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Copper(II) complexes of isomeric aminophenylhydroxamic acids. A novel 'clam-like' dimeric metallacrown and polymeric helical structure containing interlinked unique copper(II) sites

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The reaction of 3-aminophenylhydroxamic acid with $CuSO_4 \cdot 5H_2O$ in aqueous solution gives the novel helical polymer $[Cu_3(3\text{-Apha})_4(H_2O)SO_4]_n \cdot 8H_2O$ **1** the structure of which contains interlinked repeating units having three unique neutral, anionic and cationic copper(II) sites. In this complex the copper(II) sites are magnetically non-interacting. A similar reaction with 2-aminophenylhydroxamic acid gives the novel dimeric 'metallacrown' $[Cu_5(2\text{-AphaH}_{-1})_4(\mu\text{-}SO_4)(H_2O)_2]_2 \cdot 10H_2O$ **2** which has a 'clam-like' structure showing strong antiferromagnetic behaviour. In contrast to the above ligands, 4-aminophenylhydroxamic acid gives the monomeric square planar complex $Cu(4\text{-Apha})_2 \cdot H_2O$ **3** which exhibits paramagnetic behaviour. Crystal structures of all three complexes are reported.

Introduction

Hydroxamic acids, a group of weak organic acids of general formula RC(O)N(R′)OH, play a variety of roles in biology and medicine, for example as siderophores for iron(III),[1] as potent and selective inhibitors of enzymes such as peroxidases,[2] ureases,[3] matrix metalloproteinases,[4] and as hypotensive,[5,6] anti-cancer, anti-tuberculous and anti-fungal agents.[7] Many of these roles are due largely to the complexing ability of the hydroxamate group which is usually bidentate[4,8] but can also be bridging[9] or even monodentate.[10] Usually these interactions are stabilised by hydrogen bonding interactions involving the hydroxamate group and other suitable groups present in the molecule. The structures of the copper(II) complexes of the isomeric aminophenylhydroxamic acids (AphaH), which are reported herein, illustrate the diversity of structures which these ligands can produce and how these are influenced by other coordinating groups in the molecules. The structures include a novel helical polynuclear complex involving three unique copper(II) sites formed by 3-AphaH, a novel dimeric copper(II)-metallacrown type complex formed by 2-AphaH,[11] and a simple mononuclear complex formed by 4-AphaH.

Results and discussion

Synthesis and structures

The isomeric aminophenylhydroxamic acids were prepared in good yields by the reaction of NH_2OH, generated *in situ* from $(NH_2OH)_2 \cdot H_2SO_4$, with the corresponding esters. The complexes were obtained in high yield and in crystalline form, either directly or by recrystallisation, by the reaction of the hydroxamic acid with $CuSO_4 \cdot 5H_2O$ in aqueous solution. Satisfactory microanalyses were obtained. The structures of the complexes were obtained by single crystal X-ray crystallography.

The complex $[Cu_3(3\text{-Apha})_4(H_2O)SO_4]_n \cdot 8H_2O$ **1**, prepared from 3-AphaH and $CuSO_4 \cdot 5H_2O$, has a helical polymeric structure (Fig. 1, Table 1), in which the repeating units contain three interlinked unique copper(II) sites *i.e.* the neutral square planar $Cu(3\text{-Apha})_2$, the anionic square pyramidal $[Cu(3\text{-Apha})SO_4(NH_2)(...NH_2)]^-$ and the cationic square pyramidal $[Cu(3\text{-Apha})(H_2O)(NH_2)(...NH_2)]^+$ where NH_2 represents amino groups from neighbouring molecules forming both normal and elongated (…) bonds. The polymer chains are linked by an extensive hydrogen bonding network involving hydroxamate nitrogens and oxygens, sulfate oxygens and both coordinated and solvent waters. This network gives the crystal lattice a rigid structure (Fig. 2) featuring channels (dimensions ~5.5 Å × ~9 Å) which are occupied by the monodentate sulfate groups and solvent (H_2O).

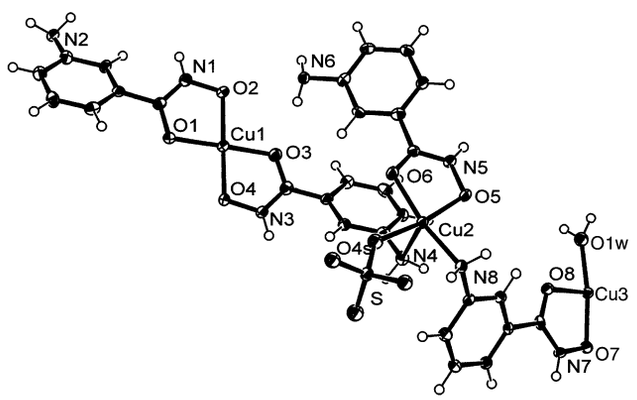

Fig. 1 ORTEP[19] diagram of **1** (solvent molecules omitted for clarity) showing a single repeating unit which contains the unique neutral (Cu1), anionic (Cu2) and the incomplete cationic (Cu3) copper(II) sites. The Cu3 site is completed by coordinated NH_2 groups from N6 (normal bond) and N2 (elongated bond) belonging to adjacent repeating units.

The dark green crystalline complex $[Cu_5(2\text{-AphaH}_{-1})_4(\mu\text{-}SO_4)(H_2O)_2]_2 \cdot 10H_2O$ **2**, was obtained by the reaction of 2-AphaH with $CuSO_4 \cdot 5H_2O$ in aqueous solution. Each monomeric unit of this dimer contains a square of copper(II) ions,

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Table 1 Selected bond lengths (Å) and angles (°) with estimated standard deviations for $[Cu_3(3\text{-Apha})_4(H_2O)SO_4]_n\cdot 8H_2O$ **1**

CU(1)–O(4)	1.922(3)	Cu(3)–N(6A)	2.053(3)
Cu(1)–O(2)	1.927(3)	Cu(3)–N(2A)	2.405(3)
Cu(1)–O(3)	1.942(3)	S–O(4S)	1.460(3)
Cu(1)–O(1)	1.951(3)	O(1)–C(1)	1.293(5)
Cu(2)–O(5)	1.958(3)	O(2)–N(1)	1.376(4)
Cu(2)–O(4S)	1.964(3)	O(3)–C(8)	1.290(5)
Cu(2)–O(6)	1.981(3)	O(4)–N(3)	1.384(4)
Cu(2)–N(8)	2.034(3)	O(5)–N(5)	1.383(4)
Cu(2)–N(4)	1.408(3)	O(6)–C(15)	1.265(5)
Cu(3)–O(7)	1.956(3)	O(7)–N(7)	1.372(4)
Cu(3)–O(8)	1.974(3)	O(8)–C(22)	1.284(5)
Cu(3)–O(1W)	1.980(3)		
O(4)–Cu(1)–O(2)	175.83(14)	O(4S)–Cu(2)–N(4)	93.16(12)
O(4)–Cu(1)–O(3)	84.66(12)	O(6)–Cu(2)–N(4)	94.46(11)
O(2)–Cu(1)–O(3)	95.84(12)	N(8)–Cu(2)–N(4)	95.30(12)
O(4)–Cu(1)–O(1)	94.81(12)	O(7)–Cu(3)–O(8)	83.20(11)
O(2)–Cu(1)–O(1)	84.80(12)	O(7)–Cu(3)–O(1W)	172.00(11)
O(3)–Cu(1)–O(1)	178.40(12)	O(8)–Cu(3)–O(1W)	92.05(12)
O(5)–Cu(2)–O(4S)	170.53(12)	O(7)–Cu(3)–N(6A)	169.58(12)
O(5)–Cu(2)–O(6)	82.97(11)	O(1W)–Cu(3)–N(6A)	89.71(13)
O(4S)–Cu(2)–O(6)	89.43(12)	O(7)–Cu(3)–N(2A)	97.27(12)
O(5)–Cu(2)–N(8)	90.89(12)	O(8)–Cu(3)–N(2A)	93.41(11)
O(4S)–Cu(2)–N(8)	95.64(13)	O(1W)–Cu(3)–N(2A)	89.41(12)
O(6)–Cu(2)–N(8)	168.74(12)	N(6A)–Cu(3)–N(2A)	96.88(12)
O(5)–Cu(2)–N(4)	93.06(12)		

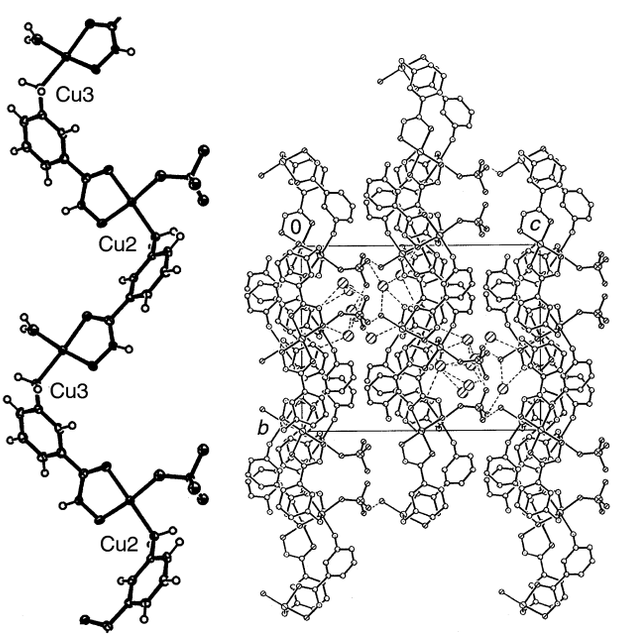

Fig. 2 ORTEP diagram of the polymeric helical chain of **1** showing only the Cu2–Cu3 backbone and a unit cell displaying channels containing coordinated sulfate groups and solvent molecules (H_2O).

Cu1–4 (Fig. 3, Table 2), linked by doubly deprotonated hydroxamate ligands, 2-AphaH_{-1}, and a central copper(II) ion, Cu5, coordinated by four hydroxamate oxygens and the oxygen of a bridging sulfate which is also weakly bonded to Cu4. A similar complex but having a monomeric structure and belonging to a family called 'metallacrowns' has previously been reported by Pecoraro *et al.* and was prepared from $Cu(OAc)_2$.[12] The structure of **2** (Fig. 3), however, is a fused dimeric metallacrown, having a novel 'clam-like' structure, the closed end of which arises from the binding of ring coppers, Cu2 and Cu2A, in two metallacrown units to oxygen atoms O2A and O2 respectively in adjacent units, and the open end of which accommodates bridging sulfate ligands. The exterior faces of the metallacrown dimer are involved in hydrogen bonding with other metallacrown units through the hydroxamate nitrogens and oxygens resulting in intermolecular Cu–Cu distances of

Table 2 Selected bond lengths (Å) and angles (°) with estimated standard deviations for $[Cu_5(2\text{-Apha}H_{-1})_4(\mu\text{-}SO_4)(H_2O)_2]_2\cdot 10H_2O$ **2**

Cu(1)–O(7)	1.901(5)	Cu(3)–N(6)	1.973(5)
Cu(1)–N(1)	1.959(6)	Cu(3)–O(8S)	2.430(6)
Cu(1)–O(8)	2.006(5)	Cu(4)–O(5)	1.919(4)
Cu(1)–N(2)	2.009(5)	Cu(4)–O(6)	1.947(4)
Cu(1)–O(7S)	2.154(5)	Cu(4)–N(7)	1.967(5)
Cu(2)–O(1)	1.904(4)	Cu(4)–N(8)	1.960(5)
Cu(2)–O(2)	1.959(4)	Cu(4)–O(10)	2.472(5)
Cu(2)–N(3)	1.963(5)	Cu(5)–O(3)	1.900(4)
Cu(2)–N(4)	1.977(5)	Cu(5)–O(7)	1.915(5)
Cu(2)–O(2A)	2.428(5)	Cu(5)–O(1)	1.937(4)
Cu(3)–O(3)	1.915(5)	Cu(5)–O(5)	1.953(5)
Cu(3)–N(5)	1.916(6)	Cu(5)–O(9)	2.258(6)
Cu(3)–O(4)	1.945(5)	O(2)–Cu(2A)	2.428(5)
O(7)–Cu(1)–N(1)	86.0(2)	O(3)–Cu(3)–N(6)	177.6(3)
O(7)–Cu(1)–O(8)	77.4(2)	N(5)–Cu(3)–N(6)	88.7(2)
N(1)–Cu(1)–O(8)	156.7(2)	O(4)–Cu(3)–N(6)	98.2(2)
O(7)–Cu(1)–N(2)	172.6(2)	O(3)–Cu(3)–O(8S)	87.8(2)
N(1)–Cu(1)–N(2)	86.8(2)	N(5)–Cu(3)–O(8S)	92.4(2)
O(8)–Cu(1)–N(2)	106.7(2)	O(4)–Cu(3)–O(8S)	102.9(2)
O(7)–Cu(1)–O(7S)	87.6(2)	N(6)–Cu(3)–O(8S)	90.3(2)
N(1)–Cu(1)–O(7S)	113.0(2)	O(5)–Cu(4)–O(6)	82.2(2)
O(8)–Cu(1)–O(7S)	84.6(2)	O(5)–Cu(4)–N(7)	89.8(2)
N(2)–Cu(1)–O(7S)	97.1(2)	O(6)–Cu(4)–N(7)	171.8(2)
O(1)–Cu(2)–O(2)	81.8(2)	O(5)–Cu(4)–N(8)	177.6(2)
O(1)–Cu(2)–N(3)	89.4(2)	O(6)–Cu(4)–N(8)	99.4(2)
O(2)–Cu(2)–N(3)	170.5(2)	O(5)–Cu(4)–O(10)	94.66(2)
O(1)–Cu(2)–N(4)	162.7(2)	N(7)–Cu(4)–O(10)	97.64(2)
O(2)–Cu(2)–N(4)	99.2(2)	N(8)–Cu(4)–O(10)	83.68(2)
N(3)–Cu(2)–N(4)	88.2(2)	O(6)–Cu(4)–O(10)	84.66(2)
O(1)–Cu(2)–O(2A)	100.3(2)	N(7)–Cu(4)–N(8)	88.7(2)
O(2)–Cu(2)–O(2A)	83.3(2)	O(3)–Cu(5)–O(7)	168.4(2)
N(3)–Cu(2)–O(2A)	101.8(2)	O(3)–Cu(5)–O(1)	88.1(2)
N(4)–Cu(2)–O(2A)	96.9(2)	O(7)–Cu(5)–O(1)	88.9(2)
O(3)–Cu(3)–N(5)	92.4(2)	O(3)–Cu(5)–O(5)	91.9(2)
O(3)–Cu(3)–O(4)	81.2(2)	O(7)–Cu(5)–O(5)	86.9(2)
N(5)–Cu(3)–O(4)	163.2(2)	O(1)–Cu(5)–O(5)	159.0(2)
O(3)–Cu(5)–O(9)	90.6(2)	Cu(2)–O(1)–Cu(5)	117.1(2)
O(7)–Cu(5)–O(9)	100.9(2)	Cu(5)–O(3)–Cu(3)	117.3(3)
O(1)–Cu(5)–O(9)	102.3(2)	Cu(4)–O(5)–Cu(5)	112.1(2)
O(5)–Cu(5)–O(9)	98.7(2)	Cu(1)–O(7)–Cu(5)	120.6(3)
Cu(2)–O(2)–Cu(2A)	96.4(2)		

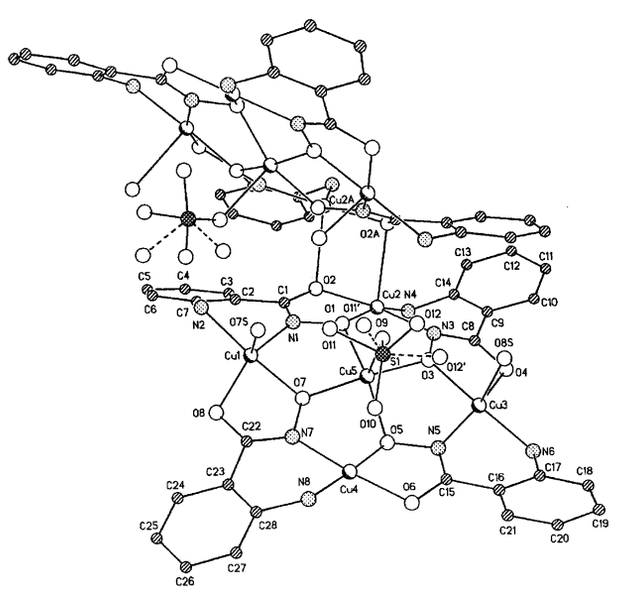

Fig. 3 ORTEP diagram of **2** (solvent molecules not shown). Only selected atoms of one metallacrown unit and the atoms of the second ring involved in binding the two metallacrowns are displayed.

~3.9 Å. The only other previously reported dimeric metallacrown is a nickel(II) complex in which metallacrown rings are almost parallel.[13] In contrast to the above complex structures, the reaction of 4-AphaH with $CuSO_4\cdot 5H_2O$ gave the simple square planar $Cu(4\text{-Apha})_2\cdot H_2O$ **3** (Fig. 4, Table 3).

Table 3 Selected bond lengths (Å) and angles (°) with estimated standard deviations for $Cu(4\text{-}Apha)_2\cdot H_2O$ **3**

Cu(1)–O(1)	1.9225(11)	O(1)–N(1)	1.3854(16)
Cu(1)–O(1A)	1.9225(11)	O(2)–C(1)	1.2864(17)
Cu(1)–O(2A)	1.9246(11)	N(1)–C(1)	1.3116(19)
Cu(1)–O(2)	1.9246(11)		
O(1)–Cu(1)–O(1A)	180.00(6)	O(2A)–Cu(1)–O(2)	180.00(6)
O(1)–Cu(1)–O(2A)	95.10(4)	N(1)–O(1)–Cu(1)	106.79(8)
O(1A)–Cu(1)–Cu(2A)	84.90(4)	C(1)–O(2)–Cu(1)	109.94(9)
O(1)–Cu(1)–O(2)	84.90(4)	C(1)–N(1)–O(1)	118.07(12)
O(1A)–Cu(1)–O(2)	95.10(4)	O(2)–C(1)–N(1)	119.37(13)

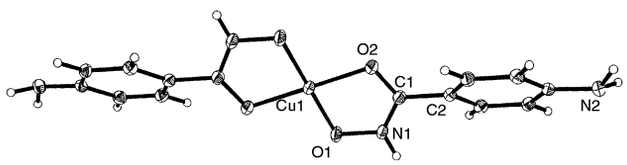

Fig. 4 ORTEP diagram of **3** displaying its simple square planar structure.

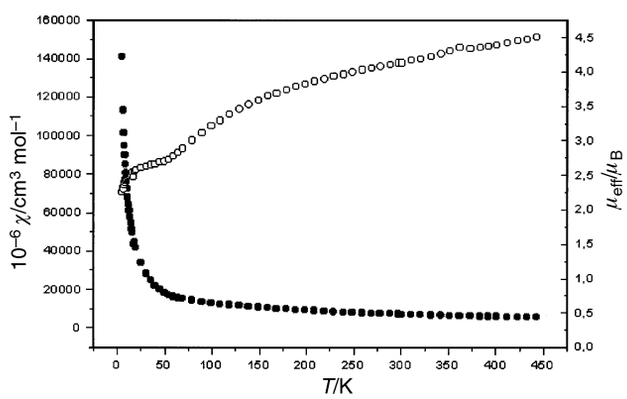

Fig. 5 Magnetic susceptibility results for **2** displayed as χ [10^{-6} cm^3 mol^{-1}] μ_{eff} [μ_B] against T [K].

Magnetic behaviour

The room temperature magnetic moment of dimeric complex **2** is 4.0 μ_B, Fig. 5, and is considerably lower than the calculated value of 5.82 μ_B for ten independent $S = \frac{1}{2}$ copper(II) ions (g assumed to be 2.125) due to antiferromagnetic coupling. This compares with the value of 2.5 μ_B reported for the monomeric metallacrown which contains five copper(II) ions[12] indicating increased inter-copper interactions in each metallacrown ring of the dimeric structure. A noteworthy feature of the magnetic behaviour is the considerable decrease in μ_{eff} between 10 K and 4 K. This behaviour has not previously been reported for copper(II) metallacrown complexes[12] and is probably due to weak antiferromagnetically coupled inter-metallacrown ring interactions through the copper and oxygen bridge connecting the two metallacrown rings. The magnetic behaviour of complex **2** is represented in Fig. 5 in terms of χ [10^{-6} cm^3 mol^{-1}] and μ_{eff} [μ_B] against T [K].

In contrast to **2** the polymeric complex **1** was found to be paramagnetic with a μ_{eff} value of 3.22 μ_B per tricopper repeating unit which is close to the calculated value for three non-interacting copper(II) centres. Complex **3** has a magnetic moment of 1.82 μ_B consistent with the simple monomeric square planar complex[14] shown by X-ray crystallography.

Conclusion

The isomeric aminophenylhydroxamic acids form structurally diverse complexes with copper(II). The 'bite' of 2-$AphaH_{-1}$ allows the formation of a pentanuclear metallacrown, which is strongly antiferromagnetically coupled and which dimerises by weak O–Cu axial interactions. The relative positioning of the amino and hydroxamate groups in 3-$Apha^-$ allows the formation of helical complex **1**, containing trimeric units having unique copper(II) sites which are magnetically non-interacting. In contrast to the above two ligands 4-$Apha^-$ forms a simple square planar 2 : 1 complex.

Experimental

Ligand synthesis

2-AphaH, 3-AphaH and 4-AphaH. The ligands were prepared from the corresponding methyl esters by modification of a previous method.[15] Methyl 3-aminobenzoate was synthesised using a previously reported method.[16] Methyl 2-aminobenzoate and methyl 4-aminobenzoate were obtained from Aldrich.

An aqueous solution (40 cm^3) of NaOH (10 g, 0.25 mol) was added to a mixture of $(NH_2OH)_2\cdot H_2SO_4$ (8.2 g, 0.05 mol) and 50 g of ice. Na_2SO_3 (1 g, 6mmol) and the corresponding ester (7.55 g, 0.05 mol) were then added. The temperature of the mixture was raised to 45 °C and stirred for 24 hours. The resulting solution was acidified with 10% H_2SO_4 to pH 6.0. Some hydroxamic acid product precipitated at this point and was collected by filtration. The filtrate was evaporated to dryness under reduced pressure yielding a yellow solid from which a further crop of hydroxamic acid was obtained by extraction into hot MeOH and evaporation to dryness under reduced pressure. Recrystallisation was performed from hot H_2O.

2-AphaH. Yield: 5.4 g, 35 mmol, 71%. Calc. (found) for $C_7H_8N_2O_2$: C, 54.26 (54.56); H, 5.26 (5.22); N, 18.42 (18.17)%. ^{1}H NMR (d_6-DMSO): δ 10.92 (s, 1H, OH), 8.85 (s, 1H, NH), 7.29 (d, J 8.2 Hz, 1H, $H^{3/6}$), 7.09 (dd, J 7.6 Hz, 8.2 Hz, 1H, $H^{4/5}$), 6.66 (d, J 8.2 Hz, 1H, $H^{3/6}$), 6.44 (dd, J 7.6 Hz, 8.2 Hz, 1H, $H^{4/5}$), 6.2 (s, 2H, NH_2).

3-AphaH. Yield: 4.5 g, 30 mmol, 60%. Calc. (found) for $C_7H_8N_2O_2$: C, 54.26 (55.03); H, 5.26 (5.37); N, 18.42 (18.26)%. ^{1}H NMR (d_6-DMSO): δ 10.97 (s, 1H, OH), 8.88 (s, 1H, NH), 7.01 (dd, J 7.2 Hz, 7.6 Hz, 1H, H^5), 6.93 (s, 1H, H^2), 6.80 (d, J 7.2 Hz, 1H, $H^{4/6}$), 6.64 (d, J 7.6 Hz, 1H, $H^{4/6}$), 5.21 (s, 2H, NH_2).

4-AphaH. Yield: 5.7 g, 38 mmol, 75%. Calc. (found) for $C_7H_8N_2O_2$: C, 54.26 (54.83); H, 5.26 (5.32); N, 18.42 (18.23)%. ^{1}H NMR (d_6-DMSO): δ 10.71 (s, 1H, OH), 8.73 (s, 1H, NH), 7.46 (d, J 8.6 Hz, 2H, aromatic H), 8.52 (d, J 8.6 Hz, 2H, aromatic H), 5.56 (s, 2H, NH_2).

Complex synthesis

$[Cu_3(3\text{-}Apha)_4(H_2O)SO_4]_n\cdot 8H_2O$ 1. To an aqueous solution (25 cm^3) of 3-AphaH (250 mg, 1.65 mmol) at 50 °C was added $CuSO_4\cdot 5H_2O$ (309 mg, 1.24 mmol) and left to stand at 10 °C. After 24 hours a bright green crystalline product was obtained and this was collected by filtration. Yield: 218 mg, 0.206 mmol, 75%. Calc. (found) for $C_{28}H_{46}N_8O_{21}S_1Cu_3$: C, 31.93 (32.53); H, 4.41 (3.90); N, 10.63 (10.62); Cu, 18.10 (18.35)%.

$[Cu_5(2\text{-}AphaH_{-1})_4(\mu\text{-}SO_4)(H_2O)_2]_2\cdot 10H_2O$ 2. To an aqueous solution (25 cm^3) of 2-AphaH (250 mg, 1.65 mmol) at 40 °C was added $CuSO_4\cdot 5H_2O$ (515 mg, 2.06 mmol) and was left to stand at room temperature. After 24 hours a dark green crystalline product was obtained and this was collected by filtration. Yield: 330 mg, 0.145 mmol, 70%. Calc. (found) for $C_{56}H_{76}N_{16}O_{38}S_2Cu_{10}$: C, 29.48 (29.48); H, 3.33 (3.16), N, 9.83 (9.36), Cu, 27.88 (26.92)%.

$Cu(4\text{-}AphaH)_2\cdot H_2O$ 3. To an aqueous solution (25 cm^3) of 4-AphaH (250 mg, 1.65 mmol) at 40 °C was added $CuSO_4\cdot 5H_2O$ (205 mg, 0.825 mmol). The pH of the solution was then raised to 7.0 using 0.2 M NaOH. The resulting light green

precipitate was filtered off, dried and recrystallised from hot water. Yield: 255 mg, 0.769 mmol, 80%. Calc. (found) for the monohydrate $C_{14}H_{16}N_4O_5Cu$ {formula from crystal structure}: C, 43.80 (42.82); H, 4.21 (3.95); N, 14.60 (14.30), Cu, 16.55 (16.05)%. Calc. for $1\frac{1}{2}$ hydrate: C, 42.80; H, 4.33; N, 14.27; Cu, 16.19%. The difference between the crystal structure formula and the formula which best fits the found microanalysis may be attributed to solvent loss.[17]

Crystallography

Crystal data and data-collection parameters. *For* ***1***. $C_{28}H_{46}N_8O_{21}S_1Cu_3$, $M_r = 1053.41$, orthorhombic, space group $Pna2_1$, $a = 15.2049(12)$, $b = 14.2017(11)$, $c = 18.5719(14)$ Å, $V = 4010.3(5)$ Å^3, $F(000) = 2164$, $Z = 4$, $T = 100$ K, μ(Mo-Kα) = 1.722 mm^{-1}, 33960 reflections collected, 10045 independent, $R_{int} = 0.0471$. Refinement converged at $wR2$ value of 0.0879, $R1$ 0.0418 [for 7521 reflections with $F_o > 2\sigma(F)$].

For ***2***. $C_{56}H_{76}N_{16}O_{38}S_2Cu_{10}$, $M_r = 2280.86$, monoclinic, space group $C2/c$, $a = 13.9633(11)$, $b = 27.574(2)$, $c = 19.966(2)$ Å, $\beta = 95.795(2)°$, $V = 7648.3(10)$ Å^3, $F(000) = 4568$, $Z = 4$, $T = 100$ K, μ(Mo-Kα) = 2.882 mm^{-1}, 36014 reflections collected, 11017 independent, $R_{int} = 0.1909$. Refinement converged at $wR2$ value of 0.0754, $R1$ 0.0520 [for 2865 reflections with $F_o > 2\sigma(F)$].

For ***3***. $C_{14}H_{16}N_4O_5Cu$, $M_r = 383.85$, monoclinic, space group $C2/c$, $a = 17.7195(9)$, $b = 5.6014(3)$, $c = 15.5028(8)$ Å, $\beta = 109.6520(10)°$, $V = 1449.09(13)$ Å^3, $F(000) = 788$, $Z = 4$, $T = 110$ K, μ(Mo-Kα) = 1.544 mm^{-1}, 6547 reflections collected, 2093 independent, $R_{int} = 0.0334$. Refinement converged at $wR2$ value of 0.0818, $R1$ 0.0301 [for 1786 reflections with $F_o > 2\sigma(F)$].

CCDC reference numbers 154909–154911.

See http://www.rsc.org/suppdata/dt/b1/b102169i/ for crystallographic data in CIF or other electronic format.

Magnetic measurements

Magnetic measurements in the temperature range 4.2–300 K were obtained using a CAHN D200 balance with a maximum accuracy of ±0.1 μg, a Leybold–Heraeus LTC60 temperature regulator with a silicon-diode or a carbon-glass-(below 70 K) resistor and in the temperature range 300–450 K using a CAHN RG balance with a maximum accuracy of ±0.3 μg, and a nickel–chrome–nickel-thermometer.[18]

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