Water-Soluble Sal$_2$en- and Reduced Sal$_2$en-Type Ligands: Study of Their Cu$^{	ext{II}}$ and Ni$^{	ext{II}}$ Complexes in the Solid State and in Solution


Keywords: Copper(II) / Nickel(II) / Reduced Schiff bases / Speciation / Crystal structure

The Cu$^{	ext{II}}$ and Ni$^{	ext{II}}$ complexes of the Schiff base pyr$_2$en $[N,N'$-ethylenebis(pyridoxyliminato)] and reduced Schiff bases Rpyr$_2$en $[N,N'$-ethylenebis(pyridoxylaminato)] and R(SO$_3$–sal)$_2$en (SO$_3$–sal = salicylaldehyde-5-sulfonate) were prepared and characterized by elemental analysis, IR, UV/Vis, and EPR spectroscopy. The structure of Ni(pyr$_2$en)$_2$3H$_2$O was determined by single-crystal X-ray diffraction. The pyr$_2$en$^2-$ligand is coordinated through two phenolate-O and imine-N atoms, in a distorted square-planar geometry. The complexation of Cu$^{	ext{II}}$ and Ni$^{	ext{II}}$ with Rpyr$_2$en in aqueous solution is studied by pH-potentiometry, UV/Vis spectroscopy, as well as by EPR spectroscopy for the Cu$^{	ext{II}}$ system and $^1$H NMR spectroscopy for the Ni$^{	ext{II}}$ system. Complex formation constants were determined and binding modes proposed. While for the Cu$^{	ext{II}}$ system all complexes present a 1:1 stoichiometry and a higher ligand excess, for the Ni$^{	ext{II}}$ system the 2:1 (L/M) complexes become important in the basic pH range at a higher ligand excess. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2006)

Introduction

The application of Green Chemistry principles in organic transformations has attracted increased attention in the development of transition metal catalysts. Sal$_2$en-type ligands derived from o-hydroxyaldehydes and diamines are one of the most important ligand systems in asymmetric, homogeneous, and heterogeneous catalysis and in stereoselective reactions.[1–5] Their transition metal complexes can be used in a large variety of applications, namely asymmetric ring opening of epoxides,[4] cyclopropanation,[6] and enantioselective epoxidation of olefins.[7] Their versatility and selectivity in chemical reactions is partly due to the ability of sal$_2$en-type ligands to complex a variety of transition metals in several oxidation states. They normally form square-planar or octahedral complexes in which the four donor atoms coordinate in an almost planar fashion. Numerous sal$_2$en-type ligands have been synthesized and investigated, but most of them show low solubility in aqueous solution, which can be overcome by changing the diamine precursor and/or the ring substituents on the aldehyde.

In solution, Schiff base (SB) ligands have the disadvantage of the hydrolysis of the C=N bond, particularly in water-containing solvents. Reduction of the SB to give an amine may present interesting advantages. The reduced SBs (hereafter designated by sal$_2$an) are not so prone to hydrolysis and are more flexible and unrestrained to remain planar when coordinated to a metal center. Several sal$_2$an complexes have been synthesized and characterized, namely with Cu$^{	ext{II}}$,[8–10] Co$^{	ext{II}}$,[9] Ni$^{	ext{II}}$[11] VO$^{	ext{IV}}$,[12,13] Fe$^{	ext{III}}$[14] and Zn$^{	ext{II}}$.[15] In the Ni$^{	ext{II}}$ and Co$^{	ext{II}}$ complexes the ligand coordinates in a slightly distorted square-planar geometry, and these complexes have shown the ability to interact with oxygen,[9,11] when dissolved in organic solvents these complexes can undergo oxidative dehydrogenation,[9,11] i.e. in the presence of O$_2$ one of the C=N bonds may be oxidized to an imine-type bond. This process has not been observed in most of the Cu$^{	ext{II}}$ complexes, which are stable in organic solutions exposed to air.

One of the guidelines in Green Chemistry research is the elimination of hazardous solvents in reaction media. As mentioned above, sal$_2$en complexes are frequently used as catalysts for several applications. As most sal$_2$en complexes are not water soluble one of our objectives is the synthesis of water-soluble ligands and complexes.

In a previous work[12] we reported the preparation and characterization of the Schiff base $N,N'$-ethylenebis(pyridoxyliminato) (pyr$_2$en) and its reduced derivative $N,N'$-ethylenebis(pyridoxylaminato) (Rpyr$_2$en). Their V$^{	ext{IV}}$O and V$^{	ext{V}}$O$_2$ complexes were characterized in the solid state and in...
solution. The molecular structure of two dioxovanadium(V) complexes with this reduced SB evidenced the tetradentate binding mode and the flexibility of the Rpyr2en when coordinated to the metal ion. The solution studies showed that Rpyr2en forms much more stable complexes with V IV and V V than the corresponding Schiff base pyr2en, and that the SB has a much higher tendency to hydrolyze in aqueous solution. This is reflected in the proton displacement constants ($K^*$), characteristic for the formation equilibrium:

$$H_6L^+ + V^{IV}O_2^+ \rightarrow [V^{IV}OLH_2]^2^+ + 4 H^+; \log K^* = -14.1 \text{ and } -5.63 \text{ for pyr2en and Rpyr2en, respectively}$$. [12]

Similar results were obtained for (SO$_3$–sal)$_2$en and R(SO$_3$–sal)$_2$en with their vanadium complexes. [16]

In this work we report on the preparation of several new moderately water-soluble Cu II and Ni II complexes (the ligands and formula names are shown in Scheme 1), one of them characterized by single-crystal X-ray diffraction. We also report on the solution study of the reduced SB Rpyr2en with CuII and NiII by pH-potentiometry, visible absorption (Vis), EPR (CuII), and $^1$H NMR (NiII) spectroscopy.

Results and Discussion

Synthesis and Characterization of the Solid Compounds

Sal$_2$en-type ligands were prepared by the condensation of ethylenediamine with the aldehyde derivative. Reduction with NaBH$_4$ yielded the reduced SB. [12,16] From solutions containing NiIII and Rpyr2en, orange crystals of the SB complex Ni(pyr2en)·3H$_2$O were obtained. This implies that the two amine bonds underwent dehydrogenation. The solid-state characterization of all complexes was done by taking into account that this process might also have occurred with the other metal complexes. For the Rpyr2en complexes the characterization (elemental analysis, IR, and UV/Vis spectroscopy) is consistent with a formulation of M(Rpyr2en) (M = NiII or CuII). Complex $K_2$(Ni[R(SO$_3$–sal)$_2$en]), although it was characterized and is included here, is not stable; its color changes from grey, immediately after the synthesis, to soft pink, and after a week to brown. The ESI mass spectrum, measured for solutions of the pink solid, confirms the presence of the reduced Schiff base showing important peaks that can be assigned to [NiL + 2K$^+$]$^+$ ($m/z = 565$) and [NiL + 3K$^+$]$^+$ ($m/z = 603$).

X-ray Diffraction Studies

$	ext{Ni(pyr2en)·3H}_2\text{O (1)}$

Figure 1 includes an ORTEP representation of the molecular structure of Ni(pyr2en)·3H$_2$O (1), and Table 1 shows selected bond lengths and angles. The molecule is neutral with both pyridinic nitrogens deprotonated, and the ligand coordinates the Ni atom through two phenolate oxygen (Ophenolate) and two imine nitrogen (Nimine) atoms. The geometry around the metal ion is distorted square planar, and there are three water molecules in the asymmetric unit (not shown). The planar arrangement Ni(ONNO) is slightly distorted due to the cis/trans angles, which are not 90° and 180°. The cis and trans angles are 84.2 and 94.8°, and 178.4 and 178.5°, respectively. The ligand forms a set of chelate rings of (6+5+6)-members, and the highest deviation from planarity is found in the ring defined by Ni(1)–N(1)–C(2)–C(1)–N(2), which has an rms value of 0.1074(75) Å (the others are less than 0.05 Å). It is noteworthy that the torsion angle between the N(1)–C(2)–C(1)–N(2) atoms is only 29.24(1.71)°, lower than those previously observed in this type of complexes. [17] The pyridoxal rings are planar, with rms values of 0.0172(63) and 0.0127(58) Å.

The Ni–O and Ni–N bond lengths are similar and in the usual range found for NiII-sal$_2$en-type complexes. [11,18–21] The C–O distances are also typical for this type of ligands. [9,11,19–21] The C–N bonds show double bond character with distances of ca. 1.3 Å. After coordination to
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**Figure 1.** ORTEP diagram of Ni(pyr₂en)·3H₂O (I) showing the atom labeling scheme. The thermal ellipsoids were drawn at the 30% probability level. The water molecules were omitted for clarity.

| Table 1. Selected bond lengths [Å] and angles [°] for complex Ni-(pyr₂en)·3H₂O (I). |
|-----------------|-----------------|-----------------|-----------------|
| Bond lengths [Å] | Bond angles [°]  |
| Ni(1)–O(3)      | 1.838(5)        | O(3)–Ni(1)–O(4) | 84.2(3)         |
| Ni(1)–O(4)      | 1.842(5)        | O(3)–Ni(1)–N(1) | 94.4(3)         |
| Ni(1)–N(2)      | 1.849(7)        | O(4)–Ni(1)–N(1) | 178.5(3)        |
| O(3)–C(5)       | 1.310(10)       | O(3)–Ni(1)–N(2) | 84.8(3)         |
| O(4)–C(12)      | 1.328(9)        | N(1)–Ni(1)–N(2) | 86.7(3)         |
| N(2)–C(10)      | 1.308(11)       | N(1)–C(2)        | 1.451(12)       |
| N(1)–C(3)       | 1.262(10)       | N(1)–C(3)        | 1.455(12)       |

The metal ion the ligand does not undergone a significant change in the C–O phenolic and C–N imine bond lengths: the C–O bonds decrease by 0.034 Å and the C=N bonds increase by 0.035 Å. In the complex the HO–(CH₂)–O groups of the pyridoxal rings are perpendicular to the apparent molecular plane, in an anti position to each other. This results in a three-dimensional crystalline structure connected by H bonds. ESI-1 shows the crystalline packing and emphasizes the intermolecular bonds. The molecular planes are approximately parallel, but overlaid in an alternate manner; this is probably because of the anti position of the hydroxy groups. The distance between neighboring Ni atoms is between 6.381 and 8.268 Å.

**Infrared Spectroscopy**

Table 2 contains selected IR bands of the complexes. The assignment was based on data from refs. [22–25] and by comparison with the spectra of the ligands. All complexes present broad bands in the 2400–3600 cm⁻¹ range, which correspond to the stretching vibration (symmetric and antisymmetric) of the CH₂O–H groups of the pyridoxal rings (for the Rpyr₂en complexes) and to the water molecules. The weak ν(N–H) band that emerged from the broad band at 3286 cm⁻¹ in Rpyr₂en [12] appears in the complexes at lower wavenumbers, in agreement with the coordination through the Namine groups. The ν(C=O) phenolate band appears in the normal range for these types of complexes [23,26]. The strong ν(C=N) band of complex Cu(pyr₂en) is assigned to the band at 1635 cm⁻¹, at a higher wavenumber than the ligand (1626 cm⁻¹),[12] and no such band is seen in the IR spectrum of Cu(Rpyr₂en). Similarly, while the ν(C=N) band of Ni(pyr₂en) appears at ca. 1620 cm⁻¹, no band is seen in the IR spectrum of Ni(Rpyr₂en), which might be assigned to this vibration. Complex Ni[(SO₃-sal)₂en] presents a very

| Table 2. Selected IR [cm⁻¹] and UV/Vis absorption bands of the prepared complexes. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| FT-IR           | ν(N–H) strech    | ν(C=N)          | ν(C=O) phenolate | ν(O–H)          | UV/Vis          | λₘₐₓ [nm] (ε [m⁻¹ cm⁻¹]) |
| ν(N–H) strech   | ν(C=N)          | ν(C=O) phenolate | ν(O–H)          | UV/Vis          | λₘₐₓ [nm] (ε [m⁻¹ cm⁻¹]) |
| ν(N–H) strech   | ν(C=N)          | ν(C=O) phenolate | ν(O–H)          | UV/Vis          | λₘₐₓ [nm] (ε [m⁻¹ cm⁻¹]) |
| ν(N–H) strech   | ν(C=N)          | ν(C=O) phenolate | ν(O–H)          | UV/Vis          | λₘₐₓ [nm] (ε [m⁻¹ cm⁻¹]) |
| ν(N–H) strech   | ν(C=N)          | ν(C=O) phenolate | ν(O–H)          | UV/Vis          | λₘₐₓ [nm] (ε [m⁻¹ cm⁻¹]) |
| ν(N–H) strech   | ν(C=N)          | ν(C=O) phenolate | ν(O–H)          | UV/Vis          | λₘₐₓ [nm] (ε [m⁻¹ cm⁻¹]) |
| ν(N–H) strech   | ν(C=N)          | ν(C=O) phenolate | ν(O–H)          | UV/Vis          | λₘₐₓ [nm] (ε [m⁻¹ cm⁻¹]) |
| ν(N–H) strech   | ν(C=N)          | ν(C=O) phenolate | ν(O–H)          | UV/Vis          | λₘₐₓ [nm] (ε [m⁻¹ cm⁻¹]) |
strong band at 1609 cm\(^{-1}\) assigned to \(\nu(C-N)\). This band is absent in the corresponding reduced SB complex \(\text{Ni}(\text{R(SO}_3\text{-sal})_2\text{en})\), which presents bands at 1593 and 1639 cm\(^{-1}\), assigned to aromatic =C–H and C=C stretching vibrations.

**UV/Vis Absorption Spectroscopy**

The UV/Vis spectra were recorded over the 250–900 nm range in DMSO or water. The results are summarized in Table 2. Some of the intense bands at low wavelengths (\(\lambda < 400\) nm) are assigned to charge transfer (CT), imine \(\pi-\pi^*\) (when appropriate), and intramolecular transitions in the aromatic rings. In the visible range (\(\lambda > 420\) nm) the bands are predominantly due to d-d transitions. The copper complexes \(2-4\) have one well-defined broad d-d band at \(\lambda_{\text{max}} = 550-650\) nm, and stronger bands at ca. \(\lambda = 380-420\) nm from the Cu\(^{II}\) \(\rightarrow\) phenolate \((\pi^*)\) transitions [and also imine \(\pi-\pi^*\) in the case of Cu(pyrr\(_2\)en)], which is in agreement with that expected for tetrahedrally distorted square-planar complexes of the Cu\(_2\)N\(_2\) type.\(^{[27,28]}\) The Ni\(^{II}\) complexes \(5-8\) have low intensity broad bands in the 400–550 nm range, assigned to transitions from the four low-lying \(d\) orbitals to the \(\sigma\) antibonding \(d_{x^2-y^2}\) orbital. At higher energies (\(\lambda < 400\) nm) a group of high intensity bands appears, and in the case of Ni(pyrr\(_2\)en) and Ni[\(\text{SO}_3\)-sal\(_2\)en] relatively intense bands from the imine \(\pi-\pi^*\) transition also show up. The UV/Vis data of the complexes in DMSO are in agreement with that expected for Ni\(^{II}\) and Cu\(^{II}\) complexes with square-planar geometries.\(^{[9,10,27]}\) The relatively high \(z\) values of the d-d bands of the Ni complexes suggest some borrowing of intensity from CT bands and/or a significant distortion of the coordination geometry.

**EPR Spectroscopy**

The EPR spectra of the Cu\(^{II}\) complexes were measured in “frozen” \((T = 77\) K) solutions of an adequate solvent. The spectrum of Cu(pyrr\(_2\)en) in DMSO showed a broad band centered at \(g = 1.995\) without hyperfine structure. This is probably because of molecular aggregation during the freezing process. No signal was detected at \(g = 4\).

The EPR spectrum of Cu(pyrr\(_2\)en) was measured in water and DMSO at 77 K. Both show well-resolved hyperfine structure and suggest axial symmetry. The spin Hamiltonian parameters were obtained by computer simulation of the experimental spectra using a program from Rockenbauer and Korecz.\(^{[29]}\) Among other factors, the \(g\) and \(A\) values depend on the nature of the donor atoms and can be used to confirm the binding mode. The parameters (DMSO: \(g_{\perp} = 2.047, A_{\perp} = 22.2\times10^{-4}\) cm\(^{-1}\), \(g_{\parallel} = 2.233, A_{\parallel} = 197.3\times10^{-4}\) cm\(^{-1}\); H\(_2\)O: \(g_{\perp} = 2.052, A_{\perp} = 38.4\times10^{-4}\) cm\(^{-1}\), \(g_{\|} = 2.237, A_{\|} = 193.5\times10^{-4}\) cm\(^{-1}\)) fit well with that expected for a \(\text{Ni}_2\text{O}_2\) binding mode.\(^{[30]}\) On the other hand, the \(g/A\) ratio of 113 in DMSO and 116 in H\(_2\)O indicates a square-planar coordination environment.\(^{[30]}\) In the spectrum of Cu(pyrr\(_2\)en), dissolved in water, superhy-
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Figure 2. Time-dependence of the UV/Vis spectra of solutions containing Ni(Rpyr$_2$en) in DMSO: (a) Bubbling air through the solution; (b) Under N$_2$ atmosphere. Insets: variation of the molar absorptivity at 412 nm. The arrows indicate increasing time (from 0 to 3 d). The spectrum of Ni(pyr$_2$en) in DMSO (dotted) is included in both figures for comparison.

Speciation Studies

The acid-base behavior of pyr$_2$en, Rpyr$_2$en, and R(SO$_3$–sal)$_2$en and their complexation with V$^{IV}$ and V$^{V}$ were previously reported.$^{[12,16]}$ The study of the Cu$^{II}$–Rpyr$_2$en systems by pH-potentiometry, Vis, EPR (for the Cu$^{II}$ system), and $^1$H NMR (for the Ni$^{II}$ system) spectroscopy is now presented.

Cu$^{II}$–Rpyr$_2$en

The pH-metric titration curves were measured between pH 2 and 11.3, and the best equilibrium model that fitted the experimental data corresponds to a model similar to that obtained for the V$^{IV}$O system.$^{[12]}$ The stability constants are listed in Table 3 and a species distribution diagram is depicted in Figure 3 (a).

Table 3. Protonation and formation constants for the M$_p$L$_q$H$_r$ species formed in the Cu$^{II}$- and Ni$^{II}$-Rpyr$_2$en systems, calculated from the pH-potentiometric and spectrophotometric data (EPR and UV/Vis) with the PSEQUAD program.$^{[31]}$

<table>
<thead>
<tr>
<th>H</th>
<th>logβ$_{H}$ (L = pyr$_2$en$^2$–)</th>
<th>logβ$_{H}$ (L = pyrN$^-$)</th>
<th>logβ (Cu$^{II}$) (L = pyr$_2$en$^2$–)</th>
<th>logβ (Cu$^{II}$) (L = pyrN$^-$)</th>
<th>logβ (Ni$^{II}$) (L = pyr$_2$en$^2$–)</th>
<th>logβ (Ni$^{II}$) (L = pyrN$^-$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$L</td>
<td>10.50 ± 0.01</td>
<td>10.41</td>
<td>28.04 ± 0.02</td>
<td>17.22</td>
<td>11.98 ± 0.02</td>
<td>6.46</td>
</tr>
<tr>
<td>H$_3$L</td>
<td>19.65 ± 0.01</td>
<td>18.56</td>
<td>35.3 ± 0.3</td>
<td>21.34</td>
<td>28.52 ± 0.01</td>
<td>–</td>
</tr>
<tr>
<td>H$_4$L</td>
<td>27.33 ± 0.01</td>
<td>22.06</td>
<td>38.91</td>
<td>24.49</td>
<td>43.59 ± 0.04</td>
<td>–</td>
</tr>
<tr>
<td>H$_5$L</td>
<td>33.30 ± 0.01</td>
<td>38.91</td>
<td>43.59 ± 0.04</td>
<td>24.49</td>
<td>51.44 ± 0.03</td>
<td>–</td>
</tr>
<tr>
<td>H$_6$L</td>
<td>36.31 ± 0.02</td>
<td>38.91</td>
<td>51.44 ± 0.03</td>
<td>24.49</td>
<td>64.6 ± 0.03</td>
<td>–</td>
</tr>
<tr>
<td>H$_7$L</td>
<td>38.60 ± 0.02</td>
<td>38.91</td>
<td>64.6 ± 0.03</td>
<td>24.49</td>
<td>78.1 ± 0.03</td>
<td>–</td>
</tr>
</tbody>
</table>

speciation}
The stability of the complexes is high, and even at pH 2 the amount of $[\text{Cu(OH}_2\text{)}_6]^{2+}$ is very small.

The Vis spectra for this system as the pH is varied (Figure 4) consists of a broad band (of d-d origin) with a maximum around 625 nm ($\varepsilon \approx 200 \text{ mol dm}^{-3} \text{ cm}^{-1}$ at pH $= 6.0$). Deprotonation of the pyridine nitrogen atoms causes significant changes in the UV/Vis spectra: the d-d transition shifts to a higher energy as the pH is increased and the shoulder at ca. 420 nm (ascribed to phenolate $\rightarrow$ Cu$^\text{II}$ CT transition) shows a bathochromic effect with increasing pH. These shifts demonstrate that the pyridoxal ring forms a connected electron system and thus deprotonation of the pyridine-NH groups will influence the donor properties of the phenolate oxygen atoms.

![Figure 4. Visible spectra of aqueous solutions containing Cu$^\text{II}$ and Rpyr$_2$en, with $C_{\text{Cu}} = 5 \text{ mmol dm}^{-3}$ and a L/M ratio of 1 at several pH values.](image)

It is clear from the speciation (Figure 3, a) and spectroscopic data (Figures 4 and 5) that for pH $\leq 2$ the amount of Cu$^\text{II}$ is already complexed by the ligand, and that the relevant data for calculation of the log $\beta_{112}$ value occurs at pH $\leq 2$. The visible absorption and room temperature EPR spectra were used to confirm the calculated stability constant obtained for $[\text{CuLH}_2]^{2+}$ and the proposed speciation model. The molar fraction of each species, obtained from both the EPR and visible absorption data for pH $\leq 2$ were introduced into the PSEQUAD program and a log $\beta_{112}$ value of 35.64 $\pm$ 0.12 was refined for CuLH$_2$. On the other hand, from the pH-potentiometry data a log $\beta_{112}$ = 35.01 $\pm$ 0.01 was obtained from data in the pH range 1.7–11, but varying the log $\beta_{112}$ in the range 35.0–35.7 hardly affects the fitting parameter of the PSEQUAD program when using only the pH-metric data. The difference may be due to (i) the ionic strength, which was not exactly constant in the spectroscopic experiments at pH $\leq 2$ and (ii) the higher error associated with the pH-metric data used in the pH range 1.7–2.0. The log $\beta_{112}$ presented in Table 3 is the average of both values and the corresponding S.D. value reflects the different calculated values.

![Figure 5. EPR X-band spectra (room temperature) of solutions containing Cu$^\text{II}$ and Rpyr$_2$en with $C_{\text{Cu}} = 5 \text{ mmol dm}^{-3}$ and a L/M ratio of 1.1 at several pH values.](image)

It should be emphasized that in complexes with the salan ligands, once each of the N$_\text{amine}$ atoms coordinates they become a stereoicenters and $R$ and $S$ configurations become possible. Therefore, for each of the stoichiometries MLH$_2$, MLH, and ML at least three diastereoisomers are possible. These diastereoisomers are schematically represented by the coordination of the coordinated amine i.e. $(R,R)$, $(S,S)$, $(S,R)$, or $(R,S)$. Only for the MLH stoichiometry does the complex represented by $(S,R)$ differ from $(R,S)$. As found by DFT calculations for the V$^\text{IV}$O$^-$ and V$^\text{V}$O$_2^-$-Rpyr$_2$en complexes, the energies of the $(S,R)$ and $(R,S)$ diastereoisomers do not differ much from $(R,R)$ or $(S,S)$ (for this pair they are the same), and we predict that in solution all of them should form. With the techniques used...
in this work it is not possible to distinguish between these different diastereoisomers. Pyridoxamine (pyrN) is a vitamin B₆ analog and Rpyr2en can be seen as two pyridoxamine molecules linked by an ethylenyl bridge. The acid-base behavior and complexation of pyrN with Cu²⁺ and Ni²⁺ has been reported and the data (pK₁ = 0.15 m NaNO₃, 37 °C) is included in Table 3 for comparison. PyrN forms complexes with Cu²⁺ with the stoichiometry 1:1 and 2:1 (L/M) in various protonation states. The stability of the complexes formed in both ligand systems can be compared based on the constants (logK*) for the displacement of four protons: H₆L + Cu²⁺ ⇌ CuLH₄ + 4H⁺ (for Rpyr2en), and 2H₆L + Cu²⁺ ⇌ Cu₂L₄H₂ + 4H⁺ (for pyrN). The logK* values are –3.3 and –11.6, respectively. As expected, because of the chelate effect, the stability of the Rpyr2en-Cu²⁺ complexes is much higher than that of the corresponding pyridoxamine complexes.

Ni²⁺–Rpyr2en

In equimolar solutions slow processes take place at pH > 8, and precipitation of a pink complex occurs. However, for solutions with L/M ratios greater than 1 the pH-metric titration curves could be measured up to 11.7. The model that best fitted the experimental data was obtained considering the formation of 1:1 and 2:1 complexes. Without bis complexes the fitting parameter of PSEQUAD was ca. five times higher. The stability constants obtained are listed in Table 3, and Figure 3b depicts a species distribution diagram.

As is usually the case for Ni²⁺ complexes the large zero-field splitting precluded the observation of any X-band resonances. Although samples were measured by EPR spectroscopy, we were not able to obtain any EPR spectra. Moreover, ¹H NMR titrations carried out in D₂O with L/M ratios of 1 and 4 confirmed that the Ni²⁺ complexes are paramagnetic. In fact, in solutions with a L/M ratio of 1, no ¹H NMR peaks were observed for pH > 3, while only metal bound ligand is present, while for pH < 3 only the peaks from the noncomplexed ligand are seen. In solutions with a L/M ratio of 4 only the free ligand peaks were observed, and for pH > 3 their areas decrease (when compared with the peak of the internal reference).

Spectroscopic data for solutions of complexes Cu²⁺(Rpyr2en) or Ni²⁺(Rpyr2en) in DMSO are consistent with a square-planar coordination of the Rpyr2en ligand. In water the spectroscopic data of Ni(Rpyr2en) is consistent with an octahedral geometry involving the donor set: O₇phen, N₇amine,N₇amine,O₇phen,O₇w,O₇w (O₇phen = phenolate-O donor atom, N₇amine = amine-N donor atom, O₇w = water-O atom).

In aqueous solutions containing Ni²⁺ and Rpyr2en the situation is more complex. To confirm the pH-metric results and the presence of the bis complexes, spectrophotometric measurements were carried out with L/M ratios of 1 and 4. Upon changing the pH the spectra show a continuous change, indicating that the speciation is much more complex than that for the Cu²⁺ system. Below pH 3 (Figure 6, a) the spectra present two d-d bands in the wavelength range shown, with maxima at ca. 725 and 395 nm, which can be assigned to the [Ni(H₂O)₆]²⁺ transitions ³T₁g(F) — ³A₂g, and ³T₁g(P) — ³A₂g, respectively.[34] As the pH is increased stronger bands progressively build up. At pH 5.0, where species NiLH₂ is ca. 100% formed, the χmax are at 620 and 430 nm, and the latter transition [³T₁g(P) — ³A₂g, using the notation for an octahedral symmetry] overlapping the O₇phen—Ni CT band tailing in from the UV region. Spectra were also measured for pH > 3 in the near IR range (see Supporting Information, Figure SI-7 in ESI-3), which show the presence of a broad band at ca. 995 nm (ε = 18 mol dm⁻³ cm⁻¹ at pH = 6.7), confirming the octahedral geometry of the complexes. This band, assigned to ³T₁g — ³A₂g, gives a measure of the ligand field and shifts to higher energies between pH 3 and 6, confirming the increase in the field strength as the ligand replaces water in the Ni²⁺ coordination sphere. For solutions with a L/M ratio of 4 (Figure 6, b), the spectral features are the same as for L/M = 1 up to pH ca. 6, but above this pH the changes in the Vis spectra, upon increasing the pH, differ. With solutions containing L/M ratios of 4 no precipitation is observed below pH ca. 9.5, but at higher pH values a slight increase in the baseline suggests the presence of a small amount of precipitate. In the pH range 7.0–8.7, and for solutions with L/M = 4 (Figure 6, b), the spectra roughly intersect at 425 and 475 nm (not exactly isosbestic points) indicating the presence of two main types of species in equilibrium (between 1:1 and 2:1 complexes). Overall the Vis spectra confirm the species distribution diagram shown in Figure 3 (b).

ESI mass spectra were also measured to confirm the presence of the 2:1 (L/M) species. For aqueous solutions containing L/M = 1, C₉Ni ≈ 1 nm and pH = 5.3 several species were found in solution: m/z = 363.5 [L + 1]⁺, 419.3 [NiL + 1]⁺, 455.0 [NiL + 2H₂O]⁺, 781.0 [NiL₂ + 1]⁺. For solutions containing L/M = 4, C₉Ni ≈ 1 nm and pH = 7.1: m/z = 363.1 [L + 1]⁺, 385.1 [L + Na]⁺, 419.1 [NiL + 1]⁺, 780.9 [NiL₂ + 1]⁺. Although NiL₂ is found in both solutions, the intensity ratio of the MS peaks NiL/NiL₂ is 10:5 in the L/M = 1 solutions and 3.5:10 in the L/M = 4 solutions, showing the much higher importance of the bis complexes in solutions containing an excess of ligand.

NiLH₂ is the dominant species in the pH range 4–6 (see Figure 3). Its coordination geometry corresponds to a O₇phen,N₇amine,N₇amine,O₇phen,O₇w,O₇w donor set, where the pyridine-N atoms are protonated. For pH > 5.5 the species Ni₂L₂H₄, Ni₂L₂H₃, Ni₂L₂H₂, Ni₂L₂H, and Ni₂L₂ successively form up to a pH ca. 10.

For 2:1 complexes with tridentate ligands containing an O₇phen,N₇mine or N₇hydrazine and N₇amine donor set binding modes corresponding to what is shown schematically as I have been characterized in the solid state by X-ray diffraction.[35–37] While in these compounds a significant part of each of the two ligands [O₇phen and N₇mine or N₇hydrazine] is constrained to be planar, the Rpyr2en ligand is much more flexible, and to the best of our knowledge this study is the first example of Ni-sal₂en- or Ni-sal₂an-type complexes reported showing the formation of bis complexes.

The intensity of the phenolate–Ni³⁺ CT band increases over the pH range ca. 5.3 to ca. 8.5. This suggests an in-
crease in the number of phenolate donor atoms in the Ni$^{II}$ coordination sphere upon the successive formation of NiLH$_2$ → NiL$_2$H$_4$ → NiL$_2$H$_3$. For pH > 8.7 the CT band remains approximately unchanged up to ca. 11.7, while the absorption over the wavelength range 450–800 nm increases until pH 10.3, and then decreases up to 11.7 (see Supporting Information, Figure SI-5 in ESI-3). However, the structure of the 2:1 Ni–Rpyr$_2$en complexes in water is not easily anticipated. Formation of 2:1 complexes possibly involves displacement of one donor atom of the first ligand and the tridentate coordination of the second ligand. Binding modes such as I are a reasonable hypothesis, but the increase in intensity of the O phen–Ni CT band may be indicative of the coordination of at least a third O phen-donor atom.

The ratio log($K_{MLH_2}/K_{ML_2H_4}$) = 0.55 indicates a favorable interaction between the side chains in the bis complexes. These may be stabilized by intramolecular H bonds formed between groups of the coordinated ligands. In fact, the Rpyr$_2$en ligand is quite flexible and contains several groups that may be involved in H bond formation: e.g. the pyridine-N atom (either as N$_{pyridine}$ or NH$_{pyridine}$), the –(CH$_2$)–OH groups of pyridoxal, or the phenolic-O atoms (O$_{phen}$ or O$_{phen}$). Many possible binding modes and types of H bonds can be envisaged but discussing these further would be mainly speculation, as the techniques used do not help in this regard.

A comparison with pyridoxamine, which forms complexes of 1:1 and 2:1 L/M stoichiometry with Ni$^{II}$, can be
done based on the log $K^*$ for the same equilibrium, as in the case of CuII (see above); the log $K^*$ = −10.08 for Rpyr$_2$en and −15.99 for pyrN$^{[12]}$ shows the higher stability of the Rpyr$_2$en complexes, and also the lower stability of the NiII–Rpyr$_2$en complexes when compared with those of CuII–Rpyr$_2$en.

Conclusions

The coordination of the sal$_2$en- and sal$_3$an-type ligands pyr$_2$en, Rpyr$_2$en, and R(SO$_3$–sal)$_2$en to CuII and NiII was investigated. These ligands form stable and moderately water-soluble complexes with CuII and NiII. From solutions containing NiII and Rpyr$_2$en, crystals of the SB complex Ni(pyr$_2$en) were obtained, resulting from oxidative dehydration of the two amine bonds, probably by molecular oxygen. The solution and solid-state characterization of the metal complexes showed that this process did not occur with the other complexes. Time-dependent visible spectroscopic studies in aqueous solution with Ni(–Rpyr$_2$en) indicated that the dehydrogenation process, facilitated by molecular O$_2$, stops after oxidation of one amine bond. On standing for longer periods Ni(pyr$_2$en) was obtained but only in the solid state.

The complexation of Rpyr$_2$en with CuII and NiII could be studied by pH-potentiometry and spectroscopic techniques in aqueous solutions. In the CuII–Rpyr$_2$en system very stable 1:1 complexes form, and at pH ca. 2 these correspond to ca. 95% of the total CuII. Characterization of the solid complex obtained indicates a square-planar coordination geometry involving the two Ophenolate and two Namine as donor atoms. In the NiII–Rpyr$_2$en system, when an excess of ligand is used bis complexes are formed in aqueous solution at pH > 6, avoiding the precipitation of the neutral NiL complex. The proton displacement constants ($K^*$) of the process $H_2L + M^{2+} \rightarrow MLH^+ + 4H^+$ are as follows: $K^*(Cu(LH)^{2+}) = −3.27$, $K^*(V(OH)L)^{2+} = −5.63$, $K^*(Ni(LH)^{2+}) = −10.08$, $K^*(Zn(LH)^{2+}) = −11.38$, i.e. the stability order is CuII > VIVO > NiII > ZnII.

We should emphasize several aspects of the ligands studied in this work (or ligands obtained using the same aldehyde precursors and other diamines), which may have considerable advantages for e.g. catalytic applications using less toxic solvents, namely their higher solubility in aqueous and alcoholic solutions, when compared with most sal$_2$en-type ligands reported so far, because of the presence of hydrophilic groups in the aromatic rings. Moreover, the lower susceptibility to hydrolysis of the reduced sal$_3$an derivatives, when compared with the corresponding SB, and the higher stability of VIVO, VIV$^{[12]}$ CuII, and NiII complexes formed with the sal$_2$en-type ligands, may be important for both improving reaction yields and catalyst recovery. Finally, the higher flexibility of the sal$_2$en-type ligands and the fact that the coordinated Namine atoms are stereogenic centers may also prove useful for asymmetric synthesis if suitable diamine and/or aldehyde precursors are chosen. In the particular case of Rpyr$_2$en, with ligands containing Npyridinic atoms, the possibility of the various protonation states for the pyridinic nitrogens, which do not participate in coordination to the metal ions, allowing the formation of neutral and cationic complexes with the same coordination mode, may also help in tuning the redox characteristics of the complexes formed.

Experimental Section

The synthesis of pyr$_2$en, Rpyr$_2$en, and R(SO$_3$–sal)$_2$en was previously reported$^{[12–16]}$.

Synthesis of Complexes

Crystals of Ni(pyr$_2$en)·H$_2$O (1): From the filtrate solution of the reaction mixture used in the preparation of complex 6 orange crystals suitable for X-ray diffraction studies were obtained after six weeks.

Cu(pyr$_2$en) (2): The Schiff base pyr$_2$en (0.05 g, 0.2 mmol) was dissolved in water (25 mL) and the pH was adjusted to 7 by addition of KOH (3 mol). Cupric acetate (0.03 g, 0.1 mmol) was added and the mixture was heated to 50 °C for an hour. A dark pink solid precipitated, which was collected by filtration and washed with water, ethanol, and diethyl ether, and dried under vacuum. Yield: 0.063 g, 68%. $C_{18}H_{20}N_4O_4Cu·2H_2O$ (461.36) $\{[(Cu(pyr$_2$en))·2H$_2$O]:$ calculated C 46.86, H 5.37, N 12.14; found C 46.9, H 5.5, N 12.0.

Cu(Rpyr$_2$en) (3): The procedure was similar to the one used for 2. A blue solid was obtained. Yield: 0.043 g, 45%. $C_{14}H_{22}N_4O_4Cu·2H_2O$ (472.60) $\{[(Cu(Rpyr$_2$en))·2H_2O]:$ calculated C 45.75, H 6.27, N 11.86; found C 45.8, H 6.3, N 11.7.

Cu(R(SO$_3$–sal)$_2$en) (4): The procedure was similar to the one used for complex 2. A green solid was obtained. Yield: 0.053 g, 50.0%. $C_{16}H_{18}N_2O_8S_2Cu$·3H$_2$O (531.03) $\{[(Cu(R(SO_3$–sal)$_2$en))·3H_2O$: calculated C 36.26, H 4.18, N 5.29, S 12.10; found C 36.2, H 4.5, N 5.1, S 12.5.

Ni(pyr$_2$en) (5): Pyr$_2$en (0.5 g, 1.4 mmol) was dissolved in methanol (25 mL) containing a few drops of a KOH solution. Ni(II) acetate (0.35 g, 1.4 mmol) dissolved in methanol with a few drops of a KOH solution was added and the mixture was heated to 50°C for 1 h. A pink complex was obtained. Yield: 0.152 g, 51%. C$_{15}H_{18}N_2O_4Ni·3H_2O$·HCl. An orange solid precipitated and was collected by filtration and washed with water, ethanol, and diethyl ether, and dried under vacuum. Yield: 0.063 g, 68%. $C_{16}H_{12}N_2O_8S_2NiK_2·3H_2O$·HCl. An orange solid precipitated and was collected by filtration and washed with water, ethanol, and diethyl ether, and dried under vacuum. Yield: 0.063 g, 68%. $C_{16}H_{12}N_2O_8S_2NiK_2·3H_2O$·HCl. An orange solid precipitated and was collected by filtration and washed with water, ethanol, and diethyl ether, and dried under vacuum. Yield: 0.063 g, 68%. $C_{16}H_{12}N_2O_8S_2NiK_2·3H_2O$·HCl. An orange solid precipitated and was collected by filtration and washed with water, ethanol, and diethyl ether, and dried under vacuum. Yield: 0.063 g, 68%. $C_{16}H_{12}N_2O_8S_2NiK_2·3H_2O$·HCl. An orange solid precipitated and was collected by filtration and washed with water, ethanol, and diethyl ether, and dried under vacuum. Yield: 0.063 g, 68%. $C_{16}H_{12}N_2O_8S_2NiK_2·3H_2O$·HCl. An orange solid precipitated and was collected by filtration and washed with water, ethanol, and diethyl ether, and dried under vacuum. Yield: 0.063 g, 68%. $C_{16}H_{12}N_2O_8S_2NiK_2·3H_2O$·HCl. An orange solid precipitated and was collected by filtration and washed with water, ethanol, and diethyl ether, and dried under vacuum. Yield: 0.063 g, 68%. $C_{16}H_{12}N_2O_8S_2NiK_2·3H_2O$·HCl. An orange solid precipitated and was collected by filtration and washed with water, ethanol, and diethyl ether, and dried under vacuum. Yield: 0.063 g, 68%. $C_{16}H_{12}N_2O_8S_2NiK_2·3H_2O$·HCl. An orange solid precipitated and was collected by filtration and washed with water, ethanol, and diethyl ether, and dried under vacuum. Yield: 0.063 g, 68%. $C_{16}H_{12}N_2O_8S_2NiK_2·3H_2O$·HCl. An orange solid precipitated and was collected by filtration and washed with water, ethanol, and diethyl ether, and dried under vacuum. Yield: 0.063 g, 68%.
H, CH=N), 7.74 (s, 2 H, CH\textsubscript{arom}), 7.55 (d, 2 H, CH\textsubscript{arom}), 6.87 (d, 2 H, CH\textsubscript{arom}), 3.45 (s, 4 H, CH\textsubscript{2}CH\textsubscript{3}).

NiR(SO\textsubscript{2}–sal)\textsubscript{en} (8): The procedure was similar to the one used for the preparation of 5. Since there was no precipitation at pH 7 the solution was evaporated to dryness. Methanol was added to the residue, which did not dissolve everything. The solid was filtered, washed with methanol and diethyl ether, and dried under vacuum. After a few hours the grey solid obtained turned soft pink and after a week brown. Yield: 0.52 g, 62.0%. C\textsubscript{26}H\textsubscript{21}N\textsubscript{2}O\textsubscript{8}S\textsubscript{2}NiK\textsubscript{2} \[ \text{calcd. C 27.1, H 4.0, N 4.0, S 7.2. ESI-MS (H\textsubscript{2}O): m/z = 565.0 [M + 2K + 1]\] and 603.0 [M + 3K]}.  

Physical and Spectroscopic Studies: Infrared spectra were recorded with a BioRad FTS 3000 MX FTIR spectrometer. UV/Visible spectra were recorded either with a Hitachi U-2000, a Perkin-Elmer Lambda 9 UV/Vis/NIR, or an HP 8452A diode array spectrophotometer. The EPR spectra were recorded with a Bruker ESP 300E X-band spectrometer. 1H NMR spectra were recorded with a Varian Unity 300 spectrometer at probe temperature.

X-ray Crystal Structure Determination: Three-dimensional X-ray data were collected with a Bruker SMART 1000 CCD diffractometer by the \( h\otimes\) scan method. Data was collected at room temperature. Reflections were measured from a hemisphere of data collected from frames each covering 0.3° of 2\( \theta \). Reflections were measured from a hemisphere of data collected with a Bruker ESP 300E X-band spectrometer. The EPR spectra were recorded with a Bruker ESP 300E X-band spectrometer. 1H NMR spectra were recorded with a Varian Unity 300 spectrometer at probe temperature.

<table>
<thead>
<tr>
<th>Table 5. Crystal data collection and refinement.</th>
<th></th>
</tr>
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<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>( \text{C}<em>{18}\text{H}</em>{29}\text{N}<em>{4}O</em>{7}\text{Ni} )</td>
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<tr>
<td><strong>M\textsubscript{r} [g mol\textsuperscript{-1}]</strong></td>
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<tr>
<td><strong>Space group</strong></td>
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<td><strong>T [K]</strong></td>
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<tr>
<td><strong>a [\text{Å}]</strong></td>
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</tr>
<tr>
<td><strong>b [\text{Å}]</strong></td>
<td>12.637(3)</td>
</tr>
<tr>
<td><strong>c [\text{Å}]</strong></td>
<td>19.634(5)</td>
</tr>
<tr>
<td><strong>a [°]</strong></td>
<td>90</td>
</tr>
<tr>
<td><strong>b [°]</strong></td>
<td>90</td>
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<tr>
<td><strong>c [°]</strong></td>
<td>90</td>
</tr>
<tr>
<td><strong>( V [\text{Å}^3] )</strong></td>
<td>2051.3(9)</td>
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<tr>
<td><strong>( F(000) )</strong></td>
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<tr>
<td><strong>Z</strong></td>
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<tr>
<td><strong>D\textsubscript{calc} [g cm\textsuperscript{-3}]</strong></td>
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<td><strong>( \mu [mm\textsuperscript{-1}] )</strong></td>
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<tr>
<td><strong>( R_{int} )</strong></td>
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<tr>
<td><strong>No. of measured reflections</strong></td>
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<tr>
<td><strong>No. of observed reflections</strong></td>
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<td><strong>Goodness-of-fit on ( F^2 )</strong></td>
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<tr>
<td><strong>( R_1 )</strong></td>
<td>0.0593</td>
</tr>
<tr>
<td><strong>( wR_2 )</strong></td>
<td>0.2813</td>
</tr>
</tbody>
</table>

\[ a \] \( R_1 = \frac{\Sigma|F_o| - |F_r|}{\Sigma|F_o|} \), \( [b] wR_2 = \frac{\Sigma[w(\sigma(F_o)^2 - |F_r|^2)]^2}{\Sigma[w(F_o^2)]^2} \)^{1/2}.
known volumes of HCl of known concentration (ca. 0.1 mol dm$^{-3}$) with water. The Vis (300 < $\lambda$ < 900 nm) and room temperature EPR spectra of these samples were recorded and used for the determination of the speciation model at low pH, namely the log$\beta$ of CuLH$_3$ with the PSEQUAD program.$^{[31]}$

For the Ni$^{2+}$-Rpyr$_2$en system the spectral range covered was 190–820 nm (for the quantitative evaluation only the 390–820 nm range was used). The absorption spectra were recorded at L/M ratios of 1 and 4 (the total concentrations of the Ni$^{2+}$ [Ca$_2$] were 0.004 and 0.002 mol dm$^{-3}$, respectively). All other experimental conditions were as described for the pH-potentiometric titrations. For the solutions with a L/M ratio of 1 (C$_{Ca}$ = 0.004 mol dm$^{-3}$) precipitation of a pink compound occurred at pH ca. 8.3; this was not observed for solutions with L/M ratios of 4. With the latter solutions, the increasing absorbance of the baseline above pH ca. 9.2 suggested the presence of small amounts of precipitate. In order to confirm the octahedral geometry of the complexes Vis spectra with a L/M ratio of 1 and C$_{Ca}$ = 0.003 mol dm$^{-3}$ were measured at several pH values (3.0–7.7) in the 350–1100 nm range.

In the absence of ethylene glycol a relatively broad background was present in most of the frozen solution EPR spectra; therefore most spectra were run with solutions containing 5% of ethylene glycol. For the $^1$H NMR measurements, solutions containing Ni$^{2+}$ and Rpyr$_2$en with a L/M ratio of 1 (5 mmol dm$^{-3}$) and 4 (16.4 mmol dm$^{-3}$) were prepared in D$_2$O (DSS, sodium 3-trimethylsilyl-1-[2$^H$]propionate, as internal reference), and the pH was adjusted with DCl or CO$_2$ free KOD, using a Crison micropH 2002 instrument fitted with a combined Mettler Toledo U402-M3 S7/200 microelectrode. The microelectrode was previously calibrated with standard buffered aqueous solutions and log[D$^+$$] was measured directly in the NMR tubes. The final values of pH were determined from pH = pH$^*$ + 0.40, where pH$^*$ corresponds to the reading from the pH meter previously calibrated with two aqueous buffers at pH 4 and 7.

Mass spectrometer experiments were performed with a LCQ Duo (Finnigan, San Jose, CA, USA) ion trap mass spectrometer equipped with an electrospray ion source, operated in the positive mode and maintained at 4.5 kV. The temperature of the heated capillary was set to 200 °C. The flow rate of the electrospray solution was 5 μL min$^{-1}$. Other parameters, including capillary voltage, lens, and octapole voltages and sheath gas flow rate were optimized for maximum abundance of the ions of interest.

The ESI mass spectra measurements were done with solutions of nickel complexes 5–8 (1 × 10$^{-4}$ mol dm$^{-3}$) and of solutions containing Ni$^{2+}$ and Rpyr$_2$en with a L/M ratio of 1 (1 mmol dm$^{-3}$) and 4 (4:1 mmol dm$^{-3}$). All solutions were prepared with deionized water.

**Supporting Information** (see also the footnote on the first page of this article): **ESI-1** Crystalline packing in complex Ni-(pyr$_2$en)$_2$H$_3$O (1). **ESI-2** EPR spectra of complex Cu[R-(SO$_2$-sal)$]_2$en (4) and [Cu(OH)$_3$]$_2$ in H$_2$O. **ESI-3** Visible spectra for the Ni$^{2+}$-Rpyr$_2$en system with L/M = 1 and 4.

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