COMMUNICATION

## 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]

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Linking salicylaldimine units with a 2,9-diazadecane strap in high yields *via* a simple Mannich condensation generates a ligand which forms 2:2:1 assemblies of Cu : L : anion in which the anion is encapsulated in a tetra-cation cavity.

As part of a programme to develop metal recovery processes based on transporting metal *salts* we have shown<sup>1,2</sup> that relatively simple systems derived from salicylaldimines can exist in a zwitterionic form (Scheme 1), providing separate binding sites for a metal cation and its attendant anion.



Scheme 1 Schematic represention of sequestration of a divalent transition metal sulfate salt, followed by stepwise stripping of first the metal with acid and then the sulfate anion with ammonia.

Appropriate forms of the ligands 1 (Scheme 2) are good extractants for base metal sulfates and can be used in the load/ strip circuit outlined in Scheme 1, recycling the ligand.<sup>3-5</sup> As the efficiency of commercial processes based on such reagents will depend on the selectivity of both cation and anion transport we have investigated methods to increase the pre-organisation of the anion binding site. One approach involves introducing a strap, as in 2 (Scheme 2), between the pendant amino groups which on protonation bind the sulfate ion. These ligands can easily be prepared from commercially available salicylaldydes using the "bottom-up" route (Scheme 2).

Straps between the aminomethyl substituents on the salicylaldimine units are readily incorporated using a Mannich condensation of the appropriate long chain secondary diamine, and the diimines are obtained in overall yields of >80%from the salicylaldehydes. These systems are related to the dicompartmental "Robson" ligands<sup>6,7</sup> and the precursor dialdehyde can be converted to macrocyclic systems by reaction with appropriate diamines in step 2b.<sup>8</sup> Complexes analysing for 1 : 1 combinations of Cu(II) salts and ligand **2** are readily isolated from the methanolic reaction mixtures *via* slow precipitation with diethyl ether. ‡

 $R_2$ . R<sub>6</sub> R 1(a) where  $R_1 = hexyl$ ,  $R_2 = methyl$ ,  $R_3 = t$ -butyl,  $R_4 = Ph$ (2) 2(b) 2(a) 1(b) 0 0 OH HC R<sub>5.</sub> ٦N - $R_2$ ОН HC Bottom-up R<sub>6</sub> Ŕ  $R_5 = en, o-C_6H_4, trans-cyclohexane$ where R<sub>6</sub> = hexyl, piperidine

 $R_4 R_4$ 

он но

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Top-down

(1)

Scheme 2 The top-down and bottom-up synthetic routes. (1a) Ethoxy-*N*-dihexylamine methane, CH<sub>3</sub>CN, reflux, 72 h; † (1b) 1,2-ethylenediamine, CH<sub>3</sub>CN, 12 h; (2a) N,N'-bis(ethoxymethyl)-N,N'-dimethylhexane-1,6-diamine, CH<sub>3</sub>CN, reflux, 72 h; (2b) PhNH<sub>2</sub>, CH<sub>3</sub>CN, 12 h.

An X-ray structure determination of the CuSO<sub>4</sub> complex 4§ shows this to be made up of two ligands in their zwitterionic forms (deprotonated phenols and protonated amines), two Cu(II) metal centres and two SO<sub>4</sub><sup>2-</sup> anions, one of which is encapsulated inside the complex (Fig. 1). Each ligand is orientated in a helical fashion with its terminal NO-chelating unit addressing different Cu atoms and the  $-N(CH_2)_6N-$  'straps' connecting both metal centres, with the long amine wrapped around the encapsulated sulfate anion. The four trialkyl-ammonium N–H groups are all directed towards the SO<sub>4</sub><sup>2-</sup> group, forming medium to strong H-bonds (N ··· O distances, 2.65–3.23 Å) with it. The second sulfate acts as a counter ion and lies outside the complex.

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**Fig. 1** The structure of  $[Cu_2L_2(SO_4)]^{2+}$ , cation of (4) in the solid-state (H atoms have been removed for clarity). Atom disorder of approx. 50% was modelled for two atoms in one of the hexyl chains, the encapsulated sulfate anion and one *tert*-butyl group. Selected bond lengths (Å) and angles (°): Cu(1)–O(1A) 1.901(4), Cu(1)–O(1B) 1.899(4), Cu(1)–N(2A) 2.026(5), Cu(1)–N(2B) 2.083(5), Cu(1)–O(1S) 2.165(4), Cu(2)–O(1D) 1.870(5), Cu(2)–O(1C) 1.880(5), Cu(2)–O(1C) 2.064(5), Cu(2)–O(2C) 2.066(5), Cu(2)–O(2S) 2.188(10), Cu(2)–O(2S') 2.305(8); O(1A)–Cu(1)–N(2A) 91.5 (2), O(1B)–Cu(1)–N(2B) 91.3(2), O(1C)–Cu(2)–N(2D) 91.7(2), O(1D)–Cu(2)–N(2C) 92.7(2).

Each copper atom has a distorted trigonal-bipyramidal coordination environment, with the O(phenolate)–Cu–O(phenolate) angles approximately linear (173 and 170°). The equatorial Cu–N(imine) (2.026–2.083 Å) and the somewhat longer Cu–O(sulfate) bonds (2.165 and 2.188 Å) complete the distorted  $D_{3h}$  symmetry (av. 119.7°). The encapsulated sulfate anion occupies a cavity that can be thought of as a cylinder with a height of 6.4 Å (Cu ··· Cu) and a diameter of 7.7 Å (N ··· N) giving an approximate volume of 300 Å<sup>3</sup>.

The ligand architecture is similar in the related tricationic tetrafluoroborate complex ¶  $[Cu_2L_2(BF_4)]^{3+}$  of (5), but the encapsulated  $BF_4^-$  is not coordinated to the copper atoms which have tetrahedrally distorted "planar" *trans*-N<sub>2</sub>O<sub>2</sub><sup>2-</sup> donor sets (Fig. 2). The encapsulated  $BF_4^-$  anion forms H-bonds with the alkyl ammonium protons, but these are weaker (N · · · F = 2.890–3.579 Å) than in the sulfate complex as would be expected. The volume of the "cylindrical" cavity is larger (330 Å<sup>3</sup>).

The UV/Vis spectra of the  $BF_4^-$  and  $ClO_4^-$  complexes in methanol (Fig. 3) are very similar, in accordance with the solid state structure of  $[Cu_2L_2(BF_4)]^{3+}$  which suggests only a very weak interaction of the anion with the copper centres. There are small but significant differences in the spectrum of the  $SO_4^{2-}$  complex consistent with a pertubation of the charge transfer bands of the copper centres by coordinated  $SO_4^{2-}$ . This imples that the 2 : 2 : 1 assemblies of Cu : L : anion are maintained in solution. Further evidence for the stability of the assemblies is obtained from FAB mass spectrometry results. For 4 there are peaks due to the parent ion,  $[Cu_2L_2(SO_4)]SO_4$ and for the parent ion less one sulfate. No peaks are seen for the parent less two sulfate ions, because major fragmentation results once the central stabilising sulfate is lost from the assembly.

The coordination chemistry of the "strapped" systems described above confirms the effectiveness of using ligand zwitterions to complex metal *salts*. The ease of synthesis of such systems from commercial precursors using Mannich reactions offers the possibility of tuning the selectivity of anion-complexation by varying the geometry and functionality of the strap and exploiting the templating role of the metal cations in the salicylaldimato sites.



Fig. 2 Molecular structure of  $[Cu_2L_2(BF_4)]^{3+}$ , cation of (5) (H atoms have been removed for clarity). Selected bond lengths (Å) and angles (°): Cu(1)–O(1A) 1.891(5), Cu(1)–O(1B) 1.903(5), Cu(1)–N(2B) 1.993(6), Cu(1)–N(2A) 1.993(6), Cu(2)–O(1D) 1.898(4), Cu(2)–O(1C) 1.908(4), Cu(2)–N(2D) 2.000(5), Cu(2)–N(2C) 2.003(5); O(1A)–Cu(1)–N(2A) 94.4(2), O(1B)–Cu(1)–N(2B) 92.9(2), O(1C)–Cu(2)–N(2D) 94.0(2), O(1D)–Cu(2)–N(2C) 93.1(2).



Fig. 3 Comparison of the UV/Vis spectra of the Cu(II) complexes 4, 5 and 6 in methanol (20 °C, 1 mmol).

## Notes and references

† Prepared by an adaption of the method of Fenton and coworkers.<sup>9</sup> ‡ Satisfactory C, H, N, analysis was obtained for  $[Cu_2L_2(SO_4)]SO_4$ 4 (expected: C, 63.3; H, 7.0; N, 6.7. Found: C, 63.2; H, 7.0; N, 6.7%),  $[Cu_2L_2(BF_4)](BF_4)_3 \cdot 2H_2O$  5 $\cdot 2H_2O$  (expected: C, 56.8; H, 6.5; N, 6.0. Found: C, 57.0; H, 6.2; N, 5.8%) and  $[Cu_2L_2(ClO_4)](ClO_4)_3 \cdot 2H_2O$ 6 $\cdot 2H_2O$  (expected: C, 55.3; H, 6.3; N, 5.8. Found: C, 55.3; H, 6.0; N, 5.4%).

§ Diffusion of diisopropyl ether vapours into a saturated methanol solution of **4** produced green plate crystals suitable for X-ray diffraction. The structure was solved by Patterson methods (DIRDIF)<sup>10</sup> and refined against  $F^2$  (SHELXL-97).<sup>11</sup> Crystal data for **4**: C<sub>88</sub>H<sub>116</sub>N<sub>8</sub>O-<sub>12</sub>Cu<sub>2</sub>S<sub>2</sub>, M = 1669.1, orthorhombic, space group *Pbca*, a = 16.980(3), b = 25.614(5), c = 48.948(10) Å, V = 21289(7) Å<sup>3</sup>, Z = 8,  $D_c = 1.042$  g cm<sup>-3</sup>,  $\mu$ (Mo-Ka) = 0.491 mm<sup>-1</sup>, 18770 unique reflections measured ( $R_{int} = 0.0735$ ), 1008 parameters, 39 restraint, largest difference peak 1.00 e Å<sup>-3</sup>, final  $R_1[I > 4\sigma(I)] = 0.102$ ,  $\omega R_2 = 0.320$ , goodness of fit on  $F^2 = 1.008$ . Diffuse solvent was treated in the manner described by Van der Sluis and Spek.<sup>12</sup> CCDC reference number 191879.

¶ Diffusion of diethyl ether vapours into a saturated methanol solution of **5** produced brown block crystals suitable for X-ray diffraction. Crystal data for **5**·1.5(CH<sub>3</sub>OH)·1.5(CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub>)·0.625H<sub>2</sub>O: C<sub>88</sub>H<sub>116</sub>N<sub>8</sub>O<sub>4</sub>Cu<sub>2</sub>B<sub>4</sub>F<sub>16</sub>·1.5(CH<sub>3</sub>OH)·1.5(CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub>)·0.625H<sub>2</sub>O, M = 1990.4, triclinic, space group  $P\bar{I}$ , a = 13.636(3), b = 18.598(4),

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c = 22.746(5) Å, a = 90.040(3),  $\beta$  = 106.749(3),  $\gamma$  = 101.869(3)°, V = 5394(2) Å<sup>3</sup>, Z = 2,  $D_c = 1.225$  g cm<sup>-3</sup>,  $\mu$ (Mo-K $\alpha$ ) = 0.474 mm<sup>-1</sup>, 21671 unique reflections measured ( $R_{int} = 0.0445$ ), 1216 parameters, 1 restraint, largest difference peak 1.42 e Å<sup>-3</sup>, final  $R_1[I > 4\sigma(I)] = 0.106$ ,  $\omega R_2 = 0.328$ , goodness of fit on  $F^2 = 1.045$ . CCDC reference number 191880. See http://www.rsc.org/suppdata/dt/b2/b208062a/ for crystallographic data in CIF or other electronic format.

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