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Formation of folded complexes retaining intramolecular H-bonding in the extraction of nickel(II) by phenolic oxime and aliphatic diamine ligands

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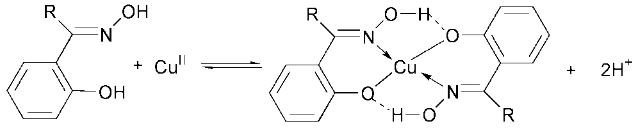
Solvent extraction of Ni^{II} by phenolic oximes is enhanced significantly by addition of aliphatic diamines; octahedral [Ni(II)(phenolate-oxime)$_2$(diamine)] complexes have been characterised that contain a novel folded conformation, retaining intramolecular hydrogen bonding between the two oxime ligands.

Hydrometallurgical processes based on solvent extraction are becoming increasingly important[1] in the recovery of metals. Approximately 20% of the worldwide production of copper now involves solvent extraction using phenolic oximes (H_2SaloxR, Scheme 1) derived from salicylaldehydes (R = H) or *o*-ketophenols (R = alkyl). These reagents are able to transfer Cu^{II} from acidic sulfate media containing a high concentration of Fe^{III}.[2,3] An important aspect of the chemistry involved in this solvent extraction is the formation of square-planar [Cu(HSaloxR)$_2$] complexes, stabilised by interligand hydrogen bonding (Scheme 1).[4]



H_2SaloxR [Cu(HSaloxR)$_2$]

Scheme 1 The 'pH-swing' equilibrium for the acid leach/solvent extraction/electrowinning circuits for copper production; the phenolic oximes (H_2SaloxR) are derived from a salicylaldehyde (R = H) or an *o*-ketophenol (R = alkyl).[2,3]

Phenolic oxime reagents (H_2SaloxR) are not effective extractants for nickel in commercial solvent extraction processes because their $pH_{1/2}$ (the pH for 50% loading of the extractant as [Ni(HSaloxR)$_2$]) values are not sufficiently low to allow recovery from acidic feeds and the kinetics of the extraction process tend to be poor.[3] We have investigated the use of aliphatic acyclic polyamines (B) as agents for enhancing the solvent extraction of Ni^{II} by phenolic oximes. This approach was based on earlier observations that the extraction of Ni^{II} from aqueous media is enhanced when combinations of ligands are used, *e.g.* salicylic acid plus an aliphatic acyclic diamine[5] or salicylaldoxime plus a monodentate *N*-heterocycle.[6]

The extraction experiments accomplished and the results obtained are summarised in Table 1. The extent of the extraction of Ni^{II}, from H_2O into CH_2Cl_2, was significantly greater for H_2SaloxH plus a diamine, as compared with the extent of extraction by either reagent alone. The addition of a diamine (B) to a mixture of Ni^{II} and H_2SaloxH would be expected to favour extraction of the Ni^{II}, since B will act as a base and displace the equilibrium of Scheme 1 and, therefore, increase the amount of [Ni(HSaloxH)$_2$] **1** formed. However, the improvement in the efficiency of the extraction that we have observed may also involve two other contributing effects.

Firstly, we have obtained evidence for ligand assembly[7] between H_2SaloxH and representatives of the diamines listed in Table 1. In particular, the isolation and crystallographic characterisation of [(H_2SaloxH)$_2$(Me$_4$en)], plus ^{1}H NMR spectra recorded for a combination of these two reagents in $CDCl_3$ solution,[8] clearly demonstrate that H_2SaloxH and Me$_4$en form a 2:1 assembly. This ligand assembly would make a favourable contribution to the entropy of formation of [Ni(HSaloxH)$_2$(Me$_4$en)] **2** and related complexes.[7]

Secondly, the addition of each of the diamines (B) to a solution of **1** in CH_2Cl_2 (1 : 1) produced a colour change from the dark green of **1** to a shade of blue or red, depending upon the nature of B, and produced 1 : 1 complexes, [Ni(HSaloxH)$_2$B].† These processes have been followed by UV–VIS–NIR spectroscopy and the general result obtained is exemplified in Fig.1, for the addition of aliquots of pn to a solution of **1** in CH_2Cl_2. In each case, a stepwise increase in the absorbance at *ca.* 900 nm was observed, together with a concomitant decrease in the absorbance and a slight shift to higher energy in the λ_{max} at *ca.* 600 nm. An isosbestic point was observed in each titration, consistent with the reaction proceeding by a simple process. The variation of the absorbance at λ_{max} of 600 and 900 nm with the reagent ratio indicated that **1** and B interact with a 1 : 1 stoichiometry.

Isolation and recrystallisation of the solids formed by reacting [Ni(HSaloxR)$_2$] and B (1 : 1) in CH_2Cl_2 produced crystalline materials of composition [Ni(HSaloxR)$_2$B]. The compounds for which R = H, B = Me$_4$en (**2**)‡ or pn and R =

Table 1 Percentage of Ni^{II} extracted from an aqueous medium into CH_2Cl_2 using a base (B) plus salicylaldoxime (H_2SaloxH)[a]

Diamine (B)	B alone (2 mM)	H_2SaloxH + B (1 mM)	H_2SaloxH + B (2 mM)	H_2SaloxH + B (3 mM)
N,N-Me$_2$en	11	100	100	100
N,N'-Me$_2$en	16	98	100	100
pn	19	93	94	93
N,N'-Me$_2$pn	32	98	100	100
Me$_4$en	37	59	86	100

[a] The extraction experiments were carried out using mechanically-shaken and stoppered vials containing $Ni(NO_3)_2\cdot 6H_2O$ (1 mM) in H_2O (5 cm^3) and H_2SaloxH (2 mM) and B (1–3 mM) in CH_2Cl_2 (5 cm^3). Each system was equilibrated for 4 h at 25 °C and the concentration of nickel in the aqueous phase was then determined by atomic absorption spectroscopy. H_2SaloxH (2 mM) alone extracted 13% of the Ni^{II}. Each of the reported values is an average of three experiments and has an estimated error of ±3%. Abbreviations for B: *N,N*-Me$_2$en = *N,N*-dimethylethylenediamine; *N,N'*-Me$_2$en = *N,N'*-dimethylethylenediamine; pn = 1,3-diaminopropane; *N,N'*-Me$_2$pn = *N,N'*-dimethyl-1,3-diaminopropane; Me$_4$en = *N,N,N',N'*-tetramethylethylenediamine.

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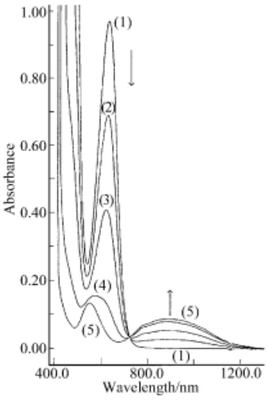

Fig. 1 The VIS–NIR absorption spectra for the addition of four [(2)–(5)] successive aliquots (2.4 mM) of pn to [Ni(HSaloxH)$_2$] (10 mM) in CH_2Cl_2; (1) is the spectrum of [Ni(HSaloxH)$_2$] prior to the addition of pn.

Me, B = *N,N'*-Me$_2$en have been characterised by X-ray crystallography.[8] Each compound is comprised of neutral mononuclear complexes with the Ni^{II} in a distorted octahedral environment, as exemplified by the molecular structure of **2** (Fig. 2). Each oxime is bound to the Ni^{II} *via* the phenolate *O*-atom and the oxime *N*-atom, to give a six-membered chelate ring that spans adjacent (*cis*) sites, and the diamine acts as a bidentate *cis-N,N*-chelate. Each [Ni(HSaloxR)$_2$B] compound that has been characterised by X-ray crystallography contains complexes exclusively in the form of the coordination isomer of the type shown in Fig. 2. An important structural feature of this isomer is that it involves retention of hydrogen bonding between the oximic hydroxyl groups and the phenolate oxygens. This type of hydrogen bonding is well established; *e.g.* in **1**[9] and [Cu(HSaloxH)$_2$],[4] it stabilises the *planar* complex (see Scheme 1). However, the [Ni(HSaloxR)$_2$B] complexes reported herein are the first examples that manifest the corresponding *folded* interligand, intramolecular H-bonding. Thus, in the octahedral [Ni(HSaloxR)$_2$B] complexes, *cis*-chelation of the diamine results in a folding about the phenolate–phenolate axis and the oxime N-atoms rotate to become mutually *cis*; the phenolate O-atoms remain mutually *trans*, but the O–Ni–O angle is reduced from 180 to 168.4(1)°. In **2**, the distances O1···O4 [2.670(4) Å] and O2···O3 [2.627(4) Å] are slightly (*ca.* 0.15 Å) longer than the corresponding distances in **1** (average 2.52 Å).[9] This difference is consistent with the increased span of the intramolecular H-bonding required to accommodate six-coordinate, high-spin, Ni^{II}, as compared to the planar four-coordinate, low-spin, Ni^{II} present in **1**.[10] Consistent with this view, the Ni–O and Ni–N$_{ox}$ bonds are longer by *ca.* 0.25 and 0.30 Å, respectively, in **2** than in **1**.[9] The oxime hydrogen atoms in **1** were located by Fourier techniques and the length of the hydrogen bonds to the phenolic oxygens (H2$_O$···O3 and H4$_O$···O1) are 1.70 and 1.88 Å, respectively. Given the importance of intramolecular H-bonding in stabilising [Cu(HSaloxR)$_2$] complexes, thereby aiding the efficacy and selectivity of the process employed for the commercial extraction of Cu^{II},[2,3] it is of considerable interest to observe that a similar, *but folded*, arrangement is present in the octahedral [Ni(HSaloxR)$_2$B] complexes.

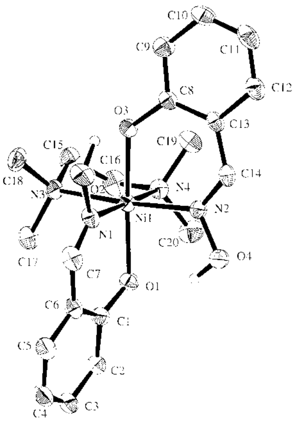

Fig. 2 ORTEP view and atomic labelling scheme for [Ni(HSaloxH)$_2$(Me$_4$en)]. Selected bond lengths (Å): Ni1–N1 2.065(4), Ni1–N2 2.057(3), Ni1–N3 2.171(4), Ni1–N4 2.170(4), Ni1–O1 2.050(3), Ni1–O3 2.041(3); selected interbond angles (°): O1–Ni1–O3 168.4(1), O1–Ni1–N1 85.4(1), O1–Ni1–N2 86.5(1), O1–Ni1–N3 97.7(1), O1–Ni1–N4 93.5(1), O3–Ni1–N1 85.8(1), O3-Ni1–N2 86.3(1), O3–Ni1–N3 90.1(1), O3–Ni1–N4 95.9(1), N1–Ni1–N2 91.7(1), N1–Ni1–N3 92.1(1), N1–Ni1–N4 175.0(1), N2–Ni1–N3 174.6(1), N2–Ni1–N4 93.1(1), N3–Ni1–N4 83.2(1); selected non-bonded distances (Å): O4···O4 3.175(7), O2···O3 2.627(4), O4···O1 2.670(4).

In view of the above, we consider that: (i) the displacement of the equilibrium of Scheme 1 by the presence of the basic diamine; (ii) the possible operation of a ligand 'assembly effect';[7] and (iii) the formation of [Ni(HSaloxR)$_2$B] with retention of the intramolecular H-bonding, could each contribute to the significant increase in the amount of Ni^{II} extracted by a combination of a phenolic oxime and a diamine, as compared with the amount of Ni^{II} extracted by either reagent alone.

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Notes and references

† [Ni(HSaloxH)$_2$][9] (0.043 g, 0.13 mmol) was dissolved in CH_2Cl_2 (5 cm^3) and Me$_4$en (20 μL, 0.13 mmol) added, producing an instantaneous change from green to blue. The solution was stirred for 10 min at RT, then layered with *n*-hexane (5 cm^3) and left to evaporate in air. The blue product was washed with a small amount of *n*-hexane and dried *in vacuo*. Yield 65%. $C_{20}H_{28}N_4O_4Ni$: found (calc.): C 53.6 (53.7), H 6.4 (6.3), N 12.6 (12.5), Ni 12.6 (13.1)%. VIS–NIR (refl.) λ_{max}/nm (rel. abs.) 975.2 (0.14), 583.2 (0.15). μ_{eff} at RT 3.13 μ_B. IR (KBr)/cm^{-1} 1644w δ_{OH}, 1597s $\nu_{C=C}$, 1544m $\nu_{C=N}$, 1189m, 907s ν_{N-O}, 1292s, 995s ν_{C-O}.

‡ *Crystal data* for $C_{20}H_{28}N_4O_4Ni$: M = 447.17, monoclinic, space group $P2_1/c$ (no. 14), a = 9.529(2) b = 14.329(3) c = 15.944(4) Å, β = 97.14(2)°, U = 2160.9(9) Å^3, T = 294(1) K, Z = 4, μ(Cu-Kα) = 15.72 cm^{-1}, 3590 reflections measured, 3366 unique, 2597 for $I > 2.50\sigma(I)$ (R_{int} = 0.085) on a Rigaku AFC5R, which were used in all calculations. The final $R1$ = 0.058, wR = 0.067. The structure was solved by direct methods with SIR92[11] and expanded using Fourier techniques.[12,13] Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in idealised positions (C–H = 0.95 Å), except for the four (O–H) that were found by difference Fourier analysis. All of the hydrogen atoms were refined isotropically to convergence, then fixed for the final rounds of refinement. The maximum and minimum peaks in the final difference Fourier map were 0.77 and −0.80 e Å^{-3}, respectively. CCDC 154046. See http://www.rsc.org/suppdata/cc/b0/b009267n/ for crystallographic data in .cif or other electronic format.

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