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Compartmental Schiff-base ligands as selective double-loaded extractants for copper(II)†

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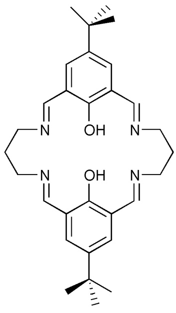
The Robson compartmental macrocyclic ligand derived from the condensation of derivatives of 2,6-diformylphenol and diamines has been prepared for the first time in its free ligand form; competitive three-phase transport and two-phase extraction studies confirm high double-loaded selectivity for the binding and delivery of Cu(II).

The Robson macrocycle has been extensively studied since the first report in 1970 of its synthesis *via* the metal-templated Schiff-base condensation of 2,6-dialdehyde- or 2,6-diketophenol with an appropriate diamine,[1] and a vast literature of complexation chemistry has been reported for these and related ligands.[2] In the absence of a metal ion, however, the cyclised product is not isolated, although more recently the diprotonated salt $[H_4L]^{2+}$ has been prepared *via* cyclisation of components under acidic conditions.[3] We report herein the first synthesis and isolation of the genuine free ligand H_2L† and its use for the selective and highly efficient extraction and transport of Cu(II).



H_2L

Reaction of equimolar amounts of 2,6-diformyl-4-*tert*-butylphenol and 1,3-diaminopropane with an excess of aqueous HBr in MeOH followed by the addition of excess NH_4PF_6 affords an orange precipitate. This was recrystallised from MeCN/diethyl ether to afford $[H_4L](PF_6)_2$ which was characterised crystallographically.§ Treatment of a vigorously stirred solution of $[H_4L](PF_6)_2$ in MeCN with five equivalents of Et_3N results in a rapid change of colour from orange to yellow leading to the formation of a yellow precipitate. The solid was collected, washed with mother liquor and dried under suction. The IR spectrum of the product shows an intense absorption at 1639 cm^{-1} assigned to the C=N bond stretching vibration which is shifted to higher energy than the corresponding absorption for $[H_4L](PF_6)_2$. The EI mass spectrum shows a peak at *m/z* 488 assigned to $[H_2L]^+$, and ^1H NMR spectroscopy confirms the assignment of the product as the free Robson ligand $[H_2L]$, which we anticipate has a zwitterionic structure.

We were interested in monitoring the metal extraction and transport of this ditopic receptor, particularly given that its monotopic oxime analogue is used commercially as a selective extractant for Cu(II) *via* the formation of a 1:2 metal:ligand complex. We were especially interested in determining whether $[H_2L]$ would act as a 'double-loaded' extractant for the selective binding of two Cu(II) centres, thus affording a more efficient extraction *via* a 2:1 metal:ligand protocol. Transport experiments employed a 'concentric cell' in which the aqueous source phase (10 cm^3) and receiving phase (30 cm^3) were separated by a $CHCl_3$ phase (50 cm^3). Details of the cell design have been reported elsewhere.[4] For each experiment both aqueous and $CHCl_3$ phases were stirred separately at 10 rpm at 25 °C. The aqueous source phase consisted of an equimolar mixture of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ag(I) and Pb(II) as their nitrate salts dissolved in a pH 4.7 buffer solution (MeCOOH/NaOOCMe).[5] The initial concentration of each metal ion in the source phase was 10^{-2} mol dm^{-3}. The $CHCl_3$ phase contained $[H_2L]$ at 1×10^{-3} mol dm^{-3}. The aqueous receiving phase was buffered at pH 3.0 (HCOOH/HCOONa).[5] All transport runs were terminated after 24 h and the amount of metal ion transported into the receiving phase over this period was determined. The quoted copper transport rate ($J = 2.0 \times 10^{-7}$ mol h^{-1}) is an average taken from duplicate runs (error ±5%) and represents the mean value measured over 24 h. Transport was performed against a back gradient of protons, and under the conditions employed, H_2L yielded highly selective transport of Cu(II) (Fig. 1).

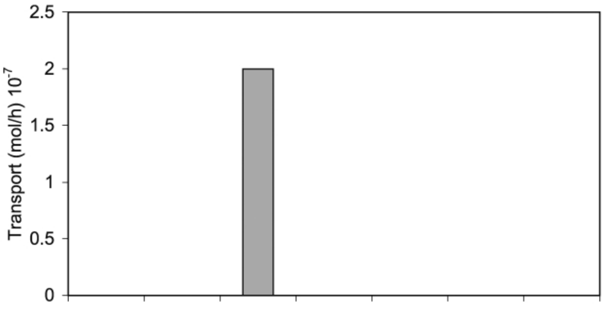


Fig. 1 Result of the competitive seven-metal three-way transport experiment (water/chloroform/water) at 25 °C.

In order to provide more insight into the nature of the transport behaviour exhibited in the bulk membrane experiment, a parallel two-phase extraction experiment was performed in which the conditions employed mirrored those used for the three-phase transport system with the aqueous phase containing equimolar concentrations of the above seven metals. The results confirm that after 24 h significant selectivity for Cu(II) was again apparent with 81% of Cu(II) initially present in the aqueous phase being extracted into the $CHCl_3$ phase together with a minor amount of Zn(II) (3.7%) and a trace of Cd(II) (Fig. 2). H_2L is seen to be an efficient extraction reagent

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† Electronic supplementary information (ESI) available: synthetic and spectroscopic data. See http://www.rsc.org/suppdata/cc/b1/b109635b/
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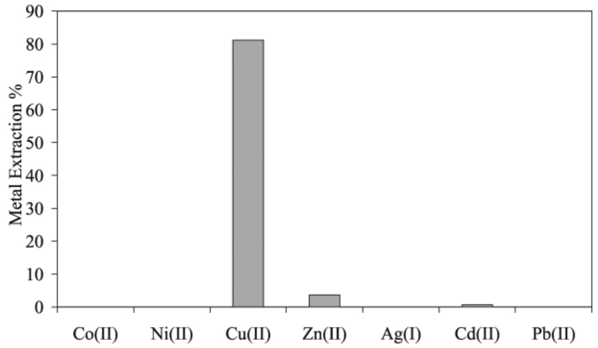

Fig. 2 Result of the competitive seven-metal two-way extraction experiment (water/chloroform) at 25 °C.

(approximately 85 percent of the ligand sites are occupied under the conditions employed) showing high specificity for Cu(II), thus paralleling the behaviour observed for the corresponding transport system.

In order to probe the binding of Cu(II) to H_2L, two equivalents of $Cu(OAc)_2 \cdot H_2O$ were treated with one equivalent of $[H_4L](PF_6)_2$ and excess Et_3N in MeCN/EtOH was added. A dark green solution resulted from which $[Cu_2(L)(MeCN)_2](PF_6)_2$ was isolated. A single crystal X-ray structure§ confirms a highly unusual dimeric structure incorporating a distorted Cu_4O_4 cubane 'core'. The Cu···Cu separation is 3.119 Å within each Cu_2O_2 unit with each Cu^{II} ion in a tetragonally distorted octahedral environment, Cu–N = 1.975(11), Cu–O = 1.992(7), Cu–N(MeCN) = 2.33(2) Å. The coordination sphere about each Cu(II) ion is completed by a long-range interaction to the phenoxy O-donor from the macrocycle in the other half of the cluster, Cu···O = 3.115 Å. While the long-range interactions between the two Cu_2O_2 units in each dimer are too long to be regarded as genuine bonds, these interactions cause each macrocycle to deviate noticeably from planarity (Fig. 3), the angle between the planes defined by the two aromatic rings being 153°. In solution, we anticipate the formation of discrete solvated $[Cu_2(L)]^{2+}$ units although aggregation in relatively non-polar solutions can not be discounted.

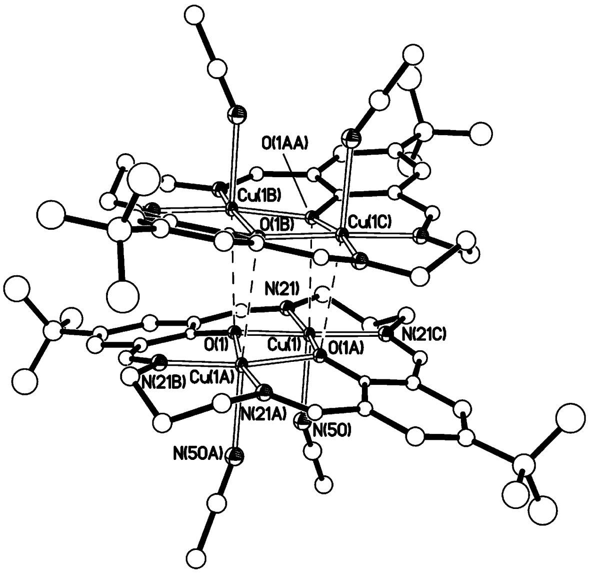

Fig. 3 Structure of $\{[Cu_2(L)(MeCN)_2]_2\}^{4+}$ with numbering scheme adopted.

In summary, we have confirmed that the Robson free ligand is an efficient and selective double-loaded system for the transport and extraction of Cu(II). Current studies aim to develop further hydrophobic and supported systems for selective metal cation binding and transport.

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Notes and references

§ *Crystal data* for $[H_6L](PF_6)_2 \cdot MeCN$: $C_{30}H_{42}N_4O_2{}^{2+}2PF_6{}^- \cdot C_2H_3N$, M = 821.67, triclinic, a = 9.576(3), b = 10.916(3), c = 18.415(4) Å, α = 89.67(3), β = 86.13(3), γ = 78.81(2)°, U = 1884.0(9) Å³, T = 150(2) K, space group $P\bar{1}$ (No. 2), Z = 2, D_c = 1.448 g cm^{-3}, μ(Mo-Kα) = 0.212 mm^{-1}, 4913 reflections measured, corrected for absorption and used in all calculations. Final R_1 [3482 $F > 4\sigma(F)$] = 0.0861 and wR (all F^2) was 0.249. One $PF_6{}^-$ anion is rotationally disordered about a general direction, leading to two sets of six fluorine sites. The group occupancies of these sets refined to 0.702(5) for the major component and 0.29(5) for the minor component. Restraints were applied to P–F distances (1.55 Å) and to F–P–F angles (90 or 180°). For $[Cu_4(L)_2(MeCN)_4](PF_6)_4$: $C_{68}H_{88}Cu_4N_{12}O_4{}^{4+}4PF_6{}^-$, M = 1971.54, tetragonal, a = 18.828(6), c = 11.477(4) Å, U = 4069(2) Å³, T = 150(2) K, space group $P4_2/nmc$ (No. 137), Z = 2, D_c = 1.609 g cm^{-3}, μ(Mo-Kα) = 1.219 mm^{-1}, 1424 unique reflections measured, corrected for absorption (R_{int} 0.173), and used in all calculations. Final R_1 [651 $F > 4\sigma(F)$] = 0.102 and wR (all F^2) was 0.281. The quality of the refinement was limited by the weakness of the data set. Also, disorder was present in the tertiary butyl groups of the cation and in the $PF_6{}^-$ counteranions: in the latter this was modelled using distance and angle restraints. CCDC reference numbers 173168 and 173169. See http://www.rsc.org/suppdata/cc/b1/b109635b/ for crystallographic data in CIF or other electronic format.

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