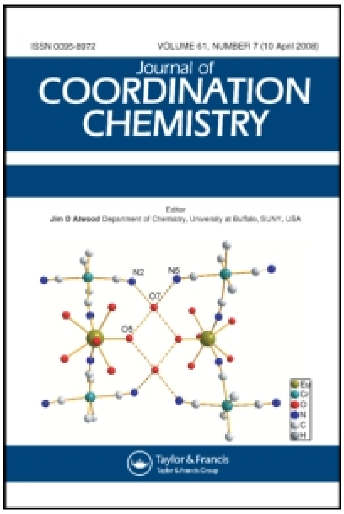

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SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF DIAQUADI(ACETATO-O)-*BIS*(2,4′-BIPYRIDYL) MANGANESE(II)

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The title complex $[Mn(H_2O)_2(ac\text{-}O)_2(2,4'\text{-bipy})_2]$ (**1**) (ac = CH_3COO^-, 2,4′-bipy = 2,4′-bipyridyl) has been synthesized and characterized by elemental and thermal analysis, IR, magnetic and conductivity studies. The structure of $[Mn(H_2O)_2(ac\text{-}O)_2(2,4'\text{-bipy})_2]$ has been determined by single crystal X-ray methods; the complex crystallizes in the monoclinic system, space group $P2_1/c$ with $Z = 2$, $a = 8.035(1)$, $b = 5.660(1)$, $c = 26.130(5)$ Å, $\beta = 97.05(1)°$, $V = 1179.36$ Å^3. The structure was solved by the Patterson method and refined by full-matrix least-squares techniques using F^2 values to conventional $R = 0.050$ for 2322 independent reflections with $F_o > 4\sigma(F_o)$. The central Mn atom lies on a centre of symmetry and is six-coordinated to two CH_3COO^- groups, two water molecules and two bipyridyl groups.

Keywords: Manganese(II); 2,4′-bipyridyl; crystal structure

INTRODUCTION

Acetate ion can coordinate manganese(II) ions in various ways: as a simple unidentate ligand,[1] or as a bidentate bridging or chelating, symmetric or unsymmetric group.[2–5] It is also stated, that in the same molecular structure individual acetate groups may coordinate manganese in different ways (bidentate symmetrical and unsymmetrical[6] or unidentate groups[7]). Manganese(II) complexes with N-donor ligands, for example, bipyridyls, form an

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important class of coordination compounds. Several studies have been made on complexes of 2,2′-bipyridyl and 4,4′-bipyridyl with some manganese(II) salts.[2,8–12] Ahuja *et al.*[2] have reported the preparation and characterization of $Mn(ac)_2(2,2'\text{-bipy})$ and $Mn(ac)_2(4,4'\text{-bipy})$. IR studies of these complexes indicate that 2,2′-bipy acts as bidentate chelating ligand, while the isomeric molecule 4,4′-bipy acts as a bidentate bridging ligand, and the acetate groups are bound as bidentate chelating ligands.[2] 2,4′-Bipyridyl can coordinate *via* N(2) or N(4′) atom, or *via* two N atoms as a bridging ligand.[13–16] It was thus of interest to examine the behaviour of 2,4′-bipy and acetate groups in mixed-ligand manganese(II) complexes. Crystal structures are described only for a few complexes with 2,4′-bipy in which the N(4′) atom is substituted with an alkyl group or H^+.[13,14]

EXPERIMENTAL

Chemicals

2,4′-Bipyridyl (m. p. 61°C) and methanol (anhydroscan) were obtained from Aldrich Chem. Co. and from Lab-scan., respectively. Other chemicals were p. a. from POCh-Gliwice.

Preparations

A solution of 4.3 mmol of manganese(II) acetate in 20 cm^3 of water was added to a solution of 12.8 mmol of 2,4′-bipy in 10 cm^3 of water containing a few drops of 95% EtOH. The mixture was heated at 80°C for 15 min and then allowed to cool. During several days a crystalline complex $[Mn(H_2O)_2(ac\text{-}O)_2(2,4'\text{-bipy})_2]$ was obtained. The light-yellow product was collected by filtration, washed with cold EtOH and Et_2O, and dried at room temperature. Anal.: calc. for $Mn(H_2O)_2(CH_3COO)_2(C_{10}N_2H_8)_2$ (%): Mn, 10.53; C, 55.28; H, 5.02; N, 10.75. Found: Mn, 10.56; C, 55.30; H, 5.10; N, 10.90.

Crystal Structure Determination

A single crystal of dimensions 0.26 × 0.33 × 0.51 mm was chosen for data collection on a Siemens P3 diffractometer with graphite-monochromatized MoKα radiation at 20°C, using the $\theta/2\theta$ scan technique. Data were corrected by empirical absorption (*psi* scans, max. and min. transmission factors = 1.00, 0.71). All details concerning data collection and refinement parameters are summarized in Table I.

TABLE I Crystal data and structure refinement parameters for $[Mn(H_2O)_2(ac\text{-}O)_2\text{-}(2,4'\text{-}bipy)_2]$ (1)

Identification code	(1)
Empirical formula	$C_{24}H_{26}N_4O_6Mn$
Formula weight	521.43
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2(1)/c$
Unit cell dimensions	$a = 8.035(1)$ Å
	$b = 5.660(1)$ Å
	$c = 26.130(5)$ Å
	$\beta = 97.050(10)$ deg.
Volume	1179.4(3) $Å^3$
Z	2
Density (calculated)	1.468 Mg/m^3
Absorption coefficient	0.608 mm^{-1}
$F(000)$	542
Crystal size	0.51 × 0.33 × 0.26 mm
Theta range for data collection	2.55 to 29.00 deg.
Index ranges	$-11 < = h < = 11, -1 < = k < = 7, -36 < = l < = 1$
Reflections collected	3898
Independent reflections	3026 $[R_{(int)} = 0.0329]$
Refinement method	Full-matrix least - squares on F^2
Data/restraints/parameters	2917/0/162
Goodness-of-fit on F^2	1.080
Final R indices $[I > 2\sigma(I)]$	$R = 0.0496$, $wR2 = 0.1229$

The structure was solved by the Patterson method and subsequent difference Fourier syntheses and refined by full-matrix least-squares methods with anisotropic thermal factors for all non-hydrogen atoms and hydrogen atoms in calculated positions (C–H = 0.96 Å, $U = 1.2 \times U(C)$). The weighting scheme applied was $w = 1/[\sigma^2(F_o^2) + (a \times P)^2 + b \times P]$, where $P = [$fx maximum of $(\phi$ or $F_o^2) + (1 - f) \times F_c^2]$, where $f = 0.33333$. The parameters a and b were optimized in each least-squares cycle to give a flat analysis of variance in terms of F_c^2. All calculations were performed with the program SHELXTL[17] and final refinements with the program SHELXL93.[18] Additional material available from the authors comprises anisotropic thermal parameters H-atom coordinates and lists of observed and calculated structure factors.

Other Measurements

Elemental analyses were carried out using a Carbo-Erba C, H, N-analyser. Mn was determined chelatometrically after decomposition of the complex by dilute HNO_3. IR spectra were obtained using KBr pellets on a Shimadzu spectrophotometer (4000–400 cm^{-1}). Conductivity measurement was performed on a conductivity meter of the OK-102/1 type equipped with an OK 902 electrode at 25 ± 0.05°C. Molar conductivity (Λ_M) of the complex was measured using a 1.0×10^{-3} mol · dm^{-3} solution in methanol. The magnetic measurement was carried out at room temperature using the Guoy method with $Hg[Co(NCS)_4]$ as calibrant. Correction for diamagnetism of the constituent atoms was calculated by Pascal's constants.[19] Thermal decomposition studies were carried out on a derivatograph type Q-1500 over a temperature range at 20–1000°C, at a heating rate of 5°C min^{-1}, in air. The sample mass was 100 mg; α-Al_2O_3 served as the reference. Analyses of the solid decomposition products were performed using derivatographic curves, analytical data and X-ray powder methods analysed using the Powder Diffraction File.[20]

RESULTS AND DISCUSSION

The obtained compound is air stable and fairly soluble in water. The observed magnetic moment of 5.82 B.M. indicates five unpaired electrons (similarly for Mn(2,2′-bipy)$_2$Br$_2$).[8] The molar conductivity value of $\Lambda_M = 54.70\,\Omega^{-1}\,cm^2\,mol^{-1}$ in methanol show a behaviour intermediate between those of non and 1 : 1 electrolytes.[21] Our compound dissociates partially in MeOH.

Crystal Structure of [Mn(H$_2$O)$_2$(ac-O)$_2$(2,4′-bipy)$_2$]

Final atomic coordinates are given in Table II. Interatomic bond distances and angles are reported in Table III. A projection of the molecule together with the labelling scheme and a view along the bipyridyl groups are given in Figures 1(a) and 1(b), respectively. Figure 2 shows the octahedral environment of the manganese atom.

The manganese atom occupies special position *b* of the space group $P2_1/c$ at 1/2, 0, 0 (No. 14, Vol. A, p. 176, *International Tables for Crystallography*[22]) with site symmetry $\bar{1}$. Therefore, there are two molecules of the complex in the unit cell. The coordination of the metal is octahedral with two unidentate acetate groups, two N(1) and N(1A) atoms of pyridine rings in 2,4′-bipyridyl and two oxygen atoms of water molecules. This octahedron is of very regular shape (Figure 2). The bond distances Mn–O are 2.167(2) to the O(1) atom of the acetate group and 2.189(2) Å to the water oxygen O(3). The Mn–N(1) distance is 2.295(2) Å. The pyridine rings are

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) 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)*
Mn	5000	0	0	29(1)
N(1)	4111(3)	281(4)	800(1)	37(1)
C(1)	3202(4)	−1449(5)	972(1)	44(1)
C(2)	2701(4)	−1472(5)	1461(1)	43(1)
C(3)	3156(3)	370(5)	1797(1)	36(1)
C(4)	4087(4)	2204(5)	1615(1)	41(1)
C(5)	4533(4)	2086(5)	1123(1)	41(1)
C(6)	2668(3)	442(5)	2329(1)	38(1)
C(7)	1846(4)	−1409(6)	2533(1)	53(1)
N(2)	1387(4)	−1238(7)	3026(1)	72(1)
C(8)	1806(4)	797(7)	3305(1)	53(1)
C(9)	2663(5)	2531(7)	3081(1)	57(1)
C(10)	3080(4)	2404(5)	2602(1)	42(1)
O(1)	7216(2)	2061(3)	260(1)	38(1)
C(11)	8561(3)	1372(5)	521(1)	36(1)
O(2)	8764(3)	−610(4)	711(1)	76(1)
C(12)	10006(3)	3071(5)	590(1)	43(1)
O(3)	6293(3)	−3224(3)	291(1)	48(1)

planar and are inclined at 4.3(2)° to each other within the 2,4′-bipyridyl group. The mean 2,4′-bipyridyl plane forms an angle of 31.2(1)° with the plane defined by the N(1), Mn and O(1) atoms. The bond lengths in the coordinated pyridine ring average 1.386(4) and 1.338(4) Å for C–C and C–N, respectively. Mean values of the bond angles of the two rings are 119.9(3) for the coordinated ring and 120.0(3)° for the second one.

Spectroscopic Characteristics

The IR spectrum of free 2,4′-bipy undergoes a change only in the region of the ring vibration modes of the 4-substituted (4-sub) pyridine,[23] upon coordination with manganese(II). Bands for in-plane and out-of-plane CH vibration modes do not change. The characteristic ring stretching vibration ν(C=N) for 4-sub pyridine, appearing at 1595 cm^{-1} in the free ligand, is shifted by 11 cm^{-1} towards higher values in the complex. At the same time, the position of ν(C=N) for 2-substituted pyridine (1586vs cm^{-1}) does not much change in spectra of the investigated compound (1584s cm^{-1}). A bathochromic shift of the band attributed to a stretching ring vibration of 4-sub pyridine, takes place. The breathing frequency for 4-sub pyridine (a shoulder in free 2,4′-bipy at 990sh cm^{-1}) is shifted to 1015vs cm^{-1}. It is thus possible to assume that 2,4′-bipy coordinates *via* the least hindered (4′)N atom as a monodentate ligand.[13] The absorption bands at 1576s and

TABLE III Bond lengths [Å] and angles [deg] for (**1**)

Bonds	
Mn–O(1)	2.167(2)
Mn–O(3)	2.189(2)
Mn–N(1)	2.295(2)
N(1)–C(1)	1.332(4)
N(1)–C(5)	1.343(4)
C(1)–C(2)	1.387(4)
C(2)–C(3)	1.384(4)
C(3)–C(4)	1.397(4)
C(3)–C(6)	1.488(4)
C(4)–C(5)	1.378(4)
C(6)–C(10)	1.340(4)
C(6)–C(7)	1.382(4)
C(7)–N(2)	1.384(4)
N(2)–C(8)	1.383(5)
C(8)–C(9)	1.371(5)
C(9)–C(10)	1.336(4)
O(1)–C(11)	1.267(3)
C(11)–O(2)	1.229(4)
C(11)–C(12)	1.502(4)
Angles	
O(1)–Mn–O(3)	90.18(7)
O(1)–Mn–N(1)	90.72(8)
O(1)#1–Mn–N(1)	89.28(8)
O(3)–Mn–N(1)	85.93(8)
C(1)–N(1)–C(5)	117.0(2)
C(1)–N(1)–Mn	120.1(2)
C(5)–N(1)–Mn	122.9(2)
N(1)–C(1)–C(2)	123.5(3)
C(3)–C(2)–C(1)	119.6(3)
C(2)–C(3)–C(4)	117.0(2)
C(2)–C(3)–C(6)	122.3(2)
C(4)–C(3)–C(6)	120.7(2)
C(5)–C(4)–C(3)	119.6(3)
N(1)–C(5)–C(4)	123.3(3)
C(10)–C(6)–C(7)	121.3(3)
C(10)–C(6)–C(3)	116.4(3)
C(7)–C(6)–C(3)	122.3(3)
C(6)–C(7)–N(2)	120.1(3)
C(7)–N(2)–C(8)	118.3(3)
C(9)–C(8)–N(2)	118.2(3)
C(10)–C(9)–C(8)	124.0(3)
C(9)–C(10)–C(6)	118.1(3)
C(11)–O(1)–Mn	128.1(2)
O(2)–C(11)–O(1)	124.1(3)
O(2)–C(11)–C(12)	118.3(2)
O(1)–C(11)–C(12)	117.6(2)

Symmetry transformation used to generate equivalent atom #1 is $-x+1$, $-y$, $-z$.

1348s cm^{-1} are identified as OCO asymmetric and OCO symmetric stretching modes, respectively.[24,25] Comparison of these bands with those of sodium acetate shows that ν_{sym} OCO is shifted to lower frequencies (66 cm^{-1}) and ν_{asym} OCO band remains almost the same. The frequencies of these modes and separation (226 cm^{-1}) modes suggest the exclusive presence of coordinated unidentate acetate groups in the obtained complex. Both the above points are entirely consistent with the X-ray structure. A strong and broad band in the water stretching region (with maximum at 3350 cm^{-1}) and a weak peak in water bending region (1655 cm^{-1}) were present in the IR spectra. The H_2O wagging vibrations for coordinated water were observed at 559m cm^{-1}. The Mn–O stretching mode for coordinated water is masked by 2,4′-bipy. Similar behaviour has previously been observed in metal complexes with other aromatic amines.[26]

Thermal Decomposition

Thermal analysis shows that the complex is thermally stable to 65°C. The first mass losses can be assigned to water evolution. The release of H_2O

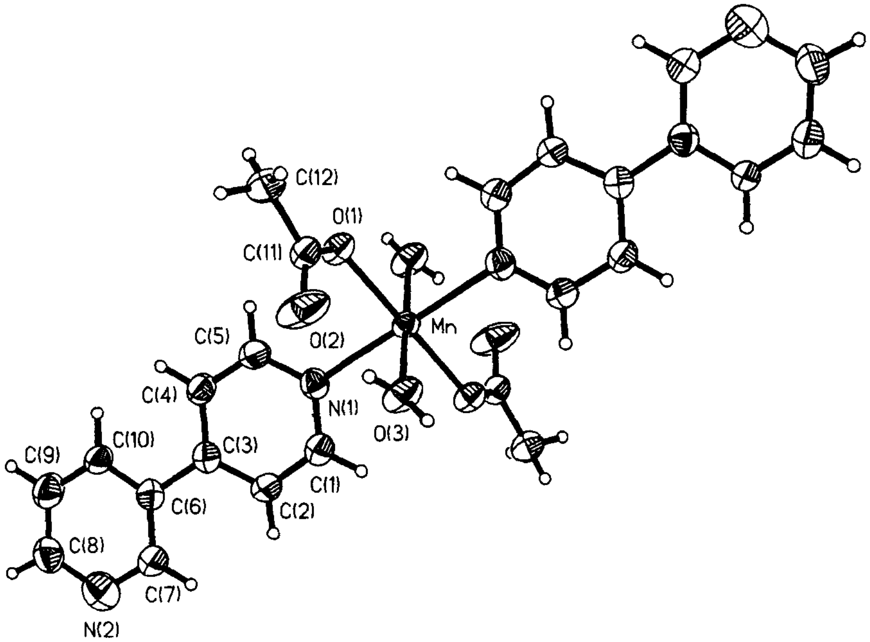

FIGURE 1(a)

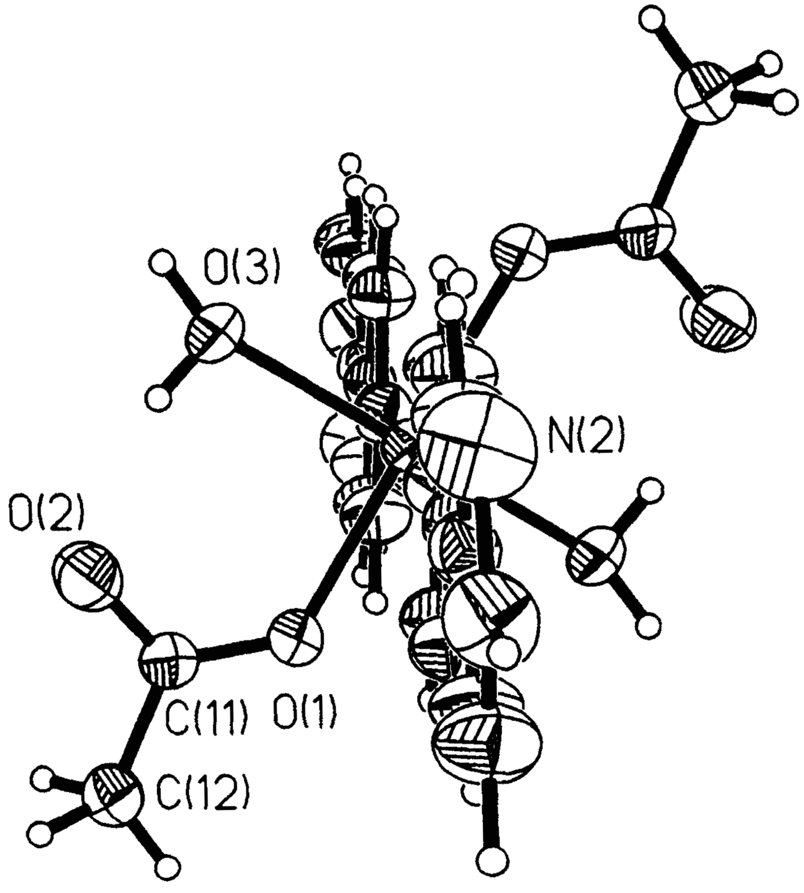

FIGURE 1(b)

FIGURE 1 (a) The structure and numbering scheme for the complex $[Mn(H_2O)_2(ac\text{-}O)_2(2,4'\text{-bipy})_2]$; (b) view of the complex along the bipyridyl groups.

molecules is a two-step process. The anhydrous complex directly decomposes to $Mn(ac)_2$ in the temperature range 138–260°C. Dehydration and deamination processes are accompanied by endothermic effects on the DTA curve. Upon further heating Mn_2O_3 forms (calcd.: 15.14%, found: 15.0%). Constant weight level for pure Mn_2O_3 was observed between 330–900°C. The decomposition of $Mn(ac)_2$ is connected with a very strongly exothermic effect at 320°C. As the temperature is raised above 900°C conversion to Mn_3O_4 occurs (cald.: 14.63%, found: 14.5%). Based on the chemical and thermal analysis, supported by powder X-ray diffraction

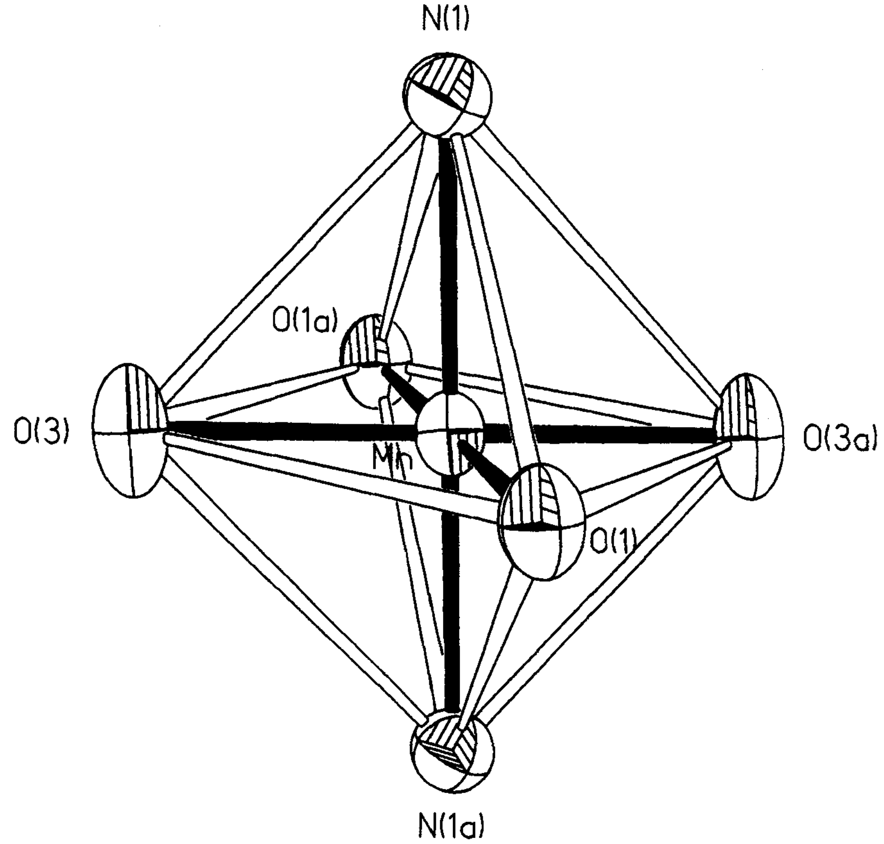

FIGURE 2 The octahedral environment of the Mn atom.

investigations, thermal decomposition of the complex proceeds according to the following sequence

$$[\mathrm{Mn(H_2O)_2(ac)_2(2,4'\text{-}bipy)_2}] \xrightarrow[78^\circ\mathrm{C\,endo}]{65\text{–}98^\circ\mathrm{C}}$$

$$[\mathrm{Mn(H_2O)(ac)_2(2,4'\text{-}bipy)_2}] \xrightarrow[100^\circ\mathrm{C\,endo}]{98\text{–}138^\circ\mathrm{C}}$$

$$\mathrm{Mn(ac)_2(2,4'\text{-}bipy)_2} \xrightarrow[245^\circ\mathrm{C\,endo}]{138\text{–}260^\circ\mathrm{C}}$$

$$\mathrm{Mn(ac)_2} \xrightarrow[320^\circ\mathrm{C\,exo}]{260\text{–}300^\circ\mathrm{C}} \mathrm{Mn_2O_3} \xrightarrow[920^\circ\mathrm{C\,endo}]{>900^\circ\mathrm{C}} \mathrm{Mn_3O_4}$$

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