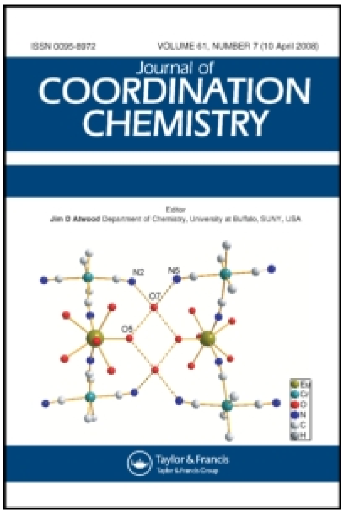

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Synthesis and crystal structure of two metal complexes involving reduced imino nitroxides

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Synthesis and crystal structure of two metal complexes involving reduced imino nitroxides

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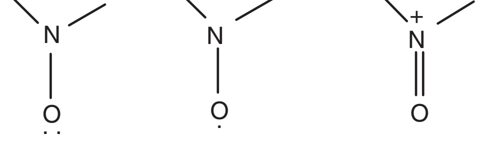
Two novel complexes, $[Co(mal)(IMH2py)_2]ClO_4$ (**1**) and $[Mn(mal)(IMH2py)_2]\cdot H_2O$ (**2**), have been synthesized and their crystal structures determined by X-ray diffraction methods. The imino nitroxide 1-oxy-2-(2′-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole (IM2py) is reduced during reaction to yield 1-hydroxy-2(2′-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole (IMH2py); mal is the malonate anion. Complexes **1** and **2** crystallize in the monoclinic space group *C*2 space group with $a = 17.004(9)$, $b = 10.753(5)$, $c = 9.207(5)$ Å, $\beta = 113.856(8)^\circ$ and $Z = 2$ for **1**, and $a = 16.721(5)$, $b = 10.897(5)$, $c = 9.253(3)$ Å, $\beta = 120.807(6)^\circ$ and $Z = 2$ for **2**. Each metal ion is six-coordinated by two imino nitrogen atoms of two imino-hydroxylamine groups, two nitrogen atoms of two pyridyl groups and two oxygen atoms of the malonate ion.

Keywords: Reduced imino nitroxide radical; Malonate; Crystal structure

1. Introduction

Imino nitroxide radicals have played a prominent role in the design and construction of molecular magnetic materials [1–4]. Nitronyl free radicals have an oxidation state intermediate between those of the hydroxylamino anion and the nitrosonium cation, as shown below,



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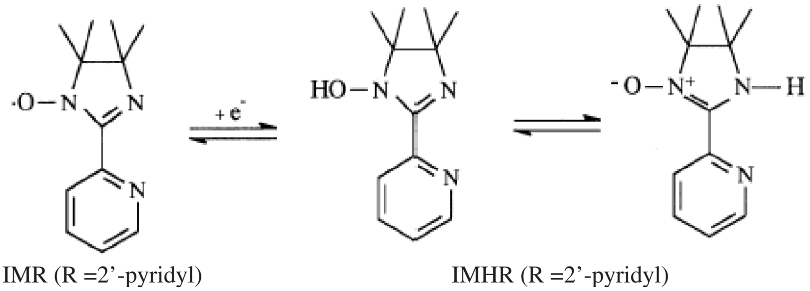

Scheme 1. Structures of IMHR and IMR.

and imino nitroxide radicals can participate in redox reactions with transition metal ions under certain experimental conditions, yielding complexes in which either the IMHR reduced form of IMR (scheme 1) acts as a diamagnetic bridging ligand [5] or both the starting IMR radical and its reduced form are present as a free paramagnetic species and a diamagnetic bridging ligand, respectively [6, 7]. In order to extend our knowledge of the extremely rich chemistry of such systems it was thus of interest to explore further the reactions between transition metal ions and IMR radicals.

The oxidation of nitroxide by some metal ions has been known for a long time, but few examples containing metal ions bound to reduced radicals have been reported [8–11]. In the present work, we report two new complexes **1** and **2**, in which 1-hydroxy-2(2′-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole (IMH2py), the diamagnetic reduced form of the imino nitroxide 1-oxy-2-(2′-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole (IM2py), (shown in scheme 1) is present as a terminal ligand. The syntheses, characterization, and crystal structures of the complexes are described.

2. Experimental

2.1. *Syntheses*

The starting material IM2-py was prepared according to a reported method [12]. A mixture of $Co(ClO_4)_2 \cdot 6H_2O$ (0.5 mmol, 0.183 g) and malonic acid (0.5 mmol, 0.052 g) in 25 cm^3 of H_2O, adjusted to pH $7 \sim 8$ with 1M NaOH, was stirred for 1.5 h. IM2py (1 mmol, 0.218 g) in 10 cm^3 of CH_3OH was added to above mixture, which was stirred for another 2 h and filtered. The filtrate was kept at room temperature for a few days to grow well-formed orange crystals of $[Co(mal)(IMH2py)_2]ClO_4$ (**1**). Yield: 32%. Anal. Calcd for $C_{27}H_{36}N_6O_{10}ClCo$ (%): C, 46.39; H, 5.19; N, 12.03. Found: C, 47.38; H, 4.98; N, 12.34. IR (KBr, cm^{-1}): $\nu_{as}(COO)$ 1650, $\nu_s(COO)$ 1455, $\Delta = \nu as - \nu s = 195$, $\nu(ClO_4)$ 1100 cm^{-1}. $[Mn(mal)(IMH2py)_2] \cdot H_2O$ (**2**) was prepared similarly, except $Mn(ClO_4)_2 \cdot 6H_2O$ was used instead of $Co(ClO_4)_2 \cdot 6H_2O$. Yield: 26%. Anal. Calcd for $C_{27}H_{38}N_6O_7Mn$ (%): C, 52.85; H, 6.24; N, 13.70. Found: 53.12; H, 6.01; N, 14.02. IR (KBr, cm^{-1}): $\nu_{as}(COO)$ 1647, $\nu_s(COO)$ 1473, $\Delta = 174\,cm^{-1}$.

2.2. *Crystal structures*

For complex **1** an orange crystal ($0.18 \times 0.16 \times 0.14\,\mathrm{mm}^3$) was selected and mounted on a glass fibre. All measurements were made on a Bruker Smart 1000 diffractometer equipped with a graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073\,\mathrm{\AA}$). Data were collected at room temperature, including a total of 3755 reflections in the $2.30^\circ < \theta < 25.10^\circ$ range with 2253 independent reflections ($R_{\mathrm{int}} = 0.0318$), of which 2024 were observed ($I > 2\sigma(I)$). Crystallographic data are given in tables 1 to 3. For complex **2** an orange crystal $0.24 \times 0.22 \times 0.18\,\mathrm{mm}^3$ was selected. Data were collected at room temperature, including a total of 3730 reflections in the $2.35^\circ < \theta < 25.01^\circ$ range with 2519 independent reflections ($R_{\mathrm{int}} = 0.0154$), of which 2457 were observed ($I > 2\sigma(I)$). Crystallographic data are given in tables 4 to 6. Absorption corrections were performed empirically. The structures were solved by direct methods using SHELXS97 [13] and refined with SHELXL 97 [14] by full-matrix least-squares techniques on F^2. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were located geometrically and refined isotropically.

3. Results and discussion

Reduction of nitroxide is promoted by acidic species [15, 16], so IMH2py formed in the presence of mal in the system. The reduced species IMH2py can in principle exist in two tautomeric forms, the iminohydroxylamine and amidinooxide shown in scheme 1, of which the former coordinates as a bidentate through the imino nitrogen atom of the iminohydroxylamine and the nitrogen atom of the pyridyl groups. Evidence for

Table 1. Crystal data and structure refinement details for **1**.

Empirical formula	$C_{27}H_{36}N_6O_{10}ClCo$
Formula weight	698.996
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, *C*2
Unit cell dimensions (Å, °)	$a = 17.004(9)$ $b = 10.753(5)$, $\beta = 113.856(8)$ $c = 9.207(5)$
Volume (Å^3)	1539.6(14)
Z, Calculated density ($\mathrm{Mg\,m^{-3}}$)	2, 1.504
Absorption coefficient ($\mathrm{mm^{-1}}$)	0.710
F(000)	724
Crystal size ($\mathrm{mm^3}$)	$0.18 \times 0.16 \times 0.14$
θ range for data collection (°)	2.30 to 25.10
Limiting indices	$-20 \le h \le 20$, $-12 \le k \le 11$, $-9 \le l \le 10$
Reflections collected/unique	3755/2253 [*R*(int) = 0.0318]
Completeness to $\theta = 25.10^\circ$	95.4%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.712
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2253/47/228
Goodness-of-fit on F^2	1.037
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0502$, $wR_2 = 0.1257$
R indices (all data)	$R_1 = 0.0583$, $wR_2 = 0.1311$
Absolute structure parameter	0.00(3)
Largest diff. peak and hole ($\mathrm{e\,\AA^{-3}}$)	1.136 and −0.285

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å $\times 10^3$) for **1**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U_{eq}
Co(1)	0	2966(1)	0	23(1)
O(1)	2667(3)	271(5)	1583(6)	54(1)
N(1)	944(2)	2952(6)	2091(4)	30(1)
N(2)	695(3)	1686(5)	−407(6)	30(1)
N(3)	1979(3)	850(5)	361(6)	36(1)
C(1)	1005(4)	3674(6)	3338(7)	41(1)
C(2)	1730(5)	3682(7)	4707(7)	50(2)
C(3)	2409(4)	2954(10)	4861(6)	55(2)
C(4)	2368(4)	2229(6)	3584(7)	41(1)
C(5)	1620(3)	2257(5)	2218(6)	30(1)
C(6)	1446(3)	1556(5)	746(6)	28(1)
C(7)	1453(4)	97(7)	−1023(8)	47(2)
C(8)	1162(5)	−1095(6)	−433(10)	63(2)
C(9)	1946(5)	−262(10)	−2006(10)	76(3)
C(10)	705(4)	1039(6)	−1831(7)	37(1)
C(11)	944(4)	2000(7)	−2807(7)	47(2)
C(12)	−129(4)	418(6)	−2823(7)	47(2)
C(13)	666(4)	5320(6)	−340(9)	47(2)
O(2)	638(3)	4147(4)	−573(5)	33(1)
O(3)	1251(3)	5981(4)	−385(8)	67(2)
C(14)	0	6006(10)	0	80(4)
Cl(1)	0	6536(3)	5000	69(1)
O(4)	506(9)	5474(12)	5755(17)	98(4)
O(5)	634(14)	6370(30)	6572(17)	194(10)
O(6)	595(12)	7528(16)	5700(30)	155(7)
O(7)	476(10)	6873(18)	4042(18)	120(5)

Table 3. Bond lengths [Å] and bond angles [°] for **1**.

Co(1)–O(2)	1.879(4)	O(2)–Co(1)–O(2)#1	95.0(3)
Co(1)–N(1)	1.945(4)	O(2)–Co(1)–N(1)#1	93.8(2)
Co(1)–N(2)	1.947(5)	O(2)–Co(1)–N(1)	86.8(2)
O(1)–N(3)	1.400(6)	N(1)#1–Co(1)–N(1)	179.1(4)
N(1)–C(5)	1.336(7)	O(2)–Co(1)–N(2)#1	175.0(2)
N(1)–C(1)	1.354(8)	N(1)–Co(1)–N(2)#1	97.2(2)
N(2)–C(6)	1.296(7)	O(2)–Co(1)–N(2)	87.67(16)
N(2)–C(10)	1.490(8)	N(1)–Co(1)–N(2)	82.1(2)
N(3)–C(6)	1.336(7)	N(2)#1–Co(1)–N(2)	90.0(3)
N(3)–C(7)	1.469(8)	C(5)–N(1)–C(1)	118.6(5)
C(13)–O(3)	1.238(8)	C(5)–N(1)–Co(1)	115.3(4)
C(13)–O(2)	1.277(8)	C(1)–N(1)–Co(1)	125.8(4)
		C(6)–N(2)–C(10)	108.2(5)

Symmetry transformation used to generate equivalent atoms at #1: $-x$, y, $-z$.

the presence of the iminohydroxylamine tautomeric form is provided by the structures. The specific structural feature which identifies this ligand as a reduced species rather than an oxidized one is the N–O bond distance of 1.400(6) Å for complex **1** and 1.406(4) Å for complex **2**, values close to those reported for analogous reduced IMHPh species 1.37–1.39 Å) [5, 8], and longer than the N–O bond in nitroxide radicals (1.25–1.34 Å) [17–21]. In addition, starting cobalt(II) has been oxidized to cobalt(III) in complex **1**.

Table 4. Crystal data and structure refinement details for **2**.

Empirical formula	$C_{27}H_{38}MnN_6O_7$
Formula weight	613.57
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, *C*2
Unit cell dimensions (Å, °)	$a = 16.721(5)$
	$b = 10.897(5)$, $\beta = 120.807(6)$
	$c = 9.253(3)$
Volume (Å^3)	1448.1(9)
Z, Calculated density (Mg m^{-3})	2, 1.403
Absorption coefficient (mm^{-1})	0.511
F(000)	642
Crystal size (mm^3)	$0.24 \times 0.22 \times 0.18$
θ range for data collection (°)	2.35 to 25.01
Limiting indices	$-19 \le h \le 14$, $-12 \le k \le 12$, $-11 \le l \le 11$
Reflections collected/unique	3730/2519 [*R*(int) = 0.0154]
Completeness to $\theta = 25.01°$	100.0%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.755
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2519/2/190
Goodness-of-fit on F^2	1.107
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0401$, $wR_2 = 0.1069$
R indices (all data)	$R_1 = 0.0418$, $wR_2 = 0.1091$
Absolute structure parameter	0.0(2)
Extinction coefficient	0.0155(19)
Largest diff. peak and hole (e Å^{-3})	0.745 and −0.294

Table 5. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å $\times 10^3$) for **2**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U_{eq}
Mn(1)	0	8734(1)	0	23(1)
O(1)	2991(2)	6064(3)	1978(4)	53(1)
O(2)	546(2)	10059(3)	−768(5)	51(1)
O(3)	587(3)	11863(3)	−1778(5)	72(1)
N(1)	1213(2)	8698(5)	2419(3)	39(1)
N(2)	815(3)	7434(3)	−286(5)	35(1)
N(3)	2223(2)	6662(3)	643(4)	42(1)
C(1)	1366(3)	9326(4)	3748(5)	49(1)
C(2)	2198(4)	9283(5)	5259(6)	60(1)
C(3)	2899(3)	8573(6)	5392(5)	63(1)
C(4)	2753(3)	7905(5)	4020(5)	50(1)
C(5)	1909(3)	7976(3)	2545(5)	36(1)
C(6)	1648(2)	7333(3)	983(5)	34(1)
C(7)	1623(3)	5896(4)	−827(6)	49(1)
C(8)	1384(4)	4722(5)	−222(8)	73(2)
C(9)	2105(4)	5589(7)	−1799(7)	82(2)
C(10)	786(3)	6795(4)	−1730(5)	40(1)
C(11)	−141(3)	6136(4)	−2787(6)	52(1)
C(12)	932(3)	7751(5)	−2743(6)	53(1)
C(13)	388(3)	11188(4)	−930(6)	49(1)
C(14)	0	11819(13)	0	116(4)
O(4)	10000	3215(8)	5000	113(2)

Table 6. Bond lengths [Å] and angles [°] for (**2**).

Mn(1)–O(2)	2.022(3)	O(2)#1–Mn(1)–O(2)	88.88(19)
Mn(1)–N(2)	2.075(4)	O(2)–Mn(1)–N(2)	89.92(11)
Mn(1)–N(1)	2.116(3)	O(2)–Mn(1)–N(2)#1	167.68(15)
O(1)–N(3)	1.406(4)	N(2)–Mn(1)–N(2)#1	93.8(2)
O(2)–C(13)	1.251(6)	O(2)–Mn(1)–N(1)#1	90.13(15)
O(3)–C(13)	1.238(6)	N(2)–Mn(1)–N(1)#1	100.87(15)
N(1)–C(1)	1.312(5)	O(2)–Mn(1)–N(1)	91.38(16)
N(1)–C(5)	1.360(5)	N(2)–Mn(1)–N(1)	77.65(15)
N(2)–C(6)	1.287(5)	N(1)#1–Mn(1)–N(1)	177.9(3)
N(2)–C(10)	1.485(5)	C(13)–O(2)–Mn(1)	129.7(3)
N(3)–C(6)	1.367(5)	C(1)–N(1)–C(5)	118.3(3)
N(3)–C(7)	1.468(5)	C(1)–N(1)–Mn(1)	127.1(3)
		C(5)–N(1)–Mn(1)	114.6(3)
		C(6)–N(2)–C(10)	107.6(3)
		C(6)–N(2)–Mn(1)	114.6(3)
		C(10)–N(2)–Mn(1)	135.6(3)

Symmetry transformation used to generate equivalent atoms at #1: $-x$, y, $-z$.

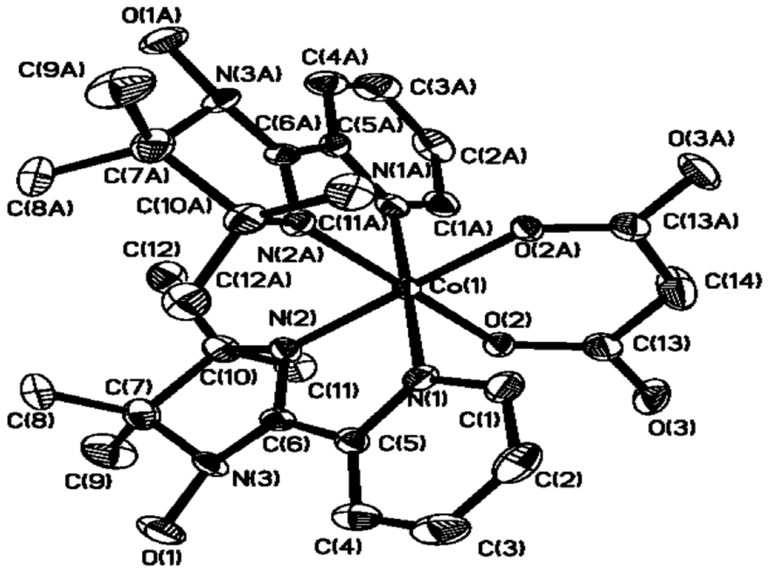

Figure 1. ORTEP view of the cation $[Co(mal)(IMH2py)_2]^+$ in **1** showing the atom labelling scheme. Thermal ellipsoids are drawn at the 30% possibility level. H atoms are omitted for clarity.

3.1. *$[Co(mal)(IMH2py)_2]ClO_4$ (1)*

A labelled diagram of complex **1** is shown in figure 1. The structure consists of a mononuclear $[Co(mal)(IMH2py)_2]^+$ and a perchlorate ion. Cobalt (III) ion is octahedral with O(2), O(2A), N(2) and N(2A) in the basal plane and N1 and N (1A) from two pyridyl groups in axial positions. In-plane Co–N and Co–O distances are 1.947(5) and 1.879 Å, respectively, and are normal. The axial Co–N bond distance is 1.945(4) Å. A sketch of crystal packing is shown in figure 2. Reduced radicals form intermolecular hydrogen bonds with oxygen atoms of the malonate ion group of another unit (2.627 Å and 154.37° for O(1)$\cdots$O(3) ($1/2-x$, $-1/2+y$, $-z$) and O(1)–H(1B)$\cdots$O(3)

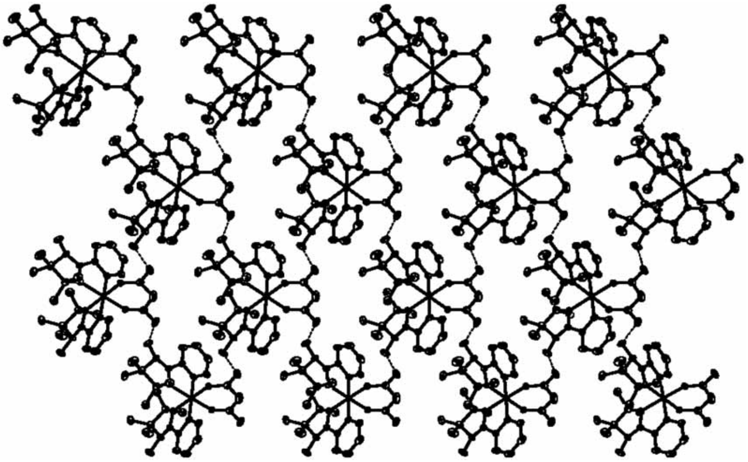

Figure 2. Packing diagram for $[Co(mal)(IMH2py)_2]^+$ along the *c* direction.

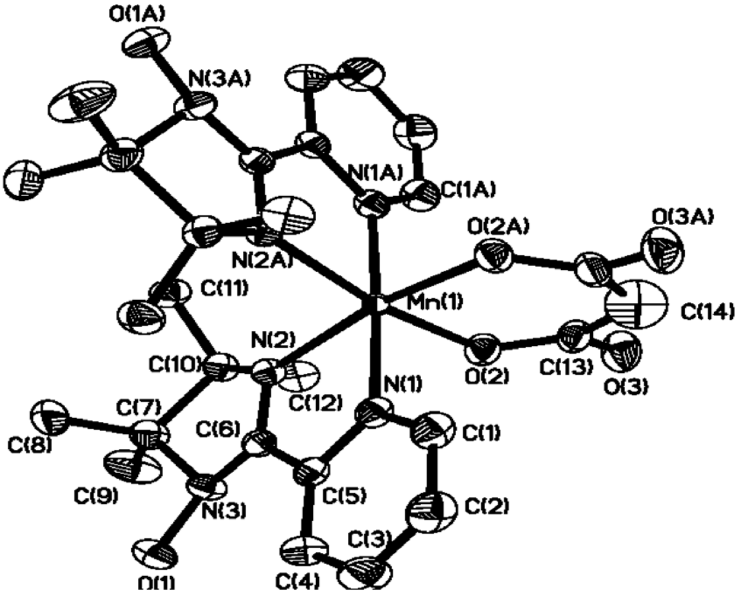

Figure 3. ORTEP view of $[Mn(mal)(IMH2py)_2]$ in **2** showing the atom labelling scheme. Thermal ellipsoids are drawn at the 30% possibility level. H atoms and the H_2O molecule are omitted for clarity.

$(1/2-x,\ -1/2+y,\ -z)$, respectively). Thus packing of the molecules along the *c* direction results in a 2D sheet. ClO_4^- ions are not coordinated.

3.2. *[Mn(mal)(IMH2py)$_2$] · H$_2$O (2)*

A labelled diagram of the complex is shown in figure 3; the non-coordinated H_2O molecule is omitted for clarity. The structure consists of a mononuclear $[Mn(mal)(IMH2py)_2]$ units. Mn(II) is hexacoordinated with O(2), O(2A), N(2) and

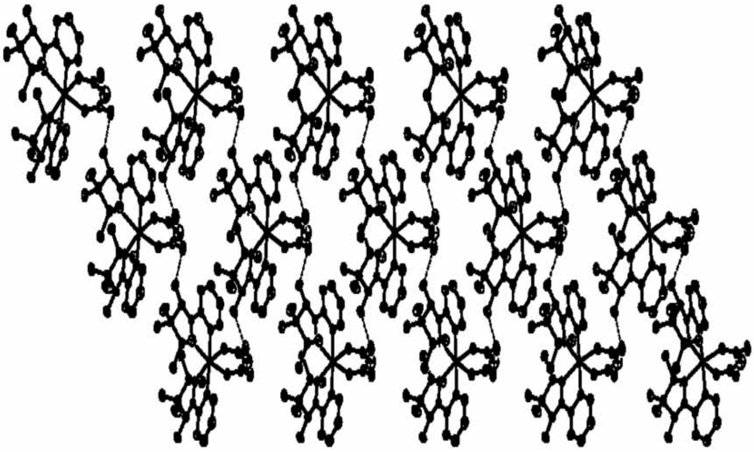

Figure 4. Packing diagram for [Mn(mal)(IMH2py)$_2$] along the *c* direction. H_2O molecules are omitted for clarity.

N(2A) in the basal plane and N1 and N (1A) from two pyridyl groups in axial positions. In-plane Mn–N and Mn–O bond distances are 1.947(5) and 1.879 Å, respectively, and are normal. The axial Mn–N bond distance is 1.945(4) Å and thus, the coordination geometry can also in this case be described as distorted octahedral. A sketch of the crystal packing is shown in figure 4. Reduced radicals form intermolecular hydrogen bonds with oxygen atoms of the malonate ion of another unit (2.635 Å and 170.86° for O(1)$\cdots$O(3) ($1/2-x$, $-1/2+y$, $-z$) and O(1)–H (1B)$\cdots$O(3) ($1/2-x$, $-1/2+y$, $-z$), respectively). Packing of the molecules along *c* also results in a 2D sheet in the crystal. Non-coordinated solvent molecules (H_2O) fill cavities that are formed.

Supplementary material

Full lists of crystallographic data are available from the Cambridge Crystallographic Data Centre (CCDC-243693 for complex **1** and CCDC-281075 for complex **2**).

Acknowledgements

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References

[1] A. Marvilliers, Y. Pei, J.C. Boquera, K.E. Vostrikova, C. Paulsen, E. Riviere, J.P. Audiere, T. Mallah. *J. Chem. Soc.*, *Chem. Commun.*, **19**, 1951 (1999).
[2] K.E. Vostrikova, D. Luneau, W. Wernsdorfer, P. Rey, M. Verdaguer. *J. Am. Chem. Soc.*, **122**, 718 (2000).
[3] H.O. Stumpf, L. Ouahab, Y. Pei, D. Grandjean, O. Kahn. *Science*, **261**, 447 (1993).

[4] P. Rey, D. Luneau. In *Supramolecular Engineering of Synthetic Metallic Materials*, J. Veciana (Ed.), Vol. 1, p. 145, Kluwer, Dordrecht (1999).
[5] M.D. Carducci, R.J. Docdens. *Inorg. Chem.*, **28**, 2492 (1989).
[6] M.H. Dickman, R.J. Doedens. *Inorg. Chem.*, **21**, 682 (1982).
[7] L.C. Porter, R.J. Doedens. *Acta Crystallogr.*, **C41**, 836 (1985).
[8] A. Caneschi, D. Gatteschi, J. Laugier, P. Rey, C. Zanchini. *Inorg. Chem.*, **28**, 1969 (1989).
[9] A. Caneschi, D. Gatteschi, M.C. Melandri, P. Rey, R. Sessoli. *Inorg. Chem.*, **29**, 4228 (1990).
[10] Q.H. Zhao, L.C.Li, Z.H. Jiang, D.Z. Liao, S.P. Yan, R.B. Fang. *J. Coord. Chem.*, **57**, 843 (2004).
[11] L.C. Li, D.Z. Liao, L.J. Bai, Z.H. Jiang, S.P. Yan. *J. Mol. Struct.*, **569**, 179 (2001).
[12] J.N. Helbert, P.W. Kopf, E.H. Poindexter, B.E. Wagner. *J. Chem. Soc., Dalton Trans.*, **11**, 998 (1975).
[13] G.M. Sheldrick. *SHELXS 97, Program for the Solution of Crystal Structures*, University of Göttingen, Germany (1997).
[14] G.M. Sheldrick. *SHELXL 97, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany (1997).
[15] E.F. Ullman, J.K. Osiecky, D.J.B. Boocock, R. Darcy. *J. Am. Chem. Soc.*, **74**, 7049 (1972).
[16] L.C. Li, C.L. Dong, D.Z. Liao, L.J. Bai, Z.H. Jiang, S.P. Yan. *Chinese J. Struct. Chem.*, **23**, 296 (2004).
[17] O.P. Anderson, T.C. Kuechler. *Inorg. Chem.*, **19**, 1417 (1980).
[18] M.H. Dickman, L.C. Porter. *Inorg. Chem.*, **25**, 3453 (1986).
[19] H. Oschio, T. Watanable, A. Ohto, T. Ito, H. Masuda. *Inorg. Chem.*, **35**, 472 (1996).
[20] M. Fettouchi, M. Khaled, A. Waheed, S. Golhen, L. Ouahab, J.P. Sutter, O. Khan. *Inorg. Chem.*, **38**, 3967 (1999).
[21] Y. Tsukahara, T. Kamatani, T. Suzuki, S. Kaizaki. *J. Chem. Soc., Dalton Trans.*, **7**, 1276 (2003).