 80.16; H, 9.18; N, 6.71. Calc. for C₅₆H₇₈N₄O₂: C, 80.14; H, 9.37; N, 6.68%. ¹H NMR (CDCl₃, 200 MHz): δ 0.48–1.37 (m, 19H, C₉H₁₉ mixed isomer chain), 1.42 (s, 2H, NCH₂CH₂CH₂), 1.56 (s, 4H, NCH₂CH₂CH₂), 2.39 (s, 4H, NCH₂CH₂CH₂), 3.52 (s, 2H, Ar-CH₂N), 7.07–7.43 (m, 6H, Ar-H), 8.53 (s, 1H, CH=N), 12.5 (br, 1H, OH). ¹³C NMR (CDCl₃, 200 MHz): δ 24.81 (NCH₂CH₂CH₂),

26.53 (NCH₂CH₂CH₂), 31.28 (CH₃), 33.76 (C(CH₃)₃), 54.58 (NCH₂CH₂CH₂), 57.36 (CCH₂N), 116.2 (Ar CH), 118.8 (Ar CH), 119.1 (Ar CH), 125.0 (Ar C), 126.6 (Ar CH), 129.08 (Ar CH), 131.4 (Ar CH), 135.1 (Ar C), 137.8 (Ar C), 139.8 (Ar C), 148.2 (Ar C), 157.5 (Ar C), 162.8 (CHN). $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 230 (36700), 278 (32400), 352 (15300). MS (FAB, thioglycerol) m/z 840 (MH⁺, 30%).

Metal sulfate complexes

A solution of ligand (0.3 mmol) in methanol (20 cm³) was stirred together with a solution of the appropriate metal sulfate (1 mol equiv.) in methanol (20 cm³) overnight. Colour changes due to complex formation were instantaneous. After removal of most of the solvent *in vacuo*, the products were recrystallised as indicated and air-dried.

[Cu(1)(SO₄)]·C₂H₅OH·2H₂O. Recrystallisation from EtOH–diethyl ether, gave a dark brown crystalline product (0.111 g, 43%); mp 268–270 °C. Found: C, 52.30; H, 7.27; N, 6.51. Calc. for C₃₆H₆₀CuN₄O₁₁S: C, 52.70; H, 7.37; N, 6.83%. $\lambda_{\text{max}}/\text{nm}$ (CH₂Cl₂) 371, 557. $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{ cm}^{-1}$) 234 (39000), 376 (12300), 556 (370). $\nu_{\text{max}}/\text{cm}^{-1}$ 1119vs (SO₄). MS (FAB, thioglycerol) m/z 734 (MH⁺, 30%). Dissolution of the product in ethanol then layering with diethyl ether produced dark brown block crystals of [Cu(1)(SO₄)]·2C₂H₅OH·½H₂O suitable for X-ray diffraction.

[Cu(4)(SO₄)]·5H₂O. Recrystallisation from pentane–diisopropyl ether gave the product as a dark brown solid (0.255 g, 87%); mp 223 °C. Found: C, 51.96; H, 7.05; N, 6.33. Calc. for C₃₆H₆₄CuN₄O₁₁S: C, 52.44; H, 7.82; N, 6.79%. $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{mol}^{-1} \text{ cm}^{-1}$) 234 (33100), 378 (10100), 555 (320). $\nu_{\text{max}}/\text{cm}^{-1}$ 1120vs (SO₄). MS (FAB, NOBA) m/z 734 (MH⁺, 30%).

[Cu(5)(SO₄)]·4H₂O. Recrystallisation from hexane–diisopropyl ether gave the product as a dark brown solid (0.254 g, 96%); mp 200–203 °C. Found: C, 59.74; H, 7.34; N, 5.65. Calc. for C₄₆H₆₆CuN₄O₁₀S: C, 59.37; H, 7.15; N, 6.02%. $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{mol}^{-1} \text{ cm}^{-1}$) 233 (46800), 254 (41700), 400 (13800), 617 (250). $\nu_{\text{max}}/\text{cm}^{-1}$ 1118vs (SO₄). (FAB, NOBA) m/z 858 (MH⁺, 20%).

[Ni(5)(SO₄)]·4.5H₂O. Recrystallisation from CH₂Cl₂–diisopropyl ether gave the product as olive green crystals (0.224 g, 85%); mp >270 °C (decomp.). Found: C, 59.04; H, 7.14; N, 5.86. Calc. for C₄₆H₆₇N₄NiO_{10.5}S: C, 59.10; H, 7.22; N, 5.99%. $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{mol}^{-1} \text{ cm}^{-1}$) 231 (43700), 382 (12100). $\nu_{\text{max}}/\text{cm}^{-1}$ 1121vs (SO₄). MS (FAB, NOBA) m/z 845 (MH⁺, 40%). Dissolution of the product in dichloromethane and layering with hexane produced olive green needle-like crystals of [Ni(5)(SO₄)]·4CH₂Cl₂ that were suitable for X-ray diffraction.

[Zn(5)(SO₄)]·4H₂O. Recrystallisation from pentane–diisopropyl ether gave a yellow powder (0.193 g, 69%); mp 190–195 °C. Found: C, 59.12; H, 6.64; N, 5.84. Calc. for C₄₆H₆₆N₄ZnO₁₀S: C, 59.25; H, 7.09; N, 6.01%. $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{ cm}^{-1}$) 237 (54100), 394 (10600). $\nu_{\text{max}}/\text{cm}^{-1}$ 1120vs (SO₄). MS (FAB, NOBA) m/z 859 (MH⁺, 50%).

Neutral complexes

The preparation of the neutral copper(II) complexes of ligands **4** and **5** was achieved by using Cu(CH₃CO₂)₂·4H₂O as the source of copper in the procedure outlined above.

[Cu(4–2H)]·4H₂O. Recrystallisation from CH₂Cl₂–diisopropyl ether gave a dark brown solid (0.208 g 98%); mp 196–198 °C. Found: C, 60.89; H, 8.64; N, 7.77. Calc. for C₃₆H₆₀CuN₄O₆: C, 61.03; H, 8.54; N, 7.91%. $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{mol}^{-1} \text{ cm}^{-1}$) 236 (38500), 380 (9200), 567 (380). MS (FAB, NOBA) m/z 636 (MH⁺, 100%). Dissolution of the product in dichloromethane

and layering with diethyl ether produced dark brown block crystals of [Cu(4–2H)] suitable for X-ray diffraction.

[Cu(5–2H)]·3H₂O. Recrystallisation from CH₂Cl₂–diisopropyl ether gave a dark brown solid (0.236 g, 99%); mp 165–167 °C. Found: C, 68.10; H, 7.55; N, 6.42. Calc. for C₄₆H₆₂CuN₄O₅: C, 67.83; H, 7.67; N, 6.88%. $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{mol}^{-1} \text{ cm}^{-1}$) 231 (42800), 286 (26000), 410 (10900), 649 (341). MS (FAB, NOBA) m/z 761 (MH⁺, 50%).

Metal salt extraction studies

Ligand recycling. Ligand **6** was taken through the loading/stripping protocol outlined in Scheme 2 as follows.

(i) *Loading.* A 0.0100 M chloroform solution of ligand **6** (15.00 cm³) was intimately mixed with a 1 M (approx) aqueous solution of copper(II) sulfate (15 cm³) at room temperature for 24 h. The mixture was allowed to separate and a sample (1.00 cm³) of the dark brown chloroform solution was removed for ICP-OES analysis to determine the copper and sulfur content.

(ii) *Copper stripping.* The remaining chloroform solution was isolated and mixed intimately with an aqueous solution adjusted to pH 1.0 (H₂SO₄) for 24 h at room temperature. The mixture was allowed to separate and an aliquot (1.00 cm³) of the resulting bright yellow chloroform solution was removed for copper and sulfur analysis by ICP-OES.

(iii) *Sulfate stripping.* The remaining chloroform solution was mixed intimately with water adjusted to pH 10 (NH₃) for 24 h at room temperature and, after separation of the phases, an aliquot (1.00 cm³) of the chloroform phase was removed for copper and sulfur analysis by ICP-OES.

(iv) *Reloading.* The remaining chloroform solution was mixed intimately with an aqueous 1 M CuSO₄ solution for 24 h at room temperature before sampling for analysis.

The pH dependence of copper and sulfate loading. A 0.01 M chloroform solution of ligand **6** (60.0 cm³) was intimately mixed with a 1 M aqueous solution of copper(II) sulfate (60.0 cm³) at room temperature for 24 h and then the phases were allowed to separate. Aliquots (5.00 cm³) were removed from the organic fraction and separately mixed with water (5.0 cm³) that had been adjusted with aqueous H₂SO₄/aqueous NH₃ to produce pH values that, after mixing for 24 h, fell in the range 1–11. After separation, a 1.00 cm³ aliquot was removed from each of the chloroform solutions for copper and sulfur analysis.

Membrane transport

The transport experiments employed a ‘concentric cell’ in which the aqueous source phase (10 cm³) and receiving phase (30 cm³) were separated by a chloroform phase (50 cm³). Details of the cell design have been reported elsewhere.⁷ For each experiment both aqueous phases and the chloroform phase were stirred separately at 10 rpm and the cell was enclosed by a water jacket and thermostatted at 25 °C. The aqueous source phase was adjusted to pH 2.3 (using H₂SO₄) and contained an equimolar mixture of the metal ions (see Results and discussion section), each at a concentration of $\approx 1 \times 10^{-2} \text{ mol dm}^{-3}$. The chloroform phase contained ligand **6** ($1 \times 10^{-3} \text{ mol dm}^{-3}$). The receiving phase was adjusted to pH 1.3 using H₂SO₄. All transport runs were terminated after 24 h and atomic absorption spectroscopy was used to determine the amount of metal ion transported over this period. The transport results are quoted as the average valued obtained from four parallel runs (error $\pm 10\%$).

Collection and reduction of X-ray data

Data for **1** were collected at 150 K on a Bruker SMART APEX CCD diffractometer using graphite monochromated Mo-K_α radiation ($\lambda = 0.71073 \text{ \AA}$). Data for **2**, [Cu(4–2H)],

Table 1 Crystallographic data

	1	2	5	[Cu(1)(SO ₄)]·2C ₂ H ₅ OH·½H ₂ O	[Cu(4-2H)]	[Ni(5)(SO ₄)]·4CH ₂ Cl ₂
Empirical formula	C ₃₄ H ₅₀ N ₄ O ₄	C ₄₁ H ₆₃ N ₄ O ₄	C ₄₆ H ₅₈ N ₄ O ₂	C ₃₈ H ₆₃ CuN ₄ O _{10.5} S	C ₃₆ H ₅₂ CuN ₄ O ₂	C ₅₀ H ₆₆ Cl ₈ N ₄ NiO ₆ S
<i>M</i>	578.78	675.95	698.96	840.53	636.36	1193.44
Crystallographic system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Tetragonal
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>P1</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P4₂/2₁</i>
<i>a</i> /Å	32.080(7)	24.786(3)	9.0272(5)	16.2663(7)	15.934(8)	18.1205(16)
<i>b</i> /Å	10.430(2)	12.9082(15)	11.5800(8)	14.7419(11)	17.260(7)	18.1205(16)
<i>c</i> /Å	20.871(5)	26.542(4)	20.5591(13)	17.4166(7)	12.692(9)	35.052(6)
<i>a</i> / ^o	90	90	74.237(3)	90	90	90
<i>b</i> / ^o	108.156(4)	91.715(18)	78.507(4)	96.663(4)	100.63(4)	90
<i>γ</i> / ^o	90	90	85.200(3)	90	90	90
<i>V</i> /Å ³	6636(3)	8488(2)	2025.9(2)	4148.2(4)	3430(3)	11510(2)
<i>D</i> _c /g cm ⁻³	1.159	1.058	1.146	1.344	1.232	1.377
<i>Z</i>	8	8	2	4	4	8
<i>F</i> (000)	2512	2952	756	1796	1364	4976
<i>μ</i> /mm ⁻¹	0.076	0.531	0.070	1.715	1.171	4.636
Independent reflections (<i>R</i> _{int})	6799 (0.0517)	7339 (0.0593)	5300 (0.1327)	6083 (0.0218)	4973 (0.0843)	8317 (0.0900)
No. parameters	387	434	478	506	395	523
Goodness of fit on <i>F</i> ²	0.906	0.944	0.960	1.013	1.037	0.930
<i>R</i>	0.0853	0.0720	0.0551	0.0462	0.0823	0.1069
<i>wR</i> ₂	0.2176	0.2059	0.1346	0.1263	0.2613	0.2957
Largest difference peak and hole/e Å ⁻³	0.781 and -0.249	0.237 and -0.209	0.240 and -0.184	0.463 and -0.410	0.785 and -0.968	1.016 and -0.766

[Cu(1)(SO₄)]·2C₂H₅OH·½H₂O and [Ni(5)(SO₄)]·4CH₂Cl₂ were collected at 220 K on a Stoe Stadi-4 4-circle diffractometer using graphite monochromated Cu-K_α radiation ($\lambda = 1.54173$ Å). Data for **5** and [Ni(5)(SO₄)]·4CH₂Cl₂ were collected at 150 K on a Nonius Kappa CCD diffractometer using graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Structures **1**, **2**, **5**, [Ni(5)(SO₄)]·4CH₂Cl₂ and [Cu(1)(SO₄)]·2C₂H₅OH·½H₂O were solved by direct methods (**1** and **5** using SHELXTL,⁸ **2**, [Ni(5)(SO₄)]·4CH₂Cl₂ and [Cu(1)(SO₄)]·2C₂H₅OH·½H₂O using SIR92⁹) and structures [Cu(4-2H)] and [Ni(5)(SO₄)]·4CH₂Cl₂ were solved by Patterson methods ([Cu(4-2H)] using SHELXTL⁸ and [Ni(5)(SO₄)]·4CH₂Cl₂ using DIRDIF¹⁰). All structures were refined against *F*² using a full matrix least squares procedure (SHELXTL).⁸ Absorption corrections were applied for **2** and [Cu(1)(SO₄)]·2C₂H₅OH·½H₂O using azimuthal measurements, and for [Ni(5)(SO₄)]·4CH₂Cl₂ using Gaussian integration. Absorption corrections were applied for **1**, **5** and [Ni(5)(SO₄)]·4CH₂Cl₂ using the multi-scan method of Blessing¹¹ (SADABS¹² for **1**, SORTAV¹¹ for **5** and [Ni(5)(SO₄)]·4CH₂Cl₂). Azimuthal measurements were performed for [Cu(4-2H)] but were very flat and were not applied.

The quaternary ammonium hydrogen atoms in the structures of [Cu(1)(SO₄)]·2C₂H₅OH·½H₂O were located on the difference map and fully refined, as were the phenolic hydrogen atoms in the structures of ligands **1** and **4**. All other hydrogen atoms were placed at calculated positions and refined as riding groups or rotating groups. The sulfate dianion in [Cu(1)(SO₄)]·2C₂H₅OH·½H₂O was refined as disordered over two sites in an occupancy ratio of 75 : 25, with the lower occupancy site being refined isotropically. 1346 electrons per unit cell in [Ni(5)(SO₄)]·4CH₂Cl₂ were modelled as 4 molecules of diffuse dichloromethane solvent per asymmetric unit, using the method of van der Sluis and Spek¹³ and the program PLATON.¹⁴ All other non-H atoms were included with anisotropic displacement parameters and final refinement statistics are presented in Table 1. The ORTEP¹⁵ plots displayed in Fig. 3–7 show 30% probability ellipsoids.

CCDC reference numbers 197885–197890.

See <http://www.rsc.org/suppdata/dt/b2/b207015b/> for crystallographic data in CIF or other electronic format.

Results and discussion

Ligand structures

The route to this type of 'salen-like' ligand, carrying pendant morpholine groups, has been described in a previous publication.³ Some of the new ligands reported here have pendant piperidine groups. This modification leads to an increase in solubility in non-polar organic solvents, a property of great importance to the solvent extraction studies discussed below.

The crystal structure of the ethane-bridged ligand **1** (Fig. 3) shows that it has an extended conformation which does not have the pendant morpholine groups arranged well for encapsulation of a sulfate ion. The intermolecular distances between the N62 amino nitrogen atoms in the two crystallographically independent molecules are 12.158(5) Å and 12.170(5) Å, comparable to 11.771(4) Å in the cyclohexane-bridged analogue **2**. An even more extended structure is observed¹⁶ in **7** which has a torsion angle of 180° about the central bond of the ethane bridge (Table 2). Incorporation of a metal ion into the salen²⁻ binding site of these ligands significantly changes³ the disposition of the pendant amine groups aligning them more effectively for sulfate binding (see below).

Ligands with a planar N₂O₂²⁻ salen-type donor set form very stable copper(II) complexes (see below). In order to facilitate the removal of copper from these binding sites, rigid bridging units could be incorporated which alter¹⁷ the disposition of the NO⁻ coordination planes to generate distortions from square

Table 2 Parameters defining the dispositions of the pendant tertiary amine atoms N62 and N62A in the ligands **1**, **2**, **5** and **7** and the complexes [Cu(**4**–2H)], [Cu(**1**)(SO₄)] and [Ni(**5**)(SO₄)]

	1 ^a	1 ^a	2	5	7 ^b	[Cu(4 –2H)]	[Cu(1)(SO ₄)]	[Ni(1)(SO ₄)]	[Ni(5)(SO ₄)]
N62 ⋯ N62A (Å)	12.158 (5)	12.170 (5)	11.771 (4)	15.203 (4)	16.22	5.789 (10)	5.294 (4)	5.163 (3)	5.904 (14)
N2–C22–C22A–N2A (°)	66.0 (4)	65.6 (4)	63.2 (3)	104.4 (4) ^c	180	39.5 (8)	29.9 (4)	38.3 (3)	50.4 (18) ^c

^a This structure has two crystallographically independent molecules of **1** per unit cell. ^b Values from ref. 16, no e.s.d.s supplied. ^c Value for the central bond of the biphenyl bridge, C22A–C27A–C27B–C22B.

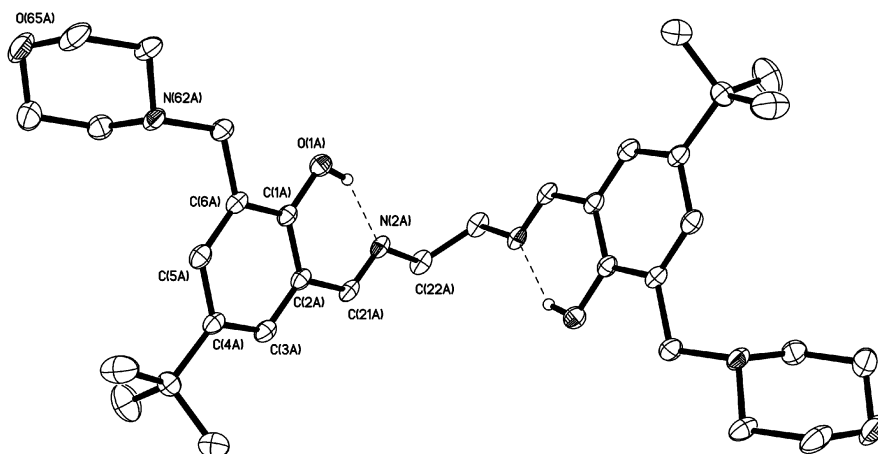


Fig. 3 An ORTEP plot of ligand **1**. The distance between the salicylaldimine chelate atoms N(2A) ⋯ O(1A) is 2.588(5) Å.

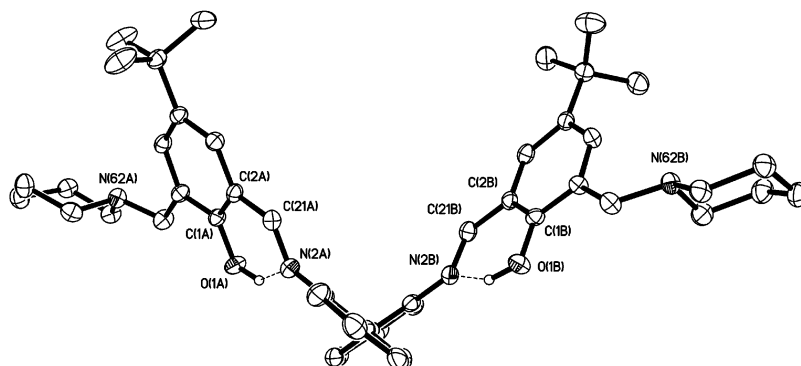


Fig. 4 An ORTEP plot of ligand **5**. The distances between the salicylaldimine chelate atoms N(2A) ⋯ O(1A) and N(2B) ⋯ O(1B) are 2.611(4) and 2.608(4) Å.

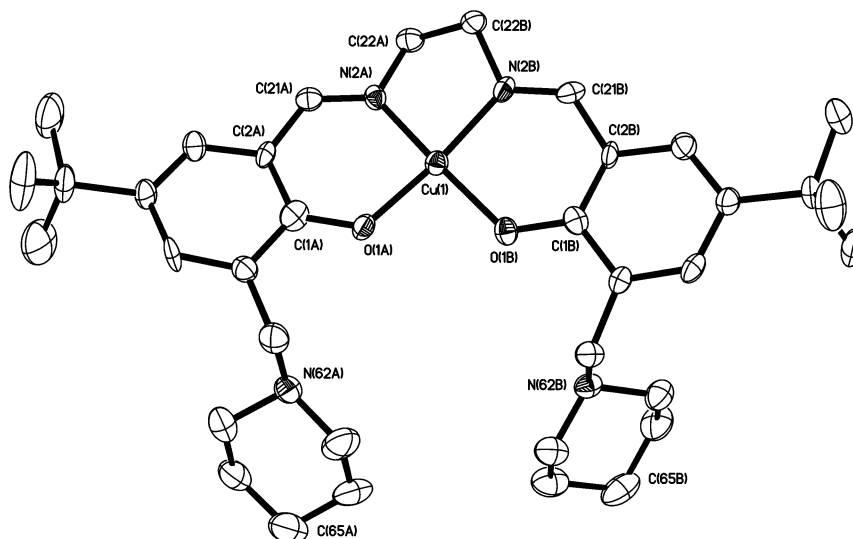


Fig. 5 An ORTEP plot of [Cu(**4**–2H)].

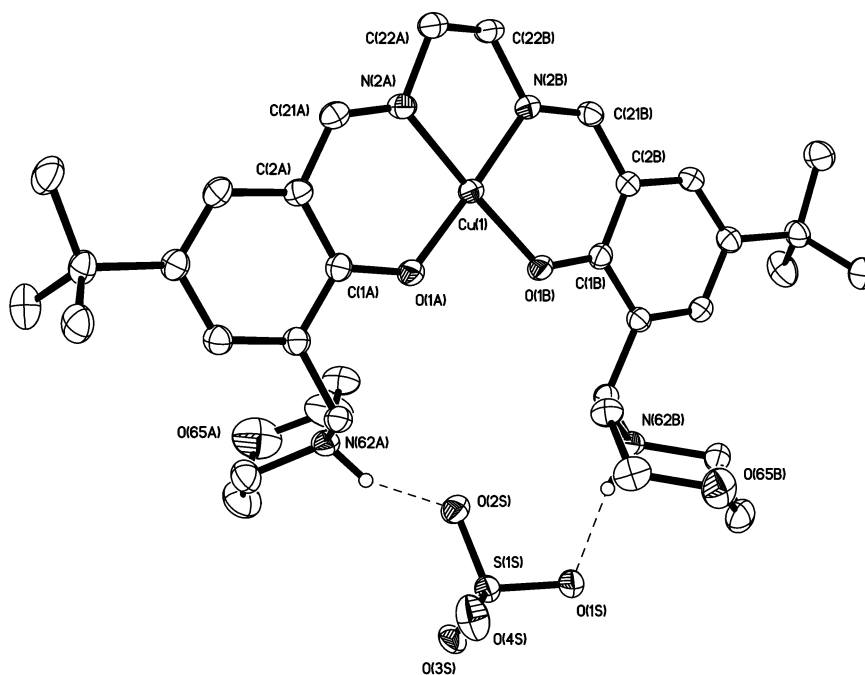


Fig. 6 An ORTEP plot of $[\text{Cu}(\mathbf{1})(\text{SO}_4)]$. For the hydrogen bonds shown $\text{N}(62\text{A}) \cdots \text{O}(2\text{S})$, 2.616(4); $\text{N}(62\text{B}) \cdots \text{O}(1\text{S})$, 2.682(3); $\text{H}(62\text{A}) \cdots \text{O}(2\text{S})$, 1.73(3); $\text{H}(62\text{B}) \cdots \text{O}(1\text{S})$, 1.79(3) Å, $\text{O}(2\text{S}) \cdots \text{H}(62\text{A})-\text{N}(62\text{A})$, 173(4) $^\circ$ and $\text{O}(1\text{S}) \cdots \text{H}(62\text{B})-\text{N}(62\text{B})$, 154(3) $^\circ$.

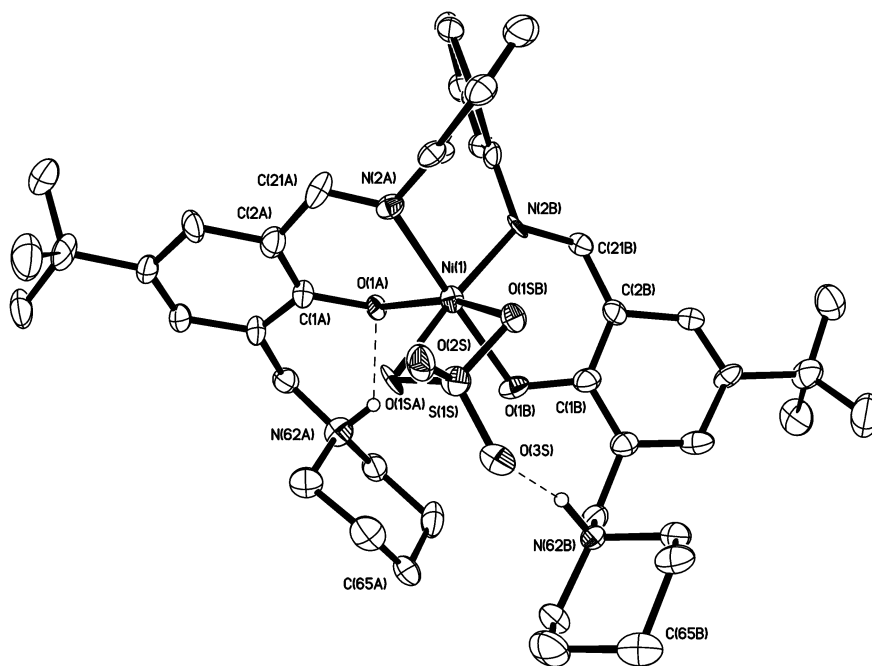


Fig. 7 An ORTEP plot of $[\text{Ni}(\mathbf{5})(\text{SO}_4)]$. For the hydrogen bonds shown $\text{N}(62\text{B}) \cdots \text{O}(3\text{S})$, 2.652(13); $\text{N}(62\text{A}) \cdots \text{O}(1\text{A})$, 2.678(13) Å.

planarity. One such group, a 2,2'-biphenylene moiety, particularly when 6,6'-substituted, favours an orthogonal arrangement of these planes and hence encourages the formation of *pseudo*-tetrahedral $\text{N}_2\text{O}_2^{2-}$ donor sets.¹⁸ The 2,2'-biphenylene-bridged ligand **5** (Fig. 4) has a dihedral angle of 104.4(4) $^\circ$ between the central phenyl groups. However, the inclination between the salicylaldimine units, which are held rigidly planar by strong intramolecular hydrogen bonding between the phenolic proton and the neighbouring imino nitrogen ($\text{N} \cdots \text{H}$ 1.66(4) and 1.73(4) Å), is 124.5 $^\circ$ because these are twisted out of the plane of their adjacent phenyl groups (see Fig. 4). It is clear from the free ligand structure that considerable strain energy would be required to define a planar $\text{N}_2\text{O}_2^{2-}$ donor set. It was assumed that this will destabilise copper-binding and hence enhance metal recovery from the loaded ligand (*vide infra*).

Metal salt complexes

The formation of divalent transition metal sulfate complexes with these ligands occurs almost immediately upon mixing in alcoholic solution. Elemental analysis and FAB mass spectrometry results confirm the formation of simple 1 : 1 : 1 metal : ligand : sulfate assemblies and these compounds exhibit characteristic absorbencies for the sulfate ion in their IR spectra. Imposition of a different coordination geometry upon the metal ion does not effect the ability of ligand **5** to form discrete metal sulfate complexes although in the case of nickel(II) the mode of metal salt binding is shown to be different as determined by crystal structure analysis of $[\text{Ni}(\mathbf{5})(\text{SO}_4)]$ (see below). The zinc(II) sulfate complex $[\text{Zn}(\mathbf{5})(\text{SO}_4)]$ is reported here to show that metal *salt* complexes can also be formed with other first row transition series metals.¹⁹ Neutral “metal-only”

Table 3 Electronic absorption spectra of ligands and metal salt complexes (CH₂Cl₂)

Compound	$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$)
4	230 (36400), 266 (50000), 324 (18200)
5	229 (39300), 276 (29600), 349 (17400)
6	230 (36700), 278 (32400), 352 (15300)
[Cu(1)(SO ₄)]	234 (39000), 376 (12300), 556 (370)
[Cu(4)(SO ₄)]	234 (33100), 378 (10100), 555 (320)
[Cu(4 –2H)]	236 (38500), 380 (9200), 567 (380)
[Cu(5)(SO ₄)]	233 (46800), 254 (41700), 400 (13800), 617 (250)
[Cu(5 –2H)]	231 (42800), 286 (26000), 410 (10900), 649 (341)
[Zn(5)(SO ₄)]	231 (43700), 382 (12100)
[Ni(5)(SO ₄)]	237 (54100), 394 (10600)

complexes, [Cu(**4**–2H)] and [Cu(**5**–2H)], can also be formed by using the acetate as the metal source, see Scheme 1. The isolation of either a metal salt or a “metal-only” complex depends on the relative basicities of the anion and the pendant tertiary amine and on the composition of the solvent system.

Electronic absorption spectroscopy

A comparison of the spectrum of the copper-only complex [Cu(**4**–2H)] with that of the corresponding copper sulfate complex, [Cu(**4**)(SO₄)], shows that sulfate binding has little effect on the electronic absorption bands in this type of complex (Table 3). This provides evidence that the cation and anion binding sites are well separated in complexes of **1**, **2**, and **4** in solution and that the anions do not interact strongly with the metal–donor chromophore. This observation is supported by the solid state structural studies (see below).

The copper complexes of **5** have different visible spectra from those of the more salen-like ligands **1** and **4**, with two features around 270 and 405 nm replacing the broad peak centred at *ca.* 380 nm for the planar complexes of **1** and **4** (see Table 3). The maximum of the weak band assigned to d–d transitions is also shifted significantly to > 617 nm from *ca.* 560 nm in the complexes of **1** and **4**. This suggests that, as expected, a different coordination environment is imposed by the biphenylene bridge in **5**. There are some small differences between the spectra of the “copper-only” and copper sulfate complexes, [Cu(**5**–2H)] and [Cu(**5**)(SO₄)] respectively, suggesting that the sulfate ion interacts weakly with the copper atom in [Cu(**5**)(SO₄)].

The nickel(II) sulfate complex of **5** is strikingly different in colour from the nickel(II) complexes³ of the “salen-like” ligands **1**–**4**, being olive green rather than a deep ruby red. This

difference can be attributed to the adoption of a *cis*-pseudo-octahedral structure incorporating a coordinate sulfate ion, confirmed by X-ray structure determination (*vide infra*). The ¹H NMR spectrum of [Ni(**5**)(SO₄)] in CDCl₃ exhibits classic paramagnetic broadening and shifting, thus supporting its formulation as a high-spin nickel(II) species in solution.²⁰

X-Ray crystallography

The structure determination of [Cu(**4**–2H)] (Fig. 5) confirms the absence of any associated anions. The CuN₂O₂ unit is approximately planar (the sum of the angles defined by *cis*-donors at the Cu atom is 361.3(8)°, with bond lengths and angles typical of those for [Cu(salen)] type complexes (Table 4).²¹ Incorporation of the copper into the salen site aligns the pendant piperidino groups such that a N62...N62 separation of 5.789(10) Å occurs compared with 12.158(5) Å and 12.170(5) Å in the related ethane-bridged free ligand **1**, and 16.22 Å in **7** (Table 2).

A comparison (Table 2) with the structure of the copper sulfate complex [Cu(**1**)(SO₄)] demonstrates how well the ligand is templated by the copper for incorporation of sulfate. This is bound between the morpholinium groups by a combination of direct electrostatic interaction as well as by two O...H–N⁺ hydrogen bonds to the ammonium nitrogen atoms N62A and N62B (Fig. 6). These O...N distances, and that in [Ni(**5**)(SO₄)] (Fig. 7) are slightly shorter than those found in [Ni(**1**)(SO₄)] which has bifurcated O₂...H–N⁺ hydrogen bonds to the sulfate.³ Protonation of the morpholine units together with sulfate-incorporation causes only minor changes in the copper geometry (Table 4). To accommodate the sulfate ion, the morpholinium groups are arranged on opposite sides of the CuN₂O₂ coordination plane creating *pseudo*-C₂ symmetry. In contrast, the copper-only structure, [Cu(**4**–2H)], has the pendant piperidines lying on the same side leading to a *pseudo*-mirror plane.

In the nickel sulfate complex³ of ligand **1** the sulfate is bound by two separate bifurcated hydrogen bonds as opposed to two single H-bonds in the copper structure, but the morpholinium N...N distances are very similar (Table 2). The sulfate is slightly closer to the metal centre than in the copper structure (M...S is 6.7996(7) Å *cf.* 6.8706(9) Å in [Cu(**1**)(SO₄)]).

It was not possible to obtain crystals suitable for structure determination of copper complexes of the ligands **5** and **6** and thus define the coordination geometry imposed by the biphenylene bridge which destabilizes extracted copper species

Table 4 Bond lengths (Å) and angles (°) in the coordination spheres of [Cu(**4**–2H)] and [Cu(**1**)(SO₄)]

	[Cu(4 –2H)]		[Cu(1)(SO ₄)]	
	Part A ^a	Part B ^b	Part A	Part B
Cu(1)–N(2)	1.909(6)	1.921(6)	1.950(3)	1.926(3)
Cu(1)–O(1)	1.881(5)	1.896(5)	1.897(2)	1.896(2)
O(1)–Cu(1)–N(2)	92.9(2)	92.9(2)	92.51(11)	93.98(10)
O(1)–Cu(1)–O(1)′	91.37(19)		88.91(9)	
N(2)–Cu(1)–N(2)	84.1(2)		84.55(11)	
O(1)–Cu(1)–N(2)′	171.0(2)		176.85(11)	
N(2)–Cu(1)–O(1)′	170.0(2)		176.80(11)	
Σ <i>cis</i> -angles	361.3(8)		360.0(5)	
N(2)–C(22)–C(22)′–N(2)′ torsion	39.3		30.1	
Inclinations (°) between the least squares plane of the N ₂ O ₂ donor set and the N(22)–C(2)–C(3)–C(1)–O(11) chelate rings	9.2	6.4	5.7	2.3
Displacement of piperidine or morpholine ring atoms (Å) from least squares plane of the N ₂ O ₂ donor set				
N(62)	0.6279	1.8447	–1.7292	0.8951
O(65) or C(65)	2.2832	4.2193	–4.5697	3.6329

^a Part A and B refer to the chemically equivalent halves of the ligand (see figures for definitions of atom labels). ^b The prime refers to the chemically equivalent atom in part B of the ligand.

Table 5 Bond lengths (Å) and angles (°) in the coordination sphere of [Ni(5)(SO₄)]

	Part A ^a	Part B ^b
Ni(1)–N(2)	2.080(9)	2.027(9)
Ni(1)–O(1)	1.966(7)	2.061(7)
Ni(1)–O(1S)	2.108(7)	2.086(7)
O(1)–Ni(1)–N(2)	89.0(4)	90.3(3)
O(1)–Ni(1)–O(1)′	93.7(3)	–
N(2)–Ni(1)–N(2)′	89.8(4)	–
O(1)–Ni(1)–N(2)′	96.0(3)	177.3(4)
O(1S)–Ni(1)–O(1)	91.9(3)	85.9(3)
O(1S)–Ni(1)–N(2)	90.9(3)	103.5(3)
O(1S)–Ni(1)–O(1S)′	68.7(3)	–
O(1S)–Ni(1)–O(1)′	160.6(3)	85.9(3)
O(1S)–Ni(1)–N(2)′	91.5(4)	172.1(3)

^a Part A and B refer to the chemically equivalent halves of the ligand (see figures for definitions of atom labels). ^b The prime refers to the chemically equivalent atom in part B of the ligand.

(*vide infra*). However, the nickel(II) sulfate complex [Ni(5)(SO₄)]·4CH₂Cl₂ crystallizes readily and has a *pseudo*-octahedral structure [Fig. 7] in which the quadridentate ligand is folded about the N(2A)–Ni–O(1B) axis. Whilst the two salicylaldimato chelate planes are not mutually perpendicular, the N₂O₂²⁻ donors are fairly close to orthogonal (Table 5). As expected, the Ni–N and Ni–O bonds are longer in this high spin six-coordinate complex (Table 5) than in related low spin four-coordinate complexes.³

The presence of the bidentate sulfate anion in the nickel(II) coordination sphere is unusual²² and appears to be favoured by the proximity of the piperidinium nitrogen atoms, which provide both electrostatic attraction and an N(62B)–H···O(3S) hydrogen bond (Fig. 7). Interestingly, the other protonated nitrogen atom N(62A) is arranged too far from the sulfate oxygens to form any hydrogen bonds and instead interacts with phenolate oxygen O(1A).

Whilst the nickel–anion–ligand package in [Ni(5)(SO₄)] provides for strong bonding of the sulfate anion, the arrangement does not have the ditopic form which meets the requirements of the loading/stripping protocol shown in Scheme 2. The extraction studies (below) and the electronic spectra of the “copper-only” and copper sulfate complexes, [Cu(5–2H)] and [Cu(5)(SO₄)], suggest that sulfate can be only weakly coordinated to the copper centre in solution. The weaker copper binding in 5 and 6 than occurs in the other ditopic ligands is presumed to result from the displacement of the N₂O₂²⁻ donor set from planarity; a dihedral angle of 37° is observed between the salicylaldimato chelating units in the copper(II) complex of the unsubstituted ligand *N,N'*-(2,2′-biphenyl)bis(salicylaldimine).¹⁸

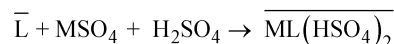
Solvent extraction of metal sulfates

It was observed that for extraction of nickel(II) by the ditopic ligands 1–6 very long equilibration times were needed. Consequently proof-of-concept for the loading/stripping protocol shown in Scheme 2 was undertaken with copper(II). The hydrophobic nonyl-substituted ligands, 3 and 6 were used in these studies.

Whilst the *o*-phenylene bridged ligand 3 gives > 95% of the theoretical Cu-loading when contacted with an excess of aqueous copper(II) sulfate solution, it proved impossible to strip the copper with 5 M sulfuric acid. The “weaker” 2,2′-biphenylene analogue, 6, meets the requirements of the flowsheet in Scheme 2; copper was loaded to > 95% of extractant capacity when a 0.01 M chloroform solution was contacted with an excess of CuSO₄ in a feed solution of pH 4.5 (no significant change in pH of the aqueous feed was observed); the loaded organic phase was stripped to < 5% of copper capacity when contacted with sulfuric acid to give an equilibrium pH = 0; the sulfate content

of the organic phase falls to < 1% of the theoretical capacity when the Cu-stripped organic is contacted with aqueous ammonia at an equilibrium pH ≥ 11.0. After one cycle of loading and stripping using this protocol the extractant 6 was reloaded to the same (> 95%) level with copper(II) sulfate, indicating that it is robust and stable to hydrolysis, oxidation and *trans*-imination when contacted with either high or low pH aqueous solutions for 24 h at room temperature. Extensive lifetimes of metal extractants under operating conditions are essential for commercial viability,¹ and tests of long term stability are in progress.¹⁹

Sulfate-loading of chloroform solutions of 6 and its copper complexes is pH dependent. As mentioned above, the ligand is converted to its free base form, or in the presence of copper salts to its “copper-only” complex, when contacted with an aqueous solution at high pH. ICP-OES analysis of chloroform solutions of both the ligand 6 and its copper complex after contacting with aqueous sulfate solutions of low pH shows their sulfur content to be greater than 1 mol per mol of 6, suggesting that HSO₄⁻ ions are also acting as counter ions for the protonated piperidinium groups under these conditions. Formation of an assembly with this stoichiometry would allow ditopic ligands of this type to transport both metal sulfate and sulfuric acid from acidic streams such as acid mine drainage streams.



The flowsheet outlined in Scheme 2 assumes that at the pH of the aqueous feed the ligand loads copper and sulfate in a 1 : 1 : 1 ratio (ligand : Cu²⁺ : SO₄²⁻). The extractant 6 shows a plateau corresponding to 1 : 1 Cu-loading in plots of loading vs. pH in the pH range 4–8 for 0.01 M chloroform solutions (see Experimental section). Sulfate loading (1 : 1 ratio) for 6 occurs in a narrow pH range and this range is very dependent on the Cu-loading levels of the organic phase. The co-operativity of sulfate/copper loading has been demonstrated recently with a related series of ligands.²³

Bulk membrane transport of metal sulfates

Competitive mixed-metal transport experiments (water/chloroform/water) have been undertaken employing 6 as the ionophore in the membrane (chloroform) phase. The aqueous source phase contained equimolar concentrations of cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) (see Experimental section). The respective pH values used for the aqueous source (pH 2.3) and receiving (pH 1.3) phases were chosen such that they span the pH_{1/2} value observed for copper sulfate loading (see Fig. 8). Under these conditions it was

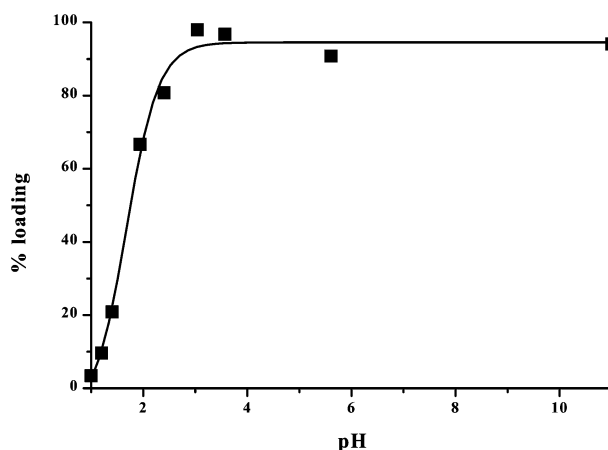


Fig. 8 Copper loading of ligand 6 as a 0.01M solution in chloroform after 24 h contacting with 1 M aqueous CuSO₄ as a function of the equilibrium pH of the aqueous phase.

assumed that both the metal-free and metal-loaded forms of **6** will be protonated and carry sulfate/bisulfate counter ions and that the resulting pH gradient across the cell will be favourable for uptake of (at least) this ion from the source phase into the membrane phase while promoting its loss from the membrane phase into the receiving phase. Overall transport (see below) was sufficiently low that no buffering was needed to maintain the pH gradient (no detectable change in the pH of each aqueous phase was observed over the 24 h used for each experiment).

Under the conditions employed, *sole* transport selectivity for copper(II) was observed over the other four metals present in the source phase. This is consistent with the CuSO₄ complex of **6** being thermodynamically favoured in the organic phase – a result in accordance with the expected Irving–Williams stability order for complexes of the present metal ion series.

Conclusions

Co-extraction of copper and sulfate has been confirmed using the hydrophobic ditopic ligand **6** and it has been shown that these can be stripped back into an aqueous medium, regenerating the ligand, by pH adjustment. The efficient sulfate extraction arises from the templating of the pendant tertiary ammonium groups by complexation of the backbone of the ligand to the copper.²³ These results have established the feasibility of using simple and inexpensive extractants based on salicylaldehydes to transport metal sulfates in flowsheets for primary metal recovery from sulfidic ores following pressure leaching. Good selectivity of sulfate transport, high hydrolytic stability of the ligands and fast metal salt complexation/decomplexation and phase transfer will also be needed if reagents of this type are to find application in robust and environmentally attractive processes. Development of reagents to meet these requirements can only be done effectively by collaboration with engineering companies and extractant suppliers who have a knowledge of the composition of process streams and expertise in formulation of hydrocarbon-based reagents.

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