Unusual metal coordination chemistry from an amino-amide derivative of 4-nitrophenol, a surprising ligand†

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The simple ligand N-(2-aminoethyl)-2-hydroxy-5-nitrobenzamide (**1**) exhibits several coordination modes depending on the reaction conditions, acting as a zwitterion on its own or being ionic in the presence of acid and depending on the concentration of metal present in a reaction, it can coordinate to the metal in either a 1:1 or a 1:2 metal:ligand mode. Furthermore, the role of solvent plays an important role in these complexation reactions with both four and six coordinate copper complexes being obtained using water as solvent but only six coordinate copper complexes obtained using acetonitrile as solvent.

Introduction

As part of our research, we have previously reported upper and lower rim functionalised calix[4]arenes, capable of binding transition metal salts.[1] In extending this theme, we targeted the design of some calix[4]arene Schiff base derivatives as potential ligands for fluorescence studies.[2] As part of our current studies, we targeted the attachment of functional groups, which did not contain imine functionalities, to the lower rim of our calix[4]arene scaffolds. We have reported our observations of the reactions of three Schiff base ligands, not calix[4]arene derivatives, with various MX_2 salts (M = Cu, Ni or Zn; X = chloride, perchlorate or acetate) which resulted in the cleavage of the imine bond and formation of metal-amine complexes.[3] With this in mind, we decided to investigate the use of the compound *N*-(2-aminoethyl)-2-hydroxy-5-nitrobenzamide (**1**), an amine which contains an amide functional group. This compound has not been reported previously but a derivative *N*-(2-aminoethyl)-2-hydroxybenzamide has been reported as a starting material for unsymmetrical Schiff bases.[4] Herein we report the synthesis, characterisation and metal complexation reactions of **1** as well as X-ray crystal structures of *N*-(2-aminoethyl)-2-hydroxy-5-nitrobenzamide (**1**), its HCl salt (**2**) and two copper(II) complexes (**3** and **4**).

Results and discussion

Ligand **1** was synthesised by the reaction of methyl 2-hydroxy-5-nitrobenzoate with 1,2-diaminoethane in a 1:1 methanol:toluene mixture. The compound showed the expected ^{1}H NMR signal pattern with three aromatic proton signals, two signals for the methylene groups and a broad signal for the amine group. Since the spectrum was obtained in d_6-DMSO, it was assumed that the hydroxyl signal was hidden by the residual water signal. A slow recrystallisation of **1** from water yielded crystals suitable for an X-ray crystallographic study. The asymmetric unit of **1** is shown in Fig. 1.[5]

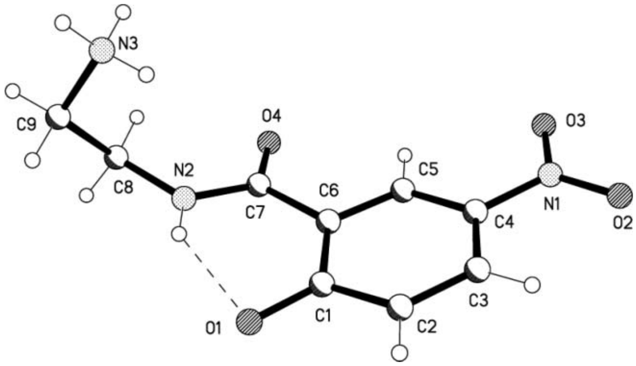

Fig. 1 Molecular structure of **1** showing selected labels. Ellipsoids are displayed at 50% probability level; the H-bond is represented by a dashed line.

The compound is a zwitterion with a complex, three-dimensional, H-bonding network (see Fig. 2), which is probably responsible for the conformation of the molecule. This also explains why the hydroxyl signal in the ^{1}H NMR spectrum is not observed. A difference map showed that the H atom in the hydrogen bond between the phenoxy oxygen O1 and the amide nitrogen N2 was localised on the N atom, indicating that the O atom is negatively charged. The phenoxy C-O bond (C1-O1) is very short at 1.3003(16) Å, whereas the typical C-O bond in a phenol is 1.362 Å.[7] The ammonium nitrogen N3 is involved in three intermolecular H-bonds, two of which involve interactions with two neighbouring phenoxide oxygens while the third interaction is with an amide oxygen.

The hydrochloride salt of N-(2-aminoethyl)-2-hydroxy-5-nitrobenzamide was readily synthesised by the reaction of **1** with HCl in water. Broad signals are clearly observed in the ^{1}H NMR spectrum for the hydroxyl and the ammonium groups, as well as signals for the aromatic and methylene protons. A slow

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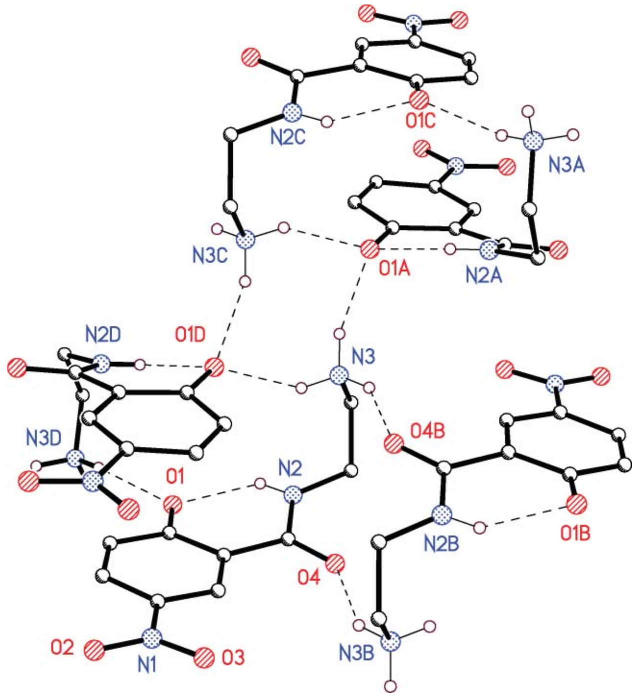

Fig. 2 Partial packing diagram for **1**, to illustrate H-bonding interactions.

recrystallisation of **2** from water yielded crystals suitable for X-ray crystallographic analysis. The asymmetric unit of **2** is shown in Fig. 3.[8]

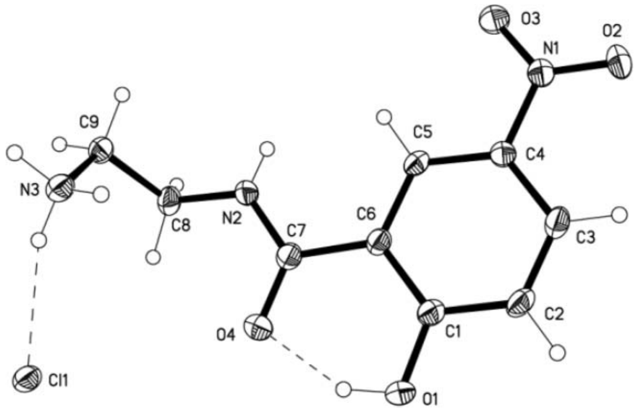

Fig. 3 Molecular structure of **2** showing selected labels. Ellipsoids are displayed at 50% probability level; dashed lines represent H-bonds.

Several structural differences between this structure and that of **1** are clearly obvious. The structure is not zwitterionic but is instead a charged species. The most striking feature of the structure involves the orientation of the ammonium amide arm. In **2**, a rotation has occurred, compared to the orientation of the arm in **1**, so that the carbonyl group points towards the phenol instead of away from it, as in **1**. As a result of this rotation there is an intramolecular H-bond (2.5471(17) Å) linking the phenol oxygen (O1) and the amide oxygen (O4), which is within the reported range for this type of H-bond.[9] Each chloride ion acts as an acceptor for H-bonds to three symmetry-related R-NH_3^+ groups (Fig. 4). The cations are paired by two, symmetry-related, H-bonds (N2…O3′).

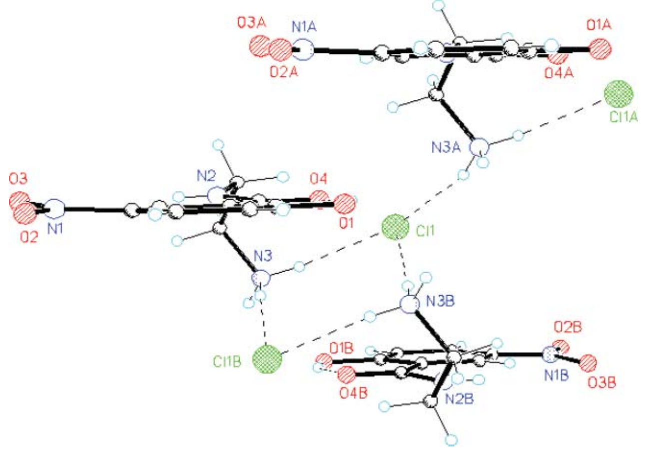

Fig. 4 Partial packing diagram for **2**, to illustrate H-bonding interactions.

As a result of these interactions, the structure consists of H-bonded sheets running diagonally across the unit cell.

Metal complexation reactions of **1** with $Cu(ClO_4)_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, $Cu(OAc)_2{\cdot}H_2O$, $Zn(ClO_4)_2{\cdot}6H_2O$ and $Zn(OAc)_2{\cdot}2H_2O$ were carried out in a 1:2 metal:ligand ratio in water, initially. The reaction of **1** with $Cu(ClO_4)_2{\cdot}6H_2O$ using a 1:2 metal:ligand ratio resulted in the formation of a brown solid (**3**) and a green solid (**4**). The X-ray crystal structure of **3** was obtained from crystals grown from a water solution.

The asymmetric unit revealed that the copper(II) ion is bound within one ligand in a square-planar geometry to the phenoxide oxygen, the amide nitrogen and the terminal amine (Fig. 5).[10] The remaining coordination site is occupied by a water solvate molecule. The overall structure consists of H-bonded layers between the water molecule and the neighbouring nitro group and amide carbonyl of two different molecules, which are further sandwiched into a double layer by H-bonding between one of the amine hydrogens and a neighbouring phenoxide oxygen. As a result of these H-bonded layers there are no further interactions between the copper centre and any other atom, reinforcing the fact that the copper atom occupies a square-planar geometry (Fig. 6 and 7).

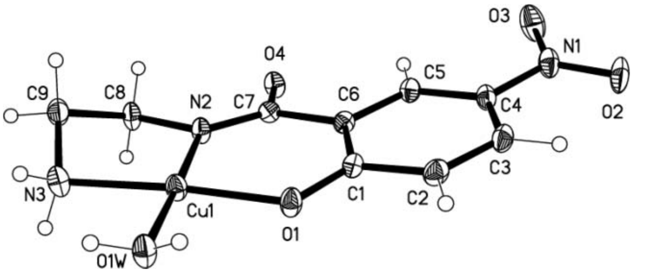

Fig. 5 Molecular structure of **3** showing selected labels, ellipsoids are shown at 50% probability level.

The coordinating role of the ligand is unusual in that it acts in a double role through loss of both the phenolic proton and the amide proton. While this loss of the amide proton has been observed in compartmental ligands[11] and in the copper(II) complexes of peptides,[12] it has not previously been reported for such a simple ligand as **1**. The mode of coordination to a metal ion through the loss of the amide proton has been observed for hydroxamic acids,

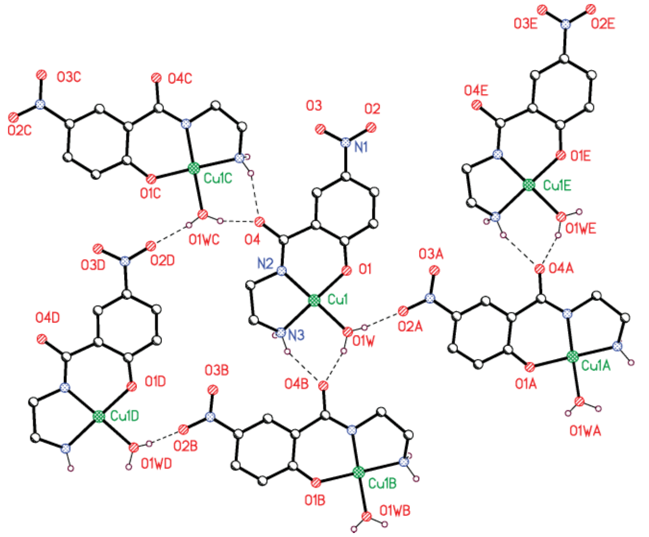

Fig. 6 Partial packing diagram for **3**, to illustrate H-bonding interactions.

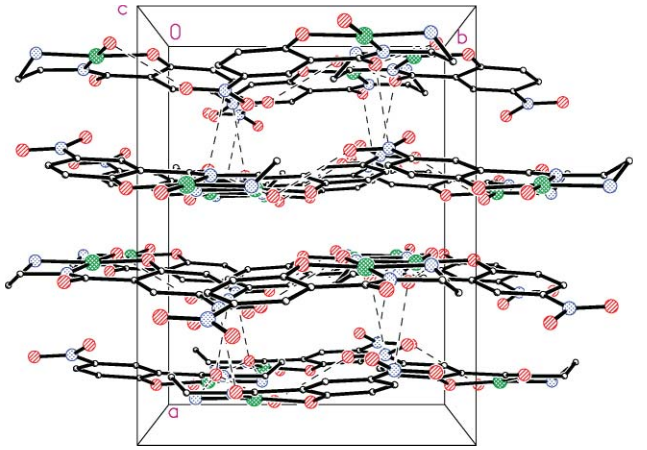

Fig. 7 Second packing diagram for **3**, to illustrate square planar geometry of copper(II) ion.

but the most common mode of metal binding for hydroxamic acids is through the deprotonated hydroxamate and carbonyl oxygen atoms, to form very stable five-membered chelate rings.[13] Presumably, the copper ion, in our case, is stripping the amide proton under these mild conditions in order to form stable five- and six-membered chelate rings. The alternative coordination possibility through the amide oxygen would result in the formation of a more unstable seven- and six-membered rings as opposed to the five- and six-membered rings depicted in the X-ray structure (Fig. 5).

A slow recrystallisation of the copper perchlorate complex (**4**) from water yielded green crystals which were structurally characterised. The asymmetric unit of **4** shows the metal in an octahedral environment with the two ligands forming the equatorial plane and the two perchlorate anions occupying the axial positions (Fig. 8).[14]

Both the copper ion and the water solvate molecule (O1w) lie on 2-fold axes. Neutrality in the molecule is maintained as the two ammonium groups and the copper(II) cation counteract the two negatively charged ligands and the two perchlorate anions. The perchlorate anions are disordered, and were modeled with 60:40 occupancy over two overlapping sites. The molecules are linked into H-bonded chains *via* the water solvate molecule, as well as further, complicated H-bonding (see Fig. 9). Interestingly, as a result of the coordination of the ligand to the copper ion, both pendant arms are on the same side of the molecule, or *cis* to each other, but point in opposite directions. From a symmetry point of view, it might be expected that having the ligands bound in such a way to have the pendant arms on opposite sides of the molecule, or *trans* to each other, would be more energetically favoured. If no steric crowding was occurring which would prevent the formation of the *cis* isomer, then the *trans* isomer would be the favoured conformation. Presumably, the hydrogen bonding interaction between the ammonium nitrogen and the water molecule, that is, the additional solvation energy of the more polar *cis* form, is largely responsible for the *cis* configuration.

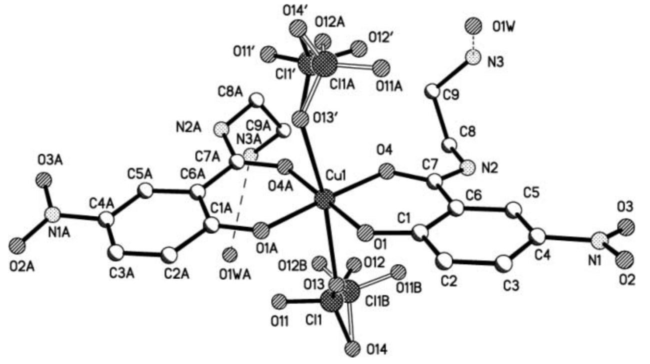

Fig. 8 Molecular structure of **4** showing selected labels and the disorder of the perchlorate ions. Hydrogen atoms are omitted for clarity, dashed lines represent H-bonds. Atoms with labels ending in A or B are generated by symmetry operation 1 – x, y, $\frac{1}{2}$ – z.

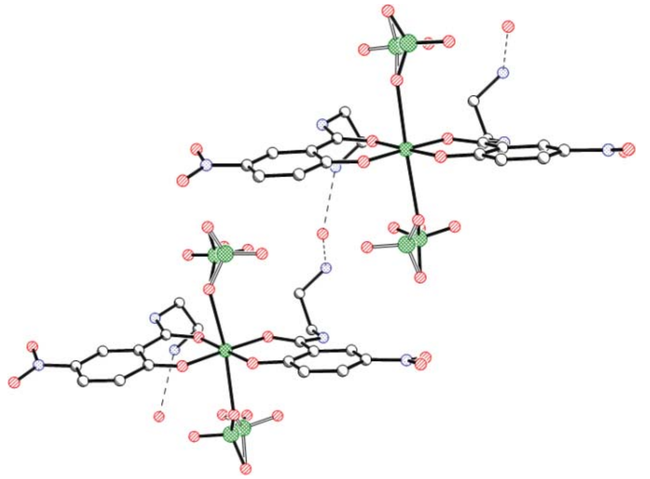

Fig. 9 Partial packing diagram for **4**, to illustrate H-bonding interactions.

The metal complexation reactions of **1** with $CuCl_2{\cdot}2H_2O$ and $Cu(OAc)_2{\cdot}H_2O$ in water yielded green (**5**) and purple (**6**) solids respectively. Elemental analyses suggested the presence of a 1:2 metal:ligand complex in the case of the green complex **5** formed from the copper chloride salt. A comparison of the IR spectra of both **4** and **5** showed that the spectra were very similar, apart from the obvious difference of the anions used in each case. This would suggest that the copper ion is involved in a

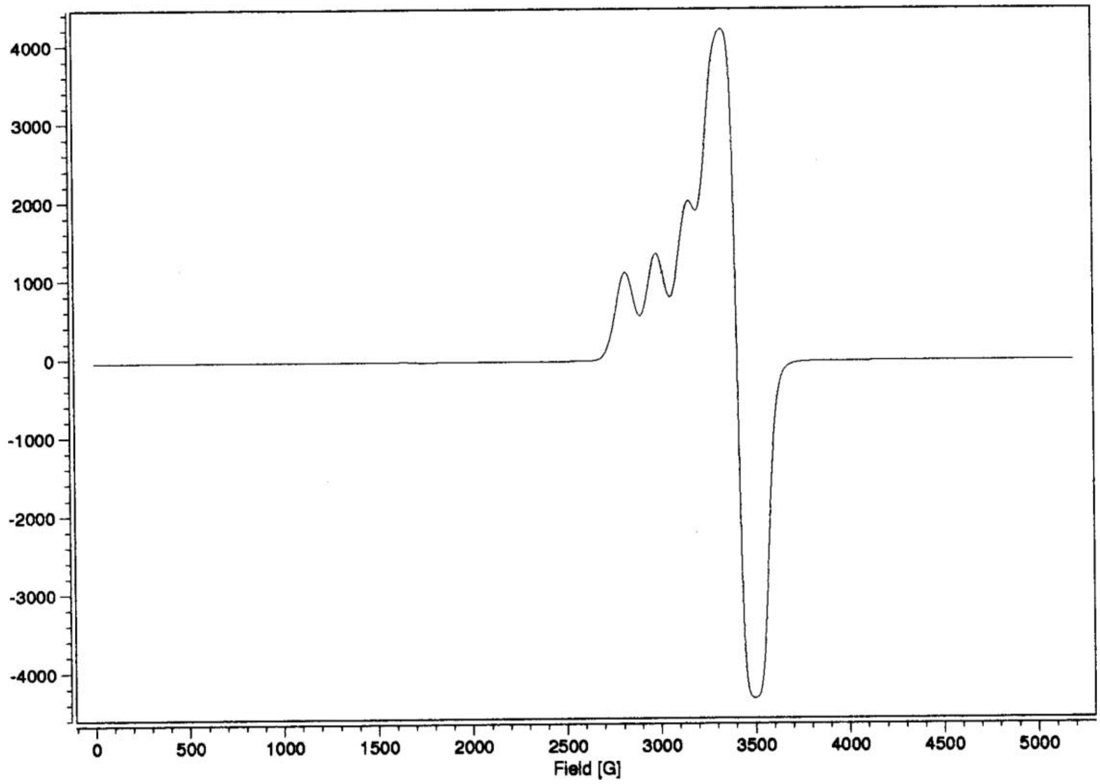

Fig. 10 ESR spectrum of **4** as a solid at RT.

similar coordination mode to that in **4**, with the anion axially bonded to the copper ion centre. EPR spectra of **4** and **5** were obtained at both room temperature and liquid nitrogen temperature as solid samples. Both EPR spectra were consistent with copper(II) being present (see Fig. 10) and were almost identical, showing jagged four-line spectra. These spectra indicate that the coordination of Cu(II) is very similar in each case. The spectrum of **4** shows a well resolved anisotropic spectrum, typical for an axially elongated octahedral geometry. The parameters ($g(\|) = 2.30$ and $g(\perp) = 2.08$, $A = 0.016$ cm^{-1}) are typical for a nearly square planar N_2O_2 coordination environment. UV-vis spectra of **4** and **5** obtained in either water or acetonitrile were also very similar, with all spectra showing metal to ligand charge transfer bands at 600 nm.

Elemental analyses suggested the presence of a 1:1 metal:ligand complex for the purple copper complex (**6**), formed from the copper acetate reaction, with no acetate anions present in the complex. One molecule of water is also included in the structure, based on the elemental analysis data. The IR spectrum of **6**, when compared to that of **3**, which is the four coordinate structure, show that both spectra are almost identical, suggesting that the complexes contain the metal ion in a four coordinate geometry similar to that found in **3** with a water molecule occupying the fourth coordination site. No solution UV-vis spectra could be obtained for **3** or **6** because, as soon as either compound was placed into solution (water, methanol or acetonitrile), the colour of the solution turned immediately to a green colour, indicating a change in the coordination geometry about copper from four to six co-ordination, with two molecules of solvent occupying the axial positions in the octahedral geometry formed. All efforts to get either solid to dissolve in a non-polar solvent failed.

The zinc complexes (**7** and **8**), which were obtained from the reaction of **1** with $Zn(ClO_4)_2 \cdot 6H_2O$ and $Zn(OAc)_2 \cdot 2H_2O$, were both pale yellow in colour. Elemental analyses suggested the presence of 1:1 metal:ligand complexes for both zinc complexes. A comparison of the IR spectrum of **3** with those of the two 1:1 zinc complexes (**7** and **8**) showed that all spectra are very similar to each other, suggesting that the zinc complexes contain the metal ion in a four coordinate geometry similar to that found in **3**. This structural assignment was confirmed when the ^{1}H NMR spectra of the zinc complexes were run in d_6-DMSO. When the ^{1}H NMR spectrum of **1** was compared with those of the zinc complexes, the triplet signal of the amide proton was completely absent in the metal complexes. Furthermore, the multiplicity of the methylene group attached to the amide was reduced from a multiplet to a triplet, suggesting that the zinc ion was bonded to the amide *via* a Zn-N bond. It also implied that the structural integrity was retained in solution. The EPR spectrum of **8** showed a radical signal with $g = 2.005$, due possibly to an impurity formed by air oxidation. The copper(II) doped zinc(II) complexes were prepared in the same way as the neat zinc(II) complexes with the addition of a few percent of copper(II) salt. Dilution of the copper(II) complex into the Zn host did not change the parameters of **4** significantly. The hyperfine lines are more narrow, but are not resolved into a superhyperfine pattern.

We repeated the copper complexation studies using acetonitrile as solvent instead of water. The complexation reaction of **1** with $Cu(ClO_4)_2 \cdot 6H_2O$ was carried out in a 1:1 metal:ligand ratio at room temperature. A moss green solution resulted from which no solid precipitated after several days. On removing some of the solvent under reduced pressure, a green solid (**9**) resulted. This green solid had an IR spectrum that was very similar to **4**, including the presence of bands due to the perchlorate anions and elemental analysis suggested that the complex had a 1:2 metal:ligand ratio, again similar to **4**. The difference in colour between **4** and **9** is due to the different solvent molecules present in each complex. The complexation reaction of **1** with $Cu(OAc)_2{\cdot}H_2O$ in a 1:1 metal:ligand ratio resulted in a dark green solid (**10**) precipitating from solution after several hours. The IR spectrum of **10** was very different to the IR spectra of both **3** and **4**, allowing for the differences in anion, implying that the copper ion was neither in a four coordinate square-planar geometry as in **3** nor in a six coordinate octahedral geometry as in **4**. It also confirmed the presence of an acetate group. Despite using different solvents, it proved impossible to grow crystals suitable for an X-ray crystallographic study. Elemental analysis of **10** suggested that the complex was a 1:1 metal:ligand complex with one acetate anion and one molecule of acetonitrile and one water molecule also present. The dimer, shown in Fig. 11, is a plausible structure for the data available, with the extra water molecules being present in the lattice. The reaction of **1** with $CuCl_2{\cdot}2H_2O$ was also carried out in a 1:1 metal:ligand ratio in acetonitrile, which resulted in a neon green solid (**11**) precipitating from the reaction solution after a few hours. The IR spectrum of **11** was very similar to the structure of **4** and elemental analysis on the complex suggested the presence of a 1:1 metal:ligand complex similar to the structure of **4**, previously described. The UV-vis spectra of the three complexes (**9-11**) were run in DMSO. All three showed metal to ligand charge transfer bands centered at 580 nm. Interestingly, in these reactions, there is no sign of a four coordinate copper species as we saw when the reactions were carried out using water as the solvent.

Experimental

Materials

The following chemicals were used without further purification from commercial sources: methyl 2-hydroxy-5-nitrobenzoate, 1,2-diaminoethane, copper perchlorate hexahydrate, copper chloride dihydrate, copper acetate monohydrate, zinc perchlorate hexahydrate and zinc acetate dihydrate. **Caution!** *Although not encountered in our experiments, perchlorate salts of metal ions are potentially explosive and should be manipulated with care and used only in small quantities.*

General procedures

^1H and ^{13}C NMR (δ ppm; J Hz) spectra were recorded on a Bruker Avance 300 MHz NMR spectrometer using saturated $CDCl_3$ solutions with Me_4Si reference, unless indicated otherwise, with resolutions of 0.18 Hz and 0.01 ppm, respectively. The X-band EPR spectra were recorded with a Bruker EMX Plus X spectrometer. The samples were solid powders in all cases. Infrared spectra (cm^{-1}) were recorded as KBr discs or liquid films between KBr plates using a Perkin Elmer System 2000 FT-IR spectrometer. Melting point analyses were carried out using a Stewart Scientific SMP 1 melting point apparatus and are uncorrected. Microanalysis was carried out at the Microanalytical Laboratory of either University College, Dublin, the National University of Ireland Cork or the National University of Ireland Maynooth. Standard Schlenk techniques were used throughout.

Syntheses

Synthesis of N-(2-aminoethyl)-2-hydroxy-5-nitro-benzamide (1). Methyl 2-hydroxy-5-nitrobenzoate (2 g, 10.14 mmol) and 1,2-diaminoethane (1.82 g, 30.42 mmol) were heated to reflux temperature in a toluene:methanol system (1:1, 80 cm^3) under nitrogen for 4 h. The resulting suspension was cooled to room temperature. The yellow precipitate was removed by filtration and dried in an oven overnight. Analytical data for **1**: yellow solid, yield = 2.06 g (91%); Found: C, 47.89; H, 4.93; N, 18.53. Calc. for $C_9H_{11}N_3O_4$ C, 47.98; H, 4.93; N, 18.66; m.p. 230-234 (dec.) °C; ν_{max} (KBr) 3441, 3193, 2914, 1626, 1590, 1557, 1430, 1341, 1298, 1201, 1151, 1131, 842, 755, 678 cm^{-1}; δ_H (300 MHz, d_6-DMSO): 11.43 (1 H, t, J 5.7 Hz, CONH), 8.65 (1 H, d, J 3.3 Hz, Ar-H), 7.80 (1 H, dd, J 9.5 & 3.3 Hz, Ar-H), 7.71 (2 H, br s, NH_2), 6.27 (1 H, d, J 9.5 Hz, Ar-H), 3.50 (2 H, m, NHCH_2), 2.96 (2 H, t, J 7.5 Hz, CH_2NH$_2$); δ_C (75 MHz, d_6-DMSO): 178.2, 167.8, 129.8, 128.4, 127.3, 122.6, 117.5, 39.5, 36.5.

Synthesis of 1·HCl (2). **1** (0.15 g, 0.67 mmol) was suspended in water (5 cm^3). 1 M HCl (7 cm^3) was added dropwise with stirring until the yellow solid has dissolved. Stirring was continued for 1 h. The solvent was reduced until a white solid precipitated. The white solid was removed by filtration, washed with cold water and dried in the air. Analytical data for **2**: white solid, yield = 0.14 g

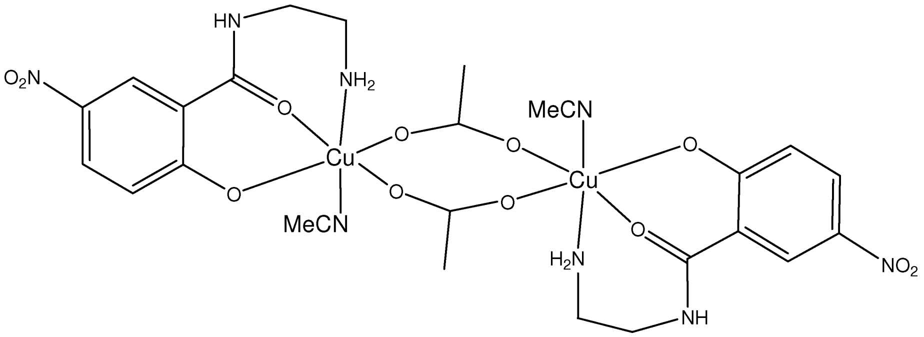

Fig. 11 Proposed structure of **11** containing bridging acetates and coordinating solvent molecules.

(82%); Found: C, 41.19; H, 4.61; N, 15.79. Calc. for $C_9H_{12}ClN_3O_4$ C, 41.29; H, 4.62; N, 16.06; m.p. 268-270 (dec.) °C; ν_{max} (KBr) 3383, 2969, 1641, 1605, 1557, 1497, 1329, 1207, 1172, 1159, 844, 749 cm^{-1}; δ_H (300 MHz, d_6-DMSO): 13.45 (1 H, br s, O*H*), 9.28 (1 H, t, *J* 4.8 Hz, CONH*H*), 8.86 (1 H, d, *J* 2.9 Hz, Ar-*H*), 8.27 (1 H, dd, *J* 9.2 & 2.7 Hz, Ar-*H*), 8.17 (3 H, br s, NH_3), 7.22 (1 H, d, *J* 9.2 Hz, Ar-*H*), 3.61 (2 H, m, CH_2NH$_3$), 3.02 (2 H, m, NHCH_2); δ_C (75 MHz, d_6-DMSO): 166.9, 164.6, 139.1, 128.5, 125.5, 118.2, 116.6, 38.2, 37.0.

Reaction of 1 with $Cu(ClO_4)_2·6H_2O$

To **1** (0.1 g, 0.44 mmol) in 15 cm^3 water was added copper perchlorate hexahydrate (0.34 g, 0.89 mmol) in water (5 cm^3) and the resulting green solution was stirred for 1 h. The resulting purple/brown precipitate was removed by filtration and dried in air. The solid was redissolved in water and allowed to stand overnight, resulting in brown crystals (**3**) and some starting material. Analytical data for **3**: brown solid, yield = 0.02 g (31%); Found: C, 35.45; H, 3.58; N, 13.45. Calc. for $C_9H_{11}CuN_3O_5$ C, 35.47; H, 3.64; N, 13.79; ν_{max} (KBr) 3438, 3225, 1611, 1569, 1525, 1435, 1317, 1283, 1231, 1142, 1131, 834, 696 cm^{-1}. The original green filtrate was allowed to stand, resulting in the formation of green crystals (**4**) after several days. The crystals were removed by filtration and dried in air. Analytical data for **4**: green solid, yield = 0.10 g (59%); Found: C, 29.40; H, 3.01; N, 11.20. Calc. for $C_{18}H_{24}Cl_2CuN_6O_{17}$ C, 29.58; H, 3.31; N, 11.50; ν_{max} (KBr) 3391, 3083, 1608, 1545, 1483, 1471, 1436, 1307, 1141, 1120, 1110, 1086, 834, 749 cm^{-1}.

Reaction of 1 with $CuCl_2·2H_2O$

To **1** (0.1 g, 0.44 mmol) in 15 cm^3 water was added copper chloride dihydrate (0.15 g, 0.88 mmol) in water (5 cm^3) and the resulting green solution was stirred for 1 h. A green solid precipitated from solution. The solid was removed by filtration and dried in air. Analytical data for **5**: green solid, yield = 0.07 g (51%); Found: C, 36.95; H, 3.79; N, 14.24. Calc. for $C_{18}H_{22}Cl_2CuN_6O_8$ C, 36.96; H, 3.79; N, 14.37; ν_{max} (KBr) 3378, 3006, 1604, 1579, 1558, 1466, 1307, 1271, 1161, 839, 750 cm^{-1}.

Reaction of 1 with $Cu(OAc)_2·H_2O$

To **1** (0.1 g, 0.44 mmol) in 15 cm^3 water was added copper acetate monohydrate (0.18 g, 0.89 mmol) in water (5 cm^3) and the resulting purple/brown solution was stirred for 1 h. A pale purple solid precipitated from solution within 2 mins. The solid was removed by filtration and dried in air. Analytical data for **6**: purple solid, yield = 0.11 g (79%); Found: C, 35.45; H, 3.58; N, 13.45. Calc. for $C_9H_{11}CuN_3O_5$ C, 35.47; H, 3.64; N, 13.79; ν_{max} (KBr) 3515, 3227, 3147, 1609, 1570, 1528, 1449, 1435, 1315, 1232, 1142, 1131, 834, 706 cm^{-1}.

Reaction of 1 with $Zn(ClO_4)_2·6H_2O$

To a zinc perchlorate hexahydrate (0.17 g, 0.44 mmol) in water (5 cm^3) solution was added dropwise a solution of **1** (0.1 g, 0.44 mmol) and sodium hydroxide (0.018 g, 0.44 mmol) in water (5 cm^3). An immediate yellow precipitate resulted and the resulting suspension was stirred for 1 h. The solid was removed by filtration, washed with water and dried in air. Analytical data for **7**: yellow solid, yield = 0.11 g (78%); Found: C, 35.45; H, 3.58; N, 13.45. Calc. for $C_9H_{11}N_3O_5Zn$ C, 35.26; H, 3.62; N, 13.71; ν_{max} (KBr) 3443, 2915, 1613, 1590, 1448, 1431, 1341, 1301, 1131, 843, 678 cm^{-1}; δ_H (300 MHz, d_6-DMSO): 8.65 (1 H, d, *J* 2.9 Hz, Ar-*H*), 7.88 (1 H, dd, *J* 9.3 & 2.9 Hz, Ar-*H*), 6.56 (1 H, d, *J* 9.3 Hz, Ar-*H*), 3.43 (2 H, br s, CH_2NCO), 2.83 (2 H, br s, CH_2NH).

Reaction of 1 with $Zn(OAc)_2·2H_2O$

Similar procedure to that of **7**, except that 0.096 g (0.44 mmol) zinc acetate dihydrate was used, with similar analytical results. Analytical data for **8**: yellow solid, yield = 0.12 g (85%); Found: C, 35.54; H, 3.84; N, 13.95. Calc. for $C_9H_{11}N_3O_5Zn$ C, 35.26; H, 3.62; N, 13.71; ν_{max} (KBr) 3515, 3227, 3147, 1609, 1570, 1528, 1449, 1435, 1315, 1232, 1142, 1131, 834, 706 cm^{-1}.

Reaction of 1 with $Cu(ClO_4)_2·6H_2O$

To **1** (0.1 g, 0.44 mmol) in 5 cm^3 acetonitrile was added copper perchlorate hexahydrate (0.18 g, 0.45 mmol) in acetonitrile (15 cm^3) and the resulting moss green solution was stirred for 10 h. No precipitate resulted and the solvent was partially removed under reduced pressure. The green solid which then precipitated was removed by filtration and dried in air (**9**). Analytical data for **9**: moss green solid, yield = 0.08 g (78%); Found: C, 31.40; H, 3.03; N, 13.20. Calc. for $C_{20}H_{25}Cl_2CuN_7O_{16}$ C, 31.86; H, 3.34; N, 13.00; ν_{max} (KBr) 3398, 1610, 1550, 1467, 1439, 1308, 1231, 1141, 1122, 834, 783, 755, 696 cm^{-1}.

Reaction of 1 with $Cu(OAc)_2·H_2O$

To **1** (0.1 g, 0.44 mmol) in 5 cm^3 acetonitrile was added copper acetate monohydrate (0.1 g, 0.49 mmol) in acetonitrile (15 cm^3) and the resulting green suspension was stirred for 10 h. The solid (**10**) was removed by filtration and dried in air. Analytical data for **10**: dark green solid, yield = 0.12 g (78%); Found: C, 38.24; H, 4.03; N, 13.46. Calc. for $C_{26}H_{30}Cu_2N_8O_{14}$ C, 38.76; H, 3.75; N, 13.91; ν_{max} (KBr) 3433, 3324, 3260, 1600, 1574, 1533, 1471, 1427, 1310, 1146, 1131, 1084, 859, 755, 706, 678 cm^{-1}.

Reaction of 1 with $CuCl_2·2H_2O$

To **1** (0.1 g, 0.44 mmol) in 5 cm^3 acetonitrile was added copper chloride dihydrate (0.08 g, 0.48 mmol) in acetonitrile (15 cm^3) and the resulting orange solution was stirred for 10 h. After 5 h, a yellow/green solid precipitated from solution. The solid (**11**) was removed by filtration and dried in air. Analytical data for **11**: neon green solid, yield = 0.11 g (84%); Found: C, 36.38; H, 4.21; N, 14.45. Calc. for $C_{18}H_{22}Cl_2CuN_6O_8$ C, 37.04; H, 4.15; N, 14.41; ν_{max} (KBr) 3375, 1610, 1556, 1465, 1358, 1321, 1273, 1163, 839, 777, 752 cm^{-1}.

Conclusions

In summary, we have shown that the simple ligand N-(2-aminoethyl)-2-hydroxy-5-nitrobenzamide (**1**) exhibits several co-ordination modes depending on the reaction conditions. It acts as a zwitterion on its own and is ionic in the presence of acid. Furthermore, depending on the concentration of metal present in a reaction, it can coordinate to the metal in either a 1:1 (as in **3**) or a 1:2 (as in **4**) metal:ligand mode. The coordination mode is also dependent on the type of metal ion present. Furthermore, when we repeat the copper complexation reactions using acetonitrile as solvent instead of water, we only get the formation of six coordinate species and no four coordinate complexes are formed.

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Notes and references

1 (*a*) B. S. Creaven, M. D. Deasy, P. M. Flood, J. McGinley and B. A. Murray, *Inorg. Chem. Commun.*, 2008, **11**, 1215; (*b*) A. D. Bond, B. S. Creaven, D. F. Donlon, T. L. Gernon, J. McGinley and H. Toftlund, *Eur. J. Inorg. Chem.*, 2007, 749; (*c*) B. S. Creaven, T. L. Gernon, J. McGinley, A.-M. Moore and H. Toftlund, *Tetrahedron*, 2006, **62**, 9066; (*d*) B. S. Creaven, T. L. Gernon, T. McCormac, J. McGinley, A.-M. Moore and H. Toftlund, *Inorg. Chim. Acta*, 2005, **358**, 2661; (*e*) B. S. Creaven, M. F. Mahon, J. McGinley and A.-M. Moore, *Inorg. Chem. Commun.*, 2006, **9**, 231; (*f*) B. S. Creaven, M. D. Deasy, J. F. Gallagher, J. McGinley and B. A. Murray, *Tetrahedron*, 2001, **57**, 8883.

2 M. F. Mahon, J. McGinley, A. D. Rooney and J. M. D. Walsh, *Tetrahedron*, 2008, **64**, 11058.

3 M. F. Mahon, J. McGinley, A. D. Rooney and J. M. D. Walsh, *Inorg. Chim. Acta*, 2009, **362**, 2353.

4 (*a*) E. A. Djurendić, T. M. Surányi and D. A. Miljković, *Collect. Czech. Chem. Commun.*, 1991, **56**, 1446; (*b*) W. Adam, C. R. Saha-Moeller and P. A. Ganeshpure, *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.*, 2004, **43A**, 56; (*c*) T. Kido, Y. Ikuta, Y. Sunatsuki, Y Ogawa, N. Matsumoto and N. Re, *Inorg. Chem.*, 2003, **42**, 398; (*d*) Q. Yu, Y. Tang, Y.-H. Feng, M.-Y. Tan and K.-B. Yu, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2003, **59**, o577.

5 All data sets were collected at 150(2) K on a Bruker APEXII CCD diffractometer. Single-crystal structure analysis of **1**. The structure was solved by direct methods and refined on F^2 using all the reflections.[6] Hydrogen atoms bonded to nitrogen were located from difference maps, those bonded to N3 were then inserted at calculated positions, but the coordinates of the hydrogen bonded to N2 were freely refined. $C_9H_{11}N_3O_4$ $M = 225.21$, $\lambda = 0.71073$ Å, monoclinic, *C2/c*, $a = 15.5904(13)$ Å, $b = 9.6611(8)$ Å, $c = 13.7196(11)$ Å, $\beta = 112.550(1)°$, $V = 1908.5(3)$ Å^3, $Z = 8$, $D_{calcd} = 1.568$ Mg/m^3, $\mu = 0.125$ mm^{-1}, GoF = 1.030, $R_{int} = 0.0359$, $R_1 = 0.0445$, wR_2(all) = 0.1307. CCDC 720239.

6 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2007, **64**, 112.

7 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.

8 Single-crystal structure analysis of **2**. The structure was solved by direct methods and refined on F^2 using all the reflections.[6] Hydrogen atoms bonded to O1 and N2 were located from difference maps and their coordinates refined. $C_9H_{12}ClN_3O_4$ $M = 261.67$, $\lambda = 0.71073$ Å, triclinic, *P-1*, $a = 5.8346(5)$ Å, $b = 8.1575(8)$ Å, $c = 11.8171(11)$ Å, $\alpha = 105.3490(10)°$, $\beta = 92.1640(10)°$, $\gamma = 91.2740(10)°$, $V = 541.69(9)$ Å^3, $Z = 2$, $D_{calcd} = 1.604$ Mg/m^3, $\mu = 0.361$ mm^{-1}, GoF = 1.047, $R_{int} = 0.0247$, $R_1 = 0.0374$, wR_2(all) = 0.0976. CCDC 720240.

9 (*a*) X.-S. Tai, J. Yin, M.-Y. Hao and Z.-P. Liang, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2007, **63**, o1727; (*b*) H.-M. Liu, L. He, X.-L. Luo and W.-Q. Zhang, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2006, **62**, o104.

10 Single-crystal structure analysis of **3**. The structure was solved by direct methods and refined on F^2 using all the reflections.[6] Hydrogen atoms on the water molecule were located from difference maps and the coordinates refined. $C_9H_{11}CuN_3O_5$ $M = 304.75$, $\lambda = 0.71073$ Å, orthorhombic, *Pbca*, $a = 13.5511(6)$ Å, $b = 10.4268(4)$ Å, $c = 14.7843(6)$ Å, $V = 2088.94(15)$ Å^3, $Z = 8$, $D_{calcd} = 1.938$ Mg/m^3, $\mu = 2.111$ mm^{-1}, GoF = 1.034, $R_{int} = 0.0428$, $R_1 = 0.0332$, wR_2(all) = 0.1027. CCDC 720242.

11 (*a*) See, for example, J. Y. Yang and D. G. Nocera, *Tetrahedron Lett.*, 2008, **49**, 4796; (*b*) R.-J. Tao, F.-A. Li, Y.-X. Cheng, S.-Q. Zang, Q.-L. Wang, J.-Y. Niu and D.-Z. Liao, *Inorg. Chim. Acta*, 2006, **359**, 2053; (*c*) S. Brooker, D. J. de Geest and G. S. Dunbar, *Inorg. Chim. Acta*, 1998, **282**, 222; (*d*) S. K. Mandal, L. K. Thompson, M. J. Newlands, A. K. Biswas, B. Adhikary, K. Nag, E. J. Gabe and F. L. Lee, *Can. J. Chem.*, 1989, **67**, 662.

12 W. Kaim and B. Schwederski, *Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life*, Wiley, Chichester, 1994.

13 C. J. Marmion, D. Griffith and K. B. Nolan, *Eur. J. Inorg. Chem.*, 2004, 3003.

14 Single-crystal structure analysis of **4**. The structure was solved by direct methods[15] and refined on F^2 using all the reflections.[6] The single independent proton bonded to the oxygen atom of a water molecule was located from difference maps and not further refined. $C_{18}H_{24}Cl_2CuN_6O_{17}$ $M = 730.87$, $\lambda = 0.71073$ Å, monoclinic, *C2/c*, $a = 10.2850(5)$ Å, $b = 14.9501(7)$ Å, $c = 18.1501(9)$ Å, $\beta = 92.915(1)°$, $V = 2787.2(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.742$ Mg/m^3, $\mu = 1.066$ mm^{-1}, GoF = 1.073, $R_{int} = 0.0268$, $R_1 = 0.0327$, wR_2(all) = 0.0951. CCDC 720241.

15 M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. D. Caro, C. Giacavazzo, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 2005, **38**, 381.