Ditopic ligands for the simultaneous solvent extraction of cations and anions

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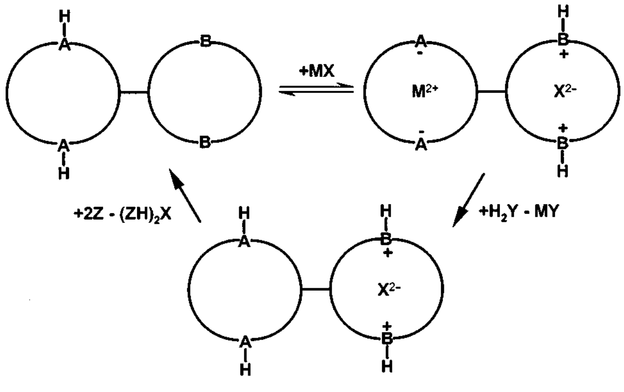
Incorporation of a dianionic binding site for transition metal cations and a dicationic binding site for anions into a lipophilic molecule has produced a ligand with a high efficacy for the solvent extraction of a transition metal salt [$M^{2+}X^{2-}$].

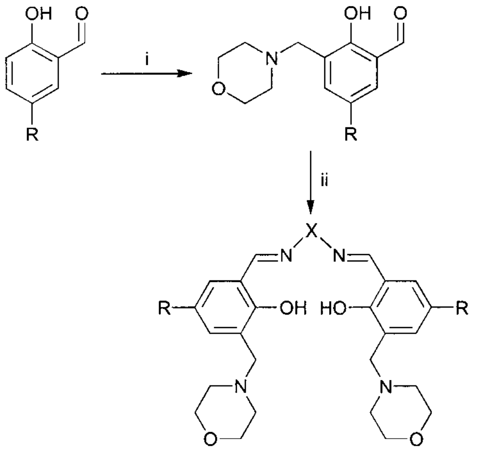
Most man-made processes to separate transition metal ions from aqueous solutions depend on ion exchange processes, in which the desired metal cation M^{n+} replaces a different metal cation (often Na^+) or protons from an anionic group in a complexing agent.[1] Such complexing agents are deployed on solid supports in processes using ion exchange resins, or in a water immiscible liquid in solvent extraction. Although toxic or detrimental metal ions may be sequestered in this way, true purification of the aqueous stream is not achieved because (i) the number of ions present in solution is, at best, unchanged and is often increased; (ii) in the case of proton exchange the pH of the stream may be significantly lowered; and (iii) the anions remain in solution. The harmful effects of anionic species such as phosphate and sulfate have led to control of environmental discharge levels for these species.

These considerations, combined with the need for novel separation technologies to process leach solutions in primary metal recovery, have led us to investigate a new class of extractant which simultaneously sequesters both a transition metal cation and its attendant anion in a ditopic system with the features illustated in Scheme 1.

There are few examples of ligands which simultaneously bind cations and anions and the majority of these address alkali or alkali earth metal or ammonium salts.[2] A recent example invovles the extraction of technetium as the [NH_4][TcO_4] ion pair.[3] Our prototype for a new class of ditopic ligand (Scheme 2) has a ligand framework similar to the uranyl salen anion receptors of Reinhoudt and coworkers,[4] but is designed to provide separate dianionic and dicationic binding sites which are derived from the zwitterionic form of the ligand created by transferring the phenolic protons to the nitrogen atoms of the pendant morpholine groups (Schemes 1 and 3). These features provide for efficient stripping to recycle the extractant and for the possibility of separately recovering the metal and anion components in articles of commerce. These new ligands, exemplified by **1** and **2** (Scheme 2), can be readily prepared in a four-step convergent synthesis from a substituted salicylaldehyde, paraformaldehyde, morpholine and a diamine of choice.†

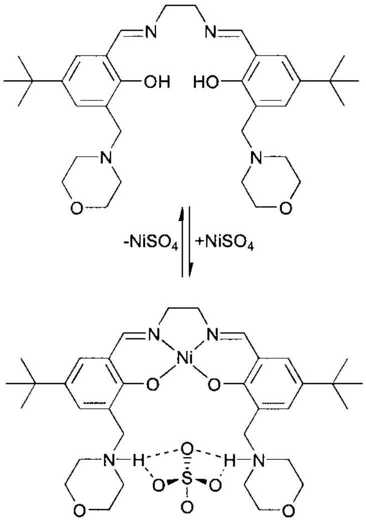


Scheme 1 Schematic representation of ditopic ligands for metal salts with diacid/dibasic sites to enable the hydrometallurgical unit operations of concentration and separation.



Scheme 2 i, 4-Ethoxyethylmorpholine, MeCN, N_2, reflux 66 h; ii, diamine, Et_2O–EtOH (1 : 1), room temp. 12 h. R = Me, Bu^t or nonyl (mixed isomer); X = CH_2CH_2 or $CH_2CH_2CH_2$, H_2NXNH_2 = (±)-*trans*-cyclohexane-1,2-diamine or benzene-1,2-diamine. Ligands referred to here are **1**: R = Bu^t, X = CH_2CH_2, **2**: R = nonyl, H_2NXNH_2 = (±)-*trans*-cyclohexane-1,2-diamine.

When a chloroform solution of the lipophilic ligand **2** (0.01 M) is contacted with aqueous $CuSO_4$ (1 M) at pH 3.8 a dark brown colour develops rapidly. Analysis of the organic phase by ICP-AES for copper and sulfur indicates close to 100% loading of $CuSO_4$. Some of the possible modes of binding of divalent transition metals and their attendant anions have been defined



Scheme 3 Sequestration of $NiSO_4$.

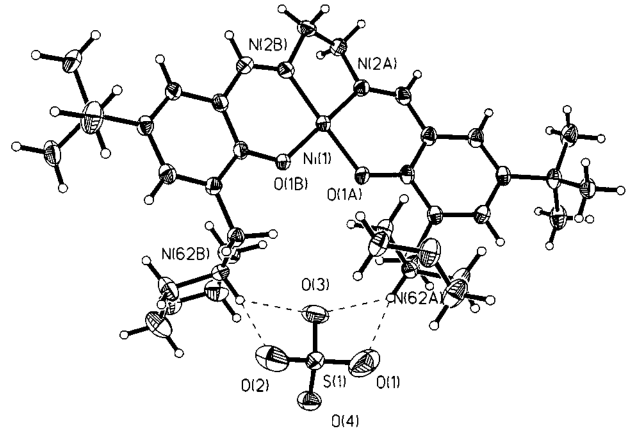


Fig. 1 Molecular structure of [Ni(**1**)SO_4]. Selected bond lengths (Å) and angles (°): Ni(1)–N(2A) 1.846(2), Ni(1)–N(2B) 1.858(2), Ni(1)–O(1A) 1.848(2), Ni(1)–O(1B) 1.854(2); O(1A)–Ni(1)–N(2A) 93.67(8), O(1B)–Ni(1)–N(2B) 94.51(8).

by X-ray structure determinations of nickel(II) complexes of ligand **1** which were readily crystallised from methanol. Reaction of **1** with $NiSO_4·7H_2O$ in methanol (Scheme 3) yields an orange precipitate with a FAB mass spectrum and micro-analysis data consistent with the formulaion of the product as [Ni(**1**)SO_4]·$6H_2O$.[5]

An X-ray crystal structure‡ shows (Fig. 1) that the Ni^{2+} cation is coordinated in the planar $N_2O_2{}^{2-}$ cavity of the salen moiety with bond distances and angles typical of such coordination environments.[6] The coordination of the Ni^{2+} ion has two important effects on the structure of the ligand. The two protons liberated from the phenols of the metal binding site have been transferred to the nitrogen atoms of the pendant morpholine groups and the ligand has been organised to bring the two morpholine groups into close proximity[7] to produce a dicationic binding site for the sulfate anion. This represents an example of cooperativity[8] in which binding of the metal cation directly enhances binding of the anion. The sulfate dianion is bound by both electrostatic interactions and two separate bifurcated hydrogen bonds, one to each quaternary amine (Table 1).

Table 1 Hydrogen bonded distances (Å) and angles (°) around the sulfate anion in [Ni(**1**)SO_4]

	N···O	N–H···O	H···O
O1···H62A–N62A	2.870(4)	166.2	1.958
O2···H62B–N62B	2.923(3)	154.1	2.322
O3···H62A–N62A	2.993(4)	128.8	2.058
O3···H62B–N62B	2.915(4)	132.1	2.209

Note: the N–H distances were fixed at 0.91 Å. H-bonds were assigned using the Platon program[15] to interactions of the oxygen and nitrogen atoms that were < 3.12 Å.

The prototype extractants exemplified by **1** have useful features for developing working systems[9] for the recovery of metal salts from process streams, acid mine drainage streams or effluents. The disposition of both the salicylaldimine units and the pendant amine functions can be separately varied in attempts to 'tune' selectivity for particular combinations of metal cation and attendant anions. The aldimine functionality is resistant to hydrolysis[10] when used in solvent extraction processes, even when contacted with relatively strong acidic media providing the options for efficient stripping protocols as otulined in Scheme 1. These and the possibility of immobilising the extractants on solid supports are the subject of current work.

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Notes and references

† *Experimental procedures:* the starting 2-hydroxy-5-alkylbenzaldehydes were prepared by the method of Levin and coworkers[11] and 4-ethoxymethyl morpholine and hydroxy-3-(morpholin-4-ylmethyl)benzaldehydes by the methods described by Fenton and coworkers.[12]

Example syntheses: **1**: 2-hydroxy-3-(morpholin-4-ylmethyl)-5-*tert*-butylbenzaldehyde (6 g, 21.7 mmol) was dissolved in diethyl ether (60 ml) and added to a solution of ethane-1,2-diamine (0.636 g, 10.6 mmol) in ethanol (60 ml). The resulting yellow solution was stirred overnight then concentrated *in vacuo* to give a yellow oil which on trituration in hexane at −78 °C gave a waxy yellow solid. This was washed with hexane (15 ml) and diethyl ether (15 ml) and dried *in vacuo* (5.8 g, 95%); mp 155–158 °C (Found: C, 70.60; H, 9.06; N, 9.67. Calc. for $C_{34}H_{50}N_4O_4$: C, 70.56; H, 8.71; N, 9.68%). MS (FAB, thioglycerol) *m/z*, 579 (MH^+ 62%).

[Ni(**1**)SO_4]: **1** (0.50 g, 86 mmol) was dissolved in hot methanol (30 ml) and added to a hot solution of $NiSO_4·7H_2O$ (0.245 g, 0.86 mmol) in methanol (20 ml), instantly producing a dark orange colour. On standing the product precipitated as a deep red solid (0.59 g, 93.6%). Recrystallisation from MeOH–H_2O (3 : 1) gave a red microcrystalline material formulated as [Ni(**1**)SO_4]·$6H_2O$; mp 235–240 °C (Found: C, 48.86; H, 7.37; N, 6.53. Calc. for $C_{34}H_{62}N_4NiO_{14}S$: C, 48.53; H, 7.43; N, 6.66%). MS (FAB, thioglycerol) *m/z* 733 [($LNiSO_4)H^+$ 10.1%]. Crystals suitable for X-ray diffraction were obtained by evaporation of a saturated methanol solution of the complex.

‡ *Crystal data*: [Ni(**1**)SO_4]·3.75MeOH: The structure was solved by Patterson methods (DIRDIF)[13] and refined against F^2 (SHELXL-97).[14] $C_{37.75}H_{65}N_4NiO_{11.75}S$, M = 518.14, monoclinic, space group $P2/c$, a = 18.9754(4), b = 12.8666(3), c = 19.7197(4) Å, β = 118.571(1)°, U = 4228.2(2), Z = 4, D_c = 1.332 g cm^{-3}, T = 150(2) K, μ(Mo-Kα) = 0.571 mm^{-1}, wR_2 = 0.1457 (8643 independent reflections), R = 0.0502 [$F > 4\sigma(F)$]. The MeOH solvate (2.701 e/cell) was treated in the manner described by van der Sluis and Spek.[15] CCDC 182/1414. See http://www.rsc.org/suppdata/cc/1999/2077/ for crystallographic files in .cif format.

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