

The rôle of 4,7-phenanthroline in coordination polymer construction

Sarah A. Barnett, Alexander J. Blake, Neil R. Champness* and Claire Wilson

School of Chemistry, The University of Nottingham, University Park, Nottingham, UK NG7 2RD. E-mail: Neil.Champness@Nottingham.ac.uk

Received 11th March 2003, Accepted 15th April 2003

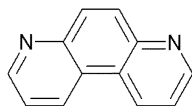
First published as an Advance Article on the web 6th May 2003

The reactions of 4,7-phenanthroline (4,7-phen) with a variety of metal salts have been investigated and the products structurally characterised by single crystal X-ray diffraction. Reaction of CoX_2 ($\text{X} = \text{Cl}, \text{Br}$) or $\text{M}(\text{NO}_3)_2$ ($\text{M} = \text{Cd}, \text{Zn}, \text{Ni}$) salts with 4,7-phen all afford one-dimensional coordination polymers, $[\text{CoX}_2(4,7\text{-phen})]_\infty$ (**1**, **2**) or $[\text{M}(\text{NO}_3)_2(4,7\text{-phen})(\text{H}_2\text{O})]_\infty$ ($\text{M} = \text{Cd}$ **3**, Zn **4**, Ni **5**), in which the metal centres are linked *via* 4,7-phen ligands which act in a bridging bidentate manner. The remaining metal coordination sites are occupied by either halide (**1**, **2**) or NO_3^- and H_2O ligands (**3–5**). In $\{[\text{Ni}(\text{NO}_3)_2(4,7\text{-phen})(\text{H}_2\text{O})] \cdot (4,7\text{-phen})\}_\infty$, **5** an additional, uncoordinated, molecule of 4,7-phen is included in the structure, hydrogen bonded to a coordinated H_2O molecule. In contrast, reaction of CuX_2 ($\text{X} = \text{Cl}, \text{Br}$) or $\text{Cu}(\text{NO}_3)_2$ with 4,7-phen leads to the formation of discrete complexes, $[\text{CuX}_2(4,7\text{-phen})_2]$ ($\text{X} = \text{Cl}$ **6**, Br **7**, NO_3 **8**) in which the N-donor ligand coordinates in a monodentate fashion and π - π interactions between coordinated 4,7-phen molecules generate an extended structure in the solid state. Investigation of the phase purity of **4** and **5** revealed that in the case of **4** the coordination polymer formed only in the presence of a previously reported hydrogen bonded structure, while **5** was shown to be contaminated with an unidentified phase. The rôle and diversity of the interactions adopted by 4,7-phen in forming coordination polymers and related species are discussed.

Introduction

Hybrid organic-inorganic frameworks can be constructed by exploiting a range of interactions, the most common being metal-ligand coordination¹ and hydrogen bonding.² For both coordination frameworks and hydrogen bonded structures the identification and design of reliable supramolecular synthons is critical for the development of new synthetic strategies.³ In the case of coordination polymers one of the most commonly studied systems are those of metal-bipyridyl arrays. The versatility of synthetic routes to bridging bipyridyls and multidentate aromatic N-donor groups makes these ligands attractive bridging units for the construction of extended arrays as a high degree of molecular design can be integrated into the system.

In comparison to ligands such as 4,4'-bipyridine,¹ relatively few examples of coordination polymers have been reported with 4,7-phen and only one of these forms a two-dimensional coordination network,⁴ with the majority adopting one-dimensional structures.^{5–7}



Reflecting the bulky nature of this ligand, in the majority of cases only two 4,7-phen ligands are coordinated to a given metal centre leading to one-dimensional 4,7-phen based polymer propagation. Indeed, in the case of the only two-dimensional coordination polymer, $[(\text{CuI})_2(4,7\text{-phen})]_\infty$, 4,7-phen provides polymer propagation in one direction and iodide bridging in the other.⁴

Previous examples of one-dimensional chains have used either Cu(I) or Cu(II) metal cations to link the 4,7-phen ligands. Thus, $\{[\text{Cu}(4,7\text{-phen})(\text{H}_2\text{O})_3](\text{ClO}_4)_2 \cdot 2(4,7\text{-phen})\}_\infty$,⁵ $\{[\text{Cu}(4,7\text{-phen})(\text{RCN})]\text{PF}_6\}_\infty$,⁶ $\{[\text{Cu}_2(4,7\text{-phen})_2(\text{RCN})]\text{BF}_4\}_\infty$,⁶ ($\text{R} = \text{Me}, \text{Ph}$), $[\text{Cu}(4,7\text{-phen})(\text{MeCN})(\text{SO}_3\text{CF}_3)]_\infty$,⁷ and $\{[\text{Cu}(4,7\text{-phen})(\text{SO}_3\text{CF}_3)] \cdot (\text{PhNO}_2)\}_\infty$,⁷ all form zigzag chains in which either tetrahedral or trigonal metal centres are bridged by the 4,7-phen ligands. These chains are linked *via* π - π interactions between the ligands using the extended aromatic functionality of 4,7-phen.

Increasing the L : M reaction stoichiometry in the reactions of 4,7-phen with $[\text{Cu}(\text{MeCN})_4]\text{SO}_3\text{CF}_3$ in either MeCN or PhCN also results in the formation of one-dimensional chains in $[\text{Cu}(4,7\text{-phen})_2(\text{SO}_3\text{CF}_3)]_\infty$ and $\{[\text{Cu}(4,7\text{-phen})(\text{SO}_3\text{CF}_3)] \cdot (\text{PhNO}_2)(\text{H}_2\text{O})\}_\infty$.⁷ However, although in these compounds the pseudo-tetrahedral Cu(I) ions are coordinated by three 4,7-phen ligands only two of these are used to bridge Cu(I) centres. The monodentate 4,7-phen ligands adopt π - π interactions in these two compounds to link the chains into two-dimensional sheets.

The last two compounds illustrate that although 4,7-phen can act as a bridging bidentate ligand the steric hindrance of the N-donors can result in the adoption of monodentate coordination modes. It is also possible for 4,7-phen to act as a hydrogen bonding bridge such that neither N-donor is coordinated to a metal centre. We,⁸ and others,⁹ have demonstrated this concept previously by using 4,7-phen to synthesise arrays of simple aquo-metal complexes in the solid state. These products, $\{[\text{M}(\text{NO}_3)_2(\text{H}_2\text{O})_4] \cdot 2(4,7\text{-phen})\}_\infty$,^{8,9} can be prepared from the reaction of $\text{M}(\text{NO}_3)_2$ salts with 4,7-phen in wet solvents.

It is clear, even from the limited number of complexes of 4,7-phen studied, that this relatively simple ligand can act in a range of different ways as a building-block for the construction of extended arrays by using coordinative, hydrogen bonding and π - π interactions. This study aims to investigate the relative importance of these interactions in the solid-state products formed from the reactions of 4,7-phen with a series of hydrated metal salts.

Results and discussion

The reactions of a variety of metal dichlorides MCl_2 ($\text{M} = \text{Co}, \text{Cu}$), dibromides MBr_2 ($\text{M} = \text{Co}, \text{Cu}$) and dinitrates, $\text{M}(\text{NO}_3)_2$ ($\text{M} = \text{Cd}, \text{Zn}, \text{Ni}, \text{Cu}$), with the potentially bridging bidentate ligand 4,7-phen have been studied. In a typical reaction, a solution of the ligand in CH_2Cl_2 was added to a solution of the metal salt in MeCN. The only exception to this was the reaction between 4,7-phen and $\text{Cu}(\text{NO}_3)_2$ where the metal salt was dissolved in $^i\text{PrOH}$. In all cases the reactions rapidly gave insoluble precipitates and were found to be independent of

M : L reaction stoichiometry. To fully understand the rôle of the 4,7-phen ligand in these compounds single crystal X-ray diffraction studies were undertaken. Single crystals were grown over a period of a few days from layered solutions of the metal salt in MeCN (1–7) or ⁱPrOH (8) and 4,7-phen in CH₂Cl₂.

Structural characterisation of 1–8 showed that 4,7-phen adopts either a bidentate mode, bridging metal centres and thereby generating one-dimensional coordination polymers, [CoX₂(4,7-phen)]_∞ (1, 2) or [M(NO₃)₂(4,7-phen)(H₂O)]_∞ (M = Cd 3, Zn 4, Ni 5) or coordinates in a monodentate fashion to afford discrete monometallic species [CuX₂(4,7-phen)₂] (X = Cl 6, Br 7, NO₃ 8). This behaviour contrasts with the previously reported examples of 4,7-phen adopting a purely hydrogen bonding, non-coordinating role in structures using [M(NO₃)₂(H₂O)₄]⁸ and [M(H₂O)₆](ClO₄)₂⁹ species.

Structures of one-dimensional zigzag polymers (1–5)

The structures of [CoX₂(4,7-phen)]_∞ (X = Cl 1, Br 2) revealed that each Co(II) cation adopts an approximately tetrahedral geometry and is coordinated by two halide anions and two bridging 4,7-phen ligands (Fig. 1) (Table 1). The ligands bridge between the Co(II) centres to form a one-dimensional zigzag structure (Fig. 2). Each 4,7-phen ligand is arranged such that the central aromatic ring points towards the interior of the chain which runs parallel to the *b*-axis in both compounds. Each [CoCl₂(4,7-phen)]_∞ chain has a pitch of 8.21 Å compared with 8.26 Å for the [CoBr₂(4,7-phen)]_∞ chains (Fig. 2).

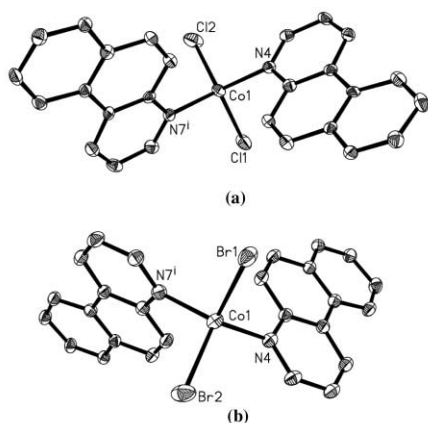


Fig. 1 The coordination environments of the Co(II) centre found in (a) [CoCl₂(4,7-phen)]_∞, 1, and (b) [CoBr₂(4,7-phen)]_∞, 2, showing the numbering schemes used. Displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Symmetry codes: [CoCl₂(4,7-phen)]_∞, 1: (i) $-x, y - 1/2, -z + 3/2$; [CoBr₂(4,7-phen)]_∞, 2: (i) $-x + 1, y - 1/2, -z + 1/2$.

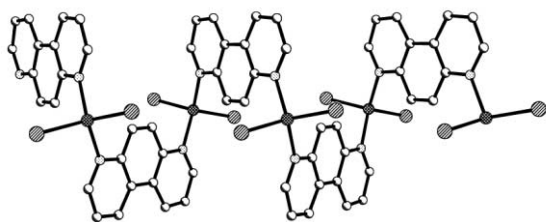


Fig. 2 A zigzag chain in [CoCl₂(4,7-phen)]_∞. Hydrogen atoms are omitted for clarity (Co - cross hatch; N - dotted; Cl - right hatch).

Adjacent zigzag chains engage in π - π interactions between the 4,7-phen ligands *via* the N-heterocyclic ring of one 4,7-phen ligand with the N-heterocycle ring of a 4,7-phen ligand in the adjacent helix {[CoCl₂(4,7-phen)]_∞: centroid-centroid separation 3.70 Å, offset 1.50 Å; [CoBr₂(4,7-phen)]_∞: centroid-centroid separation 3.79 Å, offset 1.70 Å}.¹⁰ The remaining spaces within the structures are occupied by guest MeCN molecules.

Reaction of either Cd(NO₃)₂ or Zn(NO₃)₂ with 4,7-phen yielded colourless crystals of the complexes [Cd(NO₃)₂(4,7-phen)(H₂O)]_∞ 3 or [Zn(NO₃)₂(4,7-phen)(H₂O)]_∞ 4, respectively. As with 1 and 2 the compounds were found to adopt zigzag structures with bridging bidentate 4,7-phen ligands. In 3 each Cd(II) centre adopts a coordination sphere with two mutually *cis* 4,7-phen ligands, a water ligand and two nitrate anions (Fig. 3, Table 1). One of the nitrates is coordinated in a chelating fashion whilst the other is disordered over two sites giving either η^1 or η^2 coordination. This affords either a six- or seven-coordinate geometry depending on the denticity of the disordered nitrate anion.

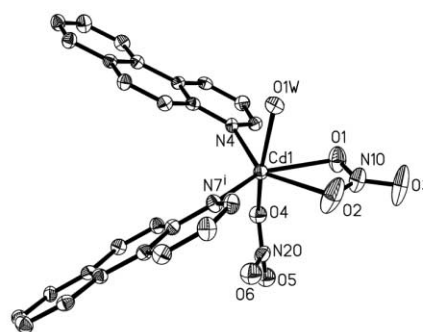


Fig. 3 The coordination environment of the Cd(II) centre found in [Cd(NO₃)₂(4,7-phen)(H₂O)]_∞, 3, showing only the major, monodentate, component of the disordered nitrate anion and showing the numbering scheme used. Displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Symmetry code: (i) $-x + 1/2, y - 1/2, -z + 1/2$.

In 4, two pseudo-trigonal bipyramidal five-coordinate Zn(II) cations are observed in the asymmetric unit. Each was found to be coordinated to two monodentate nitrates, two 4,7-phen ligands and one water molecule (Fig. 4, Table 1) and each of the crystallographically independent Zn(II) cations is involved in forming an independent zigzag chain.

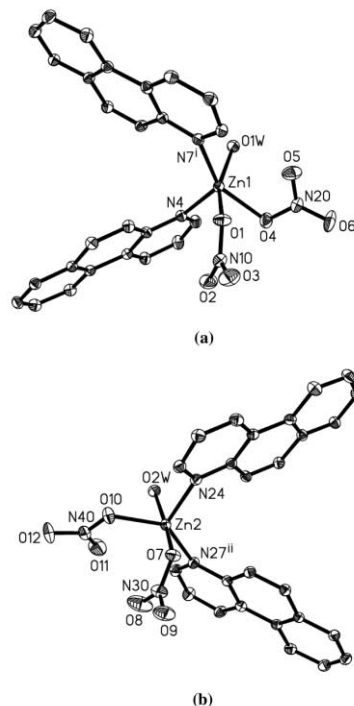


Fig. 4 The coordination environments of the two Zn(II) centres found in [Zn(NO₃)₂(4,7-phen)(H₂O)]_∞, 4, showing the numbering scheme used. Displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Symmetry codes: (i) $-x, y - 1/2, -z + 1/2$; (ii) $-x + 1, y - 1/2, -z + 1/2$.

Table 1 Selected bond lengths (Å) and angles (°) for 1–5

1		2		3		4		5	
Co1–N4	2.060(4)	Co1–N4	2.061(2)	Cd1–N7 ^c	2.257(4)	Zn1–O1	2.1437(16)	Ni1–O10	2.042(3)
Co1–N7 ^a	2.055(4)	Co1–N7 ^b	2.050(2)	Cd1–N4	2.286(4)	Zn1–O4	2.1115(17)	Ni1–O4	2.055(3)
Co1–Cl1	2.2367(16)	Co1–Br1	2.3712(5)	Cd1–O4	2.295(9)	Zn1–O1W	2.1509(17)	Ni1–N4	2.089(3)
Co1–Cl2	2.2313(16)	Co1–Br2	2.3700(5)	Cd1–O1W	2.354(4)	Zn1–N4	2.0569(18)	Ni1–O2	2.090(3)
				Cd1–O1	2.394(4)	Zn1–N7 ^d	2.0777(18)	Ni1–N7 ^d	2.107(3)
N7 ^a –Co1–N4	119.82(15)	N7 ^b –Co1–N4	119.82(9)	Cd1–O2	2.408(5)	Zn2–O7	2.1550(16)	Ni1–O1	2.156(3)
N7 ^a –Co1–Cl2	104.46(12)	N7 ^b –Co1–Br2	103.79(7)	Cd1–O4'	2.429(10)	Zn2–O10	2.0573(17)		
N4–Co1–Cl2	105.92(11)	N4–Co1–Br2	106.58(7)	Cd1–O6'	2.629(9)	Zn2–O2W	2.1216(17)	O10–Ni1–O4	174.10(12)
N7 ^a –Co1–Cl1	103.34(11)	N7 ^b –Co1–Br1	104.06(6)			Zn2–N24	2.0810(18)	O10–Ni1–N4	90.84(12)
N4–Co1–Cl1	102.78(12)	N4–Co1–Br1	102.73(7)	N7 ^c –Cd1–N	121.19(13)	Zn2–N27 ^e	2.0587(19)	O4–Ni1–N4	84.13(12)
Cl2–Co1–Cl1	121.70(6)	Br2–Co1–Br1	120.99(2)	N7 ^c –Cd1–O4	110.7(2)			O10–Ni1–O2	89.07(12)
				N4–Cd1–O4	77.17(19)	N4–Zn1–N7 ^b	121.36(7)	O4–Ni1–O2	94.10(11)
				N7 ^c –Cd1–O1W	88.20(13)	N4–Zn1–O4	90.92(7)	N4–Ni1–O2	153.91(11)
				N4–Cd1–O1W	88.93(13)	N7 ^b –Zn1–O4	147.71(7)	O10–Ni1–N7 ^d	88.00(12)
				O4–Cd1–O1W	160.4(2)	N4–Zn1–O1	106.81(7)	O4–Ni1–N7 ^d	96.77(12)
				N7 ^c –Cd1–O1	143.44(13)	N7 ^b –Zn1–O1	82.32(7)	N4–Ni1–N7 ^d	112.71(11)
				N4–Cd1–O1	94.31(13)	O4–Zn1–O1	87.95(7)	O2–Ni1–N7 ^d	93.36(11)
				O4–Cd1–O1	83.7(3)	N4–Zn1–O1W	93.45(7)	O10–Ni1–O1	88.60(12)
				O1W–Cd1–O1	83.67(14)	N7 ^b –Zn1–O1W	91.23(7)	O4–Ni1–O1	88.61(12)
				N7 ^c –Cd1–O2	91.21(14)	O4–Zn1–O1W	87.08(7)	N4–Ni1–O1	93.23(11)
				N4–Cd1–O2	144.86(15)	O1–Zn1–O1W	159.21(7)	O2–Ni1–O1	60.69(10)
				O4–Cd1–O2	105.5(3)	O10–Zn2–N27 ^c	137.79(7)	N7 ^a –Ni1–O1	153.88(11)
				O1W–Cd1–O2	78.07(18)	O10–Zn2–N24	100.61(7)		
				O1–Cd1–O2	52.24(13)	N27 ^c –Zn2–N24	121.45(7)		
				N7 ^c –Cd1–O4'	116.6(2)	O10–Zn2–O2W	89.78(7)		
				N4–Cd1–O4'	79.0(2)	N27 ^c –Zn2–O2W	91.27(7)		
				O1W–Cd1–O4'	155.2(2)	N24–Zn2–O2W	93.13(7)		
				O1–Cd1–O4'	75.9(3)	O10–Zn2–O7	83.22(7)		
				O2–Cd1–O4'	99.5(3)	N27 ^c –Zn2–O7	98.17(7)		
				N7 ^c –Cd1–O6'	77.5(2)	N24–Zn2–O7	81.99(7)		
				N4–Cd1–O6'	123.38(17)	O2W–Zn2–O7	170.56(7)		
				O4–Cd1–O6'	47.4(2)				
				O1W–Cd1–O6'	147.59(17)				
				O1–Cd1–O6'	90.7(2)				
				O2–Cd1–O6'	73.4(2)				
				O4'–Cd1–O6'	48.0(2)				

Symmetry transformations used to generate equivalent atoms: ^a $-x, y - 1/2, -z + 3/2$. ^b $-x + 1, y - 1/2, -z + 1/2$. ^c $-x + 1/2, y - 1/2, -z + 1/2$. ^d $-x, y - 1/2, -z + 1/2$. ^e $-x + 1, y - 1/2, -z + 1/2$. ^f $-x + 1, y + 1/2, -z + 3/2$.

In **3** each chain runs parallel to the crystallographic *b*-axis with a pitch of 7.95 Å. The two *cis* 4,7-phen ligands are separated by an inter-pyridyl dihedral angle of 121.2°. Adjacent zigzag chains are then arranged such that 4,7-phen ligands π - π stack *via* one N-heterocycle on each chain (Fig. 5). These have a centroid-centroid separation of 3.92 Å and are offset by 1.48 Å which represents a long interaction according to the criteria reported by Janiak.¹⁰

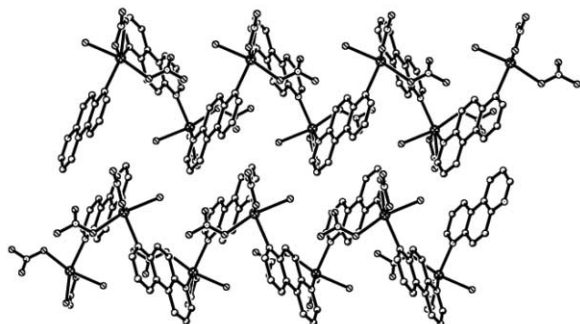


Fig. 5 View showing two adjacent helices in $[\text{Cd}(\text{NO}_3)_2(4,7\text{-phen})(\text{H}_2\text{O})]_n$, **3**, and the π - π interactions between them. Hydrogen atoms are omitted for clarity (Cd - cross hatch; N - dotted; O - left hatch).

The chains formed in **4** are very similar and have dimensions which are comparable with compound **3** with the most significant differences between the two structures being the nitrate binding modes. The inter-pyridyl dihedral angle of 121.4° for both Zn1 and Zn2 chains results in a pitch of 7.90 Å. The structure is composed of alternating rows of Zn1 chains and Zn2 chains with both zigzag polymers running parallel to the *b*-axis. Within a coplanar row of like chains, there are interactions *via* the 4,7-phen ligands. As in the previous examples, the π - π interactions occur between N-heterocycles. For the Zn1 chains, a centroid-centroid distance of 4.02 Å and an offset of 1.71 Å are observed, whereas, a centroid-centroid distance of 4.11 Å and an offset of 2.00 Å are observed for the Zn2 chains. However, on comparison of these values with those found by Janiak,¹⁰ it can be seen that these are at the higher end of the range of such interactions and are, by implication, weak in nature.

As with **3** and **4**, $\{[\text{Ni}(\text{NO}_3)_2(4,7\text{-phen})(\text{H}_2\text{O})] \cdot (4,7\text{-phen})\}_n$, **5**, also forms zigzag chains. However, in this case they are intercalated by free 4,7-phenanthroline ligands. Each Ni(II) centre is coordinated by two 4,7-phen ligands, one monodentate and one chelating nitrate anion and one water molecule, thus, completing the pseudo-octahedral coordination sphere. The same numbering scheme was used as for **3** and selected bond lengths and angles are given in Table 1.

Each zigzag chain is characterised by a pitch of 7.97 Å and runs parallel to the *b*-axis. Again the chain has a comparable inter-pyridyl dihedral ($\text{N}_{\text{phen}} \cdots \text{Ni} \cdots \text{N}_{\text{phen}}$) angle of 112.7°. Each Ni(II) centre also has a third 4,7-phen ligand associated with it *via* a $\text{OH} \cdots \text{N}_{\text{phen}}$ hydrogen bond ($\text{OH} \cdots \text{N}_{\text{phen}} = 1.98$ Å, $\text{O}-\text{H} \cdots \text{N}_{\text{phen}} = 173^\circ$) through the coordinated water molecule. This 4,7-phen ligand, which is hydrogen bonded at only one end, sits within the cavity formed between adjacent 4,7-phen ligands which constitute the chain of the nearest neighbour zigzag polymer (Fig. 6). There are no π - π interactions holding the intercalated 4,7-phen ligand within this space and it is found to be disordered over two almost equally occupied sites.

Discrete compounds formed using copper(II) salts

The reaction of the copper(II) halides, CuCl_2 or CuBr_2 with 4,7-phenanthroline yielded discrete complexes, $[\text{CuX}_2(4,7\text{-phen})_2]_n$ ($\text{X} = \text{Cl}$ **6**, $\text{X} = \text{Br}$ **7**). Single crystals were grown by the slow diffusion of CuX_2 in MeCN into a solution of 4,7-phen in

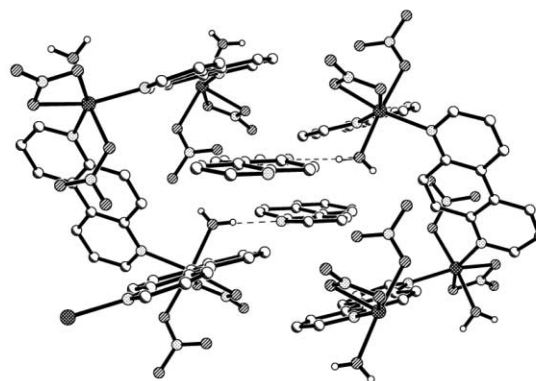


Fig. 6 View showing part of two zigzag chains of $\{[\text{Ni}(\text{NO}_3)_2(4,7\text{-phen})(\text{H}_2\text{O})] \cdot (4,7\text{-phen})\}_n$, **5**, and illustrating the associated intercalating 4,7-phen molecules. Hydrogen atoms, except those on water molecules, are omitted for clarity (Ni - cross hatch; N - dotted; O - right hatch).

CH_2Cl_2 . Structural determination by single crystal X-ray diffraction showed that in **6** and **7** each metal centre sits on an inversion centre, thus requiring a planar $\text{Cu}(\text{II})$ geometry, with only small distortions from a perfect square planar arrangement. Each metal cation is coordinated by two halide anions and two 4,7-phen ligands which act in a monodentate fashion (Table 2, Fig. 7). These units stack *via* π - π interactions between the coordinated N-heterocycle of one of the 4,7-phen ligands with the central aromatic ring of the adjacent 4,7-phen ligand (**6**, centroid-centroid = 3.92 Å, offset = 2.00 Å; **7**, centroid-centroid = 4.08 Å, offset = 2.20 Å). These weakly π - π stacked units form chains which run parallel to the *a*-axis. The second N-donor of each 4,7-phen ligand participates in a $\text{CH} \cdots \text{N}_{\text{phen}}$ hydrogen bond with an acidic aromatic proton from an adjacent 4,7-phen ligand attached to a neighbouring $[\text{CuX}_2(4,7\text{-phen})_2]_n$ stack (**6**: $\text{CH} \cdots \text{N}_{\text{phen}} = 2.39$ Å, $\text{C}-\text{H} \cdots \text{N}_{\text{phen}} = 175.5^\circ$; **7**: $\text{CH} \cdots \text{N}_{\text{phen}} = 2.43$ Å, $\text{C}-\text{H} \cdots \text{N}_{\text{phen}} = 176.4^\circ$). Each 4,7-phen ligand has one H atom and one N atom involved in hydrogen bonds such that each $[\text{CuX}_2(4,7\text{-phen})_2]_n$ unit participates in four $\text{C}-\text{H} \cdots \text{N}$ hydrogen bonds (Fig. 8). These link the units to give a two-dimensional sheet structure with (4,4) topology.

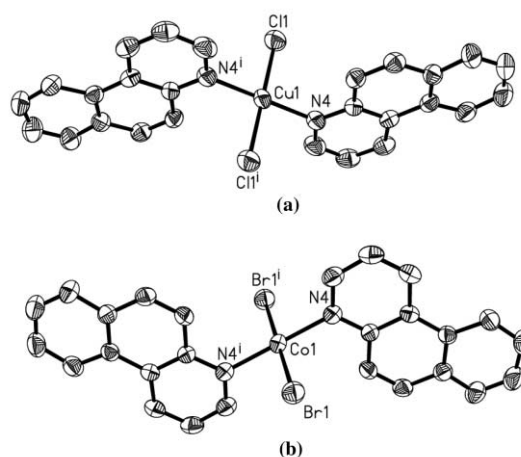


Fig. 7 The coordination environments of the $\text{Cu}(\text{II})$ centre found in (a) $[\text{CuCl}_2(4,7\text{-phen})_2]_n$, **6**, and (b) $[\text{CuBr}_2(4,7\text{-phen})_2]_n$, **7**, showing the numbering schemes used. Displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Symmetry codes: $[\text{CuCl}_2(4,7\text{-phen})_2]_n$, **6**: (i) $-x + 1, -y + 1, -z$; $[\text{CuBr}_2(4,7\text{-phen})_2]_n$, **7**: (i) $-x, -y + 1, -z + 1$.

$[\text{Cu}(\text{NO}_3)_2(4,7\text{-phen})_2]_n$, **8**, was prepared by addition of a solution of 4,7-phen in CH_2Cl_2 to a solution of $\text{Cu}(\text{NO}_3)_2$ in i PrOH, generating purple plate crystals. In a similar manner to the

Table 2 Selected bond lengths (Å) and angles (°) for **6–8**.

6		7		8	
Cu1–N4	1.985(3)	Cu1–N4	1.983(2)	Cu1–O1	1.979(3)
Cu1–Cl1	2.2552(9)	Cu1–Br1	2.4151(3)	Cu1–N4	1.9873(17)
N4–Cu1–Cl1	89.70(8)	N4–Cu1–Br1	89.40(6)	Cu1–O2'	2.038(6)
N4–Cu1–Cl1 ^a	90.30(8)	N4–Cu1–Br1 ^b	90.60(6)	O1–Cu1–N4	90.15(9)
				O1–Cu1–O2'	62.96(18)
				N4–Cu1–O2'	92.64(16)

Symmetry transformations used to generate equivalent atoms: ^a $-x + 1, -y + 1, -z$. ^b $-x, -y + 1, -z + 1$.

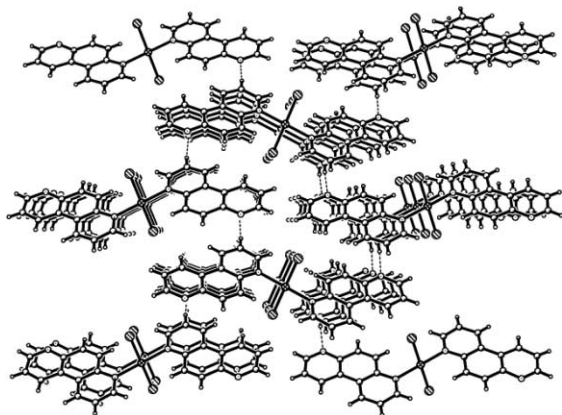


Fig. 8 View of $[\text{CuCl}_2(4,7\text{-phen})_2]$, **6**, showing the $\text{CH} \cdots \text{N}_{\text{phen}}$ hydrogen bonds as dashed lines. (Cu - cross hatch; N - dotted; Cl - left hatch).

halide complexes, **6** and **7**, the Cu(II) centre sits on an inversion centre with an approximately square planar environment, coordinated by two 4,7-phen ligands and two disordered nitrate anions (Fig. 9). On viewing the structure down the *a*-axis, it can be seen that the structure adopts a similar structure to the halide compounds. Although the stacks do not align in a parallel fashion as observed in **6** and **7**, $\text{CH} \cdots \text{N}_{\text{phen}}$ interactions between $[\text{Cu}(\text{NO}_3)_2(4,7\text{-phen})_2]$ molecules generate two-dimensional sheets with (4,4) topology ($\text{CH} \cdots \text{N}_{\text{phen}} = 2.52 \text{ \AA}$, $\text{CH} \cdots \text{N}_{\text{phen}} = 168.0^\circ$). However, in this case, the 4,7-phen ligands do not form π - π interactions within these stacks, instead the closest π - π contacts are between units which lie parallel to the *ab*-plane. The uncoordinated N-heterocycle of each 4,7-phen ligand interacts with the uncoordinated N-heterocycle of the adjacent 4,7-phen ligand (centroid-centroid = 3.85 \AA , offset = 1.59 \AA).¹⁰

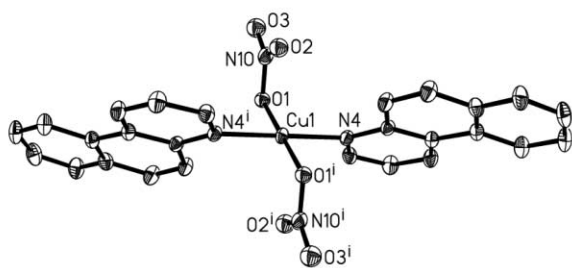


Fig. 9 The coordination environment of the Cu(II) centre in $[\text{Cu}(\text{NO}_3)_2(4,7\text{-phen})_2]$, **8**, showing the numbering scheme used (only the major nitrate disorder components are shown). Displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Symmetry code: (i) $-x, -y + 1, -z$.

H-bonding vs. coordination of 4,7-phen in its reactions with $\text{M}(\text{NO}_3)_2$ salts

As described previously, 4,7-phen has the potential to act purely as a hydrogen bonding bridge interacting with coordinated water ligands.^{8,9} Such hydrogen bonded structures can be pre-

pared from the same starting materials under extremely similar conditions. Thus, the products of rapid precipitation experiments were examined for phase purity by powder X-ray diffraction. In the case of the reactions of $\text{Mn}(\text{NO}_3)_2$ and $\text{Co}(\text{NO}_3)_2$ with 4,7-phen, pure phases of the hydrogen bonded frameworks, $\{[\text{M}(\text{NO}_3)_2(\text{H}_2\text{O})_4] \cdot 2(4,7\text{-phen})\}$,⁸ were isolated, consistent with the fact that we were unable to isolate products containing coordinated 4,7-phen with these metal salts.

However, both three-dimensional hydrogen bonded networks⁸ and one-dimensional coordination polymers have been structurally characterized for the reactions of $\text{Ni}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2$ with 4,7-phen. However, these products were obtained from different solvents, with **4** and **6** growing in $\text{MeCN}-\text{CH}_2\text{Cl}_2$ whilst the hydrogen bonded structures were prepared from ${}^i\text{PrOH}-\text{CH}_2\text{Cl}_2$. It can, therefore, be expected that these different conditions should yield either the hydrogen bonded structure or the coordination polymer under rapid precipitation conditions. Whilst this was found to be true in the case of the hydrogen bonded structures prepared from ${}^i\text{PrOH}-\text{CH}_2\text{Cl}_2$, $\{[\text{M}(\text{NO}_3)_2(\text{H}_2\text{O})_4] \cdot 2(4,7\text{-phen})\}$ ⁸ ($\text{M} = \text{Zn}, \text{Ni}$), the corresponding reactions in $\text{MeCN}-\text{CH}_2\text{Cl}_2$ gave very contrasting results. Indeed, the reaction between $\text{Zn}(\text{NO}_3)_2$ and 4,7-phen in $\text{MeCN}-\text{CH}_2\text{Cl}_2$ afforded a mixture of both the coordination polymer, **4**, and the hydrogen bonded structure $\{[\text{Zn}(\text{NO}_3)_2(\text{H}_2\text{O})_4] \cdot 2(4,7\text{-phen})\}$ ⁸ (Fig. 10). The reaction between $\text{Ni}(\text{NO}_3)_2$ and 4,7-phen under rapid precipitation conditions gave neither **6** nor the hydrogen bonded framework $\{[\text{Ni}(\text{NO}_3)_2(\text{H}_2\text{O})_4] \cdot 2(4,7\text{-phen})\}$,⁸ and yielded a previously unknown, and as yet unidentified, phase.

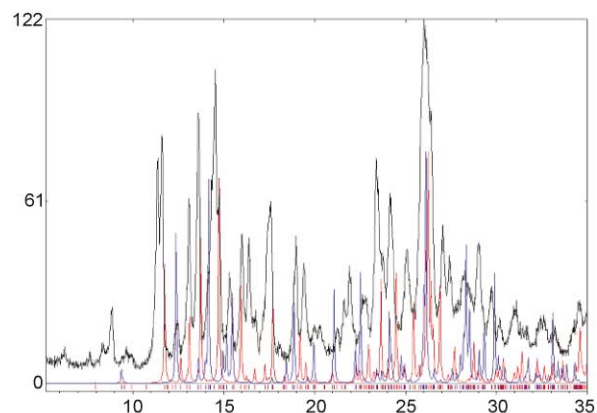


Fig. 10 The observed powder pattern for the reaction of $\text{Zn}(\text{NO}_3)_2$ with 4,7-phen in $\text{MeCN}-\text{CH}_2\text{Cl}_2$ (black line) compared with the calculated data for the helical structure, **4**, (red line) and the three-dimensional hydrogen bonded framework, $\{[\text{Zn}(\text{NO}_3)_2(\text{H}_2\text{O})_4] \cdot 2(4,7\text{-phen})\}$ ⁹ (blue line).

Conclusions

It is clear from these studies that 4,7-phen can act in a variety of ways when reacting with metal salts. Despite the sterically hindered nature of the N-donors, 4,7-phen is capable of coordinating to metal centres and acting as a coordinating bridge in order to form coordination polymers. However, it is

noticeable that for none of the polymers reported here, or previously in the literature,⁴⁻⁷ do more than three 4,7-phen ligands coordinate to a given metal centre and no more than two participate in bridging metal centres. This contrasts with 4,4'-bipyridine which forms a wide variety of tris- and tetrakis-pyridyl complexes with $M(\text{NO}_3)_2$ salts¹¹ ($M = \text{Ni},^{12} \text{Zn},^{13} \text{Cd}^{14}$). Thus, despite the bridging nature of the 4,7-phen ligands in the examples reported here, this N-donor ligand allows polymeric propagation only in one dimension.

In the case of the three Cu(II) complexes, **6-8**, the 4,7-phen ligand acts in a monodentate fashion and, as a result, the products formed are discrete, non-polymeric species. As one end of the ligand remains uncoordinated these discrete complexes could be interpreted as giving some indication that the coordinative ability of the 4,7-phen ligand may be reduced in comparison to less sterically hindered bipyridyl donors. However, it may simply be the case that these discrete complexes are insoluble in the reaction solvents and, thus, are isolated preferentially from the reaction mixture.

The formation of both coordination polymers and hydrogen bonded networks from the same building-blocks, $M(\text{NO}_3)_2$ salt and 4,7-phen, is perhaps surprising although a range of bridging modes have also been reported for 4,4'-bipyridine.¹⁵ The different bridging modes for 4,7-phen reported in this study may be attributed to differences in the reaction solvents used. Small changes in reaction conditions, including solvent, have been shown previously to result in very different products for coordination polymer species¹⁶ and this study confirms that the subtle balances between coordination polymer products and hydrogen bonded frameworks, when using appropriate building blocks, can also be influenced by small changes in solvent properties. This study illustrates that 4,7-phen can be used as either a coordinating or as a hydrogen bonding bridge. In this sense 4,7-phen is a potentially versatile building-block for crystal engineering.

Experimental

Infrared spectra were measured as KBr disks using a Nicolet Avatar 380 FT-IR spectrometer over the range 400–4000 cm^{-1} . Microanalyses were performed by the University of Nottingham Chemistry Department microanalytical service on a Perkin Elmer 240B analyser. Powder X-ray diffraction patterns (PXRD) data were collected using a Philips XPERT θ - 2θ diffractometer with Cu-K α radiation. Samples were mounted on flat glass plate sample holders. *Ca.* 50 min scans were run for each sample to assess phase purity. Short scans were run over the range $5 \leq 2\theta \leq 80^\circ$ with step size $0.02^\circ 2\theta$ and time per step of 0.65 s. The simulated powder patterns were generated from the single crystal structural data using the PC software packages APD, part of the Philips software package, and POWDERCELL.¹⁷ All chemicals were purchased from Aldrich Chemicals Company and used without further purification.

$\{[\text{CoCl}_2(4,7\text{-phen})_2] \cdot \text{MeCN}\}_{\infty}, \mathbf{1}$

A solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (12 mg, 0.10 mmol) in MeCN (15 cm^3) was added to a solution of 4,7-phen (17 mg, 0.10 mmol) in CH_2Cl_2 (5 cm^3). The blue precipitate was filtered off and dried *in vacuo*. Yield 48% (Found: C, 47.31; H, 2.86; N, 11.94. Calc. for $\text{C}_{14}\text{H}_{11}\text{Cl}_2\text{CoN}_3$: C, 47.89; H, 3.16; N, 11.97%). IR (KBr)/ cm^{-1} : 3396s, 3073m, 2931m, 1651w, 1622w, 1586m, 1504s, 1441w, 1409m, 1395w, 1367w, 1303m, 1260w, 1233w, 1114w, 1074w, 1024w, 831m, 801m, 742w, 718w, 498w, 451w, 424w. Single crystals were grown by slow diffusion of layered solutions of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in MeCN over 4,7-phen in CH_2Cl_2 .

$\{[\text{CoBr}_2(4,7\text{-phen})_2] \cdot \text{MeCN}\}_{\infty}, \mathbf{2}$

A solution of CoBr_2 (20 mg, 0.09 mmol) in MeCN (5 cm^3) was added to a solution of 4,7-phen (17 mg, 0.09 mmol) in CH_2Cl_2

(2 cm^3). The blue precipitate was filtered off and dried *in vacuo*. Yield 61% (Found: C, 38.30; H, 2.47; N, 9.22. Calc. for $\text{C}_{14}\text{H}_{11}\text{Br}_2\text{CoN}_3$: C, 38.21; H, 2.52; N, 9.55%). IR (KBr)/ cm^{-1} : 3384s, 3070m, 1651w, 1621m, 1585m, 1504s, 1441w, 1408m, 1385m, 1303m, 1114w, 1072w, 1022w, 830m, 801m, 742w, 720w, 668w. Single crystals were grown by slow diffusion of layered solutions of CoBr_2 in MeCN over 4,7-phen in CH_2Cl_2 .

$[\text{Cd}(\text{NO}_3)_2(4,7\text{-phen})(\text{H}_2\text{O})]_{\infty}, \mathbf{3}$

A solution of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (64 mg, 0.21 mmol) in MeCN (3 cm^3) was added to a solution of 4,7-phen (38 mg, 0.21 mmol) in CH_2Cl_2 (2 cm^3). The white precipitate was filtered off and dried *in vacuo*. Yield 96% (Found: C, 32.98; H, 2.54; N, 13.51. Calc. for $\text{C}_{12}\text{H}_{10}\text{CdN}_4\text{O}_7$: C, 33.16; H, 2.32; N, 12.89%). IR (KBr)/ cm^{-1} : 3423m, 1767w, 1649w, 1587w, 1505m, 1383s, 1322m, 1301m, 1116w, 1071w, 1038w, 1020w, 860w, 830m, 805w, 786w, 738w. Single crystals were grown by slow diffusion of layered solutions of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in MeCN over 4,7-phen in CH_2Cl_2 .

$\{[\text{Zn}(\text{NO}_3)_2(4,7\text{-phen})(\text{H}_2\text{O})] \cdot \text{MeCN}\}_{\infty}, \mathbf{4}$

A solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (65 mg, 0.22 mmol) in MeCN (3 cm^3) was added to a solution of 4,7-phen (40 mg, 0.22 mmol) in CH_2Cl_2 (2 cm^3). The white precipitate was filtered off and dried *in vacuo*. Yield 84% (Found: C, 39.05; H, 2.98; N, 16.04. Calc. for $\text{C}_{14}\text{H}_{13}\text{N}_5\text{O}_7\text{Zn}$: C, 39.22; H, 3.06; N, 16.34%). IR (KBr)/ cm^{-1} : 3422m, 1655w, 1589w, 1508m, 1475m, 1440m, 1384s, 1302m, 1120w, 1079w, 1045w, 1025w, 836m, 808m, 744w, 578w, 503w, 420w, 409w. Single crystals were grown by slow diffusion of layered solutions of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in MeCN over 4,7-phen in CH_2Cl_2 .

$\{[\text{Ni}(\text{NO}_3)_2(4,7\text{-phen})(\text{H}_2\text{O})] \cdot (4,7\text{-phen})\}_{\infty}, \mathbf{5}$

Attempts to prepare bulk quantities of **5** by rapid precipitation were unsuccessful. Crystals suitable for single crystal X-ray diffraction were grown by slow diffusion of layered solutions of $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in MeCN over 4,7-phen in CH_2Cl_2 .

$[\text{CuCl}_2(4,7\text{-phen})_2], \mathbf{6}$

A solution of $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ (8.5 mg, 0.05 mmol) in MeCN (5 cm^3) was added to a solution of 4,7-phen (9.0 mg, 0.05 mmol) in CH_2Cl_2 (2 cm^3). The green precipitate was filtered off and dried *in vacuo*. Yield 38% (Found: C, 57.90; H, 3.57; N, 10.58. Calc. for $\text{C}_{24}\text{H}_{16}\text{Cl}_2\text{CuN}_4$: C, 58.25; H, 3.27; N, 11.32%). IR (KBr)/ cm^{-1} : 3423s, 3075m, 1655w, 1638m, 1619m, 1586m, 1561w, 1503s, 1444w, 1407w, 1385m, 1304m, 1264w, 1151w, 1112w, 1073w, 824w, 897m, 735w, 493w, 458w, 419w. Single crystals were grown by slow diffusion of layered solutions of $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ in MeCN over 4,7-phen in CH_2Cl_2 .

$[\text{CuBr}_2(4,7\text{-phen})_2], \mathbf{7}$

A solution of CuBr_2 (9.3 mg, 0.04 mmol) in MeCN (5 cm^3) was added to a solution of 4,7-phen (7.5 mg, 0.04 mmol) in CH_2Cl_2 (2 cm^3). The green precipitate was filtered off and dried *in vacuo*. Yield 51% (Found: C, 48.40; H, 2.75; N, 9.43. Calc. for $\text{C}_{24}\text{H}_{16}\text{Br}_2\text{CuN}_4$: C, 49.38; H, 2.77; N, 9.60%). IR (KBr)/ cm^{-1} : 3552m, 3010w, 3073w, 3053w, 3007w, 2964w, 1618w, 1589w, 1526w, 1479s, 1447w, 1404m, 1388m, 1305m, 1106m, 1073w, 1055w, 1012w, 839m, 830s, 798s, 780w, 739w, 725w, 563w, 493w, 454w, 421w. Single crystals were grown by slow diffusion of layered solutions of CuBr_2 in MeCN over 4,7-phen in CH_2Cl_2 .

$[\text{Cu}(\text{NO}_3)_2(4,7\text{-phen})_2], \mathbf{8}$

A solution of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (17 mg, 0.07 mmol) in $^i\text{PrOH}$ (5 cm^3) was added to a solution of 4,7-phen (26 mg, 0.14 mmol) in CH_2Cl_2 (2 cm^3). The purple precipitate was filtered off and dried *in vacuo*. Yield 56% (Found: C, 52.33; H, 2.93; N, 15.10.

Table 3 Crystallographic data summary for complexes 1–8

	1	2	3	4	5	6	7	8
Empirical formula	C ₁₄ H ₁₁ Cl ₂ CoN ₃	C ₁₄ H ₁₁ Br ₂ CoN ₃	C ₁₄ H ₁₃ CdN ₅ O ₇	C ₁₄ H ₁₂ N ₅ O ₇ Zn	C ₂₄ H ₁₉ N ₆ NiO _{7.9}	C ₂₄ H ₁₆ Cl ₂ CuN ₄	C ₂₄ H ₁₆ Br ₂ CuN ₄	C ₁₂ H ₈ Cu _{0.5} N ₃ O ₃
<i>M</i>	351.09	440.01	475.69	428.66	577.37	494.85	583.77	273.98
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	10.517(3)	10.7897(8)	13.9304(12)	22.3308(11)	15.3438(13)	5.1490(15)	5.4065(6)	6.6182(6)
<i>b</i> /Å	8.206(3)	8.2552(7)	7.9527(7)	7.8991(4)	7.9690(7)	18.613(6)	18.709(2)	24.671(2)
<i>c</i> /Å	16.959(4)	17.0335(13)	15.5626(14)	18.5781(9)	21.943(2)	10.889(3)	10.7551(12)	7.1845(6)
<i>β</i> /°	99.04(2)	97.471(1)	101.007(1)	96.296(1)	110.107(2)	103.242(5)	103.348(2)	107.596(1)
<i>U</i> /Å ³	1445.4(5)	1504.5(4)	1692.4(5)	3257.3(5)	2519.5(7)	1015.8(9)	1058.5(4)	1118.2(3)
<i>Z</i>	4	4	4	8	4	2	2	4
<i>T</i> /K	150(2)	150(2)	150(2)	150(2)	150(2)	298(2)	298(2)	150(2)
<i>μ</i> /mm ⁻¹	1.548	6.444	1.341	1.561	0.831	1.359	4.827	1.034
Reflections collected	4985	15525	14329	29503	12631	6147	12246	5970
Unique reflections (<i>R</i> _{int})	4985 (–)	3866 (0.039)	4276 (0.049)	8392 (0.033)	6217 (0.049)	2365 (0.026)	2541 (0.024)	2662 (0.025)
Final <i>R</i> ₁ [<i>I</i> > 4σ(<i>I</i>)]	0.0512	0.0306	0.0438	0.0341	0.0530	0.0531	0.0291	0.0363
<i>wR</i> ₂ (all data)	0.1187	0.0696	0.1049	0.0912	0.1492	0.1203	0.0739	0.0958

Calc. for C₂₄H₁₆CuN₆O₆: C, 52.60; H, 2.95; N, 15.34%. IR (KBr)/cm⁻¹: 3589w, 3073w, 3054w, 3033w, 3008w, 1618w, 1589w, 1527w, 1498m, 1474w, 1447w, 1384s, 1306m, 1281w, 1240w, 1106w, 1174w, 1014w, 839m, 830m, 798m, 780w, 740w, 493w, 454w, 420w. Single crystals were grown by slow diffusion of layered solutions of Cu(NO₃)₂·2.5H₂O in ⁱPrOH over 4,7-phen in CH₂Cl₂.

Crystallography experimental

All single crystal X-ray experiments were performed on either a Bruker AXS SMART1000 (2–5, 8) or a Bruker AXS SMART APEX (6, 7) CCD detector diffractometer [graphite monochromated Mo-Kα radiation (λ = 0.71073 Å); ω scans] or on a Stoe Stadi-4 circle diffractometer (1) [graphite monochromated Mo-Kα radiation (λ = 0.71073 Å)]. All diffractometers were equipped with an Oxford Cryosystems open flow cryostat.¹⁸ Absorption corrections were applied by a semi-empirical approach (2–8). Other details of crystal data, data collection and processing are given in Table 3. All of the single-crystal structures were solved using direct methods using SHELXS-97¹⁹ and all non-hydrogen atoms were located using subsequent difference-Fourier methods.²⁰ In all cases, hydrogen atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms.

For [Cd(NO₃)₂(4,7-phen)(H₂O)]_∞ 3 the oxygen atoms of the nitrate anion N20 (O4, O5, O6) showed high displacement parameters and were modelled isotropically over two equally occupied sets of sites. The N–O bond distances and O–N–O bond angles were restrained to be the same for each disorder component.

For {[Ni(NO₃)₂(4,7-phen)(H₂O)](4,7-phen)}_∞ 5 the free 4,7-phenanthroline shows high displacement parameters and part of it has been modelled over two sets of sites with the occupancy ratio 55 : 45. The chains of solvent molecules running through channels in the structure do not model convincingly as dichloromethane, as the bond lengths and peak height ratios are not ideal. Instead, they have been modelled as two sets of water molecules, (O2W + O2WA) and (O3W + O3WA), and hydrogen atoms in this region were not located.

All crystal structure diagrams were generated using the SHELXTL program suite.²¹

CCDC reference numbers 205821–205828.

See <http://www.rsc.org/suppdata/dt/b3/b302807k/> for crystallographic data in CIF or other electronic format.

References

- A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. Schröder and M. A. Withersby, *Coord. Chem. Rev.*, 1999, **183**, 117; P. J. Hagrman, D. Hagrman and J. Zubietta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2638; M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460.
- D. Braga and F. Grepioni, *Acc. Chem. Res.*, 2000, **33**, 601; A. L. Gillon, G. R. Lewis, A. G. Orpen, S. Rotter, J. Starbuck, X.-M. Wang, Y. Rodriguez-Martin and C. Ruiz-Perez, *J. Chem. Soc., Dalton Trans.*, 2000, 3897; B. Dolling, A. L. Gillon, A. G. Orpen, J. Starbuck and X.-M. Wang, *Chem. Commun.*, 2001, 567; J. C. Mareque Rivas and L. Brammer, *Inorg. Chem.*, 1998, **37**, 4756; L. Brammer, J. K. Swearingen, E. A. Bruton and P. Sherwood, *Proc. Natl. Acad. Sci. USA*, 2002, **99**, 4956.
- G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311.
- A. J. Blake, N. R. Brooks, N. R. Champness, P. A. Cooke, M. Crew, A. M. Deveson, L. R. Hanton, P. Hubberstey, D. Fenske and M. Schröder, *Cryst. Eng.*, 1999, **2**, 181.
- M.-L. Tong, Y.-M. Wu, S.-L. Zheng, X.-M. Chen, T. Yuen, C.-L. Lin, X. Huang and J. Li, *New J. Chem.*, 2001, **25**, 1482.
- S. Lopez and S. W. Keller, *Inorg. Chem.*, 1999, **38**, 1883.
- S. Lopez and S. W. Keller, *Cryst. Eng.*, 1999, **2**, 101.
- S. A. Barnett, A. J. Blake, N. R. Champness and C. Wilson, *J. Supramol. Chem.*, 2003, in press.
- D. A. Beauchamp and S. J. Loeb, *Chem. Eur. J.*, 2002, **8**, 5084.

-
- 10 C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885.
- 11 S. A. Barnett and N. R. Champness, *Coord. Chem. Rev.*, 2003, submitted.
- 12 C. J. Kepert and M. J. Rosseinsky, *Chem. Commun.*, 1999, 375; M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka and S. Kitagawa, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1725.
- 13 B. D. Wagner, G. J. McManus, B. Moulton and M. J. Zaworotko, *Chem. Commun.*, 2002, 2176.
- 14 M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151; S. D. Huang, B. J. Lewandowski, C. Liu and Y. Shan, *Acta Crystallogr., Sect. C*, 1999, **55**, 2016; J. T. Sampanthar and J. J. Vittal, *Cryst. Eng.*, 1999, **2**, 251.
- 15 K. Abu-Shandi, C. Janiak and B. Kersting, *Acta Crystallogr., Sect. C*, 2001, **57**, 1261; O. M. Yaghi, H. Li and T. L. Groy, *Inorg. Chem.*, 1997, **36**, 4292; Y.-B. Dong, M. D. Smith, R. C. Layland and H.-C. zur Loye, *J. Chem. Soc., Dalton Trans.*, 2000, 775; M.-L. Tong, H. K. Lee, X.-M. Chen, R.-B. Huang and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1999, 3657; L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Chem. Soc., Dalton Trans.*, 1997, 1801; S.-I. Noro, M. Kondo, T. Ishii, S. Kitagawa and H. Matsuzaka, *J. Chem. Soc., Dalton Trans.*, 1999, 1569; L.-M. Zheng, X. Fang, K.-H. Lii, H.-H. Song, X.-Q. Xin, H.-K. Fun, K. Chinnakali and I. A. Razak, *J. Chem. Soc., Dalton Trans.*, 1999, 2311; S.-I. Noro, M. Kondo, S. Kitagawa, T. Ishii and H. Matsuzaka, *Chem. Lett.*, 1999, 727; N. Moliner, J. A. Real, M. C. Munoz, R. Martinez-Manez and J. M. C. Juan, *J. Chem. Soc., Dalton Trans.*, 1999, 1375.
- 16 M. A. Withersby, A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li and M. Schröder, *Inorg. Chem.*, 1999, **38**, 2259.
- 17 G. Nolze and W. Kraus, *Powder Diffr.*, 1998, **13**, 256.
- 18 J. Cosier and A. M. Glazer, *J. Appl., Crystallogr.*, 1986, **19**, 105.
- 19 G. M. Sheldrick, SHELXS-97, University of Göttingen, Germany, 1997.
- 20 G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany, 1997.
- 21 Bruker SHELXTL. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA, 1997.