Reactions of Copper(II) Nitrate with Pyridazine (pydz) and Crystal Structures of *catena*-$[\mathrm{Cu}(\mu\text{-}\eta^2\text{-pydz})(\mu\text{-OH})(\mu\text{-O}_2\mathrm{NO})]\cdot\mathrm{H_2O}$ and $[\mathrm{Cu}_3(\mu\text{-}\eta^2\text{-pydz})_4(\text{pydz})_2(\mu\text{-NO}_3)_2(\mathrm{NO}_3)_4]$†

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The reactions of $\mathrm{Cu(NO_3)_2\cdot 3H_2O}$ with pyridazine (pydz) in water and ethanol solutions have been investigated. In water, using a 1:1 salt:pydz molar ratio, the polymeric species *catena*-$[\mathrm{Cu}(\mu\text{-}\eta^2\text{-pydz})(\mu\text{-OH})(\mu\text{-O}_2\mathrm{NO})]\cdot\mathrm{H_2O}$ **1** was obtained, whilst with a ratio of 1:2 the trinuclear complex $[\mathrm{Cu}_3(\mu\text{-}\eta^2\text{-pydz})_4(\text{pydz})_2(\mu\text{-NO}_3)_2(\mathrm{NO}_3)_4]$ **2** was isolated. In ethanol a different species **3**, not yet characterized, was obtained on employing a ratio of 1:1. With a salt:pydz molar ratio close to 1:2 the trinuclear species **2** was recovered through a cleaner reaction, while, when a ratio of *ca.* 1:3 was used the mononuclear complex $[\mathrm{Cu(pydz)_3(O_2NO)(NO_3)}]$ **4** was obtained. The structures of compounds **1** and **2** have been characterized by single-crystal X-ray analysis: **1**, monoclinic, space group $I2/m$ (no. 12), $a = 10.239(1)$, $b = 6.643(1)$, $c = 12.363(2)$ Å, $\beta = 103.74(1)°$, $Z = 4$, $R = 0.022$ for 651 $[F_o > 4\sigma(F_o)]$ reflections; **2**, monoclinic, space group $P2_1/n$ (no. 14), $a = 8.957(2)$, $b = 13.687(4)$, $c = 14.945(4)$ Å, $\beta = 96.06(2)°$, $Z = 2$, $R = 0.038$ for 2430 $[F_o > 4\sigma(F_o)]$ reflections. Compound **1** is a linear polymer [Cu $\cdots$ Cu 3.3215(5) Å], with each metal atom pair symmetrically bridged by a η^2-pydz molecule, a hydroxide group and a nitrate. Compound **2** contains a linear trinuclear centrosymmetric array of copper atoms, with the two equivalent Cu $\cdots$ Cu interactions [3.4057(8) Å] symmetrically bridged by two η^2-pydz molecules and a nitrate. Both **1** and **2** exhibit strong exchange coupling between the copper atoms, the room-temperature μ_{eff} being reduced to 1.08 **1** and 2.62 μ_B **2**.

Heterocyclic diazines, such as pyrazine, pyrimidine and pyridazine, are known to have the ability to bond to different metal centres, acting as *exo*-bidentate ligands; they can form, therefore, oligo- and poly-meric metal complexes, which display a variety of geometries.[1] Such polymers are of interest, among other things, in connection with material science, for their potential properties such as electrical conductivity [for instance, in (phthalocyaninato)metal–pyrazine polymers][2] and magnetism [see ref. 1(*a*) and refs. therein], particularly in one- or two-dimensional solids, whereas three-dimensional solids are of interest in the design of new phases, *e.g.* 'scaffolding-like materials'.[3] A recently reported copper(I)–pyrazine system is an example of this latter category of compounds.[4] Moreover, polynuclear complexes have potential applications in multi-metal-centred catalysis.[5]

Many of the polymeric species obtained with these compounds are almost intractable solids, insoluble in common organic solvents and, therefore, difficult to analyse with conventional techniques; most give powders or microcrystalline samples, unsuitable for single-crystal X-ray studies.

A relatively limited number of structural characterizations have been reported so far on such systems. While polynuclear pyrazine (1,4-diazine) metal complexes have been more widely structurally investigated in the past years (see ref. 4 and the numerous refs. cited therein), few compounds containing pyridazine (1,2-diazine, pydz) or closely related heterocyclic ligands have been fully characterized. These mainly include species with one or two bridging(N,N) pydz molecules in coordination[6,7] or organometallic[8–11] compounds. There are also few known examples of structurally characterized species containing the related bases 3-methylpyridazine,[12] phthalazine[13] or benzo[*c*]cinnoline.[14,15] The structures of only two polymeric complexes of pydz have been reported, namely the copper(I) species $[\{\mathrm{Cu(CN)(pydz)}\}_n]$ characterized in 1972[16] and, recently, $[\{\mathrm{CuCl_2(pydz)}\}_n]$ single crystals of which were obtained by gel-crystallization techniques.[17] It must be mentioned, however, that the Cambridge Crystallographic Database reports a great number of 3,6-disubstituted pyridazine complexes with a variety of substituent groups containing additional donor atoms, so that the ligand acts as a tetradentate chelating agent. These compounds are suitable for the preparation of interesting binuclear species but not polymers.

Many studies have been devoted to the complexes of pydz with metal dihalides, especially in the late 1960s and early 1970s.[18–29] The polymeric nature of these products was inferred by their insolubility and high stability, and hypothetical structures were proposed on the basis of far-IR data and of the low-temperature antiferromagnetic behaviour of the $\mathrm{CuX_2}$ adducts (see refs. 22 and 25). No direct structural characterization, however, was possible until that of the above mentioned $[\{\mathrm{CuCl_2(pydz)}\}_n]$ in 1990.[17]

We have begun a systematic investigation on the reactions of pydz and related bases with transition-metal salts containing anions of different donor abilities, with the aim of obtaining and structurally characterizing ternary polynuclear diazine–metal–counter ion species. To this end we have studied the structural relationships within the family $[\{\mathrm{MX_2(pydz)}\}_n]$ (M = Mn, Fe, Co, Ni, or Cu; X = Cl or Br) by X-ray powder diffraction methods.[30] We describe here the reactions of pydz with $\mathrm{Cu(NO_3)_2\cdot 3H_2O}$ in water and ethanol, and the results of the single-crystal X-ray analyses of the crystalline products isolated.

Results and Discussion

Reactions of Copper(II) *Nitrate with pydz.*—We have investigated the reactions of $\mathrm{Cu(NO_3)_2\cdot 3H_2O}$ in water and ethanol solution, using different salt:pydz molar ratios. When the salt is treated in water at room temperature (r.t.) with pydz both in 1:1 and 1:2 molar ratios an immediate darkening of the blue

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.
Non-SI unit employed: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

solution takes place, indicating the formation of complicated equilibrium mixtures of mononuclear Cu–pydz complexes.[31] Indeed, on monitoring by UV/VIS spectroscopy the addition of pydz to a *ca.* 4×10^{-2} mol dm^{-3} water solution of copper nitrate up to a molar ratio of about 12:1 reveals a progressive lowering of the λ_{max} of the broad band, from 806 to 648 nm, accompanied by a marked increase in absorbance. No precipitate is obtained from these water solutions, even on standing for many days. However, addition of ethanol to the 1:1 mixture leads, after 2 or 3 d, to the formation of small blue crystals. On standing for many days the crystalline product can be recovered in moderate yield (*ca.* 35%) and the beautiful crystals are suitable for single-crystal X-ray analysis. The compound was shown to be the polymeric species *catena*-[Cu(μ-η^2-pydz)(μ-OH)(μ-O$_2$NO)]·H$_2$O **1**. The polymerization is driven by the fact that the polymer is insoluble in ethanol. The presence of bridging hydroxide groups is clearly related to the basicity of the pydz ligand ($pK_a = 2.30$[32]). This finding also explains the non-quantitative nature of the reaction under these conditions. The same product **1** was also obtained, but much more slowly, from solutions slightly acidified with HNO_3. Complex **1** is, to our knowledge, a unique diazine polymer containing three different bridging groups.

When the reaction is performed with a $Cu(NO_3)_2$:pydz molar ratio of 1:2 under the same reaction conditions no precipitate is obtained on addition of ethanol. However, upon heating the water solution and reducing it to a very small volume (almost to dryness) a change from blue to green occurs. Working up this system with ethanol and leaving it to stand overnight yields dark green crystals, together with some unidentified pale blue amorphous impurities, removed under a microscope. The crystals were shown to contain the trinuclear species [Cu$_3$(μ-η^2-pydz)$_4$(pydz)$_2$(μ-NO$_3$)$_2$(NO$_3$)$_4$] **2**, with a stoichiometry corresponding exactly to the 1:2 molar ratio used for the reaction. The same compound can be obtained more readily from reaction in ethanol (see below).

The reactions of $Cu(NO_3)_2 \cdot 3H_2O$ in ethanol were performed by adding pydz, in the appropriate molar ratio, to an ethanolic solution of the salt (the inverse mixing is described later). Under these conditions we observed, after the addition of a few drops of the base, the immediate formation of small amounts of a jelly-like light blue impurity, which is partially dissolved upon further addition of pydz and may be eliminated by filtration.

With a salt:pydz molar ratio of *ca.* 1:1 the reaction leads, upon stirring for 1 h, to the formation of a blue-green microcrystalline precipitate **3**, in good yield. Elemental analyses of **3**, indicative of an approximate $Cu(NO_3)_2$:pydz ratio of 1:1.5, show some differences on repeating the reaction, due, probably, to the presence of impurities, which cannot be eliminated. The IR spectra show bands due to co-ordinated pydz and nitrate groups. X-Ray powder diffraction data for **3**, compared with those obtained from **1**, show that the former is a more complex species, with a larger cell. Compound **3** is thermally stable and decomposes at *ca.* 160 °C. To date its formulation remains uncertain; however, attempts to characterize it by *ab initio* X-ray powder methods, as successfully carried out for the above-mentioned pydz–halide complexes,[30] are presently under way.

When increasing amounts of base, up to $Cu(NO_3)_2$:pydz molar ratios of 1:3, are employed the pydz must be added quickly with stirring to the ethanolic solution of the metal salt at r.t. We observed that sometimes, on heating, these ethanolic solutions become dark red-brown, indicative of decomposition. Using a 1:2 molar ratio, after having removed the initially formed by-product, a mixture of the trinuclear complex **2** and of a monomer, characterized as [Cu(pydz)$_3$(O$_2$NO)(NO$_3$)] **4**, is obtained within a few hours. However, in these solutions compound **4** is converted completely, within a few days, into pure **2**. This indicates that the formation of **4** is kinetically favoured under these conditions but that the more stable product is **2**, and **4** is slowly converted into **2**, owing to its very modest solubility in ethanol. However, on leaving **4**, obtained as described below, in ethanol for long times no spontaneous reaction is observed. Compound **2** can be better obtained by employing a molar ratio in the range 1:1.5–1:1.7, due to the above described initial loss of some copper. The reaction performed with molar ratios close to 1:3 always gives, within a few hours, crystals of pure **4**, in high yield.

Addition of an ethanolic solution of the salt to an ethanolic solution of the base (1:1 molar ratio) with stirring does not result in the formation of the initial by-product and leads, more slowly, to the separation of compound **3**. When a salt:pydz molar ratio 1:2 is employed the rapid formation of monomeric **4** is observed. On leaving this solution to stand overnight a mixture of crystals of **2** and **4** is obtained, which transforms completely into **2** within 1 d.

These complexes are air-stable species, practically insoluble in ethanol and in most common organic solvents (except for **4** in MeCN); they are soluble in water with dissociation, giving the equilibrium mixtures of mononuclear species mentioned above. Spectroscopic analyses can be, therefore, performed only on the solids. The infrared spectra in Nujol and in hexachlorobuta-1,3-diene mulls are characterized by a number of bands due to the bonded pydz molecules, modified with respect to free pydz as previously reported for similar complexes,[20,23] and by the strong bands of the nitrate ligands (in the range 1500–1270 cm^{-1}),[33] eventually overlapping with bands due to the pydz molecules or to the mull media. Weak bands near 1750 cm^{-1}, due to the nitrate $\nu_1 + \nu_4$ combination mode,[33a] were observed for all compounds. In the case of **1** two strong bands due to the O–H stretchings of the hydroxide groups and the water molecules (3416 and 3294 cm^{-1}, in Nujol mull) and the bending mode of water (1651 cm^{-1}) are also present. The magnetic susceptibilities μ_{eff} at 293 K for **1** and **2**, 1.08 and 2.62 μ_B (1.51 μ_B per copper atom), respectively, are indicative of strong exchange coupling between the copper atoms in both cases. For comparison, the polymeric pyrazolate (pz) species [{Cu(pz)$_2$}$_n$] displays a magnetic susceptibility of 1.47 μ_B at 299 K, which decreases to 0.19 μ_B at 4.2 K.[34] Similar reduced r.t. magnetic susceptibilities are shown by many dinuclear copper(II) species bridged by 1,2-diazines, the effect being more marked in the presence of bridging OH groups.[35,36] The pydz–halide polymers [{CuX$_2$(pydz)}$_n$] show, as already mentioned, low-temperature antiferromagnetic coupling,[22,25] but they display normal μ_{eff} at r.t. in the range 1.7–1.9 μ_B.[23,24]

Crystals of compounds **1**, **2** and **4** were subjected to single-crystal X-ray analyses. During the preparation of this paper a communication appeared[37] reporting the crystal structure of compound **4**. We have therefore decided to omit the description of this structure, our results being in accordance with those reported therein. The distorted-octahedral complex, with three terminally bonded pydz molecules, an anisochelating and a terminal nitrate ion, is shown in Fig. 1; crystal data, details of the data collection and the final positional and thermal parameters are given as Supplementary Material.

Structures of Compounds **1** *and* **2**.—The crystal structure of the complex *catena*-[Cu(μ-η^2-pydz)(μ-OH)(μ-O$_2$NO)]·H$_2$O **1** consists of the packing of polymeric one-dimensional chains, developing along the crystallographic *b* axis, with the Cu atoms linearly disposed [Cu ··· Cu 3.3215(5) Å], each metal atom pair being symmetrically bridged by a η^2-pydz molecule, a hydroxo group and a nitrate, as illustrated in Fig. 2. The crystal packing is shown in Fig. 3 and bond distances and angles in Table 1. The chains are cross-linked by a system of hydrogen bonds involving the solvated water molecules. These dispose their oxygen atoms toward the OH$^-$ bridging groups of one polymer [O(W) ··· H 2.00(3) Å, O ··· H–O 171(5)°] and their hydrogen atoms towards the oxygen atoms of the bridging nitrates of an adjacent polymer [O(1) ··· H 2.04(2) Å, O ··· H–O 174(3)°]. The metals lie on crystallographic inversion centres (*f* positions in Wyckoff notation), so that the ligands of each type are mutually *trans* to themselves and are bonded to the linear framework of metals in a zig-zag fashion. Each copper atom displays an octahedral *trans*-diaxially elongated co-ordination (4 + 2). The $CuN_2O_2O'_2$ chromophore, of idealized D_{2h} symmetry, shows Cu–N (pydz) and Cu–O (OH) bond lengths of 2.079(2) and 1.902(1) Å, respectively; the Cu–O interactions with the bidentate nitrates, 2.449(2) Å, are Jahn–Teller elongated. The *cis* angles at the metal atoms are in the range 87.16(8)–92.84(7)°, those between the ligands bridging the same pair of metal atoms (or internal to the bridges) being, on average, acute (mean 88.84°).

Within the pydz bridges the Cu–N–N–Cu torsion angles are equal to 0°, in accordance with the crystallographic site symmetry. The dihedral angles between the planes of the bridges around the Cu···Cu axis are as follows: [Cu(OH)Cu]/[Cu(N,N pydz)Cu] 149.0(1), [Cu(OH)Cu]/[Cu(O,O nitrate)-Cu] 111.9(2) and [Cu(N,N pydz)Cu]/[Cu(O,O nitrate)Cu] 99.1(1)°. The same bridging system for a $Cu^{II}\cdots Cu^{II}$ interaction, with one OH^-, one O_2NO^- and one 1,2-diazine, was previously observed in the dinuclear complex $[Cu_2L^1(OH)(H_2O)_2(NO_3)_2]NO_3$ [L^1 = 1,4-bis(4-methyl-2-pyridylamino)-phthalazine], which exhibits a strong antiferromagnetic exchange, mediated by the bridging groups, and a μ_{eff} of 1.02 μ_B at r.t.[39] In this complex the Cu–OH [1.856(2), 1.859(2) Å], Cu–O (NO_3) [2.428(3), 2.330(3) Å] and Cu–N (diazine) [2.022(3), 2.042(3) Å] bonds are comparable with the corresponding interactions in **1**. The Cu···Cu contact in this dinuclear complex, 3.138(1) Å, is notably shorter, due to the presence of the tetradentate phthalazine ligand. As a consequence the Cu–OH–Cu angle is also smaller, 115.3(1) *vs.* 121.6(1)° in **1**. The Cu···Cu contact in the polymer is dictated by the steric requirements of the bridging ligands. It is somewhat shorter than that found in the related polymer $[\{CuCl_2(\mu\text{-}\eta^2\text{-pydz})\}_n]$ (3.3785 Å), which displays similar bonding parameters for the bridging pydz molecules [Cu–N 2.045(3) Å].[17]

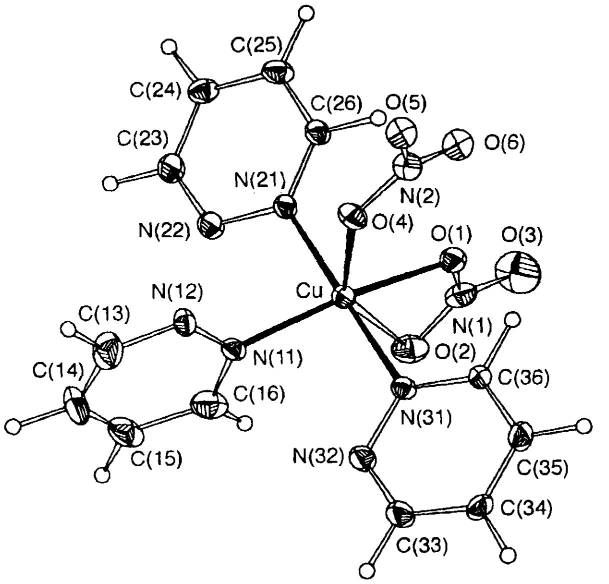

Fig. 1 An ORTEP[38] drawing of $[Cu(pydz)_3(O_2NO)(NO_3)]$ **4**. Thermal ellipsoids were drawn at the 30% probability level. Hydrogen atoms were given arbitrary radii

There are few other known examples of structurally characterized polymeric complexes containing N–N *exo*-bidentate ligands spanning *all* the metal–metal interactions. These are, to our knowledge, all copper compounds and include chloro(2,3-diazabicyclo[2.2.1]hept-2-ene)copper(I) (Cu··· Cu 3.355 Å),[40] dichloro(1,2,4-triazole)copper(II) (Cu···Cu 3.405 Å)[41] and

Table 1 Bond lengths (Å) and angles (°) for compound **1** *

$Cu\cdots Cu^{II}$	3.3215(5)	$C(2)–C(2^{II})$	1.344(5)
Cu–O(H)	1.902(1)	N(2)–O(1)	1.242(2)
Cu–N(1)	2.079(2)	N(2)–O(2)	1.220(4)
Cu–O(1)	2.449(2)	O(H)–H(1)	0.76(3)
$N(1)–N(1^{II})$	1.336(4)	O(W)–H(4)	0.81(2)
N(1)–C(1)	1.324(3)	O(1)···H(4)	2.04(2)
C(1)–C(2)	1.380(4)	$O(W^{IV})\cdots H(1)$	2.00(3)
$O(H^{I})–Cu–N(1)$	87.16(8)	$C(1)–N(1)–N(1^{II})$	118.8(1)
O(H)–Cu–O(1)	88.16(8)	N(1)–C(1)–C(2)	123.8(2)
$N(1)–Cu–O(1^{I})$	91.20(8)	$C(1)–C(2)–C(2^{II})$	117.4(2)
O(H)–Cu–N(1)	92.84(7)	Cu–O(1)–N(2)	126.9(2)
$O(H^{I})–Cu–O(1)$	91.84(8)	O(1)–N(2)–O(2)	119.9(2)
N(1)–Cu–O(1)	88.80(8)	$O(1)–N(2)–O(1^{III})$	120.1(3)
$Cu–O(H)–Cu^{II}$	121.6(1)	$H(4)–O(W)–H(4^{II})$	96(4)
Cu–O(H)–H(1)	115.3(9)	O(W)–H(4)···O(1)	174(3)
$Cu–N(1)–N(1^{II})$	118.53(5)	$O(H)–H(1)\cdots O(W^{IV})$	171(5)
Cu–N(1)–C(1)	122.6(2)		

* Symmetry operations used to generate equivalent atoms: I $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$; II $x, -y, z$; III $x, -y + 1, z$; IV $x - \frac{1}{2}, y + \frac{1}{2}, z - \frac{1}{2}$.

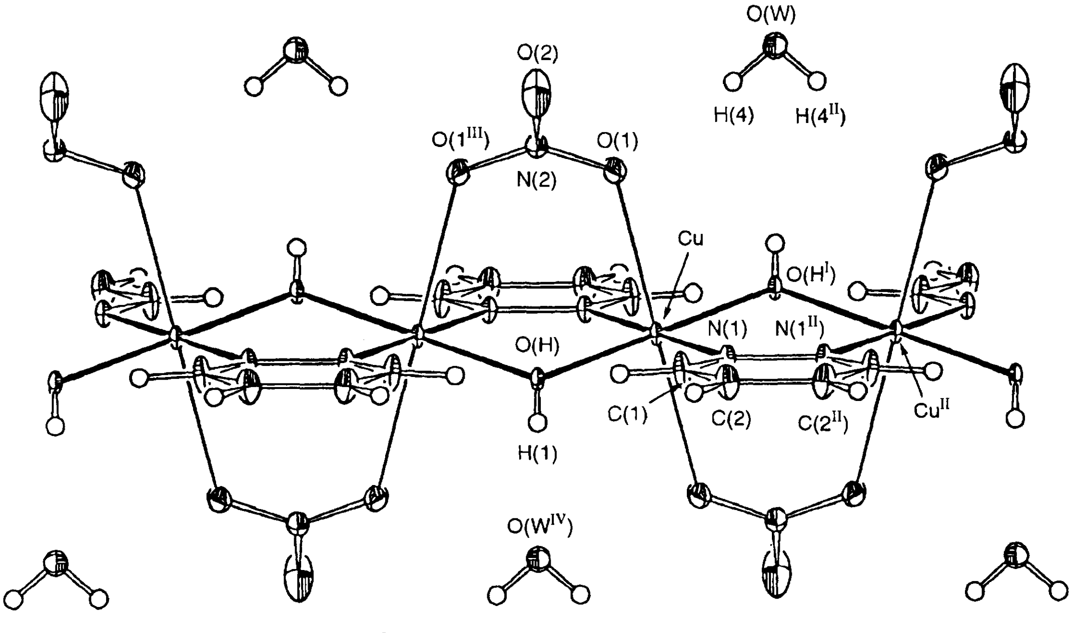

Fig. 2 An ORTEP view of the complex *catena*-$[Cu(\mu\text{-}\eta^2\text{-pydz})(\mu\text{-}OH)(\mu\text{-}O_2NO)]\cdot H_2O$ **1**. Details as in Fig. 1

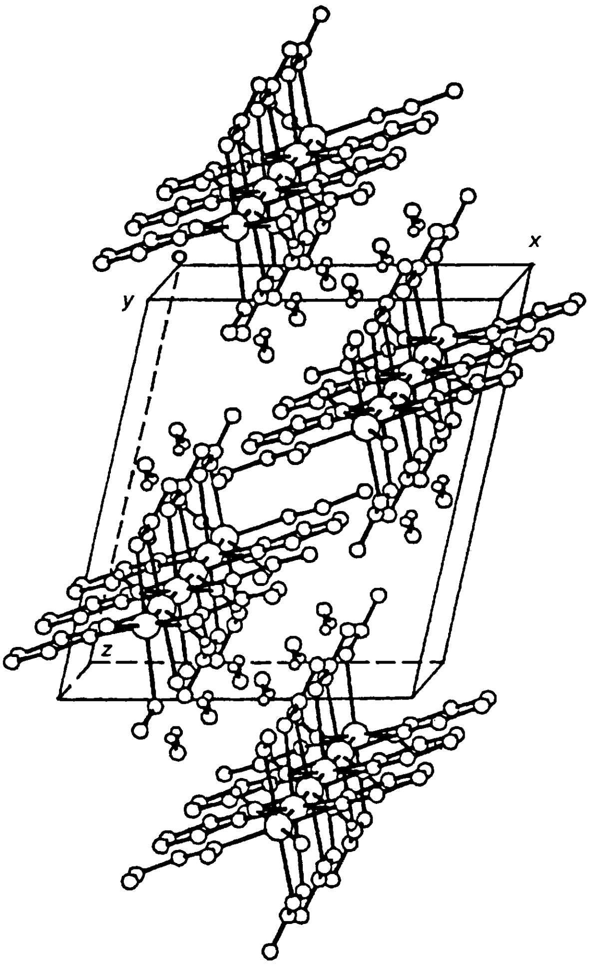

Fig. 3 A view of the crystal packing within complex **1**, showing the hydrogen-bond network. For clarity the pydz hydrogen atoms were omitted

(4-amino-3-methyl-1,2,4-triazole)dichlorocopper(II) (Cu ⋯ Cu 3.520 Å),[42] all polymers, [{Cu(pz)$_2$}$_n$] (pz = pyrazolate) (Cu ⋯ Cu 3.889 Å),[34] [{Cu(mpz)$_2$}$_n$] (mpz = 4-methylpyrazolate) (Cu ⋯ Cu 3.874 Å),[43] and [{Cu(cpz)$_2$}$_n$] (cpz = 4-chloropyrazolate) (Cu ⋯ Cu 3.858 Å),[43] and, lastly, polymeric aquabis(benzotriazolato)copper(II) (Cu ⋯ Cu 3.447 Å).[44]

The crystal structure of [Cu$_3$(μ-η^2-pydz)$_4$(pydz)$_2$(μ-NO$_3$)$_2$(NO$_3$)$_4$] **2** consists of the packing of discrete neutral trinuclear molecules, separated by normal van der Waals contacts. The complex, illustrated in Fig. 4, contains a linear trinuclear array of copper atoms, with the central Cu lying on a crystallographic inversion centre. Bond distances and angles are given in Table 2. The two equivalent Cu ⋯ Cu interactions [3.4057(8) Å] are symmetrically bridged by two η^2-pydz molecules and a nitrate. The external copper atoms complete their co-ordination sphere with a terminally *N*-bonded pydz molecule and two terminal nitrates. The central Cu atom exhibits a tetragonally distorted-octahedral geometry (4 + 2), the CuN$_4$O$_2$ chromophore showing four normal bonds with the N atoms of the pydz ligands (mean 2.063 Å), while the two Cu–O (NO$_3$) bonds are elongated [Cu(1)–O(11) 2.242(2) Å]. The external Cu atoms (CuN$_3$O$_3$ chromophores) display a distorted octahedral (4 + 1 + 1) geometry, the two asymmetrically elongated *trans* bonds being those involving the bridging nitrate [Cu(2)–O(11) 2.263(2) Å] and one of the two terminal nitrates. This ligand exhibits a disorder (see Experimental section) which has been rationalized using two slightly displaced NO$_3$ groups, each with a 50% population. The Cu(2)–O contact involving this nitrate, averaged on the two half-weight groups, is 2.494 Å. The other terminal nitrate shows a very much shorter Cu(2)–O bond of 1.979(3) Å. The Cu(2)–N interaction within the terminally bonded pydz ligand is slightly shorter [1.999(3) Å] than those involving the bridging groups (mean 2.050 Å).

The *cis* interligand angles at the central copper atom display values in the range 86.4(1)–93.6(1)°, those internal to the bridges all being acute. The external copper atoms exhibit a more distorted co-ordination, with *trans* angles in the range 170.0(2)–174.6(1)° and *cis* ones in the range 79.1(2)–101.2(1)°. The Cu(1)–O(11)–Cu(2) angle involving the bridging nitrate, 98.24(9)°, is larger than in the dinuclear [Cu$_2$L^2(OH)(NO$_3$)$_3$]·

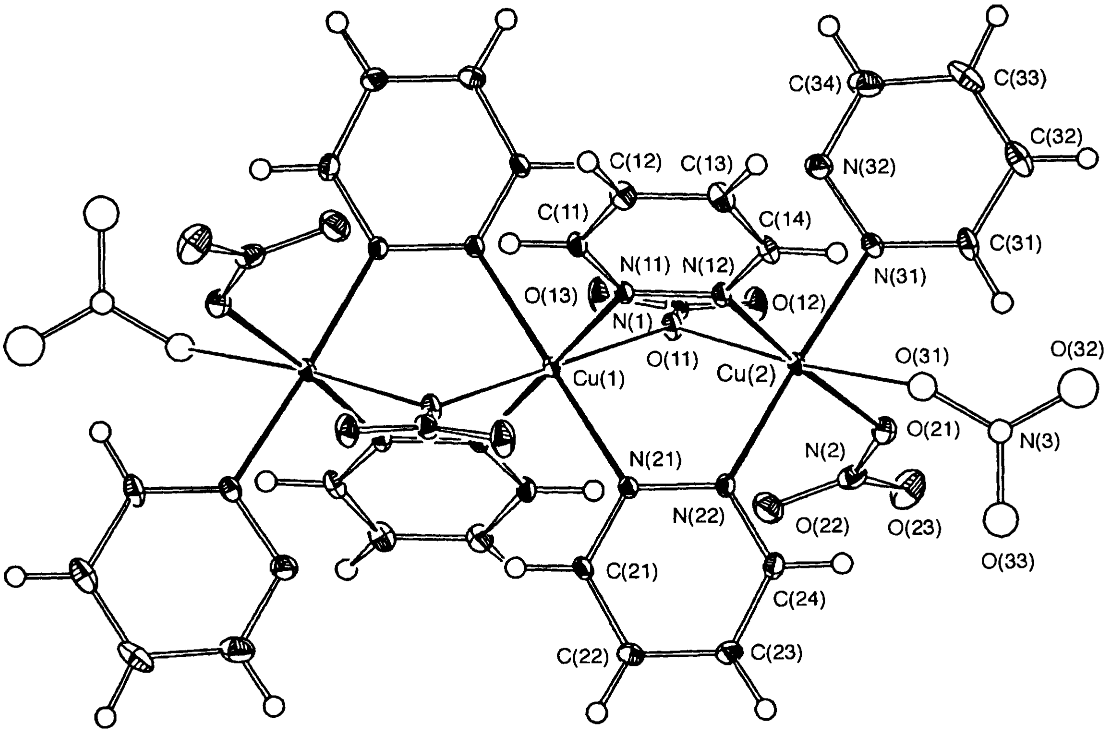

Fig. 4 An ORTEP drawing of [Cu$_3$(μ-η^2-pydz)$_4$(pydz)$_2$(μ-NO$_3$)$_2$(NO$_3$)$_4$] **2**. Atom Cu(1) lies on a crystallographic inversion centre. Only one model for the disordered (see text) nitrate ligand containing N(3) is shown. Other details as in Fig. 1

Table 2 Selected bond lengths (Å) and angles (°) for compound **2** *

Cu(1) ··· Cu(2)	3.4057(8)	C(22)–C(23)	1.359(5)	N(11)–N(12)	1.352(4)	N(2)–O(21)	1.287(4)
Cu(1)–N(11)	2.075(3)	C(23)–C(24)	1.385(5)	N(11)–C(11)	1.327(4)	N(2)–O(22)	1.248(5)
Cu(1)–N(21)	2.051(3)	N(31)–N(32)	1.333(5)	N(12)–C(14)	1.328(5)	N(2)–O(23)	1.227(4)
Cu(1)–O(11)	2.242(2)	N(31)–C(31)	1.321(5)	C(11)–C(12)	1.396(5)	N(3)–O(31)	1.247(3)
Cu(2)–N(12)	2.067(3)	N(32)–C(34)	1.336(5)	C(12)–C(13)	1.353(6)	N(3)–O(32)	1.244(3)
Cu(2)–N(22)	2.034(3)	C(31)–C(32)	1.399(6)	C(13)–C(14)	1.389(5)	N(3)–O(33)	1.243(3)
Cu(2)–N(31)	1.999(3)	C(32)–C(33)	1.356(7)	N(21)–N(22)	1.342(4)	N(3′)–O(31′)	1.248(3)
Cu(2)–O(11)	2.263(2)	C(33)–C(34)	1.393(7)	N(21)–C(21)	1.324(4)	N(3′)–O(32′)	1.240(3)
Cu(2)–O(21)	1.979(3)	N(1)–O(11)	1.295(4)	N(22)–C(24)	1.331(4)	N(3′)–O(33′)	1.248(3)
Cu(2)–O(31)	2.545(5)	N(1)–O(12)	1.219(4)	C(21)–C(22)	1.394(5)		
Cu(2)–O(31′)	2.442(5)	N(1)–O(13)	1.231(4)				
N(11)–Cu(1)–O(11)	86.4(1)	Cu(1)–N(11)–N(12)	119.6(2)	N(12)–Cu(2)–O(11)	87.1(1)	O(12)–N(1)–O(13)	123.2(3)
N(11)–Cu(1)–O(11^{I})	93.6(1)	Cu(2)–N(12)–C(14)	120.7(2)	N(12)–Cu(2)–O(31)	83.2(1)	Cu(2)–O(21)–N(2)	121.8(2)
N(21)–Cu(1)–N(11)	89.7(1)	Cu(2)–N(12)–N(11)	119.7(2)	N(12)–Cu(2)–O(31′)	92.9(2)	O(21)–N(2)–O(22)	119.7(3)
N(21)–Cu(1)–N(11^{I})	90.3(1)	Cu(1)–N(21)–C(21)	119.7(2)	N(22)–Cu(2)–N(12)	88.5(1)	O(21)–N(2)–O(23)	117.6(4)
N(21)–Cu(1)–O(11)	87.65(9)	Cu(1)–N(21)–N(22)	120.6(2)	N(22)–Cu(2)–O(11)	88.1(1)	O(22)–N(2)–O(23)	122.7(4)
N(21)–Cu(1)–O(11^{I})	92.35(9)	Cu(2)–N(22)–C(24)	120.2(2)	N(22)–Cu(2)–O(31)	93.4(2)	Cu(2)–O(31)–N(3)	127.3(5)
O(11)–Cu(2)–O(31)	170.1(1)	Cu(2)–N(22)–N(21)	120.1(2)	N(22)–Cu(2)–O(31′)	81.9(2)	O(31)–N(3)–O(32)	120.2(3)
O(11)–Cu(2)–O(31′)	170.0(2)	Cu(2)–N(31)–C(31)	122.9(3)	N(31)–Cu(2)–N(12)	89.4(1)	O(31)–N(3)–O(33)	119.8(3)
O(21)–Cu(2)–N(12)	171.5(1)	Cu(2)–N(31)–N(32)	114.1(2)	N(31)–Cu(2)–N(22)	174.6(1)	O(32)–N(3)–O(33)	119.3(3)
O(21)–Cu(2)–N(22)	93.2(1)	Cu(1)–O(11)–Cu(2)	98.24(9)	N(31)–Cu(2)–O(11)	96.8(1)	Cu(2)–O(31′)–N(3′)	135.3(5)
O(21)–Cu(2)–N(31)	88.2(1)	Cu(1)–O(11)–N(1)	133.4(2)	N(31)–Cu(2)–O(31)	81.3(2)	O(31′)–N(3′)–O(32′)	119.6(3)
O(21)–Cu(2)–O(11)	101.2(1)	Cu(2)–O(11)–N(1)	126.8(2)	N(31)–Cu(2)–O(31′)	93.2(2)	O(31′)–N(3′)–O(33′)	119.3(3)
O(21)–Cu(2)–O(31)	88.4(1)	O(11)–N(1)–O(12)	118.9(3)	Cu(1)–N(11)–C(11)	121.1(2)	O(32′)–N(3′)–O(33′)	119.7(3)
O(21)–Cu(2)–O(31′)	79.1(2)	O(11)–N(1)–O(13)	117.9(3)				

* Symmetry operation used to generate equivalent atoms: I $-x, -y, -z$.

$0.5H_2O$ [L^2 = 1,4-bis(6-methyl-2-pyridylamino)phthalazine], showing the same nitrate co-ordination [Cu–O–Cu in two independent molecules: 74.4(3) and 70.8(1)°],[36] the subtended Cu ··· Cu contact (mean 3.134 Å) being shorter and the Cu–O bonds (mean 2.642 Å) longer than in the present case. The Cu–N–N–Cu torsion angles are small for both the independent bridging pydz ligands: Cu(1)–N(11)–N(12)–Cu(2) −4.8(3)° and Cu(1)–N(21)–N(22)–Cu(2) 1.0(3)°.

While a great variety of dinuclear copper complexes has been reported, trinuclear complexes are relatively uncommon.[45] A few linear trinuclear copper(II) complexes have been previously structurally characterized.[46–48] However, this geometry is typical of a number of trinuclear species which are μ-N,N bridged by ligands of the type substituted 1,2,4-triazole[49] or 1,3,4-thiadiazole.[50] Many of these species, studied in particular for their magnetic properties, display metal–metal interactions bridged by three such ligands. The M ··· M distances in these species are longer than in **1** and **2**: for instance, the unique copper complex characterized, $[Cu_3L^3{}_6(H_2O)_4][CF_3SO_3]_6$ (L^3 = 4-ethyl-3-methyl-1,2,4-triazole), exhibits a Cu ··· Cu contact of 3.719(7) Å.[47] The metal–metal interactions become more similar to those found in the species here described when one of the three bridges is replaced by a one-atom-bridgehead ligand (see, for instance, refs. 50 and 51).

The bond parameters within the pydz molecules in these complexes are normal. Compounds **1**, **2** and **4** display a variety of bonding situations for the nitrate ions, covering almost all the known co-ordination modes of this anion: symmetric μ-O_2NO in **1**, symmetric μ-NO_3 and terminal (both strongly and weakly bonded) in **2**, and asymmetric chelating O_2NO and terminal in **4**. As expected, the N–O bonds involving the co-ordinated oxygen atoms are slightly longer than those for the unco-ordinated ones.[33b]

Conclusion

The reactions of copper(II) nitrate with the *exo*-bidentate pydz base give different products depending upon the solvent and molar ratio of the reagents. These products include polymeric (**1**) and oligomeric (**2**) complexes, the structural characterization of which is the principal aim of our studies on these systems. The results confirm the ability of pydz to keep two metals close together, thereby allowing the formation of polynuclear complexes. The nuclearity and nature of these products depends on many factors. (*i*) Solutions with increasingly high starting base : metal ratios afford solid products with increasingly high base content, possibly because the M–N bond energy outweighs that of the M–O bonds; moreover, the terminal M–N(pydz) interactions seem to be stronger than those of the bridging ones. (*ii*) Accordingly, high base : metal ratios prevent the aggregation of the metals and/or favour the fragmentation of large polynuclear fragments, the base acting mainly as a monodentate ligand, as in the mononuclear **4** and in the external Cu atoms of **2**. (*iii*) The donor power of nitrate is, however, notable, as may be inferred by the fact that all the nitrate groups, in all the species presently characterized, are co-ordinated to copper atoms. These ligands, therefore, may compete with the presence of *bridging* pydz bases, further disfavouring metal–metal condensation (see the external Cu atoms in **2**). Finally, (*iv*) the solvent plays an important role, in the relative solubility of the different products and/or directly participating in the reaction process (see compound **1**).

A variety of nuclearities and novel structural features are therefore to be expected using counter ions with different charge and donor ability and solvents with different basicity; a systematic study of such reactions will be the subject of future investigations.

Experimental

General Comments.—All the reagents and solvents employed were commercially available high-grade purity materials (Fluka Chemie), used as supplied, without further purification. Elemental analyses were carried out at the Microanalytical Laboratory of this University. Copper determinations were by conventional complexometric titrations.

Physical Measurements.—Infrared spectra were recorded on a JASCO FT/IR-5000 spectrophotometer (range 4000–500 cm^{-1}) in Nujol and hexachlorobuta-1,3-diene mulls. It was not possible to use KBr pellets because of transformation of the samples. The UV/VIS spectra in water were collected on a Hewlett-Packard 8452 instrument. Room-temperature magnetic susceptibilities were measured on a MSB-AUTO (Sherwood Scientific Ltd.) magnetic balance. Diamagnetic corrections were estimated from Pascal's constants. X-Ray powder patterns were collected on a Rigaku D-III/MAX horizontal-scan diffractometer, equipped with parallel (Soller) slits and a graphite monochromator in the diffracted beam (Cu-Kα radiation).

Syntheses.—*catena*-[Cu(μ-η^2-pydz)(μ-OH)(μ-O_2NO)]$\cdot H_2O$ **1**. The salt $Cu(NO_3)_2\cdot 3H_2O$ (0.580 g, 2.40 mmol) was dissolved in water (10 cm^3) and pydz (0.174 cm^3, 2.40 mmol) was added with stirring in an equimolar ratio. The blue colour of the solution darkened. The solution was concentrated to *ca.* 2 cm^3 and ethanol added (8 cm^3). It was left at r.t. for many days. Blue crystals formed, which were filtered off, washed with ethanol and dried in air. Yield 0.204 g (35%). The product is insoluble in ethanol and in common polar and non-polar solvents. It begins to decompose at 210 °C (Found: C, 20.00; H, 2.75; Cu, 26.20; N, 17.25. Calc. for $C_4H_7CuN_3O_5$: C, 19.95; H, 2.95; Cu, 26.40; N, 17.45%). Magnetic susceptibility at 293 K: 1.08 μ_B. Principal IR bands (cm^{-1}): 3416s, 3294s, 1651m, 1582m, 1417vs, 1334vs, 1127m, 1062m, 1007m, 824m, 791m, 723m, 681m, 574s (Nujol mull); 1462m, 1417vs, 1386vs and 1332vs (hexachlorobutadiene mull).

[Cu_3(μ-η^2-pydz)$_4$(pydz)$_2$(μ-NO_3)$_2$(NO_3)$_4$] **2**. (*a*) *In water.* After dissolution of $Cu(NO_3)_2\cdot 3H_2O$ (0.490 g, 2.03 mmol) in water (15 cm^3) pydz (0.147 cm^3, 2.03 mmol) was added with stirring. The solution was concentrated (to *ca.* 2 cm^3) upon heating until a change in colour to dark green was observed. The mixture was treated with ethanol (10–15 cm^3) and left to stand at r.t. for many hours. Green crystals, together with an amorphous blue impurity, separated. The precipitate was filtered off, washed with ethanol and dried in air. After removing the blue impurities under a microscope the approximate yield was 50%.

(*b*) *In ethanol.* The copper salt (0.350 g, 1.45 mmol) was dissolved in ethanol (99.8%, 10 cm^3) and pydz (0.180 cm^3, 2.46 mmol) added. After the addition of a few drops of pydz a small amount of a blue jelly-like product formed, which partially dissolved upon further addition of the base and was finally removed by filtration. The solution was left to stand at r.t. overnight. Beautiful, big dark green crystals of the product were obtained, which were filtered off, washed with ethanol and dried in air. Yield 0.327 g (65%). The product is insoluble in ethanol and in common organic solvents, m.p. 110–112 °C (Found: C, 27.65; H, 2.05; Cu, 18.10; N, 24.30. Calc. for $C_8H_8CuN_6O_6$: C, 27.65; H, 2.30; Cu, 18.25; N, 24.15%). The magnetic susceptibility at 293 K is 2.62 μ_B per trimer. Main IR bands (cm^{-1}): 1580m, 1428s, 1328vs, 1284vs(br), 1172m, 1075m, 1025s, 998s, 975m, 789s, 777s, 673m (Nujol mull); 1477vs(br), 1462s, 1423s, 1390vs, 1325vs and 1280vs(br) (hexachlorobutadiene mull).

Compound **3**. The salt $Cu(NO_3)_2\cdot 3H_2O$ (1.269 g, 5.25 mmol) dissolved in ethanol (99.8%, 20 cm^3) was treated with pydz (0.381 cm^3, 5.25 mmol) with stirring. A small amount of a blue jelly-like product formed immediately, which was removed by filtration. A green-blue microcrystalline precipitate separated upon stirring the solution for 1 h. The product was filtered off, washed with ethanol and dried in air. Yield 0.905 g. The product is insoluble in ethanol and in common organic solvents, m.p. 160 °C (decomp.) (Found: C, 22.50; H, 2.10; Cu, 20.05; N, 22.15%). Main IR bands (cm^{-1}): 1584m, 1499s, 1350s, 1330s, 1282vs, 1174m, 1081m, 1007s, 775m, 675m (Nujol mull); 1502vs, 1462s, 1386vs, 1350s, 1330s and 1284vs (hexachlorobutadiene mull).

[Cu(pydz)$_3$(O_2NO)(NO_3)] **4**. The salt $Cu(NO_3)_2\cdot 3H_2O$ (0.470 g, 1.94 mmol) dissolved in ethanol (99.8%, 10 cm^3) was treated with pydz (0.424 cm^3, 1.94 mmol) with stirring. Formation of the jelly-like by-product was negligible. Deep blue crystals formed within 1 h, which were filtered off, washed with ethanol and dried in air. Yield 0.697 g (84%). The product is soluble in MeCN, sparingly soluble in ethanol and insoluble in common non-polar solvents, m.p. 90–91 °C (Found: C, 33.70; H, 2.85; Cu, 14.50; N, 26.40. Calc. for $C_{12}H_{12}CuN_8O_6$: C, 33.70; H, 2.85; Cu, 14.85; N, 26.20%). Magnetic susceptibility at 293 K: 1.89 μ_B. Main IR bands (cm^{-1}): 1576m, 1328vs, 1299vs(br), 1209m, 1160m, 1071m, 1040m, 1017m, 973s, 768s, 743s, 675m (Nujol mull); 1473vs, 1462s, 1402s, 1328vs, 1301vs(br) and 1278m (hexachlorobutadiene mull).

Crystallography.—A blue crystal of complex **1** and a green crystal of **2** were mounted under a coating of epoxy glue on an Enraf–Nonius CAD-4 diffractometer and 25 intense reflections having a θ value in the range 10.0–14.0° were centred using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Least-squares refinement of their setting angles resulted in the unit-cell parameters reported in Table 3, together with an orientation matrix relating the crystal axes to the diffractometer axes. Crystal data and details associated with data collection and structure refinement for compounds **1** and **2** are given in Table 3.

Data were collected at room temperature. Intensities were checked by monitoring three standard reflections every 60 min, no crystal decay or long-range fluctuations of the primary beam intensity were observed. The diffracted intensities were corrected for Lorentz, polarization and background effects. An empirical absorption correction was applied based on ψ-scans of three suitable reflections having χ values close to 90° (ψ 0–360, every 10°).[52]

The structures were solved by a combination of direct methods[53] and Fourier-difference methods and refined by full-matrix least squares, minimizing the function $\Sigma w\Delta I^2$, using all

Table 3 Summary of crystal data and structure refinements parameters for compounds **1** and **2**[a]

	1	**2**
Formula	$C_4H_7CuN_3O_5$	$C_{24}H_{24}Cu_3N_{18}O_{18}$
M	240.67	1043.23
Space group	$I2/m$ (no. 12)	$P2_1/n$ (no. 14)
a/Å	10.239(1)	8.957(2)
b/Å	6.643(1)	13.687(4)
c/Å	12.363(2)	14.945(4)
β/°	103.74(1)	96.06(2)
U/Å^3	816.8(2)	1821.9(8)
Z	4	2
F(000)	484	1050
D_c/g cm^{-3}	1.957	1.902
μ/mm^{-1}	2.670	1.841
Crystal size/mm	0.15 × 0.11 × 0.06	0.17 × 0.16 × 0.10
Scan interval/°	0.8	1.1
Index ranges h, k, l	−12 to 11, 0–7, 0–14	−10 to 10, 0–16, 0–17
Reflections collected	785	3183
Independent reflections	785	3183
Maximum and minimum transmission	1.00, 0.82	1.00, 0.75
Data, restraints, parameters	784, 2, 73	3175, 14, 283
a, b[b]	0.0449, 0.1905	0.0808, 0.0
Goodness of fit on F_o^2 (on all data)[c]	1.091	1.107
R_1, wR_2		
[on $F_o > 4\sigma(F_o)$][d]	0.0222, 0.0611	0.0376, 0.1052
(on all data)	0.0362, 0.0648	0.0674, 0.1156
Maximum, minimum difference peak/e Å^{-3}	0.51, −0.30	0.81, −0.75

[a] Details in common: monoclinic; T 298(2) K; ω scans; θ range 3–25°. [b] Weights during refinement were $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. [c] $[\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{\frac{1}{2}}$ where n is the number of reflections and p the number of refined parameters. [d] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{\frac{1}{2}}$.

Table 4 Atomic coordinates for complex **1**

Atom	x	y	z
Cu	0.75	0.25	0.25
O(H)	0.6567(2)	0.5	0.2298(2)
O(W)	0.9032(3)	0	0.5905(2)
O(1)	0.8335(2)	0.3381(3)	0.4467(2)
O(2)	0.7882(5)	0.5	0.5820(3)
N(1)	0.5903(2)	0.1005(3)	0.2914(2)
N(2)	0.8169(3)	0.5	0.4917(2)
C(1)	0.4916(3)	0.1967(4)	0.3221(3)
C(2)	0.3874(3)	0.1011(4)	0.3545(2)

Table 5 Atomic coordinates for complex **2**

Atom	x	y	z
Cu(1)	0	0	0
Cu(2)	0.195 73(4)	0.213 63(3)	0.005 57(3)
N(11)	0.053 9(3)	0.062 2(2)	−0.119 0(2)
N(12)	0.137 4(3)	0.144 7(2)	−0.116 2(2)
C(11)	0.011 9(4)	0.020 8(3)	−0.198 0(2)
C(12)	0.049 3(4)	0.059 3(3)	−0.279 1(2)
C(13)	0.132 2(5)	0.142 1(3)	−0.276 1(3)
C(14)	0.175 7(4)	0.182 7(3)	−0.192 3(2)
N(21)	0.222 2(3)	0.004 2(2)	0.049 7(2)
N(22)	0.299 5(3)	0.088 3(2)	0.051 1(2)
C(21)	0.288 2(4)	−0.075 7(2)	0.084 7(2)
C(22)	0.435 2(4)	−0.076 4(3)	0.126 0(2)
C(23)	0.512 8(4)	0.009 0(3)	0.127 8(3)
C(24)	0.441 1(4)	0.090 4(3)	0.088 4(3)
N(31)	0.108 6(3)	0.337 9(2)	−0.047 3(2)
N(32)	−0.031 2(4)	0.329 2(2)	−0.086 9(2)
C(31)	0.183 1(4)	0.421 3(3)	−0.043 4(3)
C(32)	0.121 2(6)	0.506 0(3)	−0.084 4(3)
C(33)	−0.019 8(7)	0.498 9(3)	−0.127 1(3)
C(34)	−0.092 9(6)	0.409 2(3)	−0.126 4(3)
N(1)	−0.103 6(3)	0.194 2(2)	0.105 0(2)
O(11)	−0.019 5(3)	0.153 2(2)	0.050 4(2)
O(12)	−0.072 0(3)	0.276 2(2)	0.132 8(2)
O(13)	−0.211 0(3)	0.147 3(2)	0.127 3(2)
N(2)	0.248 1(4)	0.264 1(3)	0.192 9(2)
O(21)	0.275 2(3)	0.289 0(2)	0.113 2(2)
O(22)	0.214 3(4)	0.177 8(2)	0.208 4(2)
O(23)	0.257 3(4)	0.327 7(3)	0.251 1(2)
N(3)	0.528 1(5)	0.321 4(3)	−0.038 2(4)
O(31)	0.419 8(5)	0.271 6(4)	−0.071 6(4)
O(32)	0.545 7(8)	0.406 4(3)	−0.064 7(6)
O(33)	0.629 2(6)	0.282 5(4)	0.013 2(4)
N(3′)	0.507 9(8)	0.324 2(4)	−0.065 2(4)
O(31′)	0.476 2(10)	0.343 8(6)	−0.146 0(4)
O(32′)	0.447 8(7)	0.252 5(4)	−0.032 0(4)
O(33′)	0.576 3(11)	0.385 4(5)	−0.014 4(5)

reflections. Anisotropic thermal displacement parameters were assigned to all non-hydrogen atoms with the exception of the disordered nitrate group containing N(3) in compound **2**. All the hydrogen atoms were located from Fourier-difference maps and introduced in the final stages of refinement as fixed atom contributions riding on their parent atoms with $d_{\text{C-H}}$ 0.93 and $d_{\text{O-H}}$ 0.82 Å and a common isotropic U factor refined to a value of 0.058(5) and 0.048(3) Å^2 for **1** and **2**, respectively.

In compound **2** the monodentate nitrate ligand containing N(3) was found to be severely disordered; two models were introduced with equal occupancies and constrained to flatness using the DFIX and FLAT instructions of the SHELXL 93[54] package. The final difference map still showed several peaks, not exceeding *ca.* 0.8 e Å^{-3}, located around the disordered nitrate.

Scattering factors for neutral non-hydrogen atoms, hydrogen atoms and anomalous dispersion corrections for scattering factors were taken from ref. 55. All calculations were performed using SHELXL 93. Final non-hydrogen atomic co-ordinates are listed in Tables 4 and 5 for compounds **1** and **2**, respectively. Molecular drawings were produced with the ORTEP program.[38]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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