

Iron(III) Tris(pyridinehydroxamate)s and Related Nickel(II) and Zinc(II) Complexes: Potential Platforms for the Design of Novel Heterodimetallic Supramolecular Assemblies

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The reaction of 3- and 4-pyhaH (pyhaH = pyridinehydroxamic acid) with hydrated metal salts (Fe^{III} , Ni^{II} , Zn^{II}) in aqueous solution affords tris(pyridinehydroxamate)s in the case of Fe^{III} and bis(pyridinehydroxamate)s in the case of Zn^{II} and Ni^{II} in both the solid state and in solution. These metal pyridinehydroxamates that have the hydroxamato moiety coordinated in an O,O'-bidentate fashion all contain free pyridine nitrogen donor atoms that might allow them to be used

as building blocks in the construction of pyridinehydroxamato-bridged supramolecular assemblies. The crystal and molecular structures of the two novel Fe^{III} tris(pyridinehydroxamate) building blocks $[\text{Fe}^{\text{III}}(3\text{-pyha})_3] \cdot 5.125\text{H}_2\text{O}$ (**1a**) and $[\text{Fe}^{\text{III}}(4\text{-pyha})_3] \cdot 5.5\text{H}_2\text{O}$ (**2a**) are found to have different packing systems despite the similar nature of the two complexes. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2007)

Introduction

Hydroxamic acids, which were first discovered by Lossen in the late 19th century,^[1] are now firmly established as an important family of biomedical ligands with complex and well-defined chemistry and a wide variety of pharmaceutical properties.^[2] While hydroxamic acid containing compounds are most notably associated with Fe transport phenomena, they are ubiquitous in biology, playing vital roles in maintaining the proper function of enzymes in electron and oxygen transport and other life-sustaining processes.^[2] The versatile biological activity of hydroxamic acids is due to their strong metal-chelating ability and possibly their nitric oxide releasing properties.^[3]

The powerful metal-chelating ability of hydroxamic acids has been utilised to spectacular effect in the construction of a diverse host of fascinating metal complexes. These include hydroxamates,^[4] hydroximates^[4] and examples in supramolecular chemistry such as metallacrowns,^[5] coordination polymers^[6] and tetrahedral cluster complexes.^[7]

As ligands, hydroxamic acids typically coordinate in an O,O'-bidentate chelating fashion, coordinating through the carbonyl oxygen atom and the deprotonated hydroxy group to form very stable five-membered chelates. Other binding modes are possible, however, such as monodentate binding through the deprotonated nitrogen or oxygen atoms, although these modes require specially designed coordination environments to provide stabilisation.^[2,8] Bidentate binding of two metal ions has also been observed in an O, μ -O'-chelating mode.^[9] The complexation behaviour of hydroxamic acids can also be dramatically altered by the incorporation of ancillary coordinating groups at adjacent sites in the molecule.^[10] Additional deprotonation of the hydroxamato moiety can occur by metal-induced processes, leading to the formation of hydroximato complexes featuring both mono- and bidentate coordination where both the N- and O- atoms of the hydroxamic acid are deprotonated.^[11,12]

We recently reported that 2-pyridinehydroxamic acid (2-pyhaH) can coordinate to Pt^{II} to form a novel dinuclear Pt^{II} hydroximate complex, $[\{\text{cis-Pt}(\text{NH}_3)_2\}_2(\mu\text{-}(2\text{-pyhaH}_{-1}))(\text{ClO}_4)_2] \cdot \text{H}_2\text{O}$, with the di(amine) Pt^{II} moieties bridged by the doubly deprotonated pyridinehydroximato ligand, with N,N'-chelation to one $\text{cis-Pt}(\text{NH}_3)_2$ moiety and O,O'-chelation to the other (Figure 1).^[4]

We also recently utilised 3- and 4-pyridinehydroxamic acids 3- and 4-pyhaH as bridging scaffolds in the design of $\text{Pt}^{\text{II}}/\text{M}^{\text{II}}$ coordination polymers ($\text{M} = \text{Cu}$, Ni or Zn) because they can coordinate Pt^{II} in a monodentate fashion through the pyridine nitrogen atom only, thus leaving the hydroxamic acid moiety free to coordinate to a separate metal ion (Figure 2).^[6]

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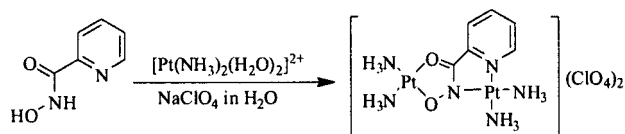


Figure 1. Coordination of 2-pyhaH to Pt^{II} to form the novel dinuclear Pt^{II} hydroxamate $[\{\text{cis-Pt}(\text{NH}_3)_2\}_2(\mu\text{-2-pyhaH})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$.

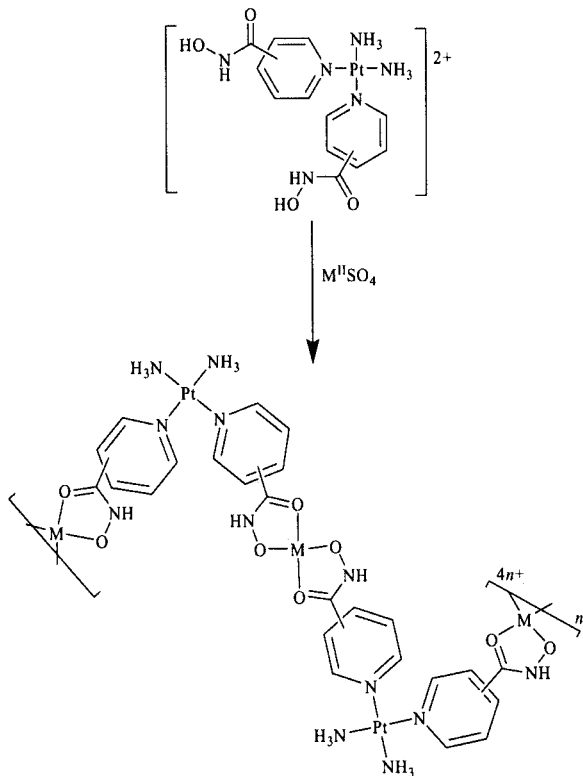


Figure 2. $\text{Pt}^{\text{II}}/\text{M}^{\text{II}}$ coordination polymers ($\text{M} = \text{Cu}$, Ni or Zn) constructed with 3- and 4-pyhaH as bridging scaffolds.

The present study extends this work to a new family of 3- and 4-pyridinehydroxamato complexes of Fe^{III} , Ni^{II} and Zn^{II} . We report the synthesis and crystal structures of $[\text{Fe}^{\text{III}}(3\text{-pyha})_3] \cdot 5.125\text{H}_2\text{O}$ and $[\text{Fe}^{\text{III}}(4\text{-pyha})_3] \cdot 5.5\text{H}_2\text{O}$ and the synthesis and characterisation of related Ni^{II} and Zn^{II} complexes. We hypothesise that such metal pyridinehydroxamates, where the hydroxamato moiety is coordinated to the metal ion in an O,O'-monoanionic way, may act as platforms for the design of novel heterodimetallic supramolecular assemblies because they contain free pyridine nitrogen donor atoms that can coordinate another metal ion. The crystal and molecular structures of the two Fe^{III} tris(pyridinehydroxamate) building blocks are found to have different packing systems despite the similar nature of the two complexes.

Results and Discussion

Syntheses of Mono- and Heteronuclear Metal Pyridinehydroxamates

Pyridinehydroxamic acids were synthesised from the corresponding methyl or ethyl esters in high yield and purity.

The metal pyridinehydroxamates were generally synthesised by dissolving the hydroxamic acid in water and adding an aqueous solution of the metal salt. This method yielded tris(pyridinehydroxamate)s in the case of Fe^{III} (Figure 3) and bis(pyridinehydroxamate)s in the case of Ni^{II} and Zn^{II} (Figure 4). Upon adjusting the pH to around 5.5, colour changes (to deep red, green and white for the Fe^{III} , Ni^{II} and Zn^{II} complexes, respectively) were observed accompanied by precipitation of the metal pyridinehydroxamates. All complexes were formed in reasonably good yields and high purity and were characterised by elemental analysis, IR spectroscopy and, where possible, UV/Vis spectroscopy. Only the Fe^{III} tris(pyridinehydroxamate)s formed crystals of good enough quality for X-ray analysis.

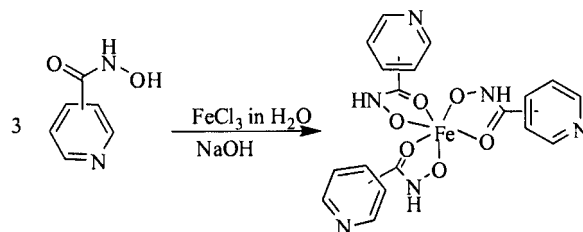


Figure 3. Synthesis of Fe^{III} tris(pyridinehydroxamate)s.

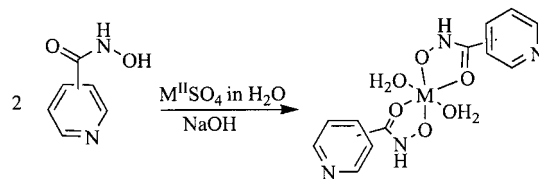


Figure 4. Synthesis of M^{II} bis(pyridinehydroxamate)s ($\text{M} = \text{Ni}$ or Zn).

IR spectroscopy proved a particularly useful technique for characterisation of the metal pyridinehydroxamates and assigning the coordination modes of the pyridinehydroxamato ligands. The IR spectra of $[\text{Fe}^{\text{III}}(3\text{-pyha})_3] \cdot 6.5\text{H}_2\text{O}$ and $[\text{Fe}^{\text{III}}(4\text{-pyha})_3] \cdot 1.5\text{H}_2\text{O}$ show a sharp and intense carbonyl stretch at 1600 and 1595 cm^{-1} , respectively, which are at lower wavenumbers than in the uncoordinated 3-pyhaH and 4-pyhaH ligands (1660 vs and 1643 cm^{-1} for 3-pyhaH and 1642 vs and 1608 cm^{-1} for 4-pyhaH). This indisputably confirms the involvement of the carbonyl oxygen atom in coordination of the Fe^{III} metal ion and is consistent with the X-ray crystallographic results. Similarly, the IR spectra of $[\text{Zn}^{\text{II}}(3\text{-pyha})_2(\text{H}_2\text{O})_2]$ and $[\text{Zn}^{\text{II}}(4\text{-pyha})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ each display a carbonyl stretch at 1618 vs and 1613 cm^{-1} , respectively, each of which has a shoulder at 1599 and 1592 cm^{-1} , respectively. Analogous shifts in the IR stretching frequencies were observed for the Ni^{II} bis(pyridinehydroxamate)s, indicative of O,O'-hydroxamato coordination. In addition, each metal complex exhibits the

characteristic C–N and N–H stretching bands of the hydroxamato moiety in the region 1555–1520 cm^{−1} and 3300–3185 cm^{−1}, respectively.

Crystal Structure of 1a

Crystals of [Fe^{III}(3-pyha)₃]·5.125H₂O formed from the mother liquor of the reaction between 3-pyhaH and FeCl₃·6H₂O. They were found to be of the monoclinic space group *P*2₁/*c* with eight formula units per unit cell. The structure consists of two independent molecules (**A** and **B**) of Fe^{III}(3-pyha)₃ (an ORTEP view of **A** and **B** at the 50% probability level is depicted in Figure 5). As expected due to the well-documented high affinity of Fe^{III} for hydroxamic acids,^[13] the Fe^{III} core is in a distorted octahedral O₆ environment with three 3-pyha chelating ligands coordinating through both oxygen atoms of the hydroxamato moiety to form stable five-membered chelate rings with the pyridinehydroxamato rings almost planar (Figure 5). The deviations of the Fe^{III} ions from the O–N–C–O planes are rather small (0.01–0.34 Å). The orientations of the pyridine rings with respect to the planes of the corresponding chelating ligands differ significantly for **A** and **B**, as shown by their respective N–C–C–C torsion angles (Table 1).

The range of torsion angles observed can be attributed to the influence of the hydrogen bonds formed between the pyridine nitrogen atoms and water molecules and also the stacking interactions between the pyridine rings. It should be noted that not all of the pyridine nitrogen atoms are involved in hydrogen bonding, whereas all of the pyridine rings are involved in stacking interactions. The degree of rotation of the pyridine ring relative to the hydroxamato functionality does not depend directly on the participation of the corresponding nitrogen atom in hydrogen bonding. For instance, in molecule **A** only two pyridine rings [containing the N(4A), N(6A) atoms], which are nearly coplanar to the connected hydroxamato rings (Table 1), are hydrogen-bonded to water molecules. The opposite situation is observed for molecule **B**, however, in which coplanar pyridine rings are not involved in hydrogen bonding while the other pyridine atom [N(5B)] forms a hydrogen bond with a water molecule. Thus, the conformation of the molecules in **1a** is defined by the effects of the crystal field, which is influenced by the hydrogen-bonding system as well as stacking interactions as a whole.

The Fe^{III}(3-pyha)₃ molecules form columns parallel to the screw axis by means of N–H···O hydrogen bonds and stacking interactions. The N(2B)–H(2NB)···O(1A) bond is formed between two independent molecules **A** and **B**, while the N(1B)–H(1NB)···O(3B) hydrogen bond connects molecules of type **B** only (see Figure S1 in the Supporting Information). All other hydrogen bonds involve water molecules. Stacking interactions exist between molecules **A** and **B**, **A** and **B''**, and **B** and **B''**. The formation of columns leaves a space between molecules which is filled with molecules from the neighbouring columns to form an interpenetrated columnar structure with stacking interactions between col-

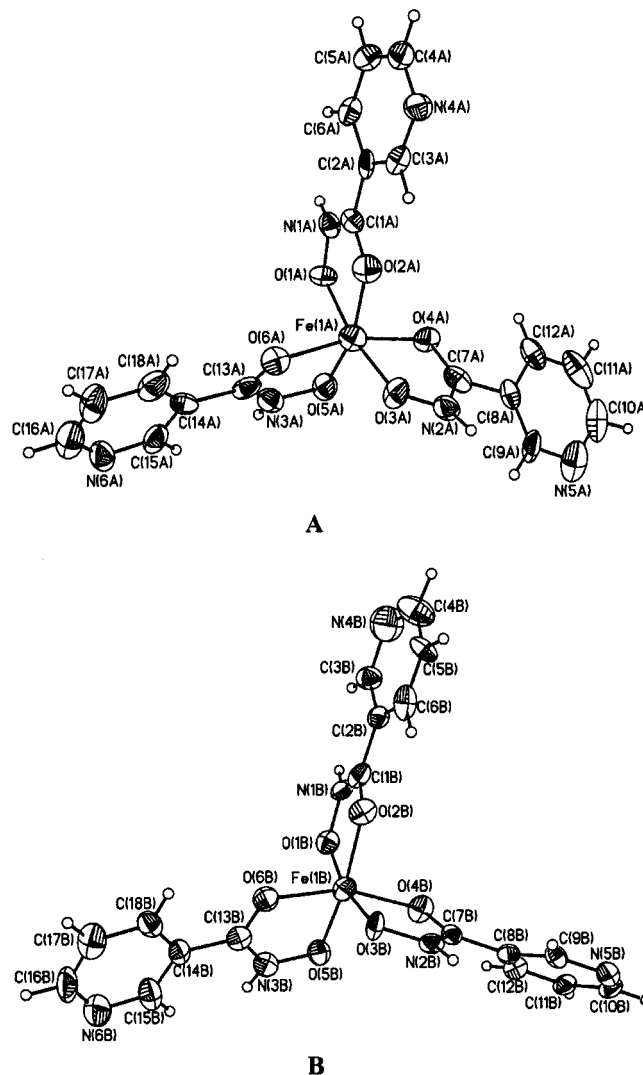


Figure 5. ORTEP drawings (50% probability) of the two independent molecules (**A** and **B**) of **1a** showing the atomic numbering scheme (water molecules of crystallisation have been omitted for clarity).

Table 1. Relative orientation of the pyridine rings and the corresponding hydroxamato rings for **1a** (**A** and **B**).

Torsion angle [°]	A	B
N(1)–C(1)–C(2)–C(3)	−174.1(5)	11.0(8)
N(2)–C(7)–C(8)–C(9)	31.5(8)	−32.7(8)
N(3)–C(13)–C(14)–C(15)	10.1(8)	−1.6(8)

umns and with channels parallel to the screw axis that are filled with water molecules (see Figure S2 in the Supporting Information).

Crystal Structure of 2a

[Fe^{III}(4-pyha)₃]·5.5H₂O crystallises in the tetragonal space group *I*4₁*a* with 5.5 water molecules of crystallisation per Fe centre and sixteen formula units in the unit cell. The molecular core consists of an Fe^{III} centre with three almost

planar 4-pyha ligands coordinating through both oxygen atoms of the pyridinehydroxamate group to form stable five-membered chelates (Figure 6). The orientations of the pyridine rings with respect to the planes of the corresponding chelating moieties are characterised by their respective N–C–C torsion angles (Table 2).

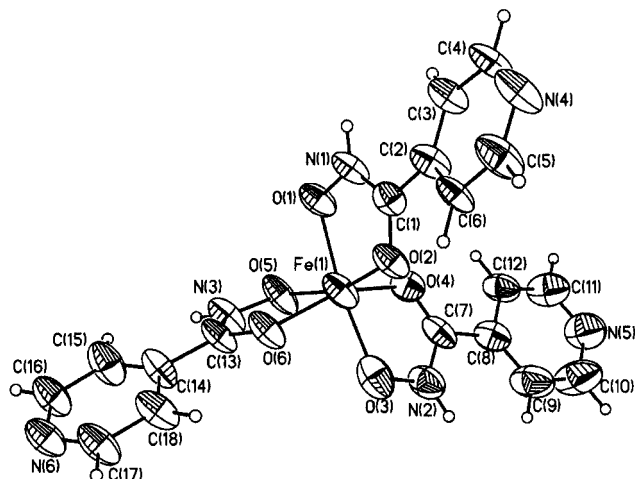


Figure 6. ORTEP view (50% probability) of **2a** showing the atomic numbering scheme (water molecules have been omitted for clarity).

Table 2. Relative orientation of the pyridine rings and corresponding hydroxamate rings in **2a**.

Atoms	Torsion angle [°]
N(1)–C(1)–C(2)–C(3)	–24.7(14)
N(2)–C(7)–C(8)–C(9)	–7.5(15)
N(3)–C(13)–C(14)–C(15)	–17.6(15)

The deviations of the Fe^{III} metal ions from the O–N–C–O planes are rather small (0.01–0.34 Å). The crystal packing motif of **2a** is based on two N(1)–H(1N)···O(1) and N(3)–H(3N)···N(6) hydrogen bonds between tris(4-pyha)Fe molecules, which results in a layered structure. Layers parallel to the *ab* crystallographic plane can be described as being built from hydrogen-bonded tetrameric fragments (Figure 7); π -stacking interactions between pyridine rings are also present in the layers (see Figure S3 in the Supporting Information). There are two types of tetrameric fragments in the layer, both of which are formed by molecules related by a fourfold screw axis. The first is formed by N(1)–H(1N)···O(1) interactions and has a butterfly structure, while the other is assembled by means of N(3)–H(3N)···N(6) bonds and is tetrahedral.

The tetrameric fragments are characterised by a chess-board order such that tetramers of the first type are connected to each other by tetramers of the second type, with each molecule participating in both types of tetramers and having four hydrogen-bonded neighbours (Figure 7).

The space between the hydrogen-bonded layers of **2a** is filled with the molecules of neighbouring layers, which results in an interpenetrated layered structure containing channels filled with water molecules. Two types of channels are found in the crystal structure of **2a**: the first is parallel

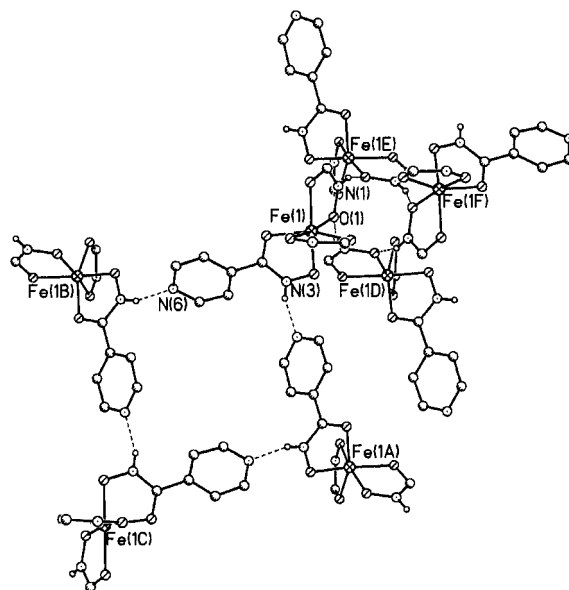


Figure 7. Two tetramers of **2a** formed by N(1)–H(1N)···O(1) and N(3)–H(3N)···N(6) hydrogen bonds (pyridine fragments not involved in hydrogen bonding have been omitted for clarity). Symmetry relations: Fe(1) [*x*, *y*, *z*], Fe(1A) [1.25 – *y*, 0.25 + *x*, 0.25 – *z*], Fe(1B) [–0.25 + *y*, 1.25 – *x*, 0.25 – *z*], Fe(1C) [1 – *x*, 1.5 – *y*, *z*], Fe(1D) [0.75 + *y*, 1.25 – *x*, 0.25 – *z*], Fe(1E) [1.25 – *y*, –0.75 + *x*, 0.25 – *z*], Fe(1F) [2 – *x*, 0.5 – *y*, *z*].

to the *b* axis and the second parallel to the *a* axis (see Figure S3 in the Supporting Information). The crystal structure of **2a** therefore represents a four-layered packing pattern.

Formation Constants and Species Distribution Curves

The protonation constants of the pyridinehydroxamic acid ligands 3-pyha (*L*¹) and 4-pyha (*L*²) and the overall stability constants for the binary ML systems (*M* = Fe^{III}, Ni^{II} or Zn^{II}; *L* = *L*¹ or *L*²) were calculated from potentiometric data. Two protonation processes were observed for each ligand upon titration with KOH (Figure 8); one proton is released from the pyridine N-atom and a second from the hydroxamate OH group (Table 3). The *pK*_{a2} value for 3-pyhaH, which corresponds to deprotonation of the hydroxamate OH group, is marginally higher than that for 4-pyhaH.

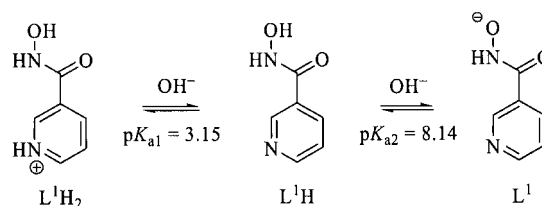


Figure 8. Protonation processes for 3-pyhaH₂ upon titration with KOH.

Table 3. Stability constants ($\log \beta$ values, which refer to the equilibrium $pM + sL + qH \rightleftharpoons M_pL_sH_q$) of the proton, Fe^{III} , Ni^{II} and Zn^{II} complexes of L^1 or L^2 ($L^1 = 3\text{-pyha}$, $L^2 = 4\text{-pyha}$) at 25 °C ($I = 0.1 \text{ M KNO}_3$).

Species	psq	$\log \beta$		
L ¹ H	011	8.14(0.01)		
L ¹ H ₂	012	11.29(0.01)		
L ² H	011	7.74(0.01)		
L ² H ₂	012	11.31(0.01)		
		Fe ^{III}	Ni ^{II}	Zn ^{II}
ML ¹	110	9.72(0.01)	4.59(0.02)	4.60(0.02)
M(L ¹) ₂	120	18.01(0.01)	8.43(0.02)	8.47(0.02)
M(L ¹) ₃	130	24.67(0.02)		
ML ¹ H ₋₁	11-1		-4.14(0.02)	-3.77(0.03)
ML ¹ H ₋₂	11-2			-12.73(0.01)
		Fe ^{III}	Ni ^{II}	Zn ^{II}
ML ²	110	9.77(0.02)	4.23(0.01)	4.22(0.02)
M(L ²) ₂	120	17.38(0.02)	7.86(0.02)	7.61(0.02)
M(L ²) ₃	130	23.13(0.03)		
ML ² H ₋₁	11-1		-4.81(0.03)	-4.41(0.03)
ML ² H ₋₂	11-2			-13.35(0.01)

For each system studied, the titration curves show significant shifts that are indicative of complex formation. The titration curves for the $Fe^{III}L^2$ system are shown in Figure 9 as a representative example of the tris(hydroxamato) systems. Fe^{III} forms ML , ML_2 and ML_3 species with both L^1 and L^2 (Figure 10) upon increasing pH, as expected, with stability constants slightly lower than those previously reported for the Fe^{III} benzohydroxamate system.^[14] We attribute this to the more electron-rich nature of the pyridine ring with respect to benzene.

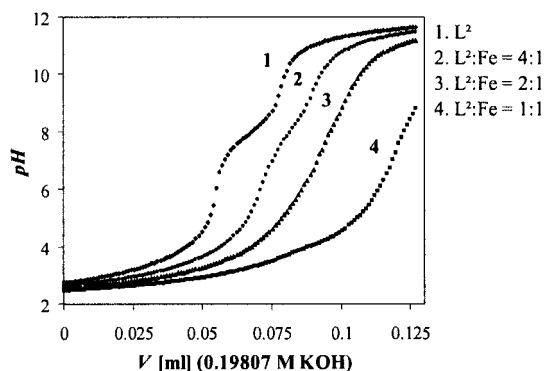


Figure 9. Titration curves for the $Fe^{III}L^2$ binary system.

The speciation studies support the presence of ML and ML_2 complexes for the Ni^{II} and Zn^{II} binary systems. The ML_2 complexes were also obtained in the solid state (3–6). The titration curves (Figure 11) and species distribution curves (Figure 12) for the $Ni^{II}L^2$ system are shown as representative examples of the bis(hydroxamato) systems. The $M(L^1)_2$ complexes ($\log \beta \approx 8.4$) were found to be slightly more stable in solution than their $M(L^2)_2$ analogues ($\log \beta \approx 7.7$).

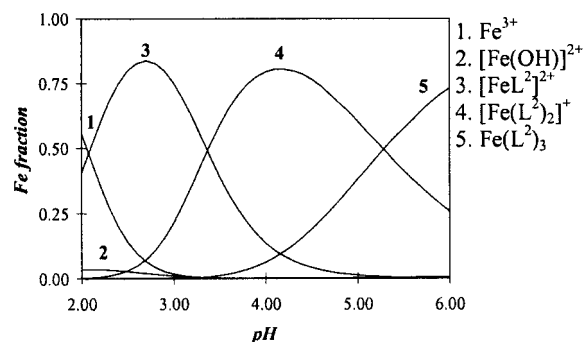


Figure 10. Distribution curves for the $Fe^{III}L^2$ system at pH = 2–6; $[Fe^{III}] = 1 \text{ mM}$; $[L^2] = 3 \text{ mM}$.

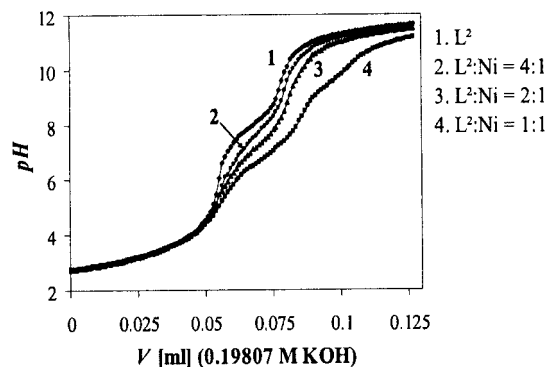


Figure 11. Titration curves for the $Ni^{II}L^2$ binary system.

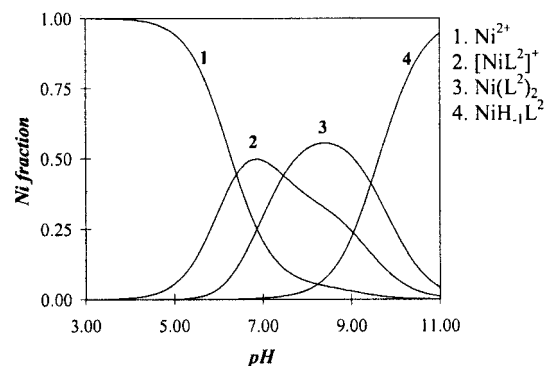


Figure 12. Distribution curves for the $Ni^{II}L^2$ system at pH = 2–6; $[Ni^{II}] = 1 \text{ mM}$; $[L^2] = 3 \text{ mM}$.

Spectrophotometric Study

Hydroxamic acids are known to form stable complexes with Fe^{III} .^[14] The Fe^{III} –hydroxamate interaction is characterised in the UV/Vis spectrum by a $\pi(\text{ligand}) \rightarrow d\pi(Fe)$ ligand-to-metal charge-transfer (LMCT) band. We monitored the reaction between Fe^{III} and L [$L = 3\text{-pyha}$ (L^1) and 4-pyha (L^2)] over the pH range of 2.11–5.97 (in line with the speciation studies reported) with an Fe^{III}/L ratio of 1:3 by spectrophotometry. Upon increasing the pH, we observed a hypsochromic shift of the LMCT band and an increase in absorption intensity corresponding to the formation of the mono-, bis- and tris(hydroxamato) complexes of Fe^{III} and also consistent with previously reported Fe^{III}

hydroxamate systems.^[14] Precipitation was observed at pH > 5.97. The 1:1 complexes give spectra with $\lambda_{\text{max}} \approx 510$ nm, the 1:2 complexes spectra with $\lambda_{\text{max}} \approx 480$ nm and the 1:3 complexes spectra with $\lambda_{\text{max}} \approx 425$ nm. The UV/Vis spectra of the $\text{Fe}^{\text{III}}\text{L}^2$ system are shown in Figure 13 as a representative example. The spectrophotometric results complement our potentiometry data and further confirm the formation of FeL , FeL_2 and FeL_3 complexes.

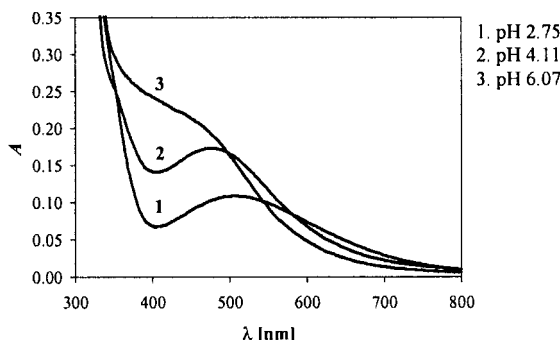


Figure 13. UV/Vis spectra of aqueous solutions of Fe^{III} (0.1 mM) and L^2 (0.3 mM) in KNO_3 (0.1 mM) at pH = 2.75, 4.11 and 6.07.

Conclusions

The affinity of hard Ni^{II} , Zn^{II} and Fe^{III} centres for hard oxygen donors facilitates the formation of a series of novel metal pyridinehydroxamates where the coordination mode is exclusively hydroxamato-O,O' with the ligand chelating to the metal centre as a monoanionic species. The crystal and molecular structures of two Fe^{III} tris(pyridinehydroxamate) building blocks have been determined and found to have different packing systems despite the similar nature of the two complexes. A comparative analysis of the crystal packing systems allows us to suggest that the different packing motifs found in **1a** and **2a** might, at least partly, be explained by the participation of the pyridine N-atom in hydrogen bonding to the pyridinehydroxamate ring in **2a**, while in **1a** hydrogen bonds are formed only between the pyridinehydroxamate rings and pyridine N-atoms are involved in hydrogen bonding with water molecules only.

These novel pyridinehydroxamato complexes of Fe^{III} , Ni^{II} and Zn^{II} lend themselves to further investigation as potential platforms for the design of novel heterodimetallic supramolecular assemblies.

Experimental Section

Materials and Methods: All reagents, deuterated solvents and metal salts were purchased from Sigma Aldrich and used without further purification. IR spectra were recorded as KBr discs with a Mattson Genesis II CSI FTIR spectrometer in the 4000–400 cm^{-1} region. UV/Vis spectra were recorded with a Helios Alpha Thermo Spectronic Spectrophotometer in a quartz cell. C, H, N, Fe, Ni and Zn elemental analyses were performed at the Microanalytical Laboratories, University College Dublin, Ireland. ^1H NMR spectra were recorded with a Bruker Advance DPX 400 FT spectrometer

at the Department of Chemistry, Trinity College Dublin, Ireland. The residual undeuterated DMSO signal was used as an internal reference at $\delta = 2.505$ ppm.

Preparation of the Ligands: These were prepared as reported previously.^[6]

3-Pyridinehydroxamic Acid (3-pyhaH, L^1): Hydroxylamine hydrochloride (5.07 g, 72 mmol) was added to sodium hydroxide (5.83 g, 146 mmol) in deionised water (37 mL) and the resulting solution was added dropwise to a solution of methyl nicotinate (5.00 g, 36 mmol) in methanol (55 mL). The solution was stirred at room temperature for 72 h, after which it was acidified to pH = 5.5 with 5% HCl. The solvent was removed in vacuo to yield a yellow solid. Methanol (60 mL) was added and sodium chloride was filtered off. The solvent was removed in vacuo to yield a light pink solid, which was recrystallised from water. Yield: 3.00 g (22 mmol, 66%). $\text{C}_6\text{H}_6\text{N}_2\text{O}_2$ (138.12): calcd. C 52.17, H 4.38, N 20.28; found C 51.98, H 4.24, N 20.14. ^1H NMR [400 MHz, $(\text{CD}_3)_2\text{SO}$, 25 °C]: $\delta = 11.41$ (s, 1 H, OH), 9.24 (br. s, 1 H, NH), 8.90 (d, $^4J_{\text{H,H}} = 2.00$ Hz, 1 H, H2), 8.70 (dd, $^3J_{\text{H,H}} = 5.04$, $^4J_{\text{H,H}} = 1.52$ Hz, 1 H, H4), 8.10 (dt, $^3J_{\text{H,H}} = 8.00$, $^4J_{\text{H,H}} = 2.00$ Hz, 1 H, H6) 7.51 (dd, $^3J_{\text{H,H}} = 8.04$, $^4J_{\text{H,H}} = 5.04$ Hz, 1 H, H5) ppm. IR (KBr disc): $\tilde{\nu}_{\text{max}} = 3196$ vs (hydroxamate N–H), 2802 s (hydroxamate O–H), 1660 vs and 1643 vs (hydroxamate C=O), 1594 s, 1557 s (hydroxamate C–N) cm^{-1} .

4-Pyridinehydroxamic Acid (4-pyhaH, L^2): This compound was prepared according to the same method as for 3-pyhaH except ethyl isonicotinate was used instead of methyl nicotinate. Yield: 55%. $\text{C}_6\text{H}_6\text{N}_2\text{O}_2$ (138.12): calcd. C 52.17, H 4.38, N 20.28; found C 51.94, H 4.29, N 20.12. ^1H NMR [400 MHz, $(\text{CD}_3)_2\text{SO}$, 25 °C]: $\delta = 11.41$ (s, 1 H, OH), 9.37 (br. s, 1 H, NH), 8.70 (d, $^3J_{\text{H,H}} = 5.6$ Hz, 2 H, H2/6), 7.68 (d, $^3J_{\text{H,H}} = 6.0$ Hz, 2 H, H3/5) ppm. IR (KBr disc): $\tilde{\nu}_{\text{max}} = 3186$ vs. (hydroxamate N–H), 2850b (hydroxamate O–H), 1642 vs. and 1608 s (hydroxamate C=O), 1551 s, 1531 s (hydroxamate C–N) cm^{-1} .

Preparation of Metal Pyridinehydroxamates

[Fe^{III} (3-pyha) $_3$] $\cdot 6.5\text{H}_2\text{O}$ (1**):** 3-pyhaH (150 mg, 1.086 mmol) was dissolved in tepid deionised water (5 mL) and, after allowing it to return to room temperature, an aqueous solution (5 mL) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (97.8 mg, 0.362 mmol) was added. The pH was adjusted to 5.5 with 5% NaOH, which resulted in the precipitation of a red solid. This was filtered, washed with water (3 mL) and dried over P_2O_5 . Yield: 141 mg (0.253 mmol, 70%). $\text{C}_{18}\text{H}_{28}\text{FeN}_6\text{O}_{12.5}$ (584.29): calcd. C 37.00, H 4.83, N 14.38, Fe 9.56; found C 37.00, H 4.87, N 14.00, Fe 9.22. IR (KBr disc): $\tilde{\nu}_{\text{max}} = 3186$ vs (hydroxamate N–H), 1600 vs (hydroxamate C=O), 1549 s, 1518 s (hydroxamate C–N) cm^{-1} . UV/Vis (H_2O): $\lambda_{\text{max}} = 430$ nm ($\epsilon = 2200 \text{ M}^{-1}\text{cm}^{-1}$, LMCT). Single crystals of [Fe^{III} (3-pyha) $_3$] $\cdot 5.125\text{H}_2\text{O}$ (**1a**) suitable for an X-ray diffraction study, were obtained from the filtrate after standing at room temperature for 2 d.

[Fe^{III} (4-pyha) $_3$] $\cdot 1.5\text{H}_2\text{O}$ (2**):** 4-pyhaH (150 mg, 1.086 mmol) was dissolved in tepid deionised water (5 mL) and, after allowing it to return to room temperature, an aqueous solution (5 mL) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (97.8 mg, 0.362 mmol) was added. The pH was adjusted to 5.5 with 5% NaOH, which resulting in the precipitation of a red solid. This was filtered, washed with water (3 mL) and dried over P_2O_5 . Yield: 120 mg (0.243 mmol, 67%). $\text{C}_{18}\text{H}_{18}\text{FeN}_6\text{O}_{7.5}$ (494.22): calcd. C 43.74, H 3.67, Fe 11.30, N 17.00; found C 43.98, H 3.38, Fe 11.40, N 16.93. IR (KBr disc): $\tilde{\nu}_{\text{max}} = 3186$ vs (hydroxamate N–H), 1595 vs (hydroxamate C=O), 1555 s (hydroxamate C–N) cm^{-1} . UV/Vis (H_2O): $\lambda_{\text{max}} = 430$ nm (ϵ

= 2800 M⁻¹ cm⁻¹, LMCT). Single crystals of Fe^{III}(4-pyha)₃·5.5H₂O (**2a**) suitable for an X-ray diffraction study were obtained from the filtrate after standing at room temperature for 2 d.

[Ni^{II}(3-pyha)₂(H₂O)₂] (3): 3-pyhaH (100 mg, 0.724 mmol) was dissolved in tepid deionised water (5 mL) and an aqueous solution (5 mL) of NiSO₄·6H₂O (95 mg, 0.362 mmol) was added. The pH was adjusted to 5.5 with 5% NaOH, which resulted in the precipitation of a green solid. This was filtered, washed with water (3 mL) and dried over P₂O₅. Yield: 79 mg (0.213 mmol, 59%). C₁₂H₁₄N₄NiO₆ (368.96): calcd. C 39.06, H 3.82, N 15.19, Ni 15.91; found C 38.69, H 3.69, N 14.70, Ni 16.50. IR (KBr disc): $\tilde{\nu}_{\max}$ = 3210 vs (hydroxamato N–H), 1611 vs (hydroxamato C=O), 1524 s (hydroxamato C–N) cm⁻¹.

[Ni^{II}(4-pyha)₂(H₂O)₂] (4): 4-pyhaH (100 mg, 0.724 mmol) was dissolved in tepid deionised water (5 mL) and an aqueous solution (5 mL) of NiSO₄·6H₂O (95 mg, 0.362 mmol) was added. The pH was adjusted to 5.5 with 5% NaOH, which resulted in the precipitation of a green solid. This was filtered, washed with water (3 mL) and dried over P₂O₅. Yield: 94 mg (0.253 mmol, 70%). C₁₂H₁₄N₄NiO₆ (368.96): calcd. C 39.06, H 3.82, N 15.19, Ni 15.91; found C 39.12, H 3.33, N 14.80, Ni 15.83. IR (KBr disc): $\tilde{\nu}_{\max}$ = 3185 vs (hydroxamato N–H), 1613 vs, 1586 vs (hydroxamato C=O), 1533 vs (hydroxamato C–N) cm⁻¹.

[Zn^{II}(3-pyha)₂(H₂O)₂] (5): 3-pyhaH (100 mg, 0.724 mmol) was dissolved in tepid deionised water (10 mL). ZnSO₄·7H₂O (104 mg, 0.362 mmol) was added to this solution and the pH was adjusted to 5.5 with 5% NaOH. The resultant white precipitate was filtered, washed with water (3 mL) and dried over P₂O₅. Yield: 61 mg (0.163 mmol, 45%). C₁₂H₁₄N₄O₆Zn (375.65): calcd. C 38.37, H 3.76, N 14.91, Zn 17.41; found C 38.16, H 3.58, N 14.70, Zn 16.37. IR (KBr disc): $\tilde{\nu}_{\max}$ = 3292 vs (hydroxamato N–H), 1618 vs (hydroxamato C=O), 1547 m (hydroxamato C–N) cm⁻¹.

[Zn^{II}(4-pyha)₂(H₂O)₂]·H₂O (6): 4-pyhaH (100 mg, 0.724 mmol) was dissolved in tepid deionised water (10 mL). ZnSO₄·7H₂O (104 mg, 0.362 mmol) was added to this solution and the pH was adjusted to 6 with 5% NaOH. The resultant white precipitate was filtered, washed with water (3 mL) and dried over P₂O₅. Yield: 79 mg (0.199 mmol, 55%). C₁₂H₁₆N₄O₇Zn (393.67): calcd. C 36.61, H 4.10, N 14.23, Zn 16.61; found C 37.06, H 3.04, N 14.28, Zn 16.56. IR (KBr disc): $\tilde{\nu}_{\max}$ = 3295 vs (hydroxamato N–H), 1613 vs, 1592 vs (hydroxamato C=O), 1536 s (hydroxamato C–N) cm⁻¹.

Potentiometric Studies: Potentiometric measurements were carried out using solutions of 0.1 M KNO₃ ionic strength at 25 °C. A carbonate-free KOH solution (0.19807 M) standardised with potassium hydrogen phthalate^[15] was used as titrant. The pH-metric studies were carried out with a Molspin pH-meter and titration controller with Thermo Russell CMAW711 combined electrode and Hamilton syringe autoburette, in the pH range of 2.5–10.5. The electrode system was calibrated daily by the method of Irving et al.^[16] (pK_w = 13.831) and the pH meter readings were converted into hydrogen ion concentrations. The initial volume of the samples was about 2 mL and the ligand concentration was 0.002 M in all systems. Three different metal/ligand ratios (1:1, 1:2 and 1:4) were used. The pH-metric data were used to determine pK_a values and the stoichiometry of the species and to calculate their concentration stability constants. The calculations were performed with the Hyperquad 2000^[17] program. Literature data were used for (hydroxido)Fe^{III} complexes: [FeH₂]²⁺: –3.21; [FeH₂]⁺: –6.73; [Fe₂H₂]⁴⁺: –4.09; [Fe₃H₄]⁵⁺: –7.58.^[18] The standard deviations quoted refer to random errors.

Spectrophotometric Studies: UV/Vis spectra for the Fe^{III}L systems (L¹ = 3-pyha and L² = 4-pyha) were obtained with a Helios Alpha

Thermo Spectronic Spectrophotometer in the region 300–800 nm. The Fe/L ratios were 1:3 ([Fe^{III}] = 0.1 mM). The pH of the solutions was adjusted with KOH (0.02 M) and HNO₃ (0.02 M).

Crystallographic Measurements for 1a and 2a: X-ray crystallographic experiments were carried out with a SMART 1000 CCD diffractometer [$\lambda(\text{Mo-K}\alpha) = 0.71073 \text{ \AA}$, graphite monochromator, ω -scans] at 120(2) K. The details of the data collection and crystal structure refinements using the SAINT Plus,^[19] SADABS and SHELXTL-97^[20] program packages are summarised in Table 4. For both structures, hydrogen atoms attached to the nitrogen atoms and to the oxygen atoms of water molecules were located in the difference Fourier maps and were then shifted to the standard X-ray values for N–H and O–H bonds and included in the refinement using the riding approximation. All other hydrogen atoms were placed in geometrically calculated positions and refined with a riding model as well. CCDC-628980 (**1a**) and -628981 (**2a**) contain the supplementary crystallographic data for this paper. These can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.ac.uk/data_request/cif.

Table 4. Crystallographic data for **1a** and **2a**.

Compound	1a	2a
Empirical formula	C ₁₈ H _{25.25} FeN ₆ O _{11.13}	C ₁₈ H ₂₆ FeN ₆ O _{11.5}
Formula mass	559.54	566.30
Crystal colour	red	red
Crystal habit	needle	plate
Crystal size [mm]	0.25 × 0.1 × 0.05	0.15 × 0.1 × 0.02
Crystal system	monoclinic	tetragonal
Space group	P2 ₁ /c	I4 ₁ /a
<i>a</i> [Å]	15.833(4)	13.872(3)
<i>b</i> [Å]	11.804(3)	13.872(3)
<i>c</i> [Å]	27.463(6)	55.462(18)
β [°]	105.617(6)	90
<i>V</i> [Å ³]	4943(2)	10673(5)
<i>Z</i>	8	16
$\rho_{\text{calcd.}}$ [g cm ⁻³]	1.504	1.410
<i>F</i> (000)	2322	4704
μ [mm ⁻¹]	0.678	0.630
<i>T</i> _{max} , <i>T</i> _{min}	0.967, 0.793	0.987, 0.796
θ range [°]	1.54–26.00	1.84–23.03
Reflections collected	28611	21340
Indep reflections, <i>R</i> _{int}	9637, 0.1500	3670, 0.1878
Completeness to θ [%]	99.1	98.1
Refined parameters	662	333
<i>GOF</i> (<i>F</i> ²)	0.904	1.010
Reflections [<i>I</i> > 2 σ (<i>I</i>)]	3295	1544
<i>R</i> ₁ (<i>F</i>) [<i>I</i> > 2 σ (<i>I</i>)] ^[a]	0.0675	0.0860
<i>wR</i> ₂ (<i>F</i> ²) (all data) ^[b]	0.0905	0.2197

[a] $R_1 = \sum |F_o - |F_c|| / \sum (F_o)$. [b] $wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$.

Supporting Information (see footnote on the first page of this article): Crystal packing diagrams of **1a**, crystal packing diagram of **2a** and selected bond lengths for **1a** and **2a**.

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