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Synthesis, characterisation and speciation studies of heterobimetallic pyridinehydroxamate-bridged Pt(II)/M(II) complexes (M = Cu, Ni, Zn). Crystal structure of a novel heterobimetallic 3-pyridinehydroxamate-bridged Pt(II)/Cu(II) wave-like coordination polymer†

Clodagh Mulcahy,[a] Fedor M. Dolgushin,[b] Krystyna A. Krot,[a] Darren Griffith[a] and Celine J. Marmion*[a]

[a] *Centre for Synthesis & Chemical Biology, Department of Pharmaceutical & Medicinal Chemistry, Royal College of Surgeons in Ireland, 123 St. Stephens Green, Dublin 2, Ireland. E-mail: cmarmion@rcsi.ie; Fax: 353 1 402 2168; Tel: 353 1 402 2161*

[b] *X-Ray Structural Centre, General and Technical Chemistry Division, Academy of Sciences of Russia, Vavilov Str. 28, Moscow, B-334, 117813, Russia*

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The reaction of *cis*-$[Pt(NH_3)_2(3\text{-pyhaH})_2]^{2+}$ (3-pyhaH = 3-pyridinehydroxamic acid) and *cis*-$[Pt(NH_3)_2(4\text{-pyhaH})_2]^{2+}$ (4-pyhaH = 4-pyridinehydroxamic acid) with Cu(II), Ni(II) or Zn(II) in aqueous solution affords novel heterobimetallic pyridinehydroxamate-bridged complexes, {*cis*-$[Pt(NH_3)_2(\mu\text{-3-pyha})M(\mu\text{-3-pyha})]\cdot SO_4\cdot xH_2O\}_n$ and {*cis*-$[Pt(NH_3)_2(\mu\text{-4-pyha})M(\mu\text{-4-pyha})]\cdot SO_4\cdot xH_2O\}_n$ respectively. The crystal and molecular structure of one of these, {*cis*-$[Pt(NH_3)_2(\mu\text{-3-pyha})Cu(\mu\text{-3-pyha})]SO_4\cdot 8H_2O\}_n$ **3a**, has been determined and was found to be a novel heterobimetallic wave-like coordination polymer, the structure of which contains interlinked pyridinehydroxamate-bridged repeating units of Pt(II) and Cu(II) ions in slightly distorted square-planar N_4 and O_4 coordination environments respectively and extensive hydrogen-bonding through the Pt ammines and the deprotonated hydroxamate *O* and *via* the *O* of the SO_4^{2-} counterions and the H(*N*) of the hydroxamate moiety. Spectrophotometric and speciation studies on the other heterobimetallic systems confirm that very similar species are being formed in solution and based on elemental analysis and spectroscopic results analogous complexes are formed in the solid-state. In this paper, we report the first examples of coordination polymers incorporating both Pt(II)/Cu(II), Pt(II)/Ni(II) and Pt(II)/Zn(II) and containing pyridinehydroxamic acids as bridging scaffolds.

Introduction

In recent years, there has been an exponential growth in the level of research activity surrounding the rational design and synthesis of molecular architectures from both a structural and topological viewpoint as well as exploiting their potential as functional materials in relation to host–guest chemistry, electrical conductivity, magnetism, ion exchange and catalysis. The diverse range of metal coordination geometries, as well as the ability to fine-tune ligands in terms of size, shape and functionality have culminated in structural motifs[1] such as grids,[2] boxes,[2] cylinders,[2] helicates[2] and coordination polymers,[3] extended structures comprising metal centres joined by bridging, multi-functional ligands. The self-assembly of coordination polymeric chains using template counterions, although reported for a variety of metal ions including Cu(I)/Cu(II),[4] Zn(II)[3] and Ag(I),[5] is hitherto relatively unexplored in relation to Pt chemistry. In fact there are only two recent reports in the literature, both by Lang *et al.*, of Pt(II)/Ag(I) and Pt(II)/Cu(I) coordination polymers and in both cases, an alkynyl ligand bridges the two metal ions where coordination is *via* a σ-C–Pt bond and a π-C–M bond (M = Cu(I) or Ag(I)).[6,7]

Furthermore, although hydroxamic acids, a remarkable family of bioligands[8] of general formula RCONR′OH, have been extensively employed as scaffolds in metallacrown chemistry,[9,10] surprisingly they have never been utilised as building blocks in the rational design of coordination polymers. Hydroxamic acids are also involved in numerous biological processes including metal-ion transport and inhibition of metalloenzymes such as matrix metalloproteinases, ureases, lipoxygenases, cyclooxygenases and peptide deformylases.[8,11,12] Hydroxamic acids also represent a wide spectrum of bioactive compounds having hypotensive, anti-cancer, anti-malarial, anti-tuberculosis and anti-fungal properties and have been identified as key therapeutic agents targeting cardiovascular diseases, HIV, Alzheimer's disease and metal-poisoning.[8] The versatile biological activity of hydroxamic acids is due to their strong metal-chelating ability and possibly their NO-releasing properties.[13] To the best of our knowledge, there have been no reports to date of either organometallic or coordination polymers incorporating both Pt(II) and Cu(II), Ni(II) or Zn(II), nor any containing hydroxamic acids as building blocks. With this in mind, we sought to create a novel class of 2D network polymers specifically containing Pt(II) and M(II) where M = Cu, Ni or Zn and utilising hydroxamic acids as scaffolds.

Our initial strategy focussed on the design of a hydroxamic acid-containing ligand with two coordination sites juxtaposed in such a fashion that they cannot both coordinate to the same metal ion. While 2-pyridinehydroxamic acid (2-pyhaH) was recently shown to coordinate to Pt(II) forming a novel dinuclear Pt(II) hydroximate complex, $[\{cis\text{-}Pt(NH_3)_2\}_2(\mu\text{-2-pyhaH}_{-1})](ClO_4)_2\cdot H_2O$ with the diammine Pt(II) moieties bridged *via* the doubly deprotonated pyridinehydroximate ligand, and, with (*N*,*N*) chelation to one Pt and (*O*,*O*) to the other,[14] we hypothesised that 3- or 4-pyridinehydroxamic acid (3- or 4-pyhaH) could be utilised as bridging scaffolds in the design of

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† Electronic supplementary information (ESI) available: Species distribution for the **L** : Zn(II) system where **L** is *cis*-$[Pt(NH_3)_2(3\text{-pyhaH})_2]^{2+}$, pH 4–11; Titration curve for the **L** : Zn(II) system where **L** = *cis*-$[Pt(NH_3)_2(3\text{-pyhaH})_2]^{2+}$. See http://www.rsc.org/suppdata/dt/b5/b501105a/

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coordination polymers because they could coordinate Pt(II) in a monodentate fashion *via* the pyridine nitrogen, leaving the hydroxamic acid moiety free to coordinate to a separate metal ion, Fig. 1.

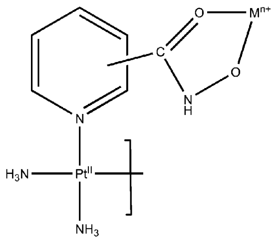


Fig. 1 Pt(II)/M(II) pyridinehydroxamate moiety (M = Cu, Ni, Zn).

Herein we report the synthesis and characterisation of the first examples to date of Pt(II)/M(II) heterobimetallic pyridinehydroxamate-bridged coordination polymers of general formula {*cis*-[Pt(NH$_3$)$_2$(μ-pyha)M(μ-pyha)]SO$_4$·*x*H$_2$O}$_n$, where M = Cu(II), Ni(II) or Zn(II) and pyha is 3- or 4-pyridinehydroxamate. The crystal structure of {*cis*-[Pt(NH$_3$)$_2$(μ-3-pyha)Cu(μ-3-pyha)]SO$_4$·8H$_2$O}$_n$, is also described. Speciation and spectroscopic studies of related systems are also reported.

Experimental

Materials and methods

All reagents, deuterated solvents and metal salts were purchased from Sigma Aldrich and used without further purification. Iodoplatin was synthesised by a previously reported literature method.[15] IR spectra were recorded on KBr discs on a Mattson Genesis II CSI FTIR spectrometer in the 4000–400 cm^{-1} region. UV-Vis spectra were performed on a Helios α Thermo Spectronic Spectrophotometer in a quartz cell. C, H, N, Cu, Ni and Zn elemental analysis were peformed at the Microanalytical laboratories, University College Dublin, Ireland. ^{1}H NMR spectra were recorded on 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 2.505 ppm. ESR spectra were recorded on a Varian E9 X-band spectrometer at a temperature of 158 K. Variable-temperature magnetic measurements were carried out on polycrystalline samples using a Faraday type magnetometer (Oxford Instruments), equipped with a continuous-flow cryostat, and an electromagnet operating at a magnetic field of 0.8 T. Diamagnetic corrections were estimated from Pascal constants.

Syntheses

3-Pyridinehydroxamic acid (3-pyhaH). Hydroxylamine hydrochloride (5.07 g, 72 mmol) was added to sodium hydroxide (5.83 g, 146 mmol) in deionised water (37 cm^3). The resulting solution was added dropwise to methylnicotinate (5.00 g, 36 mmol) in methanol (55 cm^3). The solution was stirred at room temperature for 72 h, after which the solution was acidified to pH 5.5 using 5% HCl. The solvent was removed *in vacuo* yielding a yellow solid. Methanol (60 cm^3) was added and sodium chloride was filtered. The solvent was removed *in vacuo* yielding a light pink solid, which was recrystallised from water (3.00 g, 22 mmol, 66%). (Found: C, 51.98; H, 4.24; N, 20.14. $C_6H_6N_2O_2$ requires C, 52.17; H, 4.38; N, 20.28%); δ_H (d^6-DMSO) 11.41 (s, 1H, OH), 9.24 (sb, 1H, NH), 8.90 (d, ^4J 2.00 Hz, 1H, H^2), 8.70 (dd, ^3J 5.04 Hz, ^4J 1.52 Hz, 1H, H^4), 8.10 (dt, ^3J 8.00 Hz, ^4J 2.00 Hz, 1H, H^6) 7.51 (dd, ^3J 8.04 Hz, ^4J 5.04 Hz, 1H, H^5); ν_{max}/cm^{-1} (KBr disc) 3196vs, 2950m, 2802s, 1660vs, 1643vs, 1594s, 1557s, 1496s, 1422s, 1306m, 1025vs, 713vs, 646vs.

4-Pyridinehydroxamic acid (4-pyhaH). This was prepared by the same method as for 3-pyhaH except ethylisonicotinate was used instead of methylnicotinate. Yield: 55%. (Found: C, 51.94; H, 4.29; N, 20.12. $C_6H_6N_2O_2$ requires C, 52.17; H, 4.38; N, 20.28%); δ_H (d^6-DMSO) 11.60 (s, 1H, OH), 9.37 (sb, 1H, NH), 8.70 (d, ^3J 5.6 Hz, 2H, H$^{2/6}$), 7.68 (d, ^3J 6.0 Hz, 2H, H$^{3/5}$); ν_{max}/cm^{-1} (KBr disc) 3186vs, 3061s, 2999s, 2850b, 1642vs, 1608s, 1551s, 1531s, 1321s, 1164s, 1009s 906s, 850vs, 688vs, 639vs.

***cis*-[Pt(NH$_3$)$_2$(3-pyhaH)$_2$](BPh$_4$)$_2$·4H$_2$O, 1.** Iodoplatin (*cis*-Pt(NH$_3$)$_2$I$_2$) (0.40 g, 0.83 mmol) was stirred with AgNO$_3$ (0.27 g, 1.60 mmol) in deionised water (10 cm^3) at 40 °C in darkness for 24 h. The AgI precipitate was filtered off and 3-pyridinehydroxamic acid, 3-pyhaH (0.27 g, 1.98 mmol) in deionised water (10 cm^3) was added to the filtrate. This reaction solution was stirred at room temperature for 24 h. NaBPh$_4$ (0.58 g, 2.1 mmol) was added and the resulting yellow precipitate was filtered and dried over P$_2$O$_5$. The solid was subsequently recrystallised from an aqueous/methanol solution, filtered and dried over P$_2$O$_5$. Yield: 0.72 g, 0.59 mmol, 71%. (Found: C, 59.83; H, 5.28; N, 6.66. $PtC_{60}H_{66}N_6O_8B_2$ requires C, 59.27; H, 5.47; N, 6.91%; δ_H (d^6-DMSO): 11.61 (s, 2H, OH), 9.49 (s, 2H, NH), 9.10 (s, 2H, H^2), 8.65 (d, 2H, H^4), 8.22 (d, 2H, H^6), 7.50 (m, 2H, H^5), 7.17 (s, 8H, phenyl H), 7.05 (t, 8H, phenyl H), 6.97 (t, 4H, phenyl H), 4.08 (s, 6H, NH$_3$); ν_{max}/cm^{-1} (KBr disc) 3253vs, 2879s, 1650vs, 1612s, 1558s, 750vs, 706vs.

***cis*-[Pt(NH$_3$)$_2$(4-pyhaH)$_2$](BPh$_4$)$_2$·4H$_2$O, 2.** This was synthesised by the same method as *cis*-[Pt(NH$_3$)$_2$(3-pyhaH)$_2$](BPh$_4$)$_2$·4H$_2$O but using 4-pyhaH in place of 3-pyhaH. Yield: 69%. (Found: C, 59.83; H, 5.28; N, 6.66. $PtC_{60}H_{66}N_6O_8B_2$ requires C, 59.27; H, 5.47; N, 6.91%); δ_H (d^6-DMSO) 11.72 (s, 2H, OH), 9.57 (s, 2H, NH), 8.82 (d, 2H, H$^{2/6}$), 7.70 (d, 2H, H$^{3/5}$), 7.10 (s, 8H, phenyl H), 6.78 (t, 8H, phenyl H), 6.64 (t, 4H, phenyl H), 4.71 (s, 6H, NH$_3$); ν_{max}/cm^{-1} (KBr disc) 3251vs, 2872s, 1661vs, 1614s, 1553s, 751vs, 705vs.

Preparation of heterobimetallic pyridinehydroxamate-bridged Pt(II)/M(II) complexes

{*cis*-[Pt(NH$_3$)$_2$(μ-3-pyha)Cu(μ-3-pyha)]SO$_4$·2H$_2$O}$_n$, 3. After stirring for 24 h at 40 °C in darkness, an aqueous suspension (15 cm^3) of *cis*-Pt(NH$_3$)$_2$I$_2$ (0.26 g, 0.55 mmol) and AgNO$_3$ (0.18 g, 1.09 mmol) generated *cis*-[Pt(NH$_3$)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ (0.55 mmol) which was subsequently reacted *in situ* with 3-pyhaH (0.15 g, 1.1 mmol) and, upon stirring at 40 °C for 24 h, yielded *cis*-[Pt(NH$_3$)$_2$(3-pyhaH)$_2$](NO$_3$)$_2$ (0.55 mmol). CuSO$_4$·5H$_2$O (0.14 g, 0.55 mmol) was added to this solution and, upon adjusting the pH to 5.5 using 5% NaOH solution, a grass-green solid precipitated which was filtered, washed with cold water and dried over P$_2$O$_5$. Single crystals suitable for an X-ray diffraction study were obtained from the filtrate, after standing at room temperature for two days, **3a** (0.17 g, 218 mmol, 40%). (Found C, 21.07; H, 2.66; N, 12.46; Cu, 9.81. $PtCuC_{12}H_{18}N_6O_9S$ requires C, 21.16; H, 2.66; N, 12.34; Cu, 9.33%); ν_{max}/cm^{-1} (KBr disc) 3434vs, 3228s, 3114s, 2929s, 1619vs, 1610s, 1570m, 1523s, 1384vs, 1116vs, 1054m, 931m, 846m, 618s. The IR spectra of the grass-green precipitate and **3a** were identical.

The following heterobimetallic pyridinehydroxamate-bridged complexes were synthesised by the method described for **3** above.

{*cis*-[Pt(NH$_3$)$_2$(μ-3-pyha)Ni(μ-3-pyha)]SO$_4$·4H$_2$O}$_n$, 4. Pale green solid. Yield 38%. (Found C, 20.85; H, 2.89; N, 12.21; Ni, 8.64. $PtNiC_{12}H_{20}N_6O_{10}S$ requires C, 20.76; H, 2.90; N, 12.11; Ni, 8.46%); ν_{max}/cm^{-1} (KBr disc) 3399vs, 3212vs 1620vs, 1539m, 1477m, 1384s, 1357s, 1223m, 1201m, 1166m, 1107s, 927s, 822m, 734m, 697s, 616s.

{*cis*-[Pt(NH$_3$)$_2$(μ-3-pyha)Zn(μ-3-pyha)]SO$_4$·8H$_2$O}$_n$, 5. Yellow solid. Yield 53%. (Found C, 19.45; H, 2.96; N, 11.73; Zn, 8.41. $PtZnC_{12}H_{24}N_6O_{12}S$ requires C, 19.56; H, 3.28; N, 11.40; Zn, 8.87%); ν_{max}/cm^{-1} (KBr disc) 3401vs, 3199s, 1620vs, 1601s, 1546s, 1476m, 1451m, 1384vs, 1356s, 1223m, 1168s, 1110s, 1054s, 929s, 964m, 697s, 618s.

{*cis*-[Pt(NH_3)$_2$(μ-4-pyha)Cu(μ-4-pyha)]SO_4·$4H_2O$}$_n$, 6. Grass-green solid. Yield 42%. (Found C, 19.86; H, 2.60; N, 12.03; Cu, 9.32. $PtCuC_{12}H_{20}N_6O_{10}S$ requires C, 20.62; H, 2.88; N, 12.02; Cu, 9.09%); ν_{max}/cm^{-1} (KBr disc) 3433vs, 3227s, 3108s, 1620s, 1570m, 1522m, 1384s, 1116vs, 931w, 846w, 726w, 619s.

{*cis*-[Pt(NH_3)$_2$(μ-4-pyha)Ni(μ-4-pyha)]SO_4·$4H_2O$}$_n$, 7. Pale green solid. Yield 53%. (Found C 19.45; H 2.76; N 12.73; Ni 7.91. $PtNiC_{12}H_{20}N_6O_{10}S$ requires C, 20.76; H, 2.90; N, 12.11; Ni, 8.46%); ν_{max}/cm^{-1} (KBr disc) 3401vs, 3199s, 1620vs, 1546s, 1451m, 1384vs, 1357s, 1223m, 1168s, 1110s, 1054s, 930s, 962m, 696s, 622s. Expect: C, 20.76; H, 2.90; N, 12.11; Ni, 8.46

{*cis*-[Pt(NH_3)$_2$(μ-4-pyha)Zn(μ-4-pyha)]SO_4·$4H_2O$}$_n$, 8. Yellow solid. Yield 67%. (Found C, 20.65; H, 2.60; N, 12.17; Zn, 9.27. $PtZnC_{12}H_{20}N_8O_{10}S$ requires C, 20.56; H, 2.88; N, 11.99; Zn, 9.33%); ν_{max}/cm^{-1} (KBr disc) 3400s, 3368s, 3231vs, 3090s, 1626m, 1602s, 1529m, 1429w, 1384vs, 1335m, 1317m, 1162m, 1054m, 923m, 847w, 723w, 619w.

Potentiometric and spectrophotometric studies

All measurements were carried out using solutions of 0.1 mol dm^{-3} ionic strength (KNO_3) at 25 ± 0.1 °C. Carbonate-free KOH solutions of known concentrations (*ca.* 0.2 mol dm^{-3}) standardised with potassium hydrogen phthalate,[16] were used as titrant. The pH-metric titrations were carried out on a Molspin pH meter and titration controller with Thermo Russell CMAW711 combined electrode and Hamilton syringe autoburette; data were analysed using HYPERQUAD.[17] The electrode system was calibrated by the method of Irving *et al.*[18] (pK_w = 13.831) so that the pH-meter readings could be converted into hydrogen ion concentration. The pK_a values of the platinum pyridinehydroxamic acids and the stability constants of the Pt(II)/M(II) pyridinehydroxamic acid systems, where M = Cu, Ni, Zn, were determined by titrating solutions (~2.0 × 10^{-3} mol dm^{-3}) in HNO_3 (5.0 × 10^{-3} mol dm^{-3}) with a KOH solution of known concentration (0.1977 mol dm^{-3}).

Crystallographic measurements on 3a

Crystal data and experimental details for **3a** are summarised in Table 1. Crystal analysis was determined on a Bruker SMART 1000 CCD diffractometer at 120(2) K using monochromated Mo–Kα radiation, (λ = 0.71073 Å) and the ϕ–ω scan method. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 in the anisotropic approximation for all non-hydrogen atoms, using SHELXTL-97 package.[19] The hydrogen atoms in **3a** were placed geometrically and were included in the structure factor calculations in the riding motion approximation. Hydrogen atoms in the solvate molecules of water were not localised. The atomic numbering scheme and atom connectivity for **3a** are shown in Fig. 2 and a selection of bond lengths and angles are gathered together in Table 2. The crystals were small and were found to have low diffraction ability which is reflected in the relatively high *R* factor. The high anisotropy of ellipsoids is most probably due to the twinning of the crystal. Although substantial effort went into resolving the twinning components, we were not successful in finding either a twinned or disordered model which would have provided a more accurate and consistent description of the structure. Therefore we returned to the original anisotropic refinement, which, according to our opinion, still gives the best possible approximation of the structure. Even though one should admit that the ellipsoids in this case may not reflect the actual thermal displacements, the overall general connectivity and ballpark geometry in fact do not raise any doubts in this structure of the first example of a heterobimetallic wave-like coordination polymer incorporating repeating units of Pt(II) and Cu(II) ions interlinked *via* 3-pyha.

CCDC reference number 246167 (**3a**).

See http://www.rsc.org/suppdata/dt/b5/b501105a/ for crystallographic data in CIF or other electronic format.

Table 1 Crystallographic data for **3a**

Compound	**3a**
Chemical formula	$C_{12}H_{32}CuN_6O_{16}PtS$
Formula weight	807.13
Crystal system	Triclinic
Space group	*P*-1
a/Å	8.268(2)
b/Å	10.003(2)
c/Å	17.156(4)
α/°	80.524(5)
β/°	81.164(5)
γ/°	72.404(5)
V/Å^3	1325.9(5)
Z	2
D_{calc}/Mg m^{-3}	2.022
μ(Mo–Kα)/mm^{-1}	6.231
T/K	120(2)
Crystal Size max/mm	0.20
Mid/mm	0.10
Min/mm	0.05
$2\theta_{max}$	52.2
Min/Max *trans.* factor	0.318/0.694
R_{int}	0.0943
R_1, wR_2 [$I > 2\sigma(I)$][a]	0.0737, 0.1517
R_1, wR_2 (all data)	0. 1402, 0.1736
Reflections: Collected	9679
Independent	5093
Observed	2777

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

Table 2 Selected bond lengths (Å) and angles (°) with estimated standard deviations for **3a**

Pt(1)–N(5)	2.007(10)	O(1)–Cu(1)–O(1)#1	180.000(2)
Pt(1)–N(3)	2.004(11)	O(1)–Cu(1)–O(2)	84.2(5)
Pt(1)–N(6)	2.017(12)	O(1)#1–Cu(1)–O(2)	95.8(5)
Pt(1)–N(1)	2.046(14)	O(1)–Cu(1)–O(2)#1	95.8(5)
		O(1)#1–Cu(1)–O(2)#1	84.2(5)
Cu(1)–O(1)	1.908(10)	O(2)–Cu(1)–O(2)#1	180.000(1)
Cu(1)–O(2)	1.933(12)		
Cu(2)–O(3)	1.882(12)	O(3)#2–Cu(2)–O(3)	180.000(2)
Cu(2)–O(4)	1.924(12)	O(3)#2–Cu(2)–O(4)#2	86.1(5)
		O(3)–Cu(2)–O(4)#2	93.9(5)
N(5)–Pt(1)–N(3)	176.3(5)	O(3)–Cu(2)–O(4)	93.9(5)
N(5)–Pt(1)–N(6)	90.9(5)	O(3)–Cu(2)–O(4)	86.1(5)
N(3)–Pt(1)–N(6)	91.9(6)	O(4)#2–Cu(2)–O(4)	180.000(2)
N(5)–Pt(1)–N(1)	90.3(5)		
N(3)–Pt(1)–N(1)	86.8(6)		
N(6)–Pt(1)–N(1)	178.1(5)		

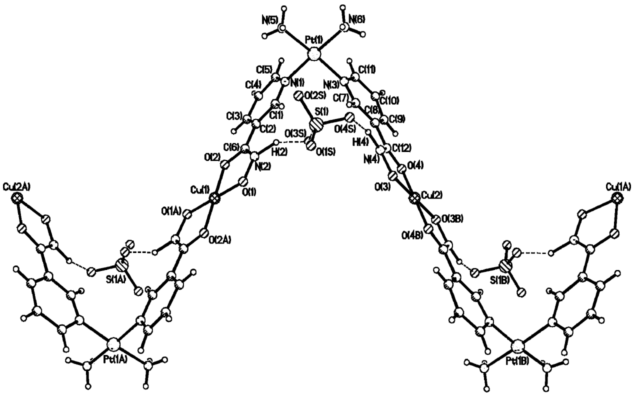


Fig. 2 Molecular structure and atomic labelling scheme of the wave-like coordination polymer, **3a**, with solvent molecules omitted for clarity.

Electron spin resonance spectroscopy

X-Band ESR spectra were recorded at 158 K using a Varian E-9 spectrometer. A 3.965 mM solution of **3**, pH = 6.5 in 50 : 50 water : ethanediol was prepared to ensure good glass formation when frozen. A modulation amplitude of 20 G and a microwave power of 5 mW were used.

Results and discussion

Syntheses of 3- and 4-pyridinehydroxamic acids

3- and 4-pyridinehydroxamic acids were synthesised from the corresponding methyl or ethyl esters in high yield and purity. They were characterised by elemental analysis, IR and ^{1}H NMR spectroscopy. Their IR spectra contained strong bands at 2802, 3196 and 1660 cm^{-1} for 3-pyhaH and 2850, 3186 and 1642 cm^{-1} for 4-pyhaH which may be assigned to ν(OH), ν(NH) and ν(C=O) respectively. These values concur with those previously reported in the literature.[20] The ^{1}H NMR spectra of 3- and 4-pyhaH show N–H and O–H resonances at *ca.* 9.3 ppm and *ca.* 11.5 ppm, respectively, both of which are concentration-dependent due to intermolecular hydrogen bonding at high concentrations. In addition, for 3-pyhaH, four main resonances at 8.90, 8.70, 8.10 and 7.51 ppm are observed and correspond to the four protons of the *meta*-substituted pyridine. In contrast, for 4-pyhaH, 2 main resonances at 8.70 and 7.68 ppm are observed for the 4 protons of the *para*-substituted pyridine ring.

Syntheses of 1 and 2

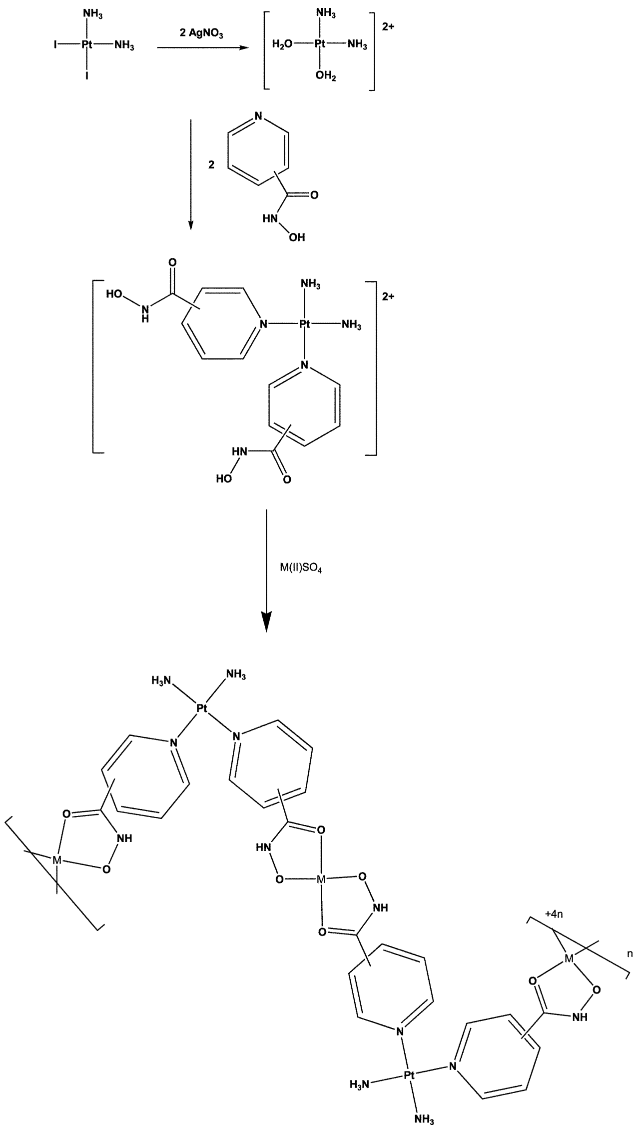
cis-[Pt(NH$_3$)$_2$(3-pyhaH)$_2$](BPh$_4$)$_2$·4H$_2$O, **1** and *cis*-[Pt(NH$_3$)$_2$(4-pyhaH)$_2$](BPh$_4$)$_2$·4H$_2$O, **2** were synthesised in high yield and purity and were charactersied by elemental analysis, IR and ^{1}H NMR spectrsocopy. Their IR and ^{1}H NMR data are similar to those of the corresponding free ligands exhibiting the expected shifts indicative of coordination to the metal ion and are consistent with the free nature of the hydroxamic acid moiety. The *cis*-configurations of both complexes were confirmed by the classic Kurnakov test.[21] Complexes **1** and **2** served as scaffolds for the subsequent formation of the heterobimetallic pyridinehydroxamate-bridged Pt(II)/M(II) coordination polymers **3–8**, where M = Cu, Ni or Zn.

Syntheses of 3–8

Reaction of an aqueous solution of *cis*-[Pt(NH$_3$)$_2$(3-pyhaH)$_2$]$^{2+}$ or *cis*-[Pt(NH$_3$)$_2$(4-pyhaH)$_2$]$^{2+}$ with M(II) salts where M is Cu, Ni or Zn in a 1 : 1 ratio at pH 5.5 resulted in deprotonation of the hydroxamic acid moieties, complexation of the metal cation, M(II), and precipitation of heterobimetallic pyridinehydroxamate-bridged Pt(II)/M(II) coordination polymers, Scheme 1. Satisfactory elemental analysis and IR data for all complexes were obtained. For complexes **3–8**, *O*,*O*-coordination of the hydroxamate moiety resulted in a significant lowering of the ν(C=O) to *ca.* 1620 cm^{-1} (*cf.* ν(C=O) is at 1660 cm^{-1} and 1642 cm^{-1} for 3-pyhaH and 4-pyhaH, respectively).

Crystal structure of 3a

Of the complexes **3–8** synthesised, only crystals of {*cis*-[Pt(NH$_3$)$_2$(μ-3-pyha)Cu(μ-3-pyha)]SO$_4$·8H$_2$O}$_n$, **3a**, materialised which were suitable for an X-ray diffraction study. The structure, shown to be {*cis*-[Pt(NH$_3$)$_2$(μ-3-pyha)Cu(μ-3-pyha)]SO$_4$·8H$_2$O}$_n$, **3a**, is the first example of a heterobimetallic wave-like coordination polymer incorporating repeating units of Pt(II) and Cu(II) ions interlinked *via* 3-pyha. It was refined in the triclinic *P*-1 space group with an asymmetric unit consisting of two formula units. The Pt(II) and Cu(II) ions, separated by a distance of 7.905 Å (for Pt(1)···Cu(1)) and 7.939 Å (for Pt(1)···Cu(2)), are in distorted square-planar N_4 and O_4 coordination environments, respectively, with a N5–Pt–N6 angle of 90.9(5)° and a N3–Pt–N1 angle of 86.8(6)° and an O–Cu–O (internal hydroxamate) angle of 84.2(5) and 86.1(5)° and an O–Cu–O (external hydroxamate) angle of 95.8(5) and 93.9(5)°. Self-assembly of the polymeric chains is achieved by inter-chain hydrogen bonds through the Pt ammines and the deprotonated hydroxamate *O* and *via* the *O* of the SO$_4$$^{2-}$ counterions and the H(*N*) of the hydroxamate moiety as can be seen in the corrugated layered structure, Fig. 3 (a). In addition to the aforementioned hydrogen bonding interactions, the polymeric arrangement is further stabilised by π–π stacking between polymeric chains, Fig. 3 (b). The distance between mean planes of neigbouring 3-pyha fragments is 3.3 Å and the shortest interatomic distances lie in the range of 3.28–3.47 Å. The use of 3-pyha as the bridging ligand and hence absence of random chain lengths undoubtedly provides structural regularity and reduced flexibility.



Scheme 1 Preparation of the Pt precursors and complexes **3–8** where M(II) = Cu, Ni or Zn.

Formation constants and species distribution curves

Speciation and spectroscopic studies were also carried out on **L** (*cis*-[Pt(NH$_3$)$_2$(3-pyhaH)$_2$]$^{2+}$) or **L**^{1} (*cis*-[Pt(NH$_3$)$_2$(4-pyhaH)$_2$]$^{2+}$) with M(II) where M is Cu, Ni or Zn salts and confirm the presence of Pt(II)/M(II) species analogous to those found in the solid state in **3–8** above.

The protonation constants of the novel Pt(II) complexes and the overall stability constants for the heterobimetallic systems were calculated from the potentiometric data. Both *cis*-[Pt(NH$_3$)$_2$(3-pyhaH)$_2$]$^{2+}$, **L**, and *cis*-[Pt(NH$_3$)$_2$(4-pyhaH)$_2$]$^{2+}$, **L**^{1}, release two protons from the hydroxamate moieties upon titration with KOH, Table 3. The pK_a values differ by one logarithmic unit probably due to intermolecular hydrogen-bonding.

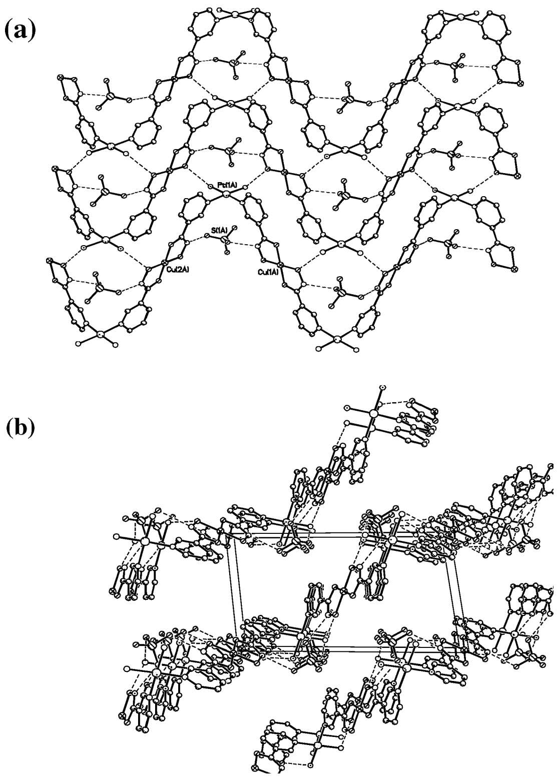


Fig. 3 (a) Cation–anion corrugated layer of **3a**. Chains in layer are bonded by weak hydrogen bonds (N5–H5B · · · O1 and N6–H6A · · · O3). (b) Fragment of crystal packing along *a* axis. Layers are parallel to (0 1 1) crystal plane. Solvate molecules of water (8 independent molecules, omitted for clarity) are located between layers.

Table 3 Stability constants (log *β* values, which refer to the equilibrium $pM + qL + rH \leftrightarrow M_pL_qH_r$) of the proton, Cu(II), Ni(II) and Zn(II) heterobimetallic complexes of **L** and **L**^{1} where **L** is *cis*-[Pt(NH$_3$)$_2$(3-pyhaH)$_2$]$^{2+}$ and **L**^{1} is *cis*-[Pt(NH$_3$)$_2$(4-pyhaH)$_2$]$^{2+}$ at 25 °C (I = 0.1 M KNO$_3$)

Species	$M_pL_qH_r$	log *β* value		
LH	0 1 1	7.66(0.004)		
L H$_2$	0 1 2	14.29(0.003)		
L^{1}H	0 1 1	7.35(0.008)		
L^{1}H$_2$	0 1 2	13.65(0.007)		
		Cu^{2+}	Ni^{2+}	Zn^{2+}
ML$_2$H$_2$	1 2 2	26.26(0.01)		
M$_2$L$_2$H	2 2 1	23.85(0.01)		
M$_2$L$_2$H$_{-1}$	2 2 −1	14.98 (0.01)		
M$_2$L$_2$H$_{-2}$	2 2 −2	8.52 (0.01)		
M$_2$L$_2$H$_{-3}$	2 2 −3	1.07 (0.01)		
M$_2$L$_2$H$_{-4}$	2 2 −4	−7.51(0.02)		
MLH	1 1 1		10.64(0.04)	10.57(0.03)
ML	1 1 0		4.50(0.01)	4.46(0.01)
MLH$_{-1}$	1 1 −1		−4.52(0.01)	−4.49(0.03)
M$_2$LH$_{-3}$	2 1 −3		−19.05(0.03)	−17.00(0.02)
ML$^1{}_2$H$_2$	1 2 2	25.41(0.01)		
M$_2$L$^1{}_2$H	2 2 1	23.45(0.02)		
M$_2$L$^1{}_2$H$_{-1}$	2 2 −1	13.05 (0.02)		
M$_2$L$^1{}_2$H$_{-2}$	2 2 −2	7.67 (0.02)		
M$_2$L$^1{}_2$H$_{-3}$	2 2 −3	1.27 (0.02)		
ML^{1}H	1 1 1		10.58(0.04)	10.47(0.03)
ML^1	1 1 0		4.24(0.02)	4.12(0.01)
M$_2$L^{1}H$_{-3}$	2 1 −3		−19.32 (0.03)	−16.90(0.03)

Titration curves of **L** and **L**^{1} with Cu show significant shifts both for **L** : Cu and **L**^{1} : Cu in the ratios of 2 : 1 and 1 : 1 suggesting the formation of heterobimetallic complexes, Fig. 4. The titration curves for the **L** : Ni and **L**^{1} : Ni systems, Fig. 4, in contrast, indicate complexation of either one or two Ni ions per **L** or **L**^{1} and were practically identical to those obtained for the L : Zn and **L**^{1} : Zn systems (see ESI†).

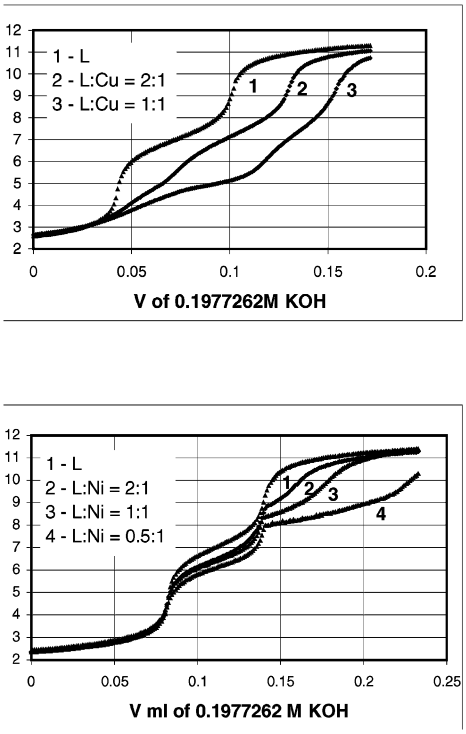


Fig. 4 Titration curves for **L** : M(II) systems where **L** = *cis*-[Pt(NH$_3$)$_2$-(3-pyhaH)$_2$]$^{2+}$ and M = Cu, Ni.

Speciation studies confirm the presence of 1 : 1 **L** : Cu and **L**^{1} : Cu species analogous to those found in the solid-state in complexes **3** and **6**, respectively. Upon coordination of Cu to **L**/**L**^{1}, consecutive deprotonations of the hydroxamate NHs are observed with increasing pH (Table 3, Fig. 5, for Zn, see ESI†). This is the first investigation to date using speciation studies involving Pt(II)/M(II) heterobimetallic systems. **L** forms slightly more stable heterobimetallic complexes than those formed by **L**^{1} and, although this difference is only very slight, it is observed in every case. We speculate that this may be due to the increased difference in the distance of the pyridine N from the hydroxamate moiety in 4-pyhaH resulting in a slightly diminished electron-donating effect.

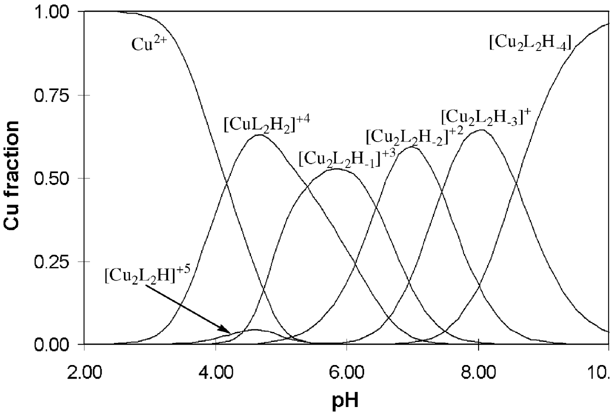


Fig. 5 Species distribution for the **L** : Cu(II) where **L** is *cis*-[Pt(NH$_3$)$_2$-(3-pyhaH)$_2$]$^{2+}$, pH 2–11, [Cu(II)] = 1 mM, [**L**] = 2 mM.

In addition, an ESR spectrum was obtained for a 3.965 mM solution of **3** in 50 : 50 water : ethanediol, pH = 6.5 where there is a 50 : 50 mixture of [Cu$_2$L$_2$H$_{-1}$]$^{3+}$ and [Cu$_2$L$_2$H$_{-2}$]$^{2+}$. We found $g_\parallel$ = 2.262 and $A_\parallel$ = 190 × 10^{-4} cm^{-1}, both of which, as expected, lie between those previously observed for acetohydroximato Cu(II) complexes [CuA$_2$H$_{-1}$]$^-$ (where $g_\parallel$ = 2.258 and $A_\parallel$ = 192 × 10^{-4} cm^{-1})[22] and [CuA$_2$H$_{-2}$]$^{2-}$ (where $g_\parallel$ = 2.219 and $A_\parallel$ = 207 × 10^{-4} cm^{-1})[22] (A is acetohydroxamic acid). The above results are also in good agreement with other previously published ESR results for Cu-hydroximato species.[22,23] The condition $g_{\parallel} > g_{\perp} > 2.0023$ (where we found $g_{\perp} = 2.053$) shows the ground state to be $dx^2–y^2$. In addition, the ratio of $g_{\parallel}/A_{\parallel}$ is 119 cm, consistent with values expected for Cu(II) chelated to a square planar array of ligands.[24] The spectrum of the solid polymeric material, **3**, appears to be similar ($g = 2.051$), although with a poorly resolved parallel component that spans the same field range as that observed in the frozen glass. These observations are consistent with the observed distorted square-planar geometry in the solid structure, while comparison with the ESR parameters of the frozen glass shows the species in solution to be similarly coordinated. Assuming that the broad, unresolved parallel feature of the spectrum of the solid represents a similar g value to that in the frozen glass, we may apply the criterion[25] $G > 4$ as a condition of insignificant exchange coupling between the paramagnetic Cu(II) centres, where $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$. This is further substantiated by magnetic measurements on **3** where the magnetic moment of **3** is 1.78 BM at 280 K and 1.95 BM at 80 K, essentially remaining unchanged with temperature, confirming the above ESR data.

Speciation studies further confirm the presence of 1 : 1 **L** : Ni, **L**^{1} : Ni, **L** : Zn and **L**^{1} : Zn species analogous to those found in the solid-state in complexes **4, 7, 5** and **8** respectively. In addition, both Pt derivatives, **L** and **L**^{1}, are able to bind up to two metal ions per Pt for Ni(II) and Zn(II) forming the species LM_2H_{-3} and $L^1M_2H_{-3}$, respectively, where the metal ions are (*O*,*O*)-coordinated by two hydroxamate moieties, Fig. 6. These complexes were not observed for Cu.

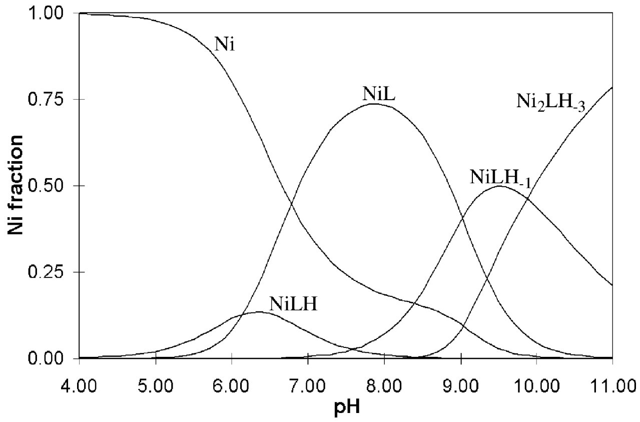


Fig. 6 Species distribution for the **L** : Ni(II) where **L** is *cis*-$[Pt(NH_3)_2(3\text{-pyhaH})_2]^{2+}$, pH 2–11, [Ni(II)] = 1 mM, [L] = 1 mM.

Furthermore, spectrophotometric studies carried out on the **L** : Cu and **L**^{1} : Cu systems are consistent with the potentiometry data described earlier where, at higher pH, deprotonation of the hydroximate NH's are observed (for **L** : Cu, pH = 4.3, λ_{max} = 765 nm, ε_{av} = 30 mol^{-1} cm^{-1}; pH = 5.7, λ_{max} = 645 nm, ε_{av} = 130 mol^{-1} cm^{-1} and for **L**^{1} : Cu, pH = 4.4, λ_{max} = 755 nm, ε_{av} = 37.5 mol^{-1}cm^{-1}; pH = 4.8, λ_{max} = 650 nm, ε_{av} = 108 mol^{-1}cm^{-1}). We also recorded spectra for the L : Ni system (pH = 6.5, λ_{max} = 660 nm, ε_{av} = 8.75 mol^{-1}cm^{-1}; pH = 8.2, λ_{max} = 660 nm, ε_{av} = 13.5 mol^{-1}cm^{-1}, pH = 10.3, λ_{max} = 660 nm, ε_{av} = 22.5 mol^{-1}cm^{-1}) and for the **L**^{1} : Ni system (pH = 6.5, λ_{max} = 670 nm, ε_{av} = 6.75 mol^{-1}cm^{-1}; pH = 8.2, λ_{max} = 670 nm, ε_{av} = 37.5 mol^{-1}cm^{-1}. Precipitation occurred at higher pH at 2 mM concentration).

Conclusions

In summary, we report the synthesis and characterisation of novel Pt(II)/M(II) pyridinehydroxamate-bridged coordination polymers where M is Cu, Ni or Zn, and where 3- or 4-pyha have proven themselves to be versatile building-blocks for the construction of these novel polymeric structures. Speciation and spectroscopic studies of related systems are also reported. The crystal structure of one of the above polymers, $\{cis\text{-}[Pt(NH_3)_2(\mu\text{-}3\text{-pyha})Cu(\mu\text{-}3\text{-pyha})]SO_4\cdot 8H_2O\}_n$, the first example to date of a Pt(II)/Cu(II) heterobimetallic pyridinehydroxamate-bridged wave-like coordination polymer, is also reported. The presence of peripheral hydrogen-bonding substituents on the hydroxamic acid moiety, the Pt-ammines and the SO_4^{2-} counterions undoubtedly play a critical role in the assembly and topology of the resulting polymer.

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