One-Dimensional Chains Formed by First-Row Transition Metal(II) Nitrates and Pyrimidine – Influence of Water Coordination on Structural Reliability

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Keywords: Coordination frameworks / Coordination polymer / Crystal structure / Metal nitrates / Pyrimidine

An isostructural family of one-dimensional coordination polymers, $[M(NO_3)_2(pym)(H_2O)_2]_\infty$ [M = Mn (**1**), Co (**2**), Ni (**3**), Zn (**4**); pym = pyrimidine], has been prepared and their phase purity assessed. It is shown that in contrast to other $M(NO_3)_2$–pyrimidine coordination polymers, **1**–**4** show a surprising preference for the structure reported herein rather the wide variety of other possible product architectures. It is also shown that a related complex $[Ni(NO_3)_2(pym)(MeCN)_2]_\infty$ (**5**), in which water ligands observed in **1**–**4** are replaced by MeCN molecules, can also be prepared. However, **5** is highly hygroscopic and readily converts to **3** in the presence of atmospheric water. The implication of the uniformity of structure is discussed in relation to the serendipitous coordination of water molecules to the metal centres.

Introduction

The construction of coordination frameworks is an extremely topical area of inorganic and materials chemistry.[1] The strong interest in this area arises because the synthetic procedure used to construct these materials allows, in principle, a high degree of design. New materials with tuneable properties have been developed from coordination frameworks over recent years and as synthetic procedures become more advanced so the properties of these materials become more highly evolved.[1] The targeted synthesis of coordination polymers requires an appreciation of not only the variety of possible coordination framework materials that can be prepared, but also an appreciation of which structures are more favourable. An assessment of phase purity of coordination polymers is both valuable from the point of view of material properties, but also gives insight into the structural reliability[2] of a given set of starting building-blocks. We,[3,4] amongst others,[5] have been interested in the use of $M(NO_3)_2$ species as building blocks in coordination polymer construction due to their structural diversity that gives rise to a variety of fascinating coordination framework architectures. We have previously commented on the lack of structural reliability of $M(NO_3)_2$ as a coordination polymer node, and in general they can be viewed as structurally unreliable due to the large number of metal nodes that are generated from such species, but also because of the variety of coordination frameworks that can be generated even when the same $M(NO_3)_2$ node configuration is adopted.[2,3]

Herein, we report a family of isostructural one-dimensional coordination polymers, $[M(NO_3)_2(pym)(H_2O)_2]_\infty$ [M = Mn (**1**), Co (**2**), Ni (**3**), Zn (**4**)], which interestingly form a single phase under the conditions of synthesis used. The serendipitous coordination of water molecules to the metal centres leads to the formation of a hydrogen-bonded array that may contribute to the favourable formation of the observed product.

Results and Discussion

Reaction of $M(NO_3)_2 \cdot xH_2O$ salts [M = Mn (**1**), Co (**2**), Ni (**3**), Zn (**4**)] dissolved in either MeCN or *i*PrOH with a solution of pyrimidine (pym) in CH_2Cl_2 leads to the formation of insoluble precipitates which are found to have the stoichiometry $[M(NO_3)_2(pym)(H_2O)_2]_\infty$ by elemental analysis. In the case of $Ni(NO_3)_2$ with pym in CH_2Cl_2/MeCN an alternative product $[Ni(NO_3)_2(pym)(MeCN)_2]_\infty$ (**5**) can also be isolated but readily undergoes conversion to **3** in the presence of atmospheric moisture. Single crystals were grown by slow diffusion of the layered solutions of the metal salt and pyrimidine in their respective solvents.

Structural characterisation of **1**–**4** by single-crystal X-ray diffraction showed the formation of one-dimensional coordination polymers with the formula $[M(NO_3)_2(pym)(H_2O)_2]_\infty$. All four compounds are isostructural and crystallize in the space groups *I*2/*a* [non-standard setting of *C*2/*c* (no. 15)]. Each M^{II} centre is pseudo-octahedral and coordinated by two pyrimidine ligands, two η^1-nitrate anions and two water molecules (Figure 1; Table 1). The bridging nature of the pyrimidine ligand results in the formation of a one-dimensional zigzag chain, which is achiral, and runs parallel to the *c* axis (Figure 2).

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Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

DOI: 10.1002/ejic.200401035

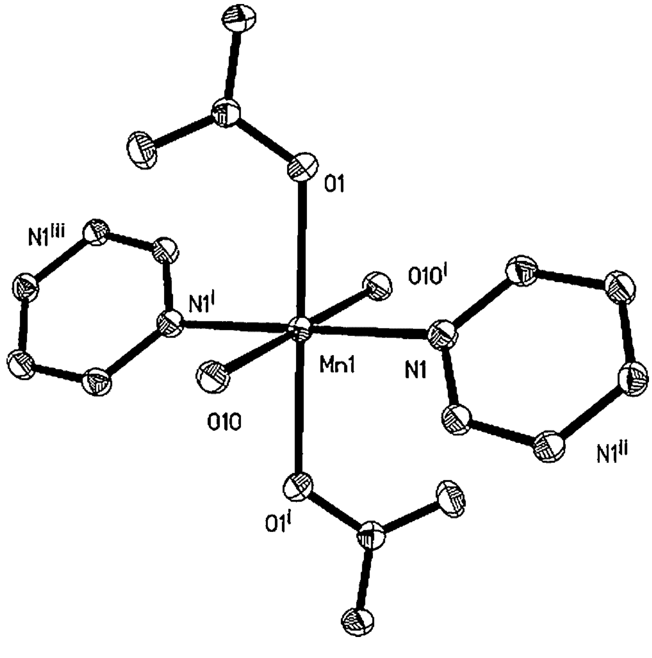

Figure 1. The Mn^{II} coordination environment observed in $[Mn(NO_3)_2(pym)(H_2O)_2]_\infty$ (**1**) showing the numbering scheme used. An analogous numbering scheme was used for compounds **2**–**4**. Displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Symmetry codes: (i) $-x + 1/2, -y + 3/2, -z + 1/2$; (ii) $-x + 1/2, y, -z$; (iii) $x, -y + 3/2, z + 1/2$.

Table 1. Selected bond lengths [Å] and angles [°] for $[M(NO_3)_2(pym)(H_2O)_2]_\infty$ [M = Mn (**1**), Co (**2**), Ni (**3**), Zn (**4**)].

1		**2**	
Mn1–N1	2.2695(11)	Co1–N1	2.1451(13)
Mn1–O1	2.2129(10)	Co1–O1	2.1413(11)
Mn1–O10	2.1742(10)	Co1–O10	2.0773(11)
N1–Mn1–O1	86.00(4)	N1–Co1–O1	86.01(5)
N1–Mn1–O10	87.12(4)	N1–Co1–O10	87.50(5)
O1–Mn1–O10	98.96(4)	O1–Co1–O10	97.85(5)
3		**4**	
Ni1–N1	2.0826(18)	Zn1–N1	2.1318(10)
Ni1–O1	2.0786(16)	Zn1–O1	2.1542(8)
Ni1–O10	2.0624(16)	Zn1–O10	2.1021(8)
N1–Ni1–O1	86.71(7)	N1–Zn1–O1	86.54(3)
N1–Ni1–O10	86.95(7)	N1–Zn1–O10	92.77(4)
O1–Ni1–O10	96.96(7)	O1–Zn1–O10	82.24(3)
5			
Ni1–N1	2.105(3)		
Ni1–O1	2.085(2)		
Ni1–N1S	2.062(3)		
N1–Ni1–O1	89.77(10)		
N1–Ni1–N1S	90.22(11)		
O1–Ni1–N1S	83.22(11)		

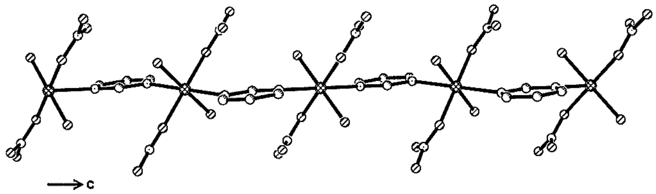

Figure 2. The one-dimensional chain formed by $[Mn(NO_3)_2(pym)(H_2O)_2]_\infty$ (**1**). Compounds **2**–**4** form analogous chains. Mn cross hatch; N dotted; O left hatch.

In addition to these coordination bonds, however, extensive hydrogen bonding interactions are observed within the structure (Figure 3). These occur between the hydrogen atoms of the coordinated water molecules and the oxygen atoms of the nitrate anions on adjacent chains. Both of the hydrogen atoms of each water molecule participate in a hydrogen bond. However, only one oxygen atom of any given nitrate anion is involved in hydrogen bonding and, in fact, interacts with two hydrogen atoms from separate, symmetry-equivalent, water molecules. Two crystallographically distinct types of $OH\cdots O(NO_3)$ hydrogen bonds are observed (Table 2); one type links $[M(NO_3)_2(pym)(H_2O)_2]_\infty$ chains parallel to the *a* axis and the second links chains in the direction of the *b* axis. Thus, the hydrogen-bonding interactions form an undulating two-dimensional hydrogen-bonded sheet parallel to the *ab* plane. Each metal node is connected to six adjacent nodes within the sheet using a total of eight hydrogen bonds, utilising all four water hydrogen atoms (two for each H_2O), and both coordinated NO_3^- anions participating in two hydrogen bonds each. These hydrogen-bonded sheets are then crosslinked by the pyrimidine ligands into a three-dimensional network of $3^6.4^{18}.5^3.6$ topology (Figure 4).

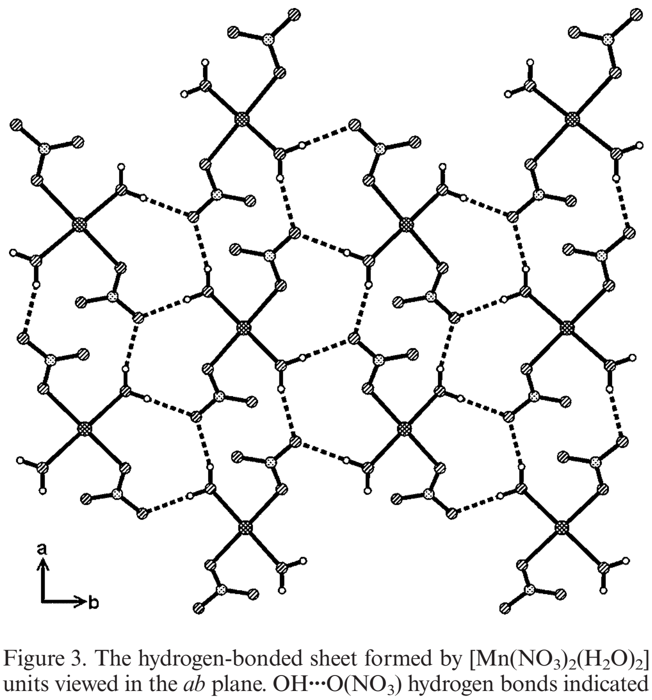

Figure 3. The hydrogen-bonded sheet formed by $[Mn(NO_3)_2(H_2O)_2]$ units viewed in the *ab* plane. $OH\cdots O(NO_3)$ hydrogen bonds indicated by dashed lines. Mn cross hatch; N dotted; O left hatch.

A single-crystal diffraction study of **5** revealed a highly related structure to that observed in **1**–**4**. Thus, each Ni^{II} centre is pseudo-octahedral and coordinated by two pyrimidine ligands, two η^1-nitrate anions and two MeCN molecules replacing the water ligands present in **1**–**4** (Figure 5; Table 1). In the absence of the water ligands no interchain

Table 2. Bonding interactions observed for $[M(NO_3)_2(pym)(H_2O)_2]_\infty$ **1**–**4**.

Compound		H···O distance [Å]	O···O distance [Å]	O–H···O angle [°]
1	O10–H10A···O2^{i}	1.98(1)	2.792(2)	166(2)
	O10–H10B···O2^{ii}	1.96(1)	2.791(2)	175(2)
2	O10–H10A···O3^{ii}	1.96(1)	2.777(2)	174(2)
	O10–H10B···O3^{iii}	1.99(1)	2.795(2)	163(2)
3	O10–H10A···O2^{ii}	1.95(1)	2.778(2)	176(2)
	O10–H10B···O2^{iii}	2.00(3)	2.811(2)	165(2)
4	O10–H10A···O3^{iv}	1.99(2)	2.800(1)	164(2)
	O10–H10B···O3^{v}	1.95(1)	2.784(1)	176(2)

Symmetry transformations used to generate equivalent atoms: (i) $-x - 1/2, -y + 3/2, -z + 1/2$; (ii) $-x, y + 1/2, -z + 1/2$; (iii) $-x - 1/2, -y + 1/2, -z + 1/2$; (iv) $x, y, z - 1$; (v) $x, -y + 1, -z - 1/2$

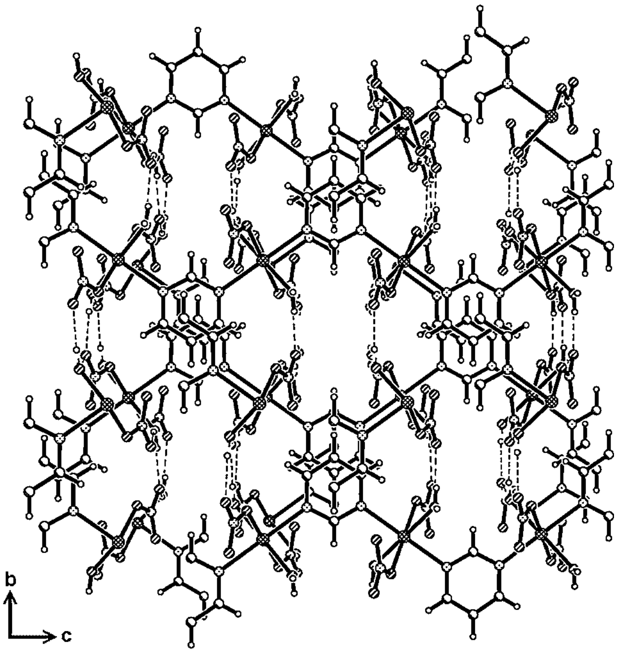

Figure 4. A view of the three-dimensional structure formed by $[Mn(NO_3)_2(pym)(H_2O)_2]_\infty$. Mn cross hatch; N dotted; O left hatch.

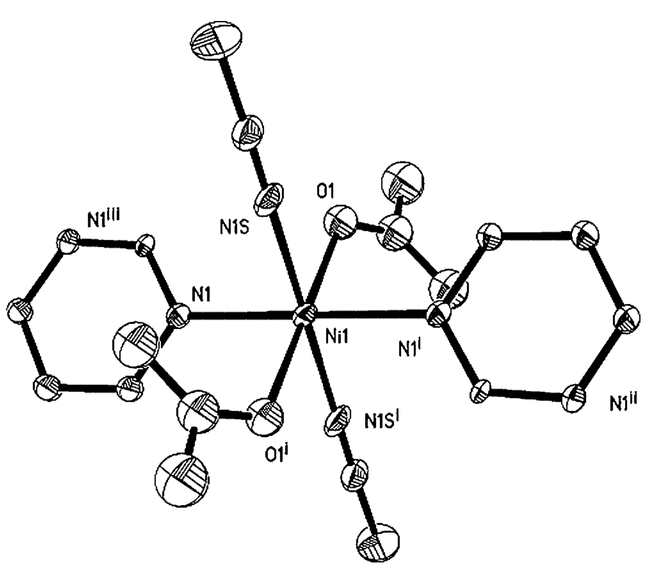

Figure 5. The Ni^{II} coordination environment observed in $\{[Ni(NO_3)_2(pym)(MeCN)_2](MeCN)\}_\infty$ (**5**) showing the numbering scheme used. Displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $x, -y, -1/2 + z$; (iii) $-x, y, 3/2 - z$.

hydrogen bonds are observed and therefore the extended structure observed in **1**–**4** is not present in **5**.

In order that phase purity of these products could be assessed, bulk samples of **1**–**4** were prepared. This is particularly important in the case of metal(II) nitrate bridging N-donor coordination polymers due to the wide variations previously observed in the products of such compounds.[3] Powders were prepared initially by L/M starting ratios of 1:1 in either an $MeCN/CH_2Cl_2$ (**1**, **2**, **4**) or an *i*PrOH/CH_2Cl_2 (**3**) solvent mixture. On comparing the results of X-ray powder diffraction with the calculated powder diffraction patterns using the single-crystal X-ray data, all the samples were confirmed to be pure single phases of the respective complexes (see Figure 6 for example).

The reaction of $Ni(NO_3)_2$ with pym in $MeCN/CH_2Cl_2$ affords crystals of both **3** and **5**. Indeed isolation of samples that contain **5** is difficult as this species proves to be highly hygroscopic, rapidly taking up atmospheric moisture and converting to **3**. All attempts to prepare bulk samples of **5** or to observe its presence in bulk samples of the reaction

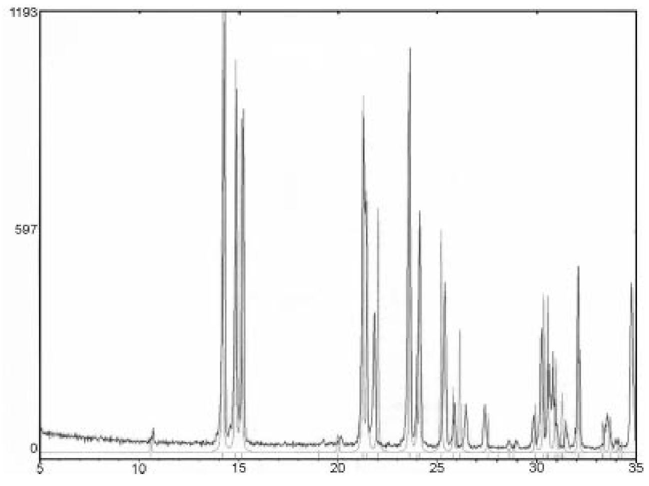

Figure 6. Comparison of the powder diffraction pattern recorded for the bulk product (black line) and that calculated from the single-crystal X-ray diffraction data (grey line) for $[Mn(NO_3)_2(pym)(H_2O)_2]_\infty$ (**1**).

products were unsuccessful with only identification of pure samples of **3**.

The structure of **1**–**4** observed here has been previously observed in the products of the reactions of other transition metal salts with pyrimidine. Indeed, compounds isostructural with **1**–**4** have previously been observed for $[Cu(NO_3)_2(pym)(H_2O)_2]_\infty$[6] and $[Cd(NO_3)_2(pym)(H_2O)_2]_\infty$.[7] However, it is worth noting that in the case of $Cu(NO_3)_2$ and $Cd(NO_3)_2$ other products with pyrimidine[8,9] are also observed indicating that these metal centres are perhaps less predictable in their behaviour than the transition metal salts reported here. The lack of structural predictability is not particular surprising for either $Cu(NO_3)_2$ or $Cd(NO_3)_2$ considering the Jahn–Teller distortion expected for Cu^{II} and the highly malleable coordination sphere of Cd^{II}.[2,3] Indeed, it is perhaps more surprising that such a uniform, isostructural family of compounds are observed for the system reported here. The uniformity of product clearly reflects the greater stability of this product in comparison to other hypothetical competing structures, but also may be attributed, in part, to the coordination of water molecules to the metal centres in **1**–**4**, which arises due to the use of hydrated $M(NO_3)_2$ starting reagents. The coordination of water molecules to the metal centres has two major effects on the resultant coordination polymer structure. Firstly, by occupying two of the coordination sites of the metal centre the number of pyrimidine ligands that can be coordinated and subsequently bridge metal centres is restricted leading to the formation of the one-dimensional chains that are observed. Secondly, the ability of water to act as a hydrogen-bond donor allows the formation of hydrogen-bonding interactions between adjacent chains undoubtedly strengthening the formation of the observed structure. The relative stability of the structure observed in **1**–**4** is further indicated by the rapid conversion of **5** to **3** by replacement of the MeCN ligands in **5** by water molecules.

In summary, a family of one-dimensional coordination polymers has been prepared and their phase purity assessed. The implications of the uniformity of structure observed have been discussed, and it can be concluded that the preferential formation of the observed products can be attributed, at least in part, to the serendipitous coordination of water molecules to the metal centres.

Experimental Section

General: Infrared spectra were measured as KBr disks with 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 with a Perkin–Elmer 240B analyser. Powder X-ray diffraction patterns (PXD) data were collected with 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 $5° \leq 2\theta \leq 80°$ with step size $2\theta = 0.02°$ and times per step of 0.65 s. The simulated powder pattern was generated using the PC software packages APD, part of the Philips software package and POWDERCELL,[10] taking the single-crystal structural data for the compound as a model. For details see Supporting information (see footnote on the first page of this article). All chemicals were purchased from Aldrich Chemicals and used without further purification. All single-crystal X-ray experiments were performed with either a Bruker AXS SMART1000 CCD detector diffractometer (**1**–**5**) equipped with an Oxford Cryosystems open flow cryostat[11] [graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å); ω scans] or with an Enraf–Nonius FAST TV Detector diffractometer [graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å)] (**3**). Absorption corrections were applied by a semi-empirical approach (**1**, **2**, **4**, **5**). Other details of crystal data, data collection and processing are given in Table 3. CCDC-258503 (**1**), -258504 (**2**), -258505 (**3**), -258506 (**4**), -258507 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. All of the single-crystal structures were solved by direct methods using SHELXS-97[12] and all non-hydrogen atoms were located using subsequent difference-Fourier methods.[13] In all cases, hydrogen atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms, except for water hydrogen atoms which were located from the difference Fourier map. The water hydrogen atoms were refined, with suitable O–H and H···H distance re-

Table 3. Crystallographic data for $[M(NO_3)_2(pym)(H_2O)_2]_\infty$ [M = Mn (**1**), Co (**2**), Ni (**3**), Zn (**4**)] and $\{[Ni(NO_3)_2(pym)(MeCN)_2](MeCN)\}_\infty$ (**5**).

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_4H_8MnN_4O_8$	$C_4H_8CoN_4O_8$	$C_4H_8N_4NiO_8$	$C_4H_8N_4O_8Zn$	$C_{10}H_{13}N_7NiO_6$
M	295.08	299.07	298.85	305.51	385.98
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*I*2/*a*	*I*2/*a*	*I*2/*a*	*I*2/*a*	*C*2/*c*
a [Å]	7.483(3)	7.4070(8)	7.3847(4)	7.4390(6)	21.548(4)
b [Å]	11.702(4)	11.5742(12)	11.4970(5)	11.5804(9)	7.0879(15)
c [Å]	12.105(4)	11.8183(12)	11.6481(4)	11.7508(8)	11.983(2)
B [°]	99.755	99,227(2)	99.125(2)	99.699(4)	117.697(3)
Z	4	4	4	4	4
T [K]	150(2)	150(2)	150(2)	150(2)	150(2)
μ [mm^{-1}]	1.305	1.760	2.032	2.505	1.240
Reflections collected	3011	3179	6117	5083	14462
Unique reflections (R_{int})	1273 (0.017)	1248 (0.022)	1108 (0.065)	1208 (0.018)	1937(0.051)
Final R_1 [$F > 4\sigma(F)$]	0.0192	0.0241	0.0333	0.0172	0.0631
wR_2 (all data)	0.0539	0.0571	0.0715	0.0486	0.1796

straints. During the refinement of the structure of **5** a region of poorly defined solvent was accounted for using SQUEEZE,[14] which calculated 87 electrons per unit cell, approximating to 4 molecules of MeCN (88 electrons) which were included in the formula. One oxygen atom and the nitrogen atom of the nitrate anion showed disorder and were modelled isotropically over two sites with occupancies 0.6 and 0.4. A large peak of residual electron density remained in a chemically nonsensical position. This may be due to some form of twinning, however, the original data all indexed cleanly using the assigned cell and application of various twin laws did not result in any improvement.

$[Mn(NO_3)_2(pym)H_2O)_2]_\infty$ (1): A solution of $Mn(NO_3)_2\cdot xH_2O$ (224 mg, 0.83 mmol) in MeCN (15 cm^3) was added to a solution of pym (67 mg, 0.83 mmol) in CH_2Cl_2 (2 cm^3). The colourless crystals which formed over a 24 h period were filtered off and dried in vacuo. Yield 70% (171 mg). $C_4H_8MnN_4O_8$ (295.1): calcd. C 16.28, H 2.74, N 18.99; found C 16.21, H 2.60, N 18.66. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3423 w, 3109 w, 3074 w, 1763 w, 1594 s, 1568 w, 1467 s, 1389 s, 1221 m, 1177 m, 1144 w, 1078 s, 1024 m, 825 m, 805 w, 694 s, 656 m. Crystals suitable for single-crystal X-ray diffraction were grown as above.

$[Co(NO_3)_2(pym)(H_2O)_2]_\infty$ (2): A solution of $Co(NO_3)_2\cdot 6H_2O$ (315 mg, 1.08 mmol) in MeCN (15 cm^3) was added to a solution of pym (87 mg, 1.08 mmol) in CH_2Cl_2 (2 cm^3). The dark pink precipitate was filtered off and dried in vacuo. Yield 87% (281 mg). $C_4H_8CoN_4O_8$ (299.1): calcd. C 16.06, H 2.70, N 18.74; found C 16.08, H 2.60, N 18.62. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3416 m, 3112 w, 3084 w, 1763 w, 1630 w, 1596 s, 1568 w, 1466 s, 1383 s, 1221 m, 1180 m, 1145 w, 1082 m, 1028 m, 825 m, 802 w, 691 s, 663 m. Single crystals were grown by slow diffusion of layered solutions of $Co(NO_3)_2\cdot 6H_2O$ in MeCN over pym in CH_2Cl_2.

$[Ni(NO_3)_2(pym)(H_2O)_2]_\infty$ (3): A solution of $Ni(NO_3)_2\cdot 6H_2O$ (240 mg, 0.83 mmol) in *i*PrOH (15 cm^3) was added to a solution of pym (66 mg, 0.83 mmol) in CH_2Cl_2 (2 cm^3). The light blue precipitate was filtered off and dried in vacuo. Yield 94% (233 mg). $C_4H_8N_4NiO_8$ (298.8): calcd. C 16.08, H 2.70, N 18.75; found C 16.10, H 2.65, N 18.31. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3405 m, 3118 w, 3091 w, 1767 w, 1636 w, 1597 s, 1570 w, 1467 m, 1386 s, 1221 w, 1182 m, 1145 w, 1085 m, 1048 w, 1031 w, 833 m, 801 w, 692 m, 666 m. Single crystals were grown by slow diffusion of layered solutions of $Ni(NO_3)_2\cdot 6H_2O$ in *i*PrOH over pym in CH_2Cl_2.

$[Zn(NO_3)_2(pym)(H_2O)_2]_\infty$ (4): A solution of $Zn(NO_3)_2\cdot 6H_2O$ (133 mg, 0.45 mmol) in MeCN (15 cm^3) was added to a solution of pym (36 mg, 0.45 mmol) in CH_2Cl_2 (2 cm^3). The colourless crystals that formed over a 24 hour period were filtered off and dried in vacuo. Yield 64% (88 mg). $C_4H_8N_4O_8Zn$ (305.5): calcd. C 15.73, H 2.65, N 18.35; found C 15.73, H 2.54, N 18.00. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3449 w, 3111 w, 1763 w, 1597 s, 1570 w, 1466 m, 1385 s, 1221 w, 1180 w, 1146 w, 1082 m, 1028 w, 825 m, 801 w, 690 s, 661 m. Crystals suitable for single-crystal X-ray diffraction were grown as above.

$[Ni(NO_3)_2(pym)(MeCN)_2]_\infty$ (5): A solution of $Ni(NO_3)_2\cdot 6H_2O$ (101 mg, 0.35 mmol) in MeCN (10 cm^3) was added to a solution of pym (28 mg, 0.35 mmol) in CH_2Cl_2 (2 cm^3). The light blue precipitate was filtered off and dried in vacuo. Yield ca. 60% (ca. 70 mg). CHN elemental analysis, powder X-ray diffraction and IR spectroscopic studies confirmed that **5** rapidly converted to **3** on exposure to atmospheric moisture. Single crystals were grown by slow diffusion of layered solutions of $Ni(NO_3)_2\cdot 6H_2O$ in MeCN over pym in CH_2Cl_2. Crystals were rapidly transferred from the reaction solution into drops of oil prior to data collection.

Acknowledgments

We would like to thank the EPSRC for support (S. A. B.). We acknowledge the use of the EPSRC National Service for Crystallography at the University of Southampton.

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Received: December 16, 2004