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Supramolecular chemistry in metal recovery; H-bond buttressing to tune extractant strength

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3-Substitution of salicylaldoximes alters their copper(II) binding strengths by buttressing stabilising hydrogen bonding.

Using solvent extraction to achieve *concentration* and *separation* in extractive hydrometallurgy is of increasing commercial importance.[1] In the high boiling hydrocarbon solvents preferred by industry, intermolecular forces between extractants, particularly hydrogen-bonding, contribute very significantly to the stability of any complexes formed in the water-immiscible phase. In this paper, we focus on hydrogen-bonding between salicylaldoxime extractants, which currently account for between 20%[2] and 30%[3] of the world's production of copper. An understanding of the supramolecular chemistry of extractants in non-polar solvents could underpin the rational design of reagents with the appropriate strength and selectivity to meet the requirements of new flowsheets.

Salicylaldoximes give 14-membered *pseudo*macrocyclic complexes (Fig. 1) with planar metal dications, in which the oxime OH groups form H-bonds to deprotonated phenolic oxygen atoms.[4,5] Such an arrangement gives particularly stable Cu^{II} complexes and ensures high selectivity of extraction over Fe^{III} and other metal cations.[1] Introduction of a substituent X with H-bond acceptor properties in the 3-position offers the possibility of buttressing the H-bonding between the two ligands, increasing the stability of the assembly and extractant strength. In contrast, a bulky 3-substituent with poor H-bond acceptor properties is likely to destabilise the assembly. These buttressing effects are expected to be observed in both preorganised ligand dimers which have planar "stepped" structures[5] and in planar complexes with divalent metal ions (Fig. 1).

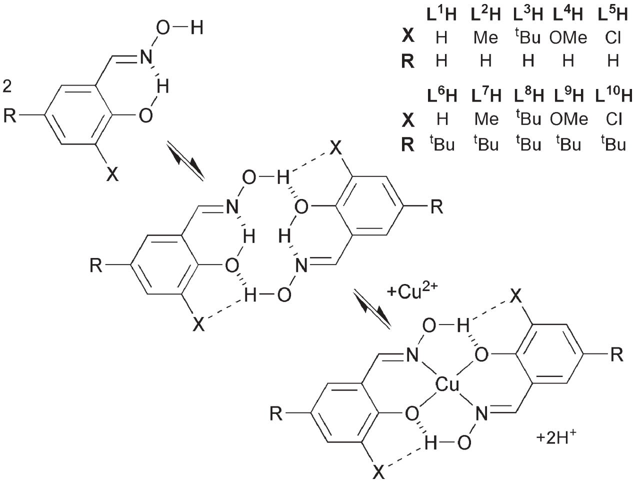

Fig. 1 Possible buttressing of interligand H-bonding by 3-substituents, X, in the formation of dimers and Cu^{II} *pseudo*macrocyclic complexes of the salicylaldoximes, **L¹H–L¹⁰H**, used in this study.

We have prepared[6] a series of 3-substituted salicylaldoximes (**L¹H–L⁵H**) to determine how substitution affects the radius of the donor set cavity (the mean distance of the donors from their centroid) in the metal-free dimer and to see whether this correlates with strength of copper extraction. Bulky *tert*-butyl substituents were needed in the 5-position to ensure that the analogous ligands (**L⁶H–L¹⁰H**) and their Cu^{II} complexes have sufficient chloroform solubility to allow the distribution of copper between chloroform and water to be determined as a function of pH of the aqueous phase,

$$2LH_{(org)} + Cu^{2+} \rightleftharpoons [CuL_2]_{(org)} + 2H^+ \qquad (1)$$

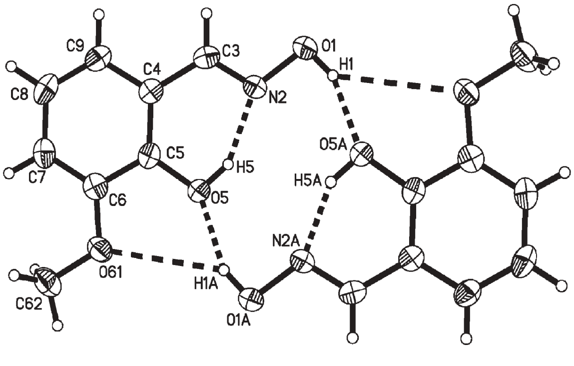

Fig. 2 Interaction of the 3-OMe group with intermolecular H-bonds in the crystal structure of $[\mathbf{L^4H}]_2$. Thermal ellipsoids at 50% probability levels; "A" refers to the symmetry operation (1 − *x*, −*y*, 1 − *z*). Selected distances (Å): H1A···O5 1.88(3), H1A···O61 2.96(3), H5···N2 1.79(3).†

The crystal structures of **L¹H–L⁵H** were determined under identical conditions to ensure comparability of data.† H-bonded *pseudo*macrocyclic dimers are formed (Fig. 2) about an inversion centre in a similar manner to that recorded previously for salicylaldoxime, $[\mathbf{L^1H}]_2$.[7] The cavities (Table 1) are significantly

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Table 1 Radii of solid state N_2O_2 donor set cavities[a] and calculated gas phase formation enthalpies[b] of the dimers of **L^1H–L^5H**

Ligand	**$[L^4H]_2$**	**$[L^5H]_2$**	**$[L^1H]_2$**	**$[L^2H]_2$**	**$[L^3H]_2$**
X	(OMe)[c]	(Cl)	(H)	(Me)	(^{t}Bu)
Cavity size/Å	1.9492(19)	1.9837(12)	2.0048(15)	2.0237(18)	2.0367(19)[d]
Dimerisation enthalpy/kJ mol^{-1}	−50.2	−45.7	−40.7	−39.3	−29.1

[a] All structures solved under identical conditions at room temperature. [b] For $2LH_{(g)} \rightleftharpoons [LH]_{2(g)}$ using Gaussian03[8] at TPSSTPSS/6-31++G(d,p)[9] and corrected for BSSE. [c] Solved previously at different temperature.[10] [d] Mean of values for two crystallographically independent molecules in the asymmetric unit.

smaller in the dimers **$[L^4H]_2$** and **$[L^5H]_2$** which have hydrogen bond accepting 3-substituents (OMe and Cl) and larger in **$[L^3H]_2$** which has a bulky 3-substituent (^{t}Bu). The calculated gas phase enthalpies for dimerisation (Table 1) follow the trend of the smaller the cavity size, the more favourable the dimer formation, suggesting that buttressing of H-bonding makes a significant contribution to the stability of the *pseudo*macrocycle.

A similar buttressing effect is expected in the formation of Cu^{II} complexes (Fig. 1) and would favour the extraction of copper from an aqueous feed solution. This was found to be the case, with extractant "strengths"‡ greater for the ligands with H-bond acceptor substituents, Cl > OMe > Me ⩾ H > ^{t}Bu (Fig. 3).

The effects of the 3-substituent on the electronic properties of the donor set also need to be taken into account when considering the formation of copper complexes. It is generally assumed that lowering the pK_a of the acidic groups in "pH-swing" extractants leads to an increase in strength.[11] If this were the major influence in the series **L^6H–$L^{10}H$**, then the incorporation of an electron-releasing group such as OMe in **L^9H** would raise the pK_a of the phenol group relative to that in the unsubstituted ligand **L^6H**, thus weakening the extractant. This is clearly not the case (Fig. 3), although the electron-releasing properties of OMe may account for **L^9H** being a slightly weaker extractant than its chloro analogue **$L^{10}H$**. A comparison of the data in Table 1 and Fig. 3 suggests that the effects of the 3-substituents on H-bond buttressing or on sterically hindering the formation of the 14-membered *pseudo*macrocycle are an important feature of ligand design to tune extractant strength.

Interaction energies within the dimers in the solid state (Table 2) were analysed by the PIXEL method, which models Coulombic-polarisation and dispersive-repulsion contributions.[12] Again the ligands with H-bond acceptor substituents, **L^4H** and **L^5H**, show the most favourable ligand–ligand attraction. The coulombic term, E_{coul}, is favourable in both cases, indicating formation of stabilising bifurcated H-bonds. A large repulsion term (E_{rep}) is seen for the ^{t}Bu substituted ligand **L^3H**, which may explain both its large hole size and poor extractive efficacy. However, the method also suggests there is a slightly stronger net attraction between the two halves of the Me and ^{t}Bu substituted dimers, **$[L^2H]_2$** and **$[L^3H]_2$**, than in the unsubstituted system **$[L^1H]_2$**. Both have large, favourable dispersion terms, E_{disp}, due to the number of electrons in the substituents, and it is possible that this term may be over estimated as it is the most parameterised.[13]

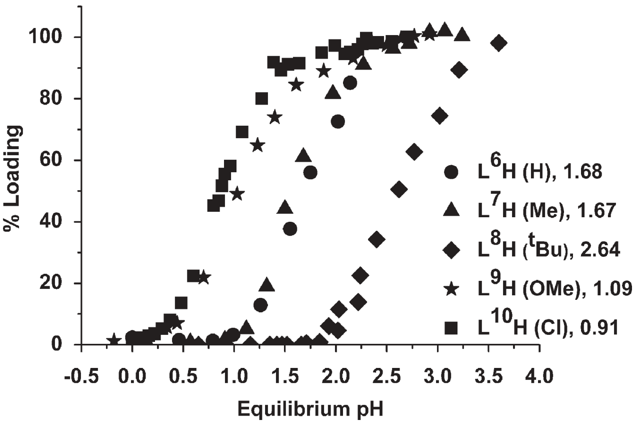

Fig. 3 Copper-loading‡ of chloroform solutions of **L^6H–$L^{10}H$** as a function of the equilibrium pH of the aqueous phase, and $pH_{0.5}$ values. The lower the $pH_{0.5}$, the stronger the extractant.

Table 2 Interaction energies[a] between halves of the dimers with 3-substituents relative to those in the unsubstituted case

Ligand	**$[L^4H]_2$**	**$[L^5H]_2$**	**$[L^1H]_2$**	**$[L^2H]_2$**	**$[L^3H]_2$**
X	(OMe)	(Cl)	(H)	(Me)	(^{t}Bu)
E_{coul}/kJ mol^{-1}	−4.8	−0.5	0	+0.2	+2.1
E_{rep}/kJ mol^{-1}	−0.4	0.0	0	+0.6	+6.2
E_{pol}/kJ mol^{-1}	−1.0	−1.0	0	−0.8	−2.7
E_{disp}/kJ mol^{-1}	−0.8	−1.5	0	−1.5	−5.8
E_{TOTAL}/kJ mol^{-1}	−7.0	−3.0	0	−1.5	−0.2

[a] Calculated by the PIXEL method as described previously.[7,12] The values are calculated for each dimer and then for the same geometry but with the substituent replaced by an H atom. The differences are reported.

These results show that buttressing of interligand H-bonding controls cavity sizes and consequently can be very effectively used to tune the relative "*strengths*" of salicylaldoxime extractants.

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Notes and references

† **L^1H–L^5H** were crystallised by slow evaporation of hexane–$CHCl_3$ solutions. Crystal structure data for **L^1H–L^5H**: see CCDC 629858, 656841, 656842, 656840 and 656839 respectively. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b712278k

‡ Solvent extraction experiments were performed by contacting 0.01 M $CHCl_3$ solutions (5 ml) of **L^6H–$L^{10}H$** with 0.01 M aqueous solutions (5 ml) of $CuSO_4$ which were prepared from 4 ml of 0.0125 M $CuSO_4$ solution and either 1 ml of 0.1 M NaOH–H_2O or 1 ml of 2.5 M H_2SO_4–H_2O solution to change pH. After stirring for 16 h at room temperature, the phases were separated, 0.5 ml aliquots of the organic phase removed for copper analysis by ICP-OES and the pH of the aqueous phase measured.

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