

# Synthesis, Spectroscopic and Thermal Investigation, and Crystal Structure of Triaqua-*trans*-bis(3,4-dimethylpyridine)-nitratomanganese(II) Nitrate

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**Summary.** A mixed ligand complex of manganese(II) nitrate (triqua-*trans*-bis(3,4-dimethylpyridine)nitratomanganese(II) nitrate,  $[\text{Mn}(\text{3,4-dimethylpyridine})_2(\text{H}_2\text{O})_3(\text{NO}_3)]\text{NO}_3$ ) has been synthesized and characterized by spectroscopic and crystallographic methods. The compound crystallizes in the orthorhombic system (space group *Pbca* (No. 61),  $a = 7.616(3)$ ,  $b = 19.230(6)$ ,  $c = 28.109(9)$  Å,  $Z = 8$ ) and consists of a discrete cation  $[\text{MnL}_2(\text{NO}_3)(\text{H}_2\text{O})_3]^+$  and a nitrate anion ( $L = 3,4$ -dimethylpyridine). In the cation, each metal atom links three water molecules ( $\text{Mn}-\text{O} = 2.148(5)$ ,  $2.194(5)$ , and  $2.198(4)$  Å) and is further coordinated to a nitrate group ( $\text{Mn}-\text{O} = 2.259(5)$  Å) and two 3,4-dimethylpyridine molecules ( $\text{Mn}-\text{N} = 2.247(5)$  and  $2.289(5)$  Å). The lattice structure is stabilized by stacking of the 3,4-dimethylpyridine groups of different asymmetric units along the *ac* plane and by hydrogen bonding along the *b* axis. The IR and ESR spectra are reported and correlated with the structure of the complex. The thermal decomposition of the solid complex was investigated derivatographically in a nitrogen atmosphere.

**Keywords.** Manganese; Pyridine; Nitrate; Complex.

## Synthese, spektroskopische und thermische Untersuchung und Kristallstruktur von Triaqua-*trans*-bis(3,4-dimethylpyridin)nitratomangan(II)nitrat

**Zusammenfassung.** Ein *Mixed-ligand*-Komplex von Mangan(II)nitrat (Triaqua-*trans*-bis(3,4-dimethylpyridine)nitratomangan(II)nitrat,  $[\text{Mn}(\text{3,4-dimethylpyridine})_2(\text{H}_2\text{O})_3(\text{NO}_3)]\text{NO}_3$ ) wurde hergestellt und mittels spektroskopischer und kristallographischer Methoden charakterisiert. Die Verbindung kristallisiert im orthorhombischen System (Raumgruppe *Pbca* (Nr. 61),  $a = 7.616(3)$ ,  $b = 19.230(6)$ ,  $c = 28.109(9)$  Å,  $Z = 8$ ) und besteht aus einem diskreten  $[\text{MnL}_2(\text{NO}_3)(\text{H}_2\text{O})_3]^+$ -Kation und einem Nitratanion ( $L = 3,4$ -Dimethylpyridin). Im Kation verbindet jedes Metallatom drei Wassermoleküle ( $\text{Mn}-\text{O} = 2.148(5)$ ,  $2.194(5)$  und  $2.198(4)$  Å) und ist weiters jeweils mit einer Nitratgruppe ( $\text{Mn}-\text{O} = 2.295(5)$  Å) und zwei 3,4-Dimethylpyridinmolekülen ( $\text{Mn}-\text{N} = 2.247(5)$  und  $2.289(5)$  Å) koordiniert. Das Gitter wird durch Stapelung der 3,4-Dimethylpyridingruppen verschiedener asymmetrischer Einheiten entlang der *ac*-Ebene und durch Wasserstoffbrückenbindungen entlang der *b*-Achse stabilisiert. Die IR- und ESR-Spektren werden diskutiert und mit der Struktur des Komplexes korreliert. Die thermische Zersetzung des festen Komplexes wurde in einer Stickstoffatmosphäre derivatographisch untersucht.

## Introduction

We have long been interested in the study of manganese(II) complexes of pyridine and pyridine derivatives with some bridging halide and pseudohalide ligands [1–4]. This, on one hand, is due to the identification of several manganese containing biomolecules including the water oxidation/oxygen evolution center, within the photosynthesis apparatus of green plants and cyanobacteria [5], the manganese catalases [6], manganese ribonucleotide reductases [7], and manganese superoxide dismutases [8]. An additional reason is the fact that many pyridine derivatives have a broad spectrum of effects on both animal and plant organisms which have been attributed to their ability to form complexes with transition metals [9]. In this regard, many complexes of manganese(II) with pyridine derivatives have been investigated, and their crystal structures have been reported [10–17]. Manganese(III) complexes have been found to exert similar effects [18, 19]. Many of these manganese(II) and manganese(III) complexes have shown quite interesting magnetic interactions when forming polymeric structures [14–19]. They contain mostly hexacoordinated chromophores; in some rare cases, seven-coordinated chromophores ( $\text{MnN}_4\text{O}_3$ ) are present (*e.g.* in  $[\text{Mn}(2,2'\text{-bipyrimidine})(\text{NO}_3)_2]$  [20] and  $[\text{Mn}(\text{TMBA})(\text{NO}_3)(\text{CH}_3\text{OH})](\text{NO}_3)\text{H}_2\text{O}$  ( $\text{TMBA}$  = tripodal (N,N,N,*tris*-(2-benzimidazolyl-methyl)amine) [21]). In the bipyridine complex described in Ref. [20] the nitrate groups show both bidentate and monodentate coordination modes. During our efforts to prepare a polynuclear manganese(II) complex with 3,4-dimethylpyridine and bridging azido ligands we obtained the title complex as a monomeric nitrate complex. The synthesis and characterization of this complex as elucidated by spectroscopic and crystallographic methods along with thermal decomposition are the subject of the present work.

## Results and Discussion

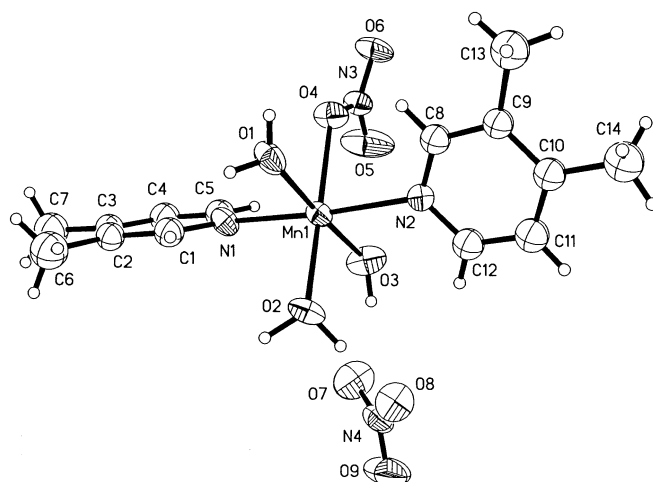
### *Properties*

The synthesis of  $[\text{Mn}(3,4\text{-dimethylpyridine})_2(\text{H}_2\text{O})_3(\text{NO}_3)]\text{NO}_3$  was achieved in reasonably good yield (75%) by reacting the free ligand (3,4-dimethylpyridine) with  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in an aqueous or aqueous/ethanolic solution. It was also obtained in lower yield as a side product during the preparation of the corresponding azido complex [4] when the free ligand was present in excess in the solution.

The complex is very well soluble in polar solvents like water, ethanol, and methanol, less soluble in organic polar solvents like  $\text{CHCl}_3$ , *DMF*, acetonitrile, and *DMSO*, and completely insoluble in non-polar solvents like  $\text{CCl}_4$  and *n*-hexane. The electrolytic conductivity of a 0.001 *M* aqueous solution is in agreement with an 1:1-electrolyte ( $950 \mu\text{S}/\text{cm}$  at  $25^\circ\text{C}$ ). The effective magnetic moment ( $\mu_{\text{eff}}$ ) of the complex was found to be 5.71 BM which is in agreement with published values for six-coordinated manganese(II) complexes [1, 14–16].

### *Structure*

The present study has shown that the title complex consists of a manganese(II) complex cation and a nitrate counter anion. The complex cation can be described

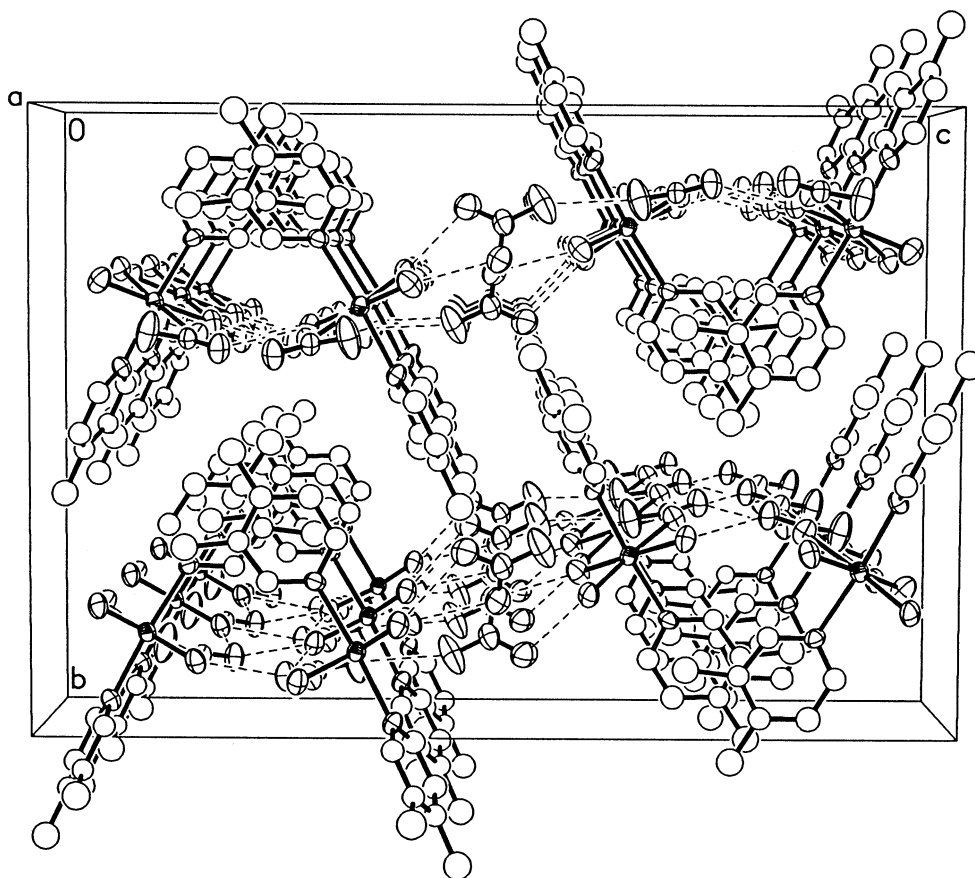


**Fig. 1.** [Mn(3,4-dimethylpyridine)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>(NO<sub>3</sub>)]NO<sub>3</sub>: molecular geometry and atom labeling scheme of the monomeric unit

by a distorted octahedral environment around the central manganese(II) ion MnN<sub>2</sub>O<sub>4</sub>. Each manganese(II) ion is *trans*-coordinated by a pair of 3,4-dimethylpyridine ligands (Mn–N(1) = 2.247(5) Mn–N(2) = 2.289(5) Å) in analogy to complexes containing N-(3,4-dimethylpyridine) and bipyrimidine [4,17]. The *trans*-angles deviate from linearity (N(1)–Mn–N(2) = 175.7(2)°) as expected due to the geometrical constraints of the nitrate anion. The planes of the two 3,4-dimethylpyridine ligands are almost perpendicular to each other (76.8(2)°, Fig. 1). The compound represents also a *mer*-triaquo complex where the manganese(II) ion is coordinated by three water molecules (Mn–O distances between 2.148(5) and 2.198(4) Å) at the equatorial plane. The Mn(II) ion coordinates in the same plane with a longer bond distance to the nitrate group relative to the water molecules (Mn–O(NO<sub>3</sub>) = 2.259(5) Å). Known Mn–O(NO<sub>3</sub>) distances range from 2.197 to 2.338 Å for mono- and bidentate nitrate ions, respectively [20,21]. The coordinated nitrate group as a trigonal planar molecule shows O–N–O angles which are larger (120.5(6) and 120.7(6)°) than the non-coordinated ones (118.8(6)°). The geometric details are comparable with angles and distances observed in previous investigations concerning other pyridine derivative manganese(II) complexes [1–4] as well as aqua- and nitratomanganese(II) complexes [18–21]. The lattice structure is stabilized by stacking interactions of the 3,4-dimethylpyridine group of different asymmetric units parallel to the *ac* plane (ring–ring distances of 3.66 and 3.78 Å; Fig. 2). The isolated complex cation and the free nitrate counter anion are held together in a polyhedral stacking interaction along the *b* axis by hydrogen bonding (O–H···O contacts; O···H: 1.822(15)–2.279(16) Å, O···O: 2.783(8)–3.061(8) Å) forming a two-dimensional network parallel to the *ac* plane. Details of the hydrogen bond sheets are listed in Table 3.

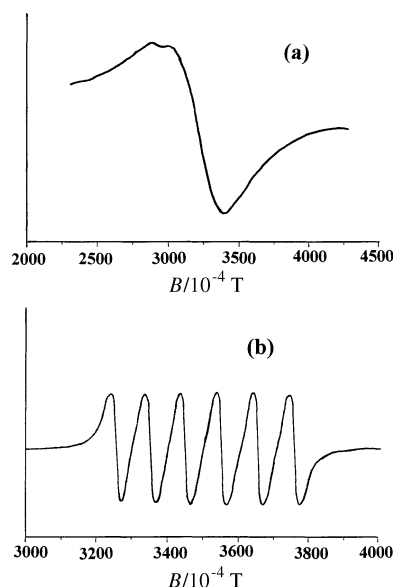
### Spectroscopy

The IR spectrum of the solid complex shows the vibration bands of the organic moiety almost at the positions of those of the free ligand with very small shifts



**Fig. 2.** Packing view of  $[\text{Mn}(\text{3,4-dimethylpyridine})_2(\text{H}_2\text{O})_3(\text{NO}_3)]\text{NO}_3$  along the  $b$ -axis of the unit cell; broken lines indicate hydrogen bonds

imposed by the coordination to the central metal ion. A very strong broad band centered around  $3360\text{ cm}^{-1}$  is attributed to  $\nu(\text{O-H})$  of the coordinated water molecules. Although in the region between  $1200$  and  $1550\text{ cm}^{-1}$  a strong interaction between ligand vibrations and nitrate group vibrations occurs, it was possible to characterize the main peaks of the nitrate group. The nitrate group shows a weak band at  $1042\text{ cm}^{-1}$  due to  $\nu(\text{N=O})$ , a very strong band at  $1333\text{ cm}^{-1}$  ( $\nu_s(\text{NO}_2)$ ), and a moderate band at  $1498\text{ cm}^{-1}$  due to  $\nu_{as}(\text{NO}_2)$  [22]. These three bands were characterized as N–O stretching vibrations for the unidentate  $\text{NO}_3^-$  group in  $C_{2v}$  symmetry [22]. We also observed a sharp moderate unsplit band at  $1760\text{ cm}^{-1}$  which was tentatively assigned to a free ionic nitrate group as was the intense sharp band at  $1380\text{ cm}^{-1}$  [23]. *Lever et al.* [24] found that this band should be split upon coordination, and the magnitude of this splitting is expected to be larger for bidentate than for unidentate ligands. The far infrared region exhibits a large number of bands in the range of  $240\text{--}390\text{ cm}^{-1}$  which could be assigned to  $\nu(\text{M-O}(\text{H}_2\text{O}))$ ,  $\nu(\text{M-O}(\text{ONO}_2))$ , and  $\nu(\text{M-N}(\text{ligand}))$ .



**Fig. 3.** ESR spectrum of solid [Mn(3,4-dimethylpyridine)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>(NO<sub>3</sub>)]NO<sub>3</sub> (a) and in *DMF* solution (b) at room temperature

The room temperature ESR spectrum of a polycrystalline sample of the title compound is given in Fig. 3a. The spectrum shows a broad intense isotropic signal centered around  $g = 2.056$ . The complex is soluble in *DMF*, *DMSO*, toluene, and acetonitrile. The room temperature ESR spectra of the complex in toluene and acetonitrile did not show hyperfine splitting whereas spectra of *DMF* and *DMSO* solutions exhibit a reproducible hyperfine structure (Fig. 3b) with a splitting factor of  $A_{av} = 94$  G. All spectra are very similar to those of hexacoordinated manganese(II) complexes with a  ${}^6S_{(5/2)}$  ground state [25, 26].

#### *Thermal analysis*

The first step of the thermal decomposition of the title complex (Fig. 4) involves the loss of one water molecule and a nitrate ion (found: 17.8, calcd.: 17.9%). The DTA curve starts with two successive endotherms with  $T_{max} = 99.3$  and  $147.6^\circ\text{C}$  and  $\Delta H = -32.7$  and  $-12.9$   $\text{kJ} \cdot \text{mol}^{-1}$ , respectively, giving rise to the diaqua cation  $[\text{MnL}_2(\text{H}_2\text{O})_2(\text{NO}_3)]^+$ . This cation is unstable and decomposes immediately under loss of two water molecules and a ligand molecule (found: 33.4, calcd.: 32.04%). This step appears in the DTA curve as a sharp exotherm ( $T_{max} = 161.3^\circ\text{C}$ ,  $\Delta H = 137.5$   $\text{kJ} \cdot \text{mol}^{-1}$ ). The anhydrous compound  $[\text{MnL}(\text{NO}_3)]^+$  gradually decomposes from  $180^\circ\text{C}$  to around  $400^\circ\text{C}$  at which it decomposes completely with an observed loss of weight of 31.2% corresponding to a loss of one ligand molecule and  $\text{NO}_2$  (calcd: 34.2%). The final residue is  $\text{MnO}$  rather than  $\text{Mn}$  (found: 17.2, calcd.: 16.1%). This last step appears in the DTA curve as a strong exotherm with  $T_{max} = 400^\circ\text{C}$  and  $\Delta H = 1051.2$   $\text{kJ} \cdot \text{mol}^{-1}$ .

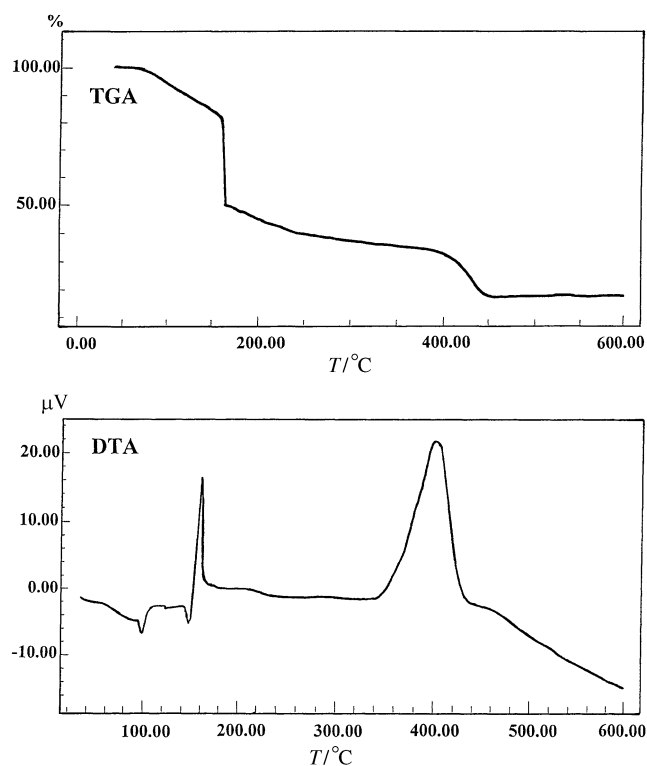


Fig. 4. Thermal decomposition of  $[\text{Mn}(\text{3,4-dimethylpyridine})_2(\text{H}_2\text{O})_3(\text{NO}_3)]\text{NO}_3$

## Experimental

### Materials

Manganese(II) nitrate tetrahydrate and 3,4-dimethylpyridine were purchased from Aldrich. All chemical were of analytical grade quality.

### Preparation of $[\text{Mn}(\text{3,4-dimethylpyridine})_2(\text{H}_2\text{O})_3(\text{NO}_3)]\text{NO}_3$

Good quality crystals of the complex were prepared by mixing a solution of manganese(II) nitrate tetrahydrate (1.0 g, 4 mmol) in  $30 \text{ cm}^3$  of a 1:1 EtOH/ $\text{H}_2\text{O}$  mixture with 3,4-dimethylpyridine (0.53 g, 5 mmol) in  $20 \text{ cm}^3$  ethanol. The colorless mixture was allowed to stand in a dark place for several days to produce colorless crystals (yield ca. 75%); found: C 37.5, H 5.5, N 12.6, Mn 12.2; calcd.: C 37.59, H 5.41, N 12.52, Mn 12.28.

### Physical measurements

IR spectra have been recorded in the range of  $200\text{--}4000 \text{ cm}^{-1}$  using a Perkin-Elmer 380-B spectrophotometer. Solid sample was measured as KBr pellets. The bulk magnetic susceptibility of the powdered sample was measured at room temperature using a modified Faraday balance. The susceptometer was calibrated with standard ferrite. Diamagnetic corrections were calculated from Pascal Tables. ESR measurements were carried out with a Varian E-9 ESR spectrometer operating at

9.5 GHz at room temperature. Thermogravimetric analysis was carried out using a Shimadzu TGA-50H system under a nitrogen atmosphere with a heating rate of 10°C/min.

#### *X-Ray crystal structure analysis*

A modified STOE four-circle diffractometer was used for single crystal X-ray analysis. Orientation matrix and lattice parameters were obtained by least-squares refinement of the diffraction data from 24 reflections in the  $\theta$  range of 10.6–14.3°. Data were collected at 295(2) K using graphite crystal monochromatized Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ) and  $\omega$ -scan technique. The intensities were corrected for Lorentz-polarization effects, for absorption [27], and also for intensity decay (intensities for standard reflections dropped during data collection by 21%). Crystallographic and refinement parameters are given in Table 1.

The structure was solved by direct methods and subsequent *Fourier* analysis. Anisotropic displacement parameters were applied to Mn, O, and N atoms in full-matrix least-squares refinements based on  $F^2$ . The hydrogen atoms were assigned with common isotropic displacement factors and in the final refinement cycles by use of geometrical restraints. Analytical expressions of neutral-atom scattering factors were employed and, anomalous dispersion corrections were incorporated [28]. The programs DIFABS [27], SHELXL-93 [29], SHELXS-86 [30], the latter two incorporated in the SHELXTL/PC [31] program package, and PLATON [32] were used for computations. Selected bond distances and bond angles are given in Table 2. Supplementary material has been deposited with the Cambridge Crystallographic Data Center (deposition number 103052).

**Table 1.** Crystal data and structure refinement for [Mn(3,4-dimethylpyridine)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>(NO<sub>3</sub>)]NO<sub>3</sub>

Molecular formula	C <sub>14</sub> H <sub>24</sub> MnN <sub>4</sub> O <sub>9</sub>
Formula weight	447.31
Temperature	295(2) K
Wavelength	0.71069 Å
Crystal system	Orthorhombic
Space group	Pbca
Unit cell dimensions	$a = 7.616(3) \text{ \AA}$ $b = 19.230(6) \text{ \AA}$ $c = 28.109(9) \text{ \AA}$
Volume	4117(3) Å <sup>3</sup>
Z	8
Density (calculated)	1.443 Mg/m <sup>3</sup>
Absorption coefficient	0.693 mm <sup>-1</sup>
Crystal size	0.44 × 0.44 × 0.22 mm
Reflections collected	2052
Independent reflections	1823 ( $R(\text{int}) = 0.0247$ )
Parameters	188
Goodness-of-fit on $F^2$	1.040
Final $R$ indices ( $I > 2\sigma(I)$ )	$R_1 = 0.0552$ , $wR_2 = 0.1347$
Largest diff. of peak and hole	0.315 and $-0.278 \text{ e. \AA}^{-3}$

$$R_1 = \sum ||F_o| - |F_c| / \sum |F_o|, wR_2 = (\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2)^2))^{1/2}$$

**Table 2.** Selected bond lengths (Å) and angles (°) for [Mn(3,4-dimethylpyridine)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>(NO<sub>3</sub>)]NO<sub>3</sub>

Mn(1)–O(3)	2.148(5)	Mn(1)–O(1)	2.194(5)
Mn(1)–O(2)	2.198(4)	Mn(1)–N(1)	2.247(5)
Mn(1)–O(4)	2.259(5)	Mn(1)–N(2)	2.289(5)
N(3)–O(5)	1.223(7)	N(3)–O(6)	1.235(7)
N(3)–O(4)	1.251(7)	N(4)–O(9)	1.225(8)
N(4)–O(8)	1.238(8)	N(4)–O(7)	1.249(8)
O(3)–Mn(1)–O(1)	177.2	O(3)–Mn(1)–O(2)	88.4(2)
O(1)–Mn(1)–O(2)	93.6(2)	O(3)–Mn(1)–N(1)	93.0(2)
O(1)–Mn(1)–N(1)	88.9(2)	O(2)–Mn(1)–N(1)	92.2(2)
O(3)–Mn(1)–O(4)	95.5(2)	O(1)–Mn(1)–O(4)	82.4(2)
O(2)–Mn(1)–O(4)	175.5(2)	N(1)–Mn(1)–O(4)	89.9(2)
O(3)–Mn(1)–N(2)	89.0(2)	O(1)–Mn(1)–N(2)	89.0(2)
O(2)–Mn(1)–N(2)	91.7(2)	N(1)–Mn(1)–N(2)	175.7(2)
O(4)–Mn(1)–N(2)	86.2(2)	O(5)–N(3)–O(6)	118.8(6)
O(5)–N(3)–O(4)	120.5(6)	O(6)–N(3)–O(4)	120.7(6)
N(3)–O(4)–Mn(1)	127.4(4)	O(9)–N(4)–O(7)	117.7(8)
O(8)–N(4)–O(7)	118.2(7)		

**Table 3.** Hydrogen bonds (distances in Å, angles in °) for [Mn(3,4-dimethylpyridine)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>(NO<sub>3</sub>)]NO<sub>3</sub>

	O–H	H···O	O–O	O–H–O
O1–H91A···O6	0.864(16)	2.279(16)	2.875(7)	126.3(14)
O1–H91A···O6	0.836(13)	2.007(16)	2.783(8)	154(2)
O2–H92A···O8	1.054(13)	1.822(15)	2.872(8)	173.5(15)
O2–H92B···O9	1.002(16)	2.089(16)	3.061(8)	162.8(14)
O3–H93A···O7	0.897(13)	1.839(14)	2.703(8)	161.0(12)
O3–H93B···O9	0.783(16)	2.192(17)	2.969(8)	71.6(16)

## Acknowledgments

The author thanks Prof. *Kratky* and Dr. *Belaj*, Graz, for access to the STOE diffractometer.

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*Received December 15, 1998. Accepted (revised) February 15, 1999*