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Copper(II), cobalt(II), nickel(II) and zinc(II) complexes containing the enolate of *N*-acetyl-3-butanoyltetramic acid (Habta) and its phenylhydrazone derivative analogues. Crystal structure of $[Cu(abta)_2(py)_2]\cdot 2H_2O$ †

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Reaction of *N*-acetyl-3-butanoyltetramic acid (*N*-acetyl-3-butanoyl-4-hydroxypyrrolidin-2-one) (Habta) with $M(CH_3CO_2)_2\cdot xH_2O$ ($x = 1$, 2 or 4; M = Cu^{II}, Co^{II} or Ni^{II}) in a 1 : 1 ratio gave $M(CH_3CO_2)(abta)\cdot yH_2O$ **1**, **3**, **5** and in 1 : 2 ratio $M(abta)_2\cdot y'H_2O$ **2**, **4**, **6**. A new ligand, the phenylhydrazone of Habta (HPhabta), has been prepared and reacts with $M(CH_3CO_2)_2\cdot xH_2O$ ($x = 2$ or 4; M = Cu^{II} or Co^{II}) in a 1 : 1 and 1 : 2 ratio to give the analogous complexes $M(CH_3CO_2)(Phabta)\cdot zH_2O$ **9**, **11** and $M(Phabta)_2\cdot z'H_2O$ **10** respectively. The solid state structure of $[Cu(abta)_2(py)_2]\cdot 2H_2O$ **2a** has been determined by single crystal X-ray diffraction. It shows that copper adopts a slightly distorted octahedral co-ordination geometry with the abta enolate ligand adopting an O,O′ mode of co-ordination *via* the functionalities associated with C^4 and the acyl group at C^3 in the pyrrolidine ring. The reaction of Habta with $Zn(CH_3CO_2)_2\cdot 2H_2O$ in 1 : 1 ratio gives a complex **7** with a deacetylated ligand whereas, with 1 : 2 ratio, $Zn(abta)_2\cdot 2H_2O$ **8** is obtained. In contrast the reaction of HPhabta with $Zn(CH_3CO_2)_2\cdot 2H_2O$, irrespective of the metal to ligand ratio, gives $Zn(CH_3CO_2)(Phbta)\cdot 2H_2O$ **12** containing the deacetylated ligand.

Introduction

The 3-acyltetramic acids (substituted pyrrolin-2-ones) (Fig. 1) constitute a growing class of natural products displaying a range of biological activities.[1] The β,β′-tricarbonyl moiety present in the 3-acyltetramic acids provides a suitable site for bidentate complexation to a metal. "Magnesidin" (Fig. 2a), a natural antibiotic, was isolated as a 1 : 1 mixture of the covalent magnesium chelates of 1-acetyl-3-hexanoyl- and -3-octanoyl-tetramic acid derivatives.[2] "Tenuazonic acid" (Fig. 2b), the simplest compound of this class, was isolated as a mixture of calcium(II) and magnesium(II) complexes, of 3-acetyl-5-*sec*-butyltetramic acid.[3] "Oleficin" (Fig. 2c) functions as an ionophore for Mg^{2+} and Ca^{2+} ions in isolated rat liver mitochondria. This property can be attributed to the ability of the β,β′-tricarbonyl moiety to form complexes with various metal ions.[4]

Thus the synthesis and spectroscopic studies of compounds containing the pyrrolidine-2,4-dione ring system is of increasing interest. The broad spectrum of biological activity of 3-acyltetramic acids prompted many research groups to synthesize related complexes and evaluate their biological properties. The mechanisms responsible for the various biological properties include complexation with various metal cations, which increases their liposolubility and permeability through cell walls.[5] Such a feature has become evident on testing copper(II) complexes containing 3-acetyl- and 3-decanoyl-

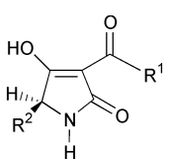

Fig. 1 3-Acyl-4-hydroxypyrrolin-2-ones.

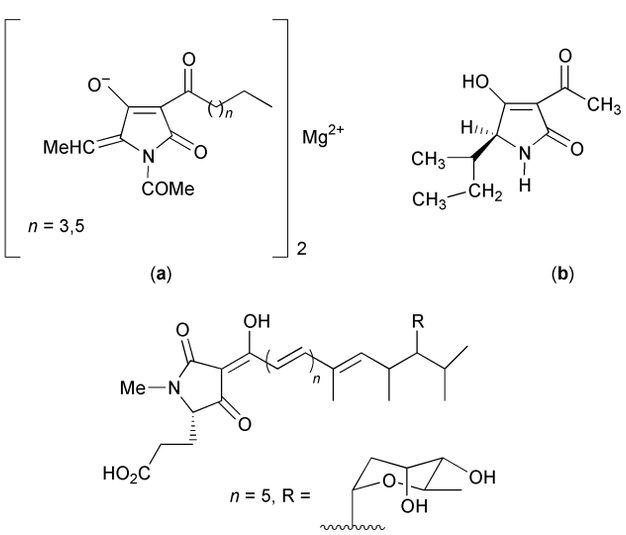

Fig. 2 Naturally occurring 3-acyltetramic acids.

† Electronic supplementary information (ESI) available: colours and elemental analysis data for complexes **1**–**12**. See http://www.rsc.org/suppdata/dt/b0/b007252o/

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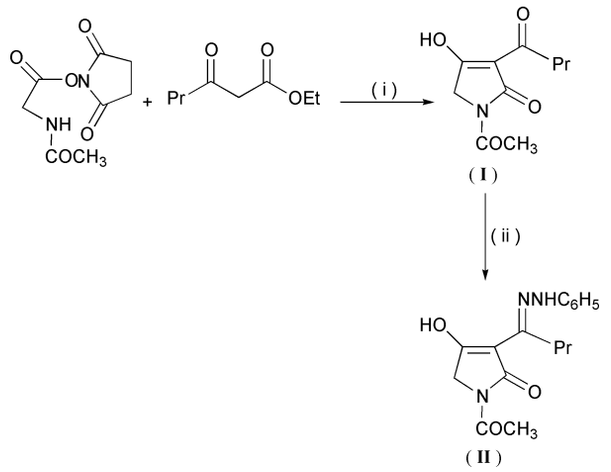
tetramic acids for antimicrobial activity[6,7] and it seems likely that their biological activity is related to their complexing ability.[8] Recently new platinum(II) complexes containing 3-alkanoyltetramic acids have been shown to have a broad spectrum of biological properties.[9]

The complexation of 3-butanoyl and 3-benzoyl N–H tetramic acids with metal(II) halides has previously been examined by our team.[10] However, the *N*-acetyl analogues are expected to adopt a different co-ordination mode. In this paper we describe the synthesis (Scheme 1) and characterization



Scheme 1 Synthesis of the ligand Habta **I** and its phenylhydrazone derivative **II**. (i) NaH, PhH, r.t.; (ii) $H_2NNHC_6H_5$, abs. ethanol, reflux 2.5 h.

of metal(II) complexes of *N*-acetyl-3-butanoyltetramic acid (Habta, **I**). The ability of Habta to substitute acetylacetonate as a chelating monoanion has been well studied for rhodium(I) complexes.[11] We have extended our studies to the acetate salts of the first row transition metals as well as zinc(II).

Moreover, our interest in the co-ordination chemistry of hydrazones[12–14] prompted us to synthesize the phenylhydrazone derivative **II** (Scheme 1) of the above mentioned tetramic acid and to test its complexing ability with copper(II), cobalt(II) and zinc(II) acetate salts. Ligands with N–N bonds have been studied much in recent years because of their relationship to the problem of conversion of dinitrogen into ammonia or hydrazine. The interest in the study of hydrazones has increased because of their use in biological systems,[15] analytical chemistry[16] and in non-linear optics.[17]

Results and discussion

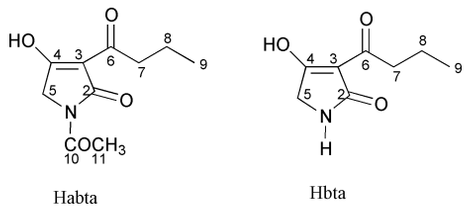
Synthesis

The synthesis of *N*-acetyl-3-butanoyltetramic acid (Habta), together with its IR, ^{1}H and ^{13}C NMR spectra and X-ray analysis, has previously been reported by our team.[18] The complexes $M(CH_3CO_2)(abta)\cdot yH_2O$ (M = Cu^{II} **1**, Co^{II} **3** or Ni^{II} **5**) and $M(abta)_2\cdot y'H_2O$ (M = Cu^{II} **2**, Co^{II} **4** or Ni^{II} **6**) are readily prepared (eqns. (1) and (2)) by reaction of the appropriate metal

$$M(CH_3CO_2)_2\cdot xH_2O + \text{Habta} \longrightarrow M(CH_3CO_2)(abta)\cdot yH_2O + CH_3CO_2H \quad (1)$$

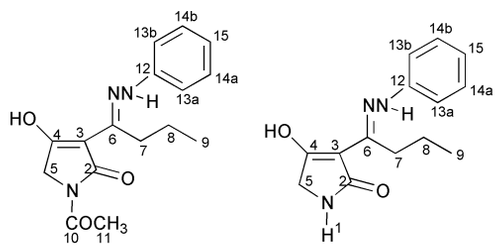
$$M(CH_3CO_2)_2\cdot xH_2O + 2\ \text{Habta} \longrightarrow M(abta)_2\cdot y'H_2O + 2\ CH_3CO_2H \quad (2)$$

acetate salt $M(CH_3CO_2)_2\cdot xH_2O$ (x = 1, 2 or 4) and Habta in MeOH under reflux by simply changing the metal to ligand ratio. The complexes can be isolated as powders, which are stable in the normal laboratory atmosphere and soluble in MeOH and DMSO. Crystals suitable for a single crystal X-ray study of $Cu(abta)_2\cdot 2H_2O$ **2** have been grown from a pyridine–



Habta Hbta

Fig. 3 The ligands Habta and Hbta.



HPhabta HPhbta

Fig. 4 The ligands HPhabta and HPhbta.

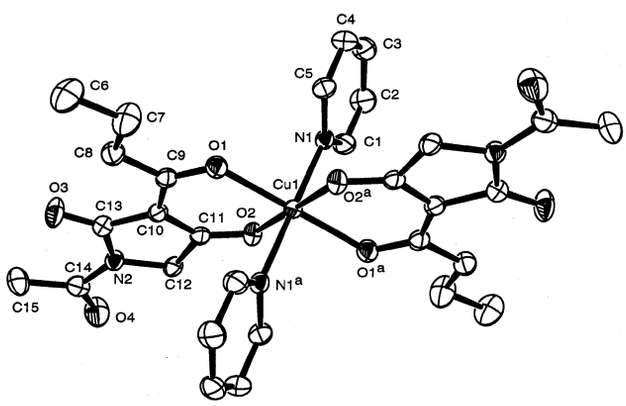


Fig. 5 Crystal structure of the complex $[Cu(abta)_2(py)_2]\cdot 2H_2O$ **2a**.

water solution in a refrigerator overnight and the elemental analysis of the resulting green crystals suggested the empirical formula $[Cu(abta)_2(py)_2]\cdot 2H_2O$ **2a** which was confirmed by X-ray analysis, see below. Efforts to prepare analogous complexes with $Zn(CH_3CO_2)_2\cdot H_2O$ gave two products; with a 1:1 ligand to metal ion molar ratio deacetylation of the ligand occurs, resulting in complexation of the N–H ligand (Hbta) (Fig. 3) to give $Zn(bta)_2\cdot 2H_2O$ **7**, whereas a 2:1 ligand to metal ion molar ratio results in the formation of $Zn(abta)_2\cdot 2H_2O$ **8**.

New complexes of general formulae $M(CH_3CO_2)(Phabta)\cdot 2H_2O$ (M = Cu^{II} **9** or Co^{II} **11**) and $Cu(Phabta)_2\cdot 4H_2O$ **10**, where HPhabta is the phenylhydrazone derivative of the ligand Habta, have been prepared and characterized. The synthesis of the phenylhydrazone of *N*-acetyl-3-butanoyltetramic acid (Scheme 1) is straightforward and the new ligand has been characterized by IR, ^{1}H–^{13}C NMR and elemental analysis (Fig. 4). As found for the reaction of Habta with Zn^{II}, loss of the acetyl group from HPhabta occurs in the analogous reaction with Zn^{II} to give $Zn(CH_3CO_2)(Phbta)\cdot 2H_2O$ **12** and the same complex is formed irrespective of the metal to ligand ratio used (2:1, 1:1, 1:2).

Crystal structure of $[Cu(abta)_2(py)_2]\cdot 2H_2O$ 2a

A view of the molecular structure of complex **2a** is shown in Fig. 5. Selected bond lengths and angles are listed in Table 1. Copper adopts a slightly distorted octahedral geometry. The Cu(1)–O(1) [2.0257(18) Å] bond is shorter than that of Cu(1)–O(2) [2.2463(18) Å], but both are much longer than Cu(1)–N(1) [2.0076(19) Å] of the two axially co-ordinated pyridines. Each abta ligand is co-ordinated to the copper ion through its butanoyl oxygen atom O(1) and the oxygen O(2) (4-hydroxyl)

Table 1 Selected bond distances (Å) and angles (°) for $[Cu(abta)_2(py)_2]\cdot 2H_2O$ **2a** with standard deviations in parentheses

Cu(1)–N(1)	2.0076(19)	O(2)–C(11)	1.247(3)
Cu(1)–O(1)	2.0257(18)	N(2)–C(12)	1.455(3)
Cu(1)–O(2)	2.2463(18)	C(8)–C(9)	1.505(4)
C(10)–C(13)	1.458(3)	O(1)–C(9)	1.252(3)
N(2)–C(13)	1.429(3)	C(7)–C(8)	1.491(4)
O(3)–C(13)	1.211(3)	C(6)–C(7)	1.515(4)
C(10)–C(11)	1.406(4)	C(14)–C(15)	1.490(4)
C(9)–C(10)	1.435(4)	N(2)–C(14)	1.384(3)
C(11)–C(12)	1.508(4)	O(4)–C(14)	1.219(3)
N(1)–Cu(1)–N(1)#1	180.0	C(9)–O(1)–Cu(1)	129.6(16)
N(1)–Cu(1)–O(1)#1	89.0(7)	C(11)–O(2)–Cu(1)	117.2(16)
N(1)–Cu(1)–O(1)	91.0(7)	N(1)–C(1)–C(2)	122.8(3)
O(1)#1–Cu(1)–O(1)	180.0	N(1)–C(5)–C(4)	121.4(2)
N(1)–Cu(1)–O(2)	89.6(7)	O(1)–C(9)–C(10)	122.0(2)
N(1)#1–Cu(1)–O(2)	90.4(7)	O(1)–C(9)–C(8)	117.7(2)
O(1)#1–Cu(1)–O(2)	93.0(7)	O(2)–C(11)–C(10)	130.7(2)
O(1)–Cu(1)–O(2)	87.0(7)	O(2)–C(11)–C(12)	120.4(2)
C(1)–N(1)–C(5)	118.5(2)	O(3)–C(13)–N(2)	123.1(2)
C(1)–N(1)–Cu(1)	120.1(16)	O(3)–C(13)–C(10)	130.2(2)
C(5)–N(1)–Cu(1)	121.3(17)	N(2)–C(13)–C(10)	106.6(2)
C(14)–N(2)–C(13)	128.9(2)	O(4)–C(14)–N(2)	118.3(2)
C(14)–N(2)–C(12)	119.9(2)	O(4)–C(14)–C(15)	122.1(2)
C(13)–N(2)–C(12)	111.1(18)	N(2)–C(14)–C(15)	119.5(2)

of the pyrrolidine ring, as a β-diketonate anion. This arrangement is probably preferred because of the higher electron density on the hydroxyl oxygen compared to that of the amide carbonyl O(3) in the 2 position. The two individual ligand molecules are *trans* with respect to chelation to the copper ion. The co-ordination environment around the copper atom is completed with two axially co-ordinated pyridine molecules. The equivalence of the O(1)–C(9) [1.252(3) Å] and O(2)–C(11) [1.247(3) Å] and also of C(9)–C(10) [1.435(4) Å] and C(10)–C(11) 1.406(4) Å] bonds indicates extensive delocalization in the chelate rings and, within experimental error, the two six-membered chelate rings are planar.

The crystal structure of complex **2a** contains two water molecules per $Cu(abta)_2(py)_2$ complex. Each forms hydrogen bonds to two copper complexes *via* O(2) and O(4), respectively. Hence, each complex is linked intermolecularly with two neighbouring complexes by four water molecules, resulting in linear chains featuring double H_2O bridges between metal complexes. The sites of co-ordination of Habta in this copper complex, as well as the geometry around the copper center, differ markedly from those found in the crystal structure of an analogous copper(II) complex containing the naturally occurring tenuazonic acid.[19] In this case tenuazonic acid chelates to copper *via* the acetyl oxygen and the amide (2-carbonyl) oxygen of the pyrrolidine ring. This difference could be due to the different substituents on the nitrogen atom of the ring. In the case presented here the free electron pair on the nitrogen atom is shared by the amide carbonyl group and the acetyl carbonyl, thus reducing the electron density on the amide carbonyl. Consequently the co-ordinating ability of the amide carbonyl is reduced, inducing co-ordination from the 4-hydroxyl oxygen which is deprotonated. On the other hand in tenuazonic acid, according to Steyn's[20] tetramic acid model, the nitrogen atom in the amide structure is better able to donate electrons to the C-2 carbonyl group, thus enhancing its co-ordinating ability.

NMR spectroscopy studies

From the ^{1}H NMR spectra of complex **7** it is evident that deacetylation of the ligand has occurred accounting for the disappearance of the singlet at δ 2.39 assigned to the methyl protons of the acetyl group. The deacetylation is further demonstrated by the ^{13}C NMR and the disappearance of the two signals at δ 24.8 and 168.5. The carbonyl atoms C-2 and C-6 are significantly shifted downfield for **7** as a result of complexation with zinc(II), while C-4 is only shifted by 1.7 ppm. In **8** the carbonyl atoms C-4 and C-6 are shifted downfield while C-2 is only shifted by 1.4 ppm. The *N*-acetyl-3-hydrazonoalkyl tetramic acids can exist as enolic "internal" tautomers **a** ⇌ **b** and **c** ⇌ **d**, in addition to "external" tautomers **ab** ⇌ **cd** (Fig. 6), demonstrating that a tautomeric equilibrium, due to the various hydrogen-bonding strengths, exists between the external tautomers **a**,**b** and **c**,**d**.[20] In $CDCl_3$ solution two sets of signals are thus observed for certain protons. The ^{1}H and ^{13}C NMR spectra of **12** also exhibit two pairs of signals for all the protons and the carbons, which must arise from the same tautomerism as found in the "free" ligand. Deacetylation of the latter on complexation to Zn^{II} is clearly shown by the NMR spectra of **12**. Thus the ^{1}H NMR verifies the existence of one acetate unit per ligand, the single resonance at δ 2.08 is assigned to the methyl protons of the acetate group. The resonance due to the 5-methylene protons at δ 3.78 is shifted significantly upfield consistent with the change in the ligand from *N*-acetyl to N–H. Major shifts are observed in the ^{13}C NMR for the carbonyl atoms C-2, C-4, C-6 which is consistent with the complexation *via* one oxygen atom and the imino nitrogen atom. Complexation *via* the amine nitrogen of the hydrazono moiety is excluded by the existence of a single resonance at δ 5.95 in the ^{1}H NMR due to N–H.

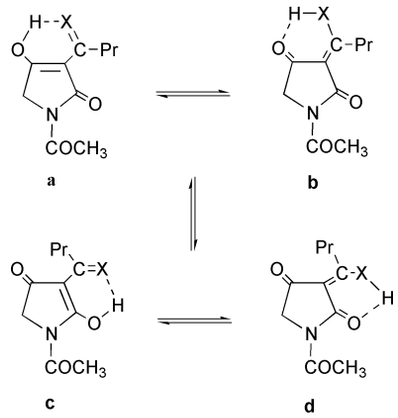


Fig. 6 Tautomeric forms of Habta and its phenylhydrazone derivative HPhabta.

Electronic spectra and magnetic moments

The high magnetic moments (4.9–5.3 μ_B) and electronic spectra of the cobalt(II) complexes are characteristic of pseudo-octahedral complexes, the two peaks in the electronic spectra being assigned to transitions from the $^4T_{1g}$ to the $^4T_{1g}$(P) and $^4A_{2g}$ states respectively. The nickel(II) complexes similarly show magnetic and electronic spectroscopic properties which are characteristic of an octahedral stereochemistry. They have magnetic moments only a little above the spin-only value and show two main peaks in the electronic spectra (the highest energy band is obscured by an intense charge-transfer absorption), assignable to transitions from the $^3A_{2g}$ ground state to the $^3T_{2g}$ and $^3T_{1g}$(F) states respectively. For the copper(II) complexes the magnetic moments indicate that no reduction to copper(I) has occurred and the electronic spectra show broad bands in the 15000–14000 cm^{-1} region with shoulders on the low frequency side typical of Jahn–Teller distorted octahedral copper(II) complexes.[21]

Vibrational spectra

The IR spectra of complexes **1**–**8** show the ν(C=O) lactam and ν(C=O) β-diketone, shifted to lower wavenumbers with respect to that of the "free" ligand, confirming that two oxygens are involved in the co-ordination of the metal. New bands at high frequencies (>3200 cm^{-1}) appear when Habta is complexed to the metals. These can be attributed to the stretching vibration

of the O–H group from water molecules, which are either co-ordinated or captured in the crystal lattice. The differences ($\Delta\nu$) of the asymmetric $\nu_{asym}(CO_2^-)$ and symmetric $\nu_{sym}(CO_2^-)$ carbonyl stretching frequencies of compounds **1**, **3**, **5** are much larger than 200 cm^{-1} (240–255 cm^{-1}), which indicates that the acetate groups are co-ordinated in a monodentate fashion, rather than as a chelate.[22] We assign the band at 1570 cm^{-1} of the phenylhydrazone of *N*-acetyl-3-butanoyltetramic acid to ν(C=N) and that at 1080 cm^{-1} to ν(N–N) in accordance with other assignments.[23] A movement of the ν(C=N) band to higher frequencies in the spectra of the complexes has been observed similar to that for complexes of other ligands containing the >C=N–N< grouping[24] in which the imino nitrogen atom donates to the metal ion. The hydrazinic ν(N–N) band shifts to higher wavenumbers in the spectra of the complexes relative to the "free" ligand, as a result of co-ordination through the imino nitrogen atom, similar to what has been observed for hydrazine[25] and other α-dihydrazone[26] complexes. Deacon and Phillips[27] have established, in the case of acetate compounds, some correlations between the $\Delta\nu$ values of the different modes of bonding of the carboxylate moiety found in the molecular structure. The $\Delta\nu$ value for compounds **9**, **11**, **12** is 150–220 cm^{-1} which is somewhere between the value for monodentate and bis chelate co-ordination of the acetate group. Therefore an unambiguous assignment of the mode of co-ordination of the acetate group is not possible.

Concluding remarks

The isolated copper(II), cobalt(II) and nickel(II) complexes of Habta all have octahedral stereochemistry with bidentate co-ordination through O(1) and O(2) (4-hydroxyl) atoms of the pyrrolidine ring. The copper(II) and cobalt(II) complexes of HPhabta have similar stereochemistry with bidentate co-ordination through O(2) (4-hydroxyl) and N-methine atoms. In contrast, complexation of Habta to Zn^{II} is different and depends on the ratio of ligand to metal ion. Using a 1:1 ratio deacetylation of the ligand occurs whereas at a 2:1 ratio the *N*-acetyl complex could be isolated. The reaction of the hydrazone analogue with Zn^{II} results in deacetylation, which occurs irrespective of the metal to ligand ratio used. The ligand co-ordination mode in the zinc(II) complexes probably involves O(1) and O(2) for Habta and O(2) and the N-methine atom for the HPhabta ligand.

Experimental

Reagents and physical measurements

All manipulations were performed under aerobic conditions using reagents and solvents as received, except benzene, which was distilled prior to use according to standard procedures.[28] Melting points were determined on a Gallenkamp MFB-595 melting point apparatus and are uncorrected. C, H and N analyses were conducted by the University of Liverpool, Chemistry Department. IR spectra (4000–250 cm^{-1}) were recorded on a Perkin-Elmer 883 spectrometer with samples prepared as KBr pellets, electronic spectra by diffuse reflectance on a Perkin-Elmer 124 spectrophotometer over the range (25000–12500 cm^{-1}) using MgO as standard. Magnetic susceptibilities of powdered samples were recorded by the Gouy method at room temperature against $Hg[Co(SCN)_4]$ as calibrant. Diamagnetic corrections were estimated from Pascal constants. ^1H, ^{13}C, 2-D HETCOR (heteronuclear correlation) NMR spectra were recorded on a Varian Gemini-2000 300 MHz spectrometer.

Syntheses

The *N*-hydroxysuccinimide ester of *N*-acetylglycine was synthesized according to a previously reported method,[29] as was the compound Hbta from Habta.[11]

***N*-Acetyl-3-butanoyltetramic acid (Habta) I.** Ethyl butyrylacetate (6.64 g, 0.042 mol) was added dropwise to sodium hydride (1.14 g, 0.028 mol, 60% sodium hydride in oil) in anhydrous benzene (120 ml) and the thick white slurry thus formed was stirred at room temperature for $1\frac{1}{2}$ h. The *N*-hydroxysuccinimide ester of *N*-acetylglycine (3 g, 0.014 mol) was added and stirring continued for $2\frac{1}{2}$ h. Water was added and the aqueous layer separated and acidified with 10% hydrochloric acid in an ice–water bath. The product was formed directly in the acidified solution as a white solid, which was filtered off, washed with cold water, light petroleum (bp range 40–60 °C) (2 × 5 ml) and dried *in vacuo* over P_2O_5 (yield 1.6 g, 55%), mp 67–69 °C (Found: C, 56.3; H, 6.3; N, 6.9%. Calc. for $C_{10}H_{13}NO_4$: C, 56.9; H, 6.2; N, 6.6%). $\tilde{\nu}_{max}/cm^{-1}$ (OH) 3330br, (N–$COCH_3$) 1740s, (C=O lactam) 1720w and (C=O and C=C of the enolic and β-diketone system) 1650br; δ_H(DMSO-d_6) 0.86 (3H, t, H^9), 1.52 (2H, mt, H^8), 2.39 (3H, s, H^{11}), 2.73 (2H, t, H^7) and 4.11 (2H, s, H^5); δ_C(DMSO-d_6) 194.2 C(6), 186.9 C(4), 169.2 C(2), 168.5 C(10), 105.1 C(3), 49.5 C(5), 39.7 C(7), 24.8 C(11), 17.8 C(8) and 13.7 C(9).

***N*-Acetyl-4-hydroxy-3-[1-(2-phenylhydrazono)butyl]pyrrolin-2-one (HPhabta) II.** A solution of phenylhydrazine (0.31 g, 2.84 mmol) in absolute ethanol was added dropwise to a solution of Habta (0.60 g, 2.84 mmol) in absolute ethanol and the mixture stirred under reflux for 2.5 h. The resulting mixture was concentrated *in vacuo* and the solid obtained was filtered off, washed with cold ethanol and dried *in vacuo* over P_2O_5. Yield 0.50 g, 60%. mp 140–141 °C (Found: C, 62.5; H, 6.3; N, 13.6%. Calc. for $C_{16}H_{19}N_3O_3\cdot\frac{1}{3}H_2O$: C, 62.5; H, 6.4; N, 13.7%). $\tilde{\nu}_{max}/cm^{-1}$ (NH and OH) 3260br, (C=N) 1570s and (N–N) 1080w; δ_H($CDCl_3$) 1.04 (3H, t, H^9), 1.65 (2H, mt, H^8), 2.56 and 2.6 (3H, 2s, H^{11}), 3.14 (2H, t, H^7), 4.07 and 4.1 (2H, 2s, H^5), 5.94 and 5.98 (1H, 2br, NH), 6.7–7.4 (5H, mt, C_6H_5), 11.5 and 12.28 (1H, 2br, OH); δ_C($CDCl_3$) 194.4/189.8 C(6), 178.0/177.5 C(4), 172.6/170.5 C(2), 169.8/168.1 C(10), 145.7/145.6 C(12), 129.8 C(13a, 13b), 122.9/122.8 C(14a, 14b), 113.7/113.6 C(15), 96.6/95.4 C(3), 53.2/51.3 C(5), 28.3/27.6 C(7), 25.2/25.1 C(11), 21.8/21.7 C(8) and 14.2/14.1 C(9).

$M(CH_3CO_2)(abta)\cdot yH_2O$. A solution of Habta (0.422 g, 2 mmol) in MeOH (10 ml) was added to a stirred solution of $M(CH_3CO_2)_2\cdot xH_2O$ (2 mmol) in the same solvent (30 ml). The homogeneous solution obtained was refluxed for 2 hours, then the solvent was evaporated *in vacuo* to yield a coloured solid which was collected by filtration, washed with cold MeOH (5 ml) and Et_2O (3 × 5 ml) and dried *in vacuo* over P_2O_5.

$M(abta)_2\cdot y'H_2O$. A solution of Habta (0.844 g, 4 mmol) in MeOH (20 ml) was added to a stirred solution of $M(CH_3CO_2)_2\cdot xH_2O$ (2 mmol) in the same solvent (30 ml). The homogeneous solution obtained was refluxed for 2 hours, then the solvent was evaporated *in vacuo* to yield a coloured solid which was collected by filtration, washed with cold MeOH (5 ml) and Et_2O (3 × 5 ml) and dried *in vacuo* over P_2O_5.

$M(CH_3CO_2)(Phabta)\cdot zH_2O$. A solution of HPhabta (0.30 g, 1 mmol) in MeOH (10 ml) was added to a stirred solution of $M(CH_3CO_2)_2\cdot xH_2O$ (1 mmol) in the same solvent (15 ml). The homogeneous solution obtained was refluxed for 2 hours, then the solvent was evaporated *in vacuo* to yield a coloured solid which was collected by filtration, washed with cold MeOH (5 ml) and Et_2O (3 × 5 ml) and dried *in vacuo* over P_2O_5.

$M(Phabta)_2\cdot z'H_2O$. A solution of HPhabta (0.60 g, 2 mmol) in MeOH (20 ml) was added to a stirred solution of $M(CH_3CO_2)_2\cdot xH_2O$ (1 mmol) in the same solvent (15 ml). The homogeneous solution obtained was refluxed for 2 hours, then the solvent was evaporated *in vacuo* to yield a coloured solid which

Table 2 Crystal data and data-collection parameters for $[Cu(abta)_2(py)_2]\cdot 2H_2O$ **2a**

Empirical formula	$C_{30}H_{38}CuN_4O_{10}$
Formula weight (M)	678.26
T/K	213(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	8.9105(14)
b/Å	10.2444(16)
c/Å	10.4369(17)
α/°	63.643(17)
β/°	65.680(18)
γ/°	75.792(18)
V/Å^3	775.6(2)
Z	1
μ/mm^{-1}	0.714
Reflections collected	4439
Independent reflections	2044 [R(int) = 0.0568]
Data/restraints/parameters	2044/0/211
Final $R1$ [$I > 2\sigma(I)$]	0.0354
$wR2$ (all data)	0.0898

was collected by filtration, washed with cold MeOH (5 ml) and Et_2O (3 × 5 ml) and dried *in vacuo* over P_2O_5.

Cu(CH$_3$CO$_2$)(abta)·H$_2$O **1**. μ_{eff} 1.92 μ_B; UV (cm^{-1} × 10^3) 14.9; $\tilde{\nu}_{max}$/cm^{-1} (OH) 3460br, 3340br, 3250br, (C=O lactam) 1675s, (C=C and C=O) 1590s, ($\nu_{asym}CO_2^-$) 1690s, ($\nu_{sym}CO_2^-$) 1450s, (Cu–O and ring def.) 530w, 475w.

Cu(abta)$_2$·2H$_2$O **2**. μ_{eff} 2.14 μ_B; UV (cm^{-1} × 10^3) 14.7; $\tilde{\nu}_{max}$/cm^{-1} (OH) 3520br, 3420br, 3240br, (C=O lactam) 1720s, 1680s, (C=C and C=O) 1600s, (Cu–O and ring def.) 555w, 470w, 385w.

Co(CH$_3$CO$_2$)(abta)·3H$_2$O **3**. μ_{eff} 4.93 μ_B; UV (cm^{-1} × 10^3) 18.9 and 21.5; $\tilde{\nu}_{max}$/cm^{-1} (OH) 3340br, (C=O lactam) 1710s, (C=C and C=O) 1570s, ($\nu_{asym}CO_2^-$) 1650s, ($\nu_{sym}CO_2^-$) 1370s, (Co–O and ring def.) 525w, 430w.

Co(abta)$_2$·3H$_2$O **4**. μ_{eff} 5.02 μ_B; UV (cm^{-1} × 10^3) 18.9 and 20.8; $\tilde{\nu}_{max}$/cm^{-1} (OH) 3380br, 3310br, 3220br, (C=O lactam) 1720s, (C=C and C=O) 1620s, (Co–O and ring def.) 530w, 430w, 380w.

Ni(CH$_3$CO$_2$)(abta)·2H$_2$O **5**. μ_{eff} 3.07 μ_B; UV (cm^{-1} × 10^3) 13.7, 14.9 and 25.6; $\tilde{\nu}_{max}$/cm^{-1} (OH) 3350br, (C=O lactam) 1715s, (C=C and C=O) 1610s, ($\nu_{asym}CO_2^-$) 1625s, ($\nu_{sym}CO_2^-$) 1370s (Ni–O and ring def.) 535w, 450w.

Ni(abta)$_2$·2H$_2$O **6**. μ_{eff} 3.1 μ_B; UV (cm^{-1} × 10^3) 13.7, 15.9 and 21.3; $\tilde{\nu}_{max}$/cm^{-1} (OH) 3380br, 3240br, (C=O lactam) 1720s, 1630s, (C=C and C=O) 1580s, (Ni–O and ring def.) 540w, 450w.

Zn(bta)$_2$·2H$_2$O **7**. $\tilde{\nu}_{max}$/cm^{-1} (OH) 3350br, (C=O lactam) 1650s, 1640s, (Zn–O) 490w, 420w; δ_H(DMSO-d_6) 0.84 (3H, t, H^9), 1.46 (2H, mt, H^8), 2.64 (2H, t, H^7), 3.44 (2H, s, H^5) and 7.68 (1H, br, NH); δ_C(DMSO-d_6) 193.5 C(6), 195.2 C(4), 178.7 C(2), 99.9 C(3), 50.0 C(5), 18.5 C(8) and 13.9 C(9).

Zn(abta)$_2$·2H$_2$O **8**. $\tilde{\nu}_{max}$/cm^{-1} (OH) 3400br, (C=O lactam) 1720s, 1660s, (Zn–O) 490w, 430w, 380w; δ_H(DMSO-d_6) 0.84 (3H, t, H^9), 1.47 (2H, mt, H^8), 2.38 (3H, s, H^{11}), 2.71 (2H, t, H^7) and 3.84 (2H, s, H^5); δ_C(DMSO-d_6) 198.8 C(6), 192.8 C(4), 170.6 C(2), 168.9 C(10), 102.6 C(3), 50.6 C(5), 24.8 C(11), 17.9 C(8) and 13.7 C(9).

Cu(CH$_3$CO$_2$)(Phabta)·2H$_2$O **9**. μ_{eff} 2.11 μ_B; UV (cm^{-1} × 10^3) 14.3; $\tilde{\nu}_{max}$/cm^{-1} (NH, OH) 3420br, (C=N) 1590s, (N–N) 1095, ($\nu_{asym}CO_2^-$) 1590s, ($\nu_{sym}CO_2^-$) 1370s, (ring def.) 550w, (Cu–O and ring def.) 470w, (Cu–N) 350w.

Cu(Phabta)$_2$·4H$_2$O **10**. μ_{eff} 2.3 μ_B; UV (cm^{-1} × 10^3) 14.3; $\tilde{\nu}_{max}$/cm^{-1} (NH, OH) 3410br, 3290br, (C=N) 1580s, (N–N) 1100s, (ring def.) 500w, (Cu–O and ring def.) 420w, 380w, (Cu–N) 350w.

Co(CH$_3$CO$_2$)(Phabta)·2H$_2$O **11**. μ_{eff} 5.28 μ_B; UV (cm^{-1} × 10^3) 19.8 and 21.3; $\tilde{\nu}_{max}$/cm^{-1} (NH, OH) 3310br, (C=N) 1575s, (N–N) 1090s, ($\nu_{asym}CO_2^-$) 1570s, ($\nu_{sym}CO_2^-$) 1420s, (ring def.) 570w, (Cu–O and ring def.) 490w, 430w, (Cu–N) 355w.

Zn(CH$_3$CO$_2$)(Phbta)·2H$_2$O **12**. $\tilde{\nu}_{max}$/cm^{-1} (OH, NH) 3500br, 3270br, (C=N) 1590s, (N–N) 1090s, ($\nu_{asym}CO_2^-$) 1580s, ($\nu_{sym}CO_2^-$) 1420s, (ring def.) 490w, (Cu–O and ring def.) 430w, 425w, (Cu–N) 360w; δ_H(CDCl$_3$) 1.02 (3H, t, H^9), 1.63 (2H, mt, H^8), 2.08 (3H, s, $CH_3CO_2^-$), 3.1 (2H, t, H^7), 3.78 (2H, s, H^5), 5.69 (1H, br, H^1), 5.95 (1H, s, NH), 6.7–7.4 (5H, mt, C_6H_5); δ_C(CDCl$_3$) 197.8/193.5 C(6), 181.3 CH_3CO_2, 176.4/175.5 C(4), 175.9/173.1 C(2), 146.5/146.2 C(12), 129.7/129.3 C(13a, 13b), 122.5/122.3 C(14a, 14b), 114.6/113.5 C(15), 95.9/94.2 C(3), 51.5/49.5 C(5), 28.0/27.3 C(7), 22.9/22.1 C(8), 21.7 CH_3CO_2 and 14.1 C(9).

X-Ray crystallography

The crystal data and data-collection parameters are summarized in Table 2. Crystal data were collected on a STOE-IPDS diffractometer, using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Structure solution and refinement were carried out using the program SHELXS 97.[30] Structure refinement (SHELXL 97)[31] by full-matrix least squares was based on all data using F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at calculated positions. The structure diagram was generated using ORTEP 3.[32]

CCDC reference number 186/2318.

See http://www.rsc.org/suppdata/dt/b0/b007252o/ for crystallographic files in .cif format.

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