

Synthesis and structures of 5-(pyridyl)tetrazole complexes of Mn(II)†

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Received 11th April 2005, Accepted 3rd June 2005

First published as an Advance Article on the web 13th June 2005

New Mn^{II} complexes containing 5-(2-pyridyl)tetrazole, 5-(3-cyano-4-pyridyl)tetrazole or 5-(4-pyridyl)tetrazole ligands are described. The complexes are prepared by reaction of the corresponding cyanopyridines with sodium azide in the presence of Mn^{II} salts. All the complexes have been characterized by X-ray crystallography, which reveals that 5-(pyridyl)tetrazole ligands can coordinate to Mn through either type of nitrogen atom in the tetrazole residue or *via* the pyridyl group. In the solid state, extended 2D and 3D structures are produced through networks of hydrogen bonding (involving water molecules and the tetrazolate residue). Acidification of the complexes produces the corresponding free 5-(pyridyl)-1*H*-tetrazole.

Introduction

Tetrazoles have found a wide range of applications in areas as diverse as coordination chemistry, medicinal chemistry and materials science.^{1–4} Although it has been known for some time that substituted tetrazoles can be prepared by the 1,3-dipolar reaction of a nitrile with azide ion, the syntheses were difficult, typically involving reaction times of days at 100–125 °C.^{5–7} It was shown some time ago that performing the reaction on a metal site facilitated the 1,3-dipolar addition.⁸ Thus, the reaction of [Co(NCR)(NH₃)₅]³⁺ (R = Me or Ph) with an excess of azide produces [Co(CRN₄)(NH₃)₅]²⁺ in which the 5-substituted tetrazole is initially coordinated to Co through N¹ but subsequently rearranges to coordinate through N². More recently, Sharpless *et al.* reported⁹ the preparation of a variety of 5-substituted-1*H*-tetrazoles using Zn^{II} salts as catalysts. In the presence of Zn^{II} the tetrazoles can be prepared in high yield in times ranging from 6 to 48 h at 100 °C. This facile metal-assisted synthesis allows us to explore the coordination chemistry of tetrazoles more extensively than in the past.

The study of complexes containing substituted tetrazole ligands is of interest to delineate the ways in which tetrazoles bind to metal centres. In addition, it is anticipated that tetrazole complexes could produce some unusual extended structures through hydrogen bonded networks because substituted 1*H*-tetrazoles have a relatively low p*K*_a (in the range 3–5), similar to those of carboxylic acids. Recently,^{4a} a series of tetrazole complexes of tetrahedral Zn have been reported in which a range of coordination modes for the tetrazoles were observed and extended 2D and 3D structures identified. Herein, we report that 5-(pyridyl)-1*H*-tetrazoles (5-1*H*-PTZ; **1a**, **2a** or **3a**) can be isolated from the room temperature reaction of cyanopyridines with sodium azide in the presence of Mn^{II} salts, within 2–4 h. Furthermore, we have isolated the octahedral Mn(II)-5-pyridyl-tetrazolato (PTZ) complexes (**1**, **2** or **3**) from their respective reaction solutions and determined their structures by X-ray crystallography.

Results and discussion

Synthesis

In general, 5-substituted-tetrazolato-ligands (RCN₄⁻) can coordinate to metal centres through either the nitrogen atoms adja-

cent to the carbon (N¹) or the nitrogen atoms (N²) remote from the carbon in the ring. Only two tetrazole complexes of Mn {Mn(I)} have been reported previously, [Mn(CO)₃{N₄C(CF₃)₂-(Ph₂PCH₂CH₂Ph₂)}] and [Mn(CO)₃{N₄C(CF₃)₂}(Et₂PCH₂CH₂-Et₂)].¹⁰ These complexes were prepared by the reaction of CF₃CN with [Mn(CO)₃(N₃)(Ph₂PCH₂CH₂Ph₂)] and [Mn(CO)₃(N₃)(Et₂PCH₂CH₂Et₂)], respectively. In both cases the tetrazole coordinated to the Mn through a nitrogen atom remote from the carbon in the ring (N²). In the 5-(pyridyl)tetrazolato ligands investigated in this paper there is the additional capability of coordination by the pyridyl group. The work reported herein shows that the donor atoms can be the pyridyl nitrogen and/or the tetrazole nitrogen atoms, as illustrated in Scheme 1.

Sharpless *et al.* reported testing a number of Lewis acids for catalytic ability in the reaction of azide ions with nitriles to form tetrazoles (Li^I, K^I, Cs^I, Mg^{II}, Ca^{II}, Ba^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Ag^I, Zn^{II}, Ce^{IV}, Sm^{III}, Yb^{III}, B^{III}, Al^{III}, Bi^{III}). However, these metal ions have shown little or no catalysis.^{9a} As reported herein, we have observed that Mn^{II} salts do facilitate the formation of tetrazoles.

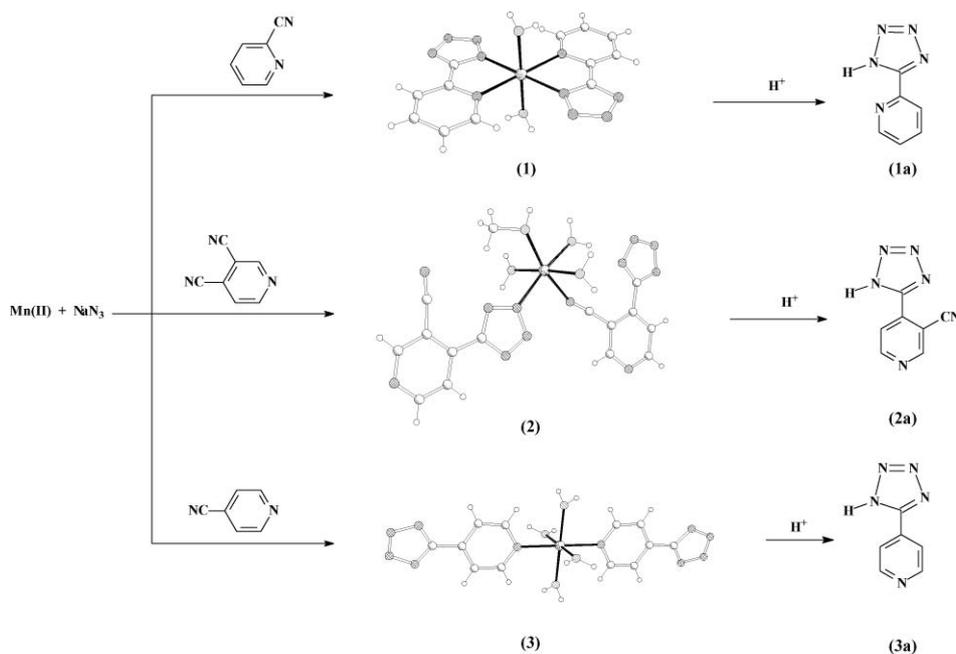
The reaction of equimolar amounts of NaN₃ and cyanopyridines with a Mn^{II} salt produces (after workup) stoichiometric yields of the corresponding 5-(pyridyl)-1*H*-tetrazole. In a typical reaction, Mn(NO₃)₂·4H₂O (2 mmol), NaN₃ (4 mmol) and a cyanopyridine (4 mmol) are added to a mixed solvent (methanol: water = 1 : 2), and then stirred at room temperature for *ca.* 2 h. After removal of all the volatiles *in vacuo*, the crude solid product {containing Mn-(PTZ) and inorganic salts} is added to water and the pH of the solution adjusted to *ca.* 4.0. Ethyl acetate (30 mL) is then added to the mixture and the organic layer is separated. The ethyl acetate is removed *in vacuo*, and the colourless microcrystalline product, a 5-(pyridyl)-1*H*-tetrazole (**1a**, **2a** or **3a**), forms in yields of 46–58% (Scheme 1).

The 5-(pyridyl)tetrazolato-complexes of Mn^{II} can be isolated by mixing Mn(NO₃)₂·4H₂O (2 mmol), NaN₃ (4 mmol) and a cyanopyridine (4 mmol), then allowing the solution to stand at room temperature, whereupon crystallization of the complexes slowly occurs.

It is important to emphasise that Mn^{II} salts do not *catalyze* the formation of the tetrazoles. Thus, the reaction of Mn(NO₃)₂·4H₂O (0.4 mmol), NaN₃ (4 mmol) and 4-cyanopyridine (4 mmol) resulted in 0.6 mmol of yield of 5-(4-pyridyl)-1*H*-tetrazole. This yield is consistent with the production of 5-(4-pyridyl)-1*H*-tetrazole (**3a**) from the stoichiometric formation of complex (**3**). Although the theoretical maximum stoichiometric yield of (**3a**) from (**3**) is 0.8 mmol, the observed yield is obtained after an extensive workup procedure.

In the presentation below we discuss the molecular structures of the 5-(pyridyl)tetrazolato-complexes of Mn^{II} and the

† Electronic supplementary information (ESI) available: Three-dimensional structure of **3** supported by hydrogen bonds, with hydrogen atoms on carbons omitted; Three layers of two-dimensional framework consisting of [Mn{5-(4-pyridyl)-tetrazolato}₂(H₂O)₄] units linked by 'intermolecule' hydrogen bonds. See <http://dx.doi.org/10.1039/b505077d>



Scheme 1 Syntheses of 5-(pyridyl)-1H-tetrazoles.

extended structures of the solids. It is worth noting that we have also attempted to use Ni^{II} , Cu^{II} and Cu^{I} salts to catalyse the reaction between cyanopyridines and NaN_3 . In no case is 5-(pyridyl)-1H-tetrazole formed. It appears that, with Ni^{II} , Cu^{II} or Cu^{I} , the reactions are hampered by the rapid precipitation of a metal complex. In the case of Cu^{II} we have shown that the precipitate is a polymeric species in which the cyanopyridine links metal centres,¹¹ similar to the known $[\text{Cu}(\text{4-cyanopyridine})_4(\text{H}_2\text{O})](\text{ClO}_4)_2$ complex.¹²

Crystal Structures of Mn^{II} Complexes

Structure of $[\text{Mn}\{5\text{-(2-pyridyl)-tetrazolato}\}_2(\text{H}_2\text{O})_2]$ (1). The molecular structure of $[\text{Mn}\{5\text{-(2-pyridyl)-tetrazolato}\}_2(\text{H}_2\text{O})_2]$ (1), Fig. 1(a), has a centrosymmetric configuration, in which the octahedral Mn is coordinated by four equatorial nitrogen atoms from two 5-(2-pyridyl)-tetrazolato-ligands (2-PTZ) and axial oxygen atoms of coordinated water molecules. Each PTZ ligand chelates to Mn through one tetrazolato-nitrogen atom at the N^1 -site of the tetrazolato-ring and through the pyridyl nitrogen atom. The tetrazolato-ring is coplanar with the pyridyl ring. Selected bond distances and angles are listed in Table 1.

In the crystal structure of **1**, eight intermolecular $\text{O}-\text{H}\cdots\text{N}(\text{tetrazole})$ hydrogen bonds (details of which are given in Table 2) link each Mn complex to four other complexes. Each $\text{O}-\text{H}$ group of the coordinated water molecules acts as a hydrogen bond donor, and tetrazole nitrogen atoms N^1 and N^2 of the PTZ moiety act as hydrogen bond acceptors, as illustrated in Fig. 1(b). In addition, $\pi-\pi$ -stacking interactions between the adjacent tetrazolato rings are present. The rings stack in a 'face to face'

Table 1 Selected bond lengths (Å) and angles (°) for **1**^a

| | | | |
|------------------|------------|-----------------|------------|
| Mn(1)–O(1) | 2.2084(18) | Mn(1)–N(1) | 2.2117(19) |
| Mn(1)–N(5) | 2.255(2) | N(1)–N(2) | 1.350(3) |
| N(2)–N(3) | 1.323(3) | N(3)–N(4) | 1.359(3) |
| N(4)–C(1) | 1.331(3) | N(1)–C(1) | 1.332(3) |
| O(1)–Mn(1)–O(1A) | 180.0 | N(1)–Mn(1)–N(5) | 75.42(7) |
| N(5)–Mn(1)–N(1A) | 104.58(7) | N(1)–N(2)–N(3) | 107.94(19) |
| N(2)–N(3)–N(4) | 109.6(2) | N(3)–N(4)–C(1) | 105.0(2) |
| N(1)–C(1)–N(4) | 111.1(2) | N(2)–N(1)–C(1) | 106.41(18) |

^a Symmetry operations for equivalent atoms: A, $(-x, 1-y, 1-z)$; B, $(x, 1/2-y, 1/2+z)$; C, $(-x, 1/2+y, 3/2-z)$.

Table 2 Hydrogen bond distances and angles^a

| D–H \cdots A | D–H | H \cdots A | D \cdots A | D–H \cdots A |
|---------------------------|---------|--------------|--------------|----------------|
| O(1)–H(1a) \cdots N(3C) | 0.79(3) | 2.04(3) | 2.820(3) | 171(3) |
| O(1)–H(1b) \cdots N(4B) | 0.83(3) | 1.94(3) | 2.758(3) | 171(3) |

^a Symmetry operations for equivalent atoms: A, $(-x, 1-y, 1-z)$; B, $(x, 1/2-y, 1/2+z)$; C, $(-x, 1/2+y, 3/2-z)$.

orientation parallel to the crystallographic c axis. The spacing between adjacent tetrazolato-rings (*ca.* 3.6 Å) falls within the range (3.3–3.8 Å), which is an acceptable distance for effectual $\pi-\pi$ -stacking interaction.¹³ In contrast, the perpendicular distance between the parallel pyridyl rings (7.38 Å) is outside the acceptable range of $\pi-\pi$ -stacking interaction distances. These non-bonding interactions link the molecular units to form independent two-dimensional layers, extending in the (100) lattice plane, as shown in Fig. 1(c). The interlayer distance is 8.064 Å, the length of the crystallographic a axis, and only van der Waals interactions hold the layers together.

The room temperature magnetic moment of **1** was determined and found to be $\mu = 5.99$ BM. This value is that expected for an isolated mononuclear high spin Mn^{II} complex (spin-only formula predicts $\mu = 5.92$ BM). We have not further explored the magnetic properties of the complexes reported in this paper.

Structure of $[\text{Mn}\{5\text{-(3-cyano-4-pyridyl)tetrazolato}\}_2(\text{H}_2\text{O})_3(\text{MeOH})]$ (2). The complex $[\text{Mn}\{5\text{-(3-cyano-4-pyridyl)tetrazolato}\}_2(\text{H}_2\text{O})_3(\text{MeOH})]$ (2), shown in Fig. 2(a), is the only product isolated from the reaction between $\text{Mn}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$, NaN_3 (4 mol-equivalents) and pyridine-3,4-dicarbonitrile (2 mol-equivalents). The molecular structure of (2) shows an asymmetric configuration, as shown in Fig. 2(a). The Mn^{II} centre has a distorted octahedral geometry, being coordinated by two PTZ ligands bound in differing configurations. The first (hereafter referred to as PTZ-C) coordinates *via* the cyano group [using N(11)] whilst the second (PTZ-T) coordinates through the N^2 atom of the tetrazolato-ring [N(1)]. The oxygen atom of a methanol [O(2)] and the oxygen atoms of three water molecules, [O(1), O(3) and O(4), respectively] complete the coordination of Mn. The methanol is *trans* to the coordinated cyano group. O(1) and O(4) occupy the axial positions in an approximately linear arrangement [O(1)–Mn(1)–O(4) 176.10(6)°] whilst O(2), O(3),

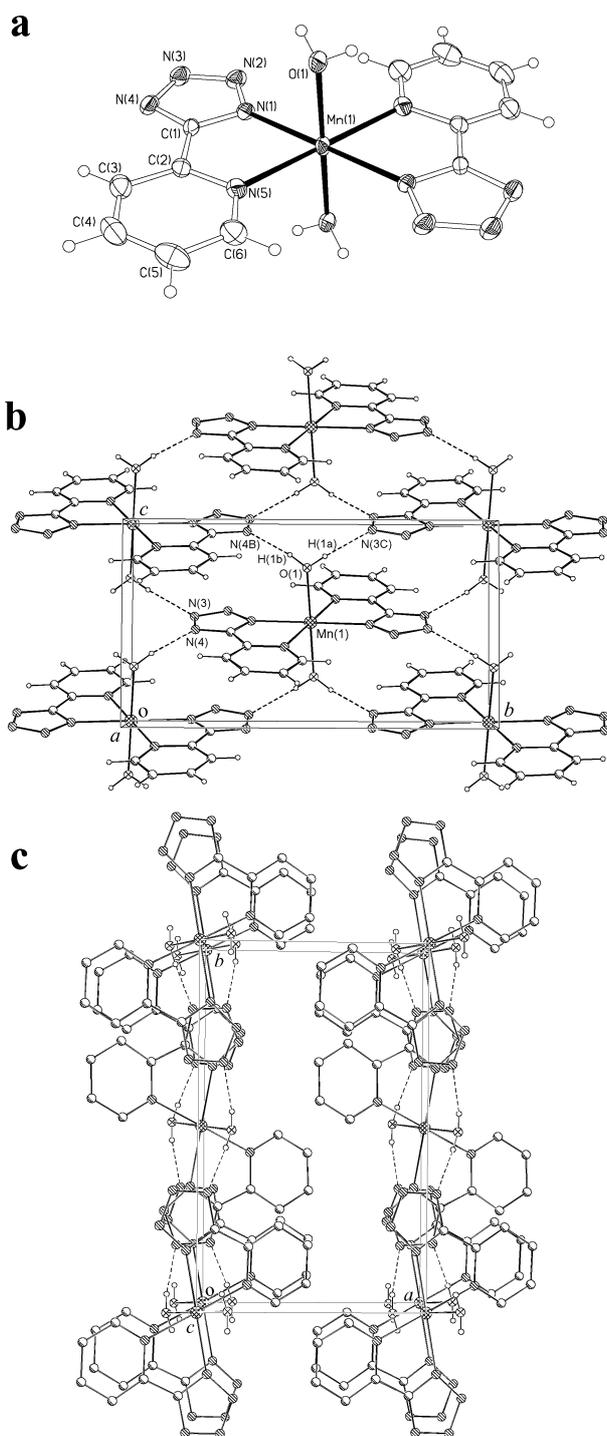


Fig. 1 Molecular structure of **1** with 50% probability displacement ellipsoids. (b) A single layer of the two-dimensional structure supported by hydrogen-bonded linking of monomer units of **1**, seen edge-on down the crystallographic *a* axis. Hydrogen bonds shown dashed. (c) The unit cell contents of compound **1** viewed along the *c* axis, showing two independent layers consisting of complex units linked by hydrogen bonds. Hydrogen atoms on carbons are omitted for clarity.

N(11) and N(1) are essentially coplanar, with the Mn centre deviating 0.011 Å from the mean plane through the four donor atoms. Selected bond distances and angles are shown in Table 3. The planes of the pyridyl and tetrazolato rings of PTZ-T are twisted by 7.5°, the equivalent torsion angle being 6.4° in PTZ-C.

In all previously described structures of tetrazolato-complexes at least one nitrogen atom from each tetrazolato-ligand is involved in coordination to the metal centre.^{2a-c,3,4,10} It seems likely that, when the tetrazolato-residue is bound to a metal, the electron density on the ring is diminished. In the case of **2**, the coordination of PTZ-C means that the electron density on the

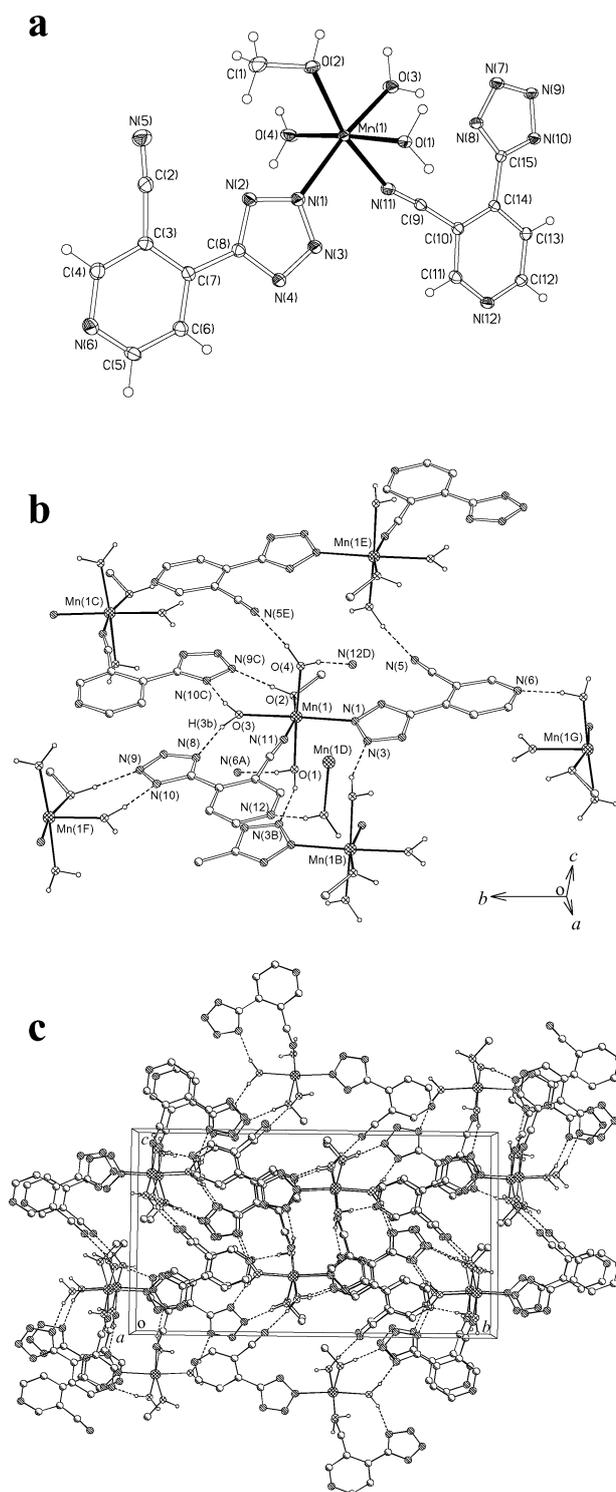


Fig. 2 Molecular structure of **2** with 50% probability displacement ellipsoids (b) View of one complex unit hydrogen bonding to seven adjacent units; partial symmetry-related units are shown for clarity. Hydrogen bonds are shown dashed and hydrogen atoms on carbons are omitted. Additional symmetry codes not in Table 3: F, $(-1/2 + x, 3/2 - y, -1/2 + z)$; G, $(3/2 - x, -1/2 + y, 3/2 - z)$. (c) Crystal packing diagram of the complex **2** with hydrogen bonds shown dashed. Hydrogen atoms on carbons are omitted.

tetrazolato-residue is less affected by the metal, thus enhancing the capability of its nitrogen atoms to act as hydrogen bond acceptors.

As illustrated in Fig. 2(b), one of the N² atoms of the PTZ-C ligand is intramolecularly hydrogen bonded to an equatorial water ligand of the same molecule of **2** [O(3) ⋯ N(8) 2.993(2) Å; O(3)–H(3b) ⋯ N(8) 167(3)°]. Furthermore, Fig. 2(b) shows how each complex interacts with seven symmetry-*2*-related molecules

Table 3 Selected bond lengths (Å) and angles (°) for **2**^a

| | | | |
|------------------|------------|------------------|------------|
| Mn(1)–O(1) | 2.1741(15) | Mn(1)–O(2) | 2.1799(14) |
| Mn(1)–O(3) | 2.1901(16) | Mn(1)–O(4) | 2.1441(16) |
| Mn(1)–N(1) | 2.2595(18) | Mn(1)–N(11) | 2.2880(16) |
| N(1)–N(2) | 1.341(2) | N(1)–N(3) | 1.332(2) |
| N(3)–N(4) | 1.327(2) | N(4)–C(8) | 1.351(2) |
| N(2)–C(8) | 1.339(2) | N(7)–N(8) | 1.343(2) |
| N(7)–N(9) | 1.326(2) | N(9)–N(10) | 1.344(2) |
| N(8)–C(15) | 1.345(2) | N(10)–C(15) | 1.338(2) |
| O(1)–Mn(1)–O(4) | 176.10(6) | O(3)–Mn(1)–N(1) | 170.32(6) |
| O(2)–Mn(1)–N(11) | 165.78(6) | N(1)–Mn(1)–N(11) | 92.11(6) |
| Mn(1)–N(11)–C(9) | 158.15(16) | Mn(1)–O(2)–C(1) | 122.04(13) |

^a Symmetry operations for equivalent atoms: A, (1/2 – x, 1/2 + y, 1/2 – z); B, (– x, – y, – z); C, (1/2 + x, 1/2 – y, 1/2 + z); D, (– 1 – x, – y, – z); E, (– x, – y, 1 – z).

Table 4 Hydrogen bond distances and angles in **2**^a

| D–H...A | D–H | H...A | D...A | D–H...A |
|---------------------|---------|---------|----------|---------|
| O(1)–H(1a)...N(6A) | 0.84(2) | 1.93(2) | 2.764(2) | 170(3) |
| O(1)–H(1b)...N(3B) | 0.81(2) | 2.03(2) | 2.802(2) | 159(3) |
| O(2)–H(2)...N(9C) | 0.87(2) | 1.91(2) | 2.785(2) | 177(3) |
| O(3)–H(3a)...N(10C) | 0.88(2) | 1.93(2) | 2.805(2) | 168(3) |
| O(3)–H(3b)...N(8) | 0.86(2) | 2.15(2) | 2.993(2) | 167(3) |
| O(4)–H(4a)...N(12D) | 0.85(2) | 1.88(2) | 2.718(2) | 168(3) |
| O(4)–H(4b)...N(5E) | 0.84(2) | 1.99(2) | 2.815(2) | 170(3) |

^a Symmetry operations for equivalent atoms: A, (1/2 – x, 1/2 + y, 1/2 – z); B, (– x, – y, – z); C, (1/2 + x, 1/2 – y, 1/2 + z); D, (– 1 – x, – y, – z); E, (– x, – y, 1 – z).

through twelve intermolecular O–H...N(tetrazole) hydrogen bonds, involving the coordinated methanol and all but one of the O–H groups of the three coordinated water molecules (the remaining water ligand forms the intramolecular interaction described above). Structural details of the hydrogen bonding are given in Table 4.

The hydrogen bonding interactions of the PTZ-C and PTZ-T ligands are similar. Three atoms of the PTZ-T ligand act as hydrogen bond acceptors: one N²-atom of the tetrazole, the cyano nitrogen atom and the pyridyl nitrogen atom. In contrast, the hydrogen bond acceptors for the PTZ-C ligand are the N¹ and N² atoms of the tetrazole and the pyridyl nitrogen atom. These hydrogen bonds produce a 3D architecture for **2**, as shown in Fig. 2c. The adjacent tetrazolate and pyridyl rings stack in an ABAB sequence along the direction parallel to the crystallographic *a* axis. The spacing between adjacent tetrazolate and pyridyl rings (*ca.* 3.6 Å centroid-centroid), lies within the acceptable range for effective π–π-stacking interactions.¹²

Structure of [Mn{5-(4-pyridyl)-tetrazolato}₂(H₂O)₄](3). The molecular structure of [Mn{5-(4-pyridyl)-tetrazolato}₂(H₂O)₄](**3**) is shown in Fig. 3(a). The Mn has an octahedral geometry and lies on a crystallographic inversion centre. Four water molecules occupy the equatorial positions with the pyridyl nitrogen atoms from two symmetry related 4-PTZ ligands coordinating in the axial positions. In **3**, each 5-(4-pyridyl)tetrazolate is a monodentate ligand, coordinating only to Mn through the pyridyl nitrogen atom. The 5-(4-pyridyl)tetrazolato-ligand has also been characterised in the coordination polymer, [Zn(4-PTZ)(HO)(H₂O)]^{4a} in which each 5-(4-pyridyl)tetrazolato-group bridges two Zn centres, bonding through the pyridyl nitrogen to one Zn and a tetrazole nitrogen to another Zn. For each Mn, two molecules of water are present within the crystal structure. Selected bond distances and angles for **3** are given in Table 5.

In each PTZ ligand, the planes of the pyridyl and tetrazolate rings are twisted by 11.2° with respect to one another. No tetrazole nitrogen atoms are coordinated to the Mn centre. Consequently, in the crystal structure of **3**, all tetrazolato-

Table 5 Selected bond lengths (Å) and angles (°) for **3**^a

| | | | |
|-----------------|----------|-----------------|----------|
| Mn(1)–N(1) | 2.294(2) | Mn(1)–O(1) | 2.162(2) |
| Mn(1)–O(2) | 2.163(2) | N(2)–N(3) | 1.340(3) |
| N(3)–N(4) | 1.320(4) | N(4)–N(5) | 1.347(4) |
| N(5)–C(6) | 1.337(4) | N(2)–C(6) | 1.339(4) |
| O(1)–Mn(1)–O(2) | 90.87(9) | N(1)–Mn(1)–O(1) | 88.66(9) |
| N(1)–Mn(1)–O(2) | 92.55(9) | N(3)–N(2)–C(6) | 104.7(2) |
| N(2)–N(3)–N(4) | 109.9(2) | N(3)–N(4)–N(5) | 108.9(2) |
| N(4)–N(5)–C(6) | 105.0(2) | N(2)–C(6)–N(5) | 111.5(3) |

^a Symmetry operation for equivalent atoms: A, (1 – x, – y, 1 – z); B, (2 – x, – y, 1 – z); C, (x, y, 1 + z); D, (x, – 1 + y, 1 + z); E, (x, – 1 + y, z); F, (2 – x, 1 – y, – z).

Table 6 Hydrogen bonds distances and angles for **3**^a

| D–H...A | D–H | H...A | D...A | D–H...A |
|--------------------|---------|---------|----------|---------|
| O(1)–H(1a)...O(3B) | 0.84(2) | 1.90(3) | 2.748(3) | 178(5) |
| O(1)–H(1b)...N(5C) | 0.85(2) | 1.97(3) | 2.801(3) | 167(3) |
| O(2)–H(2a)...O(3) | 0.84(3) | 1.90(3) | 2.734(3) | 178(5) |
| O(2)–H(2b)...N(4D) | 0.82(2) | 2.06(3) | 2.873(4) | 171(4) |
| O(3)–H(3a)...N(2E) | 0.85(2) | 1.96(2) | 2.807(3) | 175(4) |
| O(3)–H(3b)...N(3F) | 0.83(3) | 1.95(3) | 2.771(3) | 170(4) |

^a Symmetry operation for equivalent atoms: A, (1 – x, – y, 1 – z); B, (2 – x, – y, 1 – z); C, (x, y, 1 + z); D, (x, – 1 + y, 1 + z); E, (x, – 1 + y, z); F, (2 – x, 1 – y, – z).

nitrogen atoms are involved in O–H...N(tetrazole) hydrogen bonds with the coordinated or uncoordinated water molecules. These interactions link **3** into a 3D-supramolecular structure as shown in Fig. 3(b). For each molecule of **3**, eight tetrazolato-nitrogen atoms are hydrogen bond acceptors and eight O–H groups from coordinated water molecules are hydrogen bond donors. Hydrogen bonds are formed to eight adjacent complex units and eight uncoordinated water molecules. Structural details of the hydrogen bonding are given in Table 6.

The uncoordinated water molecules act as bridges in the construction of the 3D-framework of **3**, as illustrated in Fig. 3(c) (and in the ESI†). Each uncoordinated water molecule connects to four adjacent complexes of **3** through intermolecular hydrogen bonds, *via* two O–H...N(tetrazole) hydrogen bonds {O(3)–H(3a)...N(2E) and O(3)–H(3b)...N(3F)}, and two O–H...O hydrogen bonds {O(2)–H(2a)...O(3) and O(1)–H(1a)...O(3B)}.

In the crystal structure of **3**, the adjacent tetrazolate and pyridyl rings stack in an ABAB sequence along the direction parallel to the crystallographic *a* axis as shown in Fig. 3(d). The spacing between adjacent tetrazole and pyridyl rings (*ca.* 3.7 Å, centroid-centroid), lies within the acceptable range for effective π–π-stacking interaction.

Conclusions

The structures of the various 5-(pyridyl)tetrazolato-complexes of Mn^{II} described in this paper show that the coordination mode of 5-(pyridyl)tetrazolato-ligands is varied. Thus, the 5-(2-pyridyl)tetrazolato-ligand coordinates in a bidentate fashion through the pyridyl nitrogen and N¹ of the tetrazole ring, in complex (**1**). The same ligation has been observed in a tetrahedral Zn^{II} complex.^{4a} In contrast, the 5-(4-pyridyl)tetrazolato-ligand coordinates to Mn^{II} only through the pyridyl nitrogen {complex (**3**)}. Finally, the 5-(3-cyano-4-pyridyl)tetrazolato ligand can coordinate to Mn^{II} either by the cyano group or by the N²-site of the tetrazolato-residue {complex (**2**)}. Tetrazolato-ligation to Mn through the N² atom has been observed before in [Mn(CO)₃{N₄C(CF₃)}(R₂PCH₂CH₂PR₂)] (R = Et or Ph).¹⁰ Furthermore, 5-(pyridyl)tetrazolato-ligation has been observed also in coordination polymers of Zn^{II}, Cd^{II} and Sn^{IV},^{3d} in which various nitrogen atoms of the tetrazolato-ring are involved in

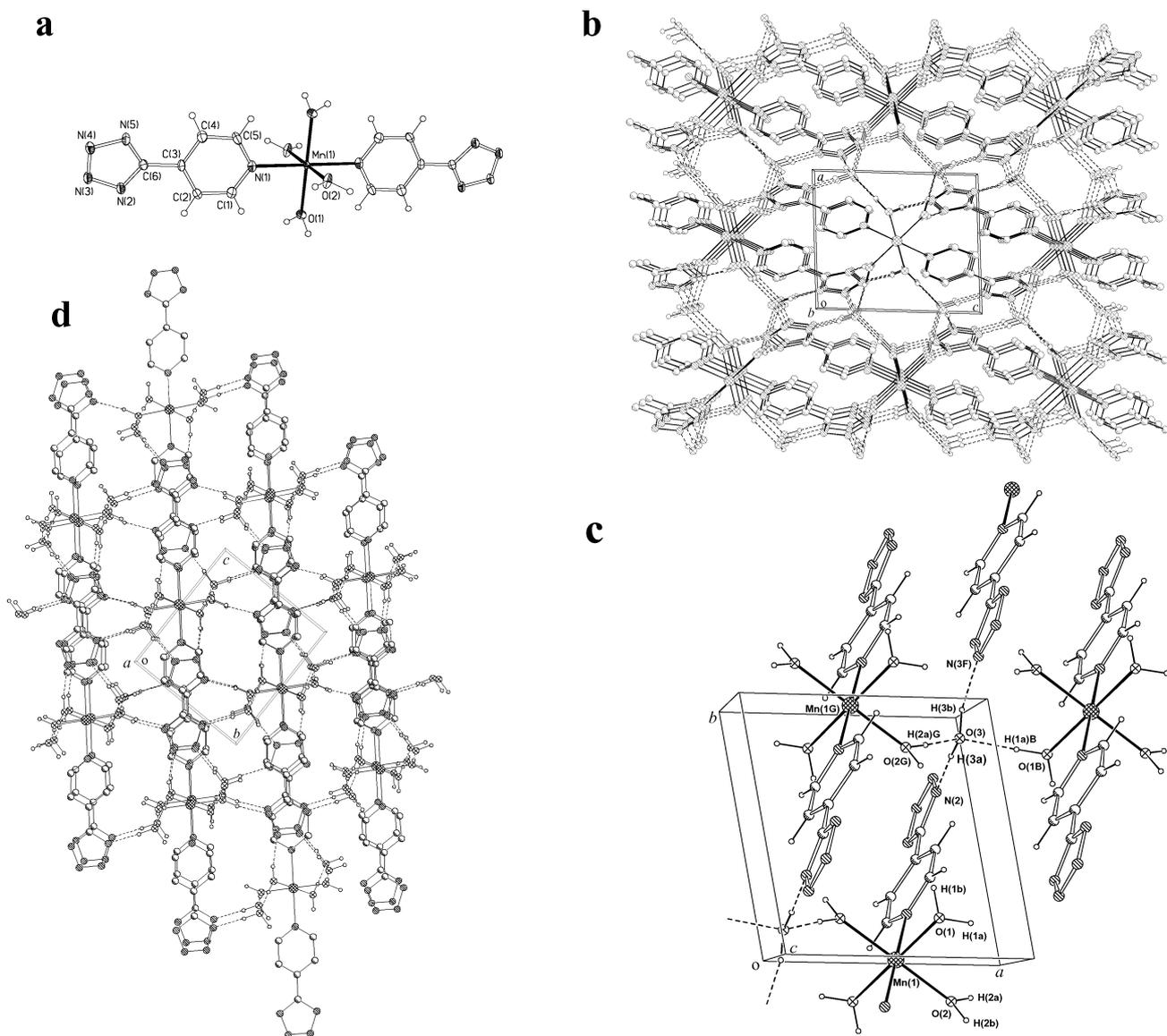


Fig. 3 Molecular structure of **3** with 50% probability displacement ellipsoids. (b) View of the crystal packing diagram of **3** along the crystallographic *b* axis, with hydrogen bonds shown dashed. Hydrogen atoms on carbons omitted. (c) Hydrogen bonding between complex molecules and uncoordinated water molecules in **3**. Additional symmetry code: G, (*x*, 1 + *y*, *z*). (d) Crystal packing diagram of **3** along the crystallographic *a* axis, with hydrogen bonds shown dashed. Hydrogen atoms on carbons omitted.

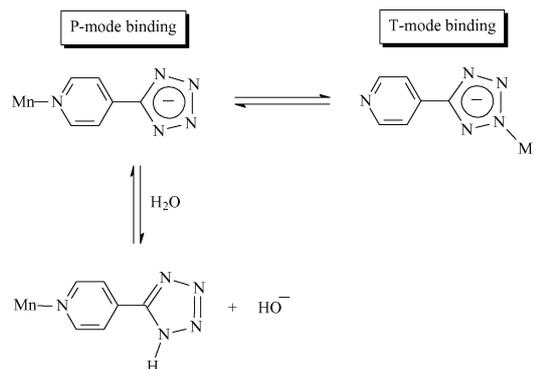
coordination to the metal centre. In the light of the structures of the Mn complexes described herein we will now briefly consider the reactions between Mn^{II} salts, cyanopyridines and NaN₃, and the nature of the species in solution.

It is a little surprising that the Mn^{II} complexes do not *catalyze* the reactions between cyanopyridines and NaN₃. Many kinetic studies on Mn^{II} complexes have established the substitution lability of Mn^{II} complexes.¹⁴ The 5-(pyridyl)tetrazolato-ligands are presumably prepared on the metal site and it might be anticipated that the lability of Mn^{II} results in this ligand dissociating from the Mn, thus regenerating a vacant site on the metal where the reaction between further cyanopyridine and NaN₃ can occur. The lack of catalysis with Mn^{II} salts indicates that dissociation of the 5-(pyridyl)tetrazole ligands is not extensive.

A further issue is the manner by which 5-(pyridyl)tetrazole coordinates to Mn in solution. A variety of different coordination modes could exist in solution, but what controls which species crystallizes from solution is solubility.

Saturated aqueous solutions of **3** are weakly basic (pH ~8, indicator paper), suggesting that slight hydrolysis of the 5-(4-pyridyl)tetrazole ligand has occurred. It is possible that the 5-(4-pyridyl)tetrazolato-ligands are bound to Mn^{II} by two binding

modes in solution: through the pyridyl ('P-mode') or the tetrazolato ('T-mode') nitrogen atoms (Scheme 2). In the 'P-mode', the tetrazolato-ring is not directly bound to Mn and it is likely that the tetrazolato-ring is sufficiently basic to be protonated. In contrast, the 'T-mode' coordinated tetrazolato-group must be appreciably less basic due to the direct coordination of the Mn to the ring, and protonation is less likely.



Scheme 2

Finally, it is interesting to note that 3,4-dicyanopyridine undergoes regioselective reaction with the azide ion in the presence of Mn^{II} at room temperature. Only the 4-cyano-group reacts with the azide, producing 5-(3-cyano-4-pyridyl)-1*H*-tetrazole (**2a**). Furthermore, **2a** is formed, even in the presence of a large (10-fold) excess of NaN_3 . Such regioselectivity opens up the potential for preparing pyridyl-substituted tetrazoles.

Experimental

All reagents were used as received from commercial sources. The C, H, N microanalyses were carried out on a Carlo Erba 1108 Elemental Analyser by the University of Newcastle upon Tyne microanalytical service. Infrared spectra (KBr pellets) were recorded on a Perkin-Elmer 598 spectrometer. ^1H NMR spectra were recorded on a Bruker Avance 300 spectrometer.

Syntheses

[Mn{5-(2-pyridyl)-tetrazolato}₂(H₂O)₂](1). $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (2 mmol), NaN_3 (4 mmol) and 2-cyanopyridine (4 mmol) were added to 30 mL mixed solvent (methanol : water, 1 : 2), then stirred at room temperature in air for 2 h. A small amount of white precipitate was generated which was removed by filtration. The filtrate (pH *ca.* 8) was slowly evaporated in air for 5 days and colourless plate-like crystals of **1** were obtained (0.41 g; 54% yield based on Mn). Crystals of **1** are slightly soluble in methanol or water and insoluble in ethyl acetate. Anal. Calc. for $\text{C}_{12}\text{H}_{12}\text{MnN}_{10}\text{O}_2$ (**1**): C, 37.61; H, 3.16; N, 36.55. Found: C, 37.63; H, 3.18; N, 36.56%. IR/ cm^{-1} : 3051w, 1608s, 1569m, 1465m, 1441s, 1291m, 1168m, 1058m, 1033m, 804s, 756s, 731s, 718m, 683m, 639m.

[Mn{5-(3-cyano-4-pyridyl)tetrazolato}₂(H₂O)₃(MeOH)](2). The procedure is identical to that of **1** except that 4 mmol of pyridine-3,4-dicarbonitrile was used in place of 2-cyanopyridine. In this case, 8 mmol NaN_3 was used and the stirring time increased to 4 h. The filtrate (pH 8–9) was slowly evaporated in air for 9 days and colourless crystals of **2** were obtained (0.50 g, 52% yield based on Mn). **2** is soluble in methanol, slightly soluble in water and insoluble in ethyl acetate. Anal. Calc. for $\text{C}_{15}\text{H}_{16}\text{MnN}_{12}\text{O}_4$ (**2**): C, 37.28; H, 3.34; N, 34.78. Found: C, 37.31; H, 3.35; N, 34.80%. IR/ cm^{-1} : 3062w, 2239m, 1701m, 1608s, 1558m, 1447s, 1399m, 1372m, 1217m, 1195m, 1067s, 854m, 812s, 726s, 691s, 591m.

[Mn{5-(4-pyridyl)-tetrazolato}₂(H₂O)₁·2H₂O(3). This was prepared as for **1**, with 4-cyanopyridine used in place of 2-cyanopyridine. The filtrate (pH *ca.* 9) was slowly evaporated in air for one week and colourless needle-like crystals of **3** were obtained (0.44 g, 48% yield based on Mn). **3** is soluble in methanol, slightly soluble in water and insoluble in ethyl acetate. Anal. Calc. for $\text{C}_{12}\text{H}_{20}\text{MnN}_{10}\text{O}_6$ (**3**): C, 31.64; H, 4.43; N, 30.77. Found: C, 31.62; H, 4.45; N, 30.74%. IR/ cm^{-1} : 3078w, 1685w, 1624s, 1562m, 1447m, 1432s, 1378m, 1221m, 1157m, 1014s, 878m, 837m, 752m, 730m, 712s, 665m, 650m, 631m.

5-(2-pyridyl)-1*H*-tetrazole (1a). The procedure is similar to that of **1** but the generated precipitate was not removed after the mixture solution was stirred for 3 h. The solvent was removed *in vacuo* and the resulting solid powder washed with 10 mL ethyl acetate to remove any unreacted 2-cyanopyridine. The crude solid product {containing Mn–(2-PTZ) complex and inorganic salts} was added to 10 mL water with stirring, and then the pH of the aqueous solution (containing a white precipitate) adjusted to *ca.* 4.0 using 3 M HCl. Upon acidification, the original precipitate dissolved and another precipitate was produced. Ethyl acetate (30 mL) was added to the mixture and stirred vigorously until no solid was present. The organic layer was separated and the aqueous layer extracted again with a further 30 mL of ethyl acetate. The ethyl acetate from the combined extracts was removed *in vacuo*, and the colourless microcrystals

talline 5-(2-pyridyl)-1*H*-tetrazole 0.27 g (yield 46% based on 2-cyanopyridine) was produced. Anal. Calc. for $\text{C}_6\text{H}_5\text{N}_5$ (**1a**): C, 48.98; H, 3.43; N, 47.60. Found: C, 48.93; H, 3.48; N, 47.58%. IR/ cm^{-1} : 3090w, 3064w, 1747w, 1639w, 1603m, 1559s, 1485s, 1450s, 1401m, 1384m, 1285m, 1261m, 1159m, 1069m, 1025s, 949m, 795s, 743s, 704m, 631m. ^1H NMR (DMSO-*d*₆ solvent): 8.86 (m, 1H), 8.28 (m, 1H), 8.14 (m, 1H), 7.70 (m, 1H).

5-(3-cyano-4-pyridyl)-1*H*-tetrazole (2a)

Method A. This was prepared as for **1a**, and 4 mmol pyridine-3,4-dicarbonitrile and 4 mmol NaN_3 were used. Yield: 0.38g, 56% based on pyridine-3,4-dicarbonitrile. Anal. Calc. for $\text{C}_7\text{H}_4\text{N}_6$ (**2a**): C, 48.84; H, 2.34; N, 48.82. Found: C, 48.79; H, 2.37; N, 48.78%. IR/ cm^{-1} : 3058w, 3024w, 2239m, 1738w, 1577s, 1548m, 1480s, 1403s, 1262m, 1215m, 1189m, 1043s, 865s, 817s, 743m, 587m. ^1H NMR (DMSO-*d*₆ solvent): 9.42 (s, 1H), 9.18 (d, 1H, *J* = 5.1 Hz), 8.27 (d, 1H, *J* = 5.1 Hz).

Method B: Similar to Method A, but 4 mmol pyridine-3,4-dicarbonitrile and 10 mmol NaN_3 were used (yield 0.40 g, 58% based on pyridine-3,4-dicarbonitrile). Microanalyses, infrared and ^1H NMR spectra confirm the identity of the product.

5-(4-pyridyl)-1*H*-tetrazole (3a)

Method A. This was prepared as for **1a**. Yield: 0.28 g, 48% based on 4-cyanopyridine. Anal. Calc. for $\text{C}_6\text{H}_5\text{N}_5$ (**3a**): C, 48.98; H, 3.43; N, 47.60. Found: C, 48.92; H, 3.47; N, 47.56%. IR (KBr pellet)/ cm^{-1} : 3084w, 3028w, 2968w, 1720w, 1594s, 1544s, 1498s, 1414s, 1384m, 1262m, 1206m, 991m, 937w, 779s, 747m, 664m. ^1H NMR (DMSO-*d*₆ solvent): 8.87 (d, 2H, *J* = 6.0 Hz), 7.88 (d, 2H, *J* = 6.0 Hz).

Method B. Similar to Method A, but the reaction solution was heated at 60 °C for 3 h (yield: 0.44 g, 74% based on 4-cyanopyridine). Microanalyses, infrared and ^1H NMR spectra confirm the identity of the product.

Investigation of Catalysis by Mn^{II}. $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.1 g, 0.4 mmol), NaN_3 (0.26 g, 4 mmol) and 4-cyanopyridine (0.416 g, 4 mmol) were added to 30 mL of mixed solvent (methanol : water, 1 : 2), and stirred at room temperature for 24 h. The methanol in the solution was removed *in vacuo* and then the pH of the solution was adjusted to *ca.* 4.0 using 3 M HCl. Upon acidification, ethyl acetate (30 mL) was added to the mixture and stirred vigorously. The organic layer was separated and the aqueous layer extracted again with another 30 mL ethyl acetate. The ethyl acetate from the combined extracts was removed *in vacuo*, and 0.32 g of white powder produced. The powder product was characterised by ^1H NMR spectroscopy; this indicated it is a mixture containing *ca.* 15% of 5-(4-pyridyl)-1*H*-tetrazole and 85% of 4-cyanopyridine.

It should be noted that 5-(4-pyridyl)-1*H*-tetrazole is more soluble in water than 4-cyanopyridine. Consequently, the amount of 5-(4-pyridyl)-1*H*-tetrazole in the reaction mixture prior to workup could be somewhat higher than 15 : 85.

X-Ray crystallography

X-Ray diffraction studies of crystals **1** (size 0.30 × 0.30 × 0.10 mm³) and **3** (size 0.22 × 0.20 × 0.14 mm³) were performed on a Bruker SMART CCD area diffractometer, using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Due to size limitations, data for **2** (size 0.04 × 0.04 × 0.04 mm³) were collected at station 9.8 of the SRS, Daresbury ($\lambda = 0.6948 \text{ \AA}$). Crystal data and other experimental information are given in Table 7, with further details in the ESI†. Semi-empirical absorption corrections, based on repeated and symmetry-equivalent reflections.¹⁵ The structures were solved by direct methods and refined by full-matrix least-squares on all unique F^2 values.¹⁶ Anisotropic displacement parameters were assigned to all the non-hydrogen atoms. In all three cases the hydrogen atoms on oxygen were refined with the O–H bond lengths restrained to 0.84(3) Å; the hydrogen atoms on carbon were placed in idealized positions and allowed to ride on their respective parent atoms.

Table 7 Crystal data and structure refinement parameters for compounds **1**, **2** and **3**

| | 1 | 2 | 3 |
|---|--|--|---|
| Formula | C ₁₂ H ₁₂ MnN ₁₀ O ₂ | C ₁₅ H ₁₆ MnN ₁₂ O ₄ | C ₁₂ H ₁₆ MnN ₁₀ O ₄ ·2H ₂ O |
| <i>M</i> _r | 383.3 | 483.3 | 455.3 |
| Crystal system | Monoclinic | Monoclinic | Triclinic |
| Space group | <i>P</i> 2 ₁ / <i>c</i> | <i>P</i> 2 ₁ / <i>n</i> | <i>P</i> $\bar{1}$ |
| <i>T</i> /K | 150 | 120 | 160 |
| <i>a</i> /Å | 8.0643(10) | 7.1817(17) | 7.3932(7) |
| <i>b</i> /Å | 13.0693(16) | 21.684(5) | 7.8646(7) |
| <i>c</i> /Å | 7.3767(9) | 12.347(3) | 8.5723(8) |
| <i>a</i> /° | | | 91.007(2) |
| <i>β</i> /° | 97.560(2) | 94.789(7) | 93.011(2) |
| <i>γ</i> /° | | | 100.789(2) |
| <i>V</i> /Å ³ | 770.71(16) | 1916.1(8) | 488.76(8) |
| <i>Z</i> | 2 | 4 | 1 |
| <i>μ</i> (Mo-Kα)/mm ⁻¹ | 0.889 | 0.745 | 0.729 |
| Reflections collected | 5268 | 7894 | 3283 |
| Independent reflections, <i>R</i> _{int} | 1361, 0.0393 | 4852, 0.0379 | 1537, 0.0344 |
| Refined parameters | 124 | 318 | 158 |
| <i>R</i> (<i>F</i> ² > 2σ) | 0.0324 | 0.0414 | 0.0407 |
| <i>R</i> _w (<i>F</i> ² , all data) | 0.0709 | 0.1086 | 0.0894 |
| GOF on <i>F</i> ² | 1.147 | 1.023 | 1.166 |
| Max, min electron density/e Å ⁻³ | 0.24, -0.32 | 0.48, -0.37 | 0.28, -0.41 |

CCDC reference numbers 222433–222435.

See <http://dx.doi.org/10.1039/b505077d> for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the EPSRC (U.K.) for equipment funding. P. L. acknowledges a studentship from the University of Newcastle. The crystallographic data for **2** were obtained through the EPSRC-funded national synchrotron service, with beamtime awarded by CCLRC.

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