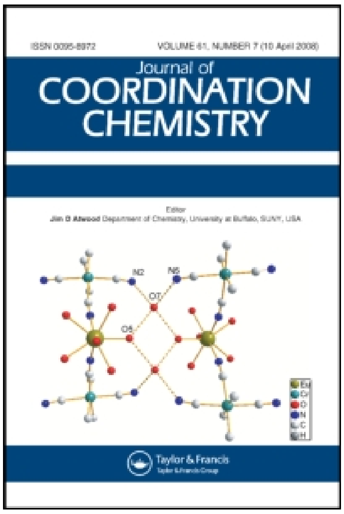

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Synthesis, Characterization and Molecular structure of bis(2,2'-Bipyridine-*N,N'*)Bis(Monochloroacetato-O) Manganese(II) Dihydrate

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SYNTHESIS, CHARACTERIZATION AND MOLECULAR STRUCTURE OF BIS(2,2′-BIPYRIDINE-*N*,*N*′)-BIS(MONOCHLOROACETATO-O) MANGANESE(II) DIHYDRATE

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$[Mn(2\text{-}bpy)_2(mcac\text{-}O)_2]\cdot 2H_2O$ (2-bpy = 2,2′-bipyridine, mcac = $ClCH_2COO^-$) has been synthesized and characterized by elemental and thermal analysis, IR, magnetic and conductivity studies. It crystallizes in space group $P2_1/n$. The manganese atom adopts a significantly distorted square bipyramidal coordination. Mn–O bonds are distinctly stronger than Mn–N bonds. Molecules of the title compound are linked by strong hydrogen bonds O–H···O(acetate) to form an infinite hydrogen-bonded chain. The hydrogen-bonded chains are assembled via weak C–H···O hydrogen bonds leading to a three-dimensional net structure.

Keywords: Manganese(II); 2,2′-Bipyridine; Monochloroacetate; Crystal structure

INTRODUCTION

The work presented here is a continuation of our studies on transition metal complexes with bipyridine isomers and carboxylates [1–6]. The crystal and molecular structures of diaqua-di(acetato-O)-bis(2,4′-bipyridyl) manganese(II) [1], and mono- and diaqua-di(acetato-O)bis(2,4′-bipyridyl) copper(II) [2] have been determined. Syntheses, properties and crystal structure of transition-metal(II) complexes with bipyridine isomers (2,2′-, 4,4′- and 2,4′-bipyridine) and carboxylates have been studied because of their complicated structures [2,7–9] and applications. They exhibit biological activity [10] and catalytic properties [11]. Especially interesting are investigations of new types of materials with potential functions as microporous solids for molecular adsorption, ion exchange, as materials for gas storage, nonlinear optical materials and several other applications [12–14]. In other work [15] on the composition and properties of

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[Mn(CH_3COO)$_2$ (2-bpy)] it was shown that 2-bpy and acetate act as bidentate chelating ligands. It is of interest to explore the influence of halogen-substituted acetate on the properties of mixed ligand bipyridine complexes.

EXPERIMENTAL

Chemicals

2,2′-Bipyridine and $ClCH_2COOH$ were obtained from Aldrich; hydroxyloamine (50%, v/v) from Fluka, methanol (anhydroscan), dimethylformamide (DMF) and dimethylsulfoxide (DMSO) from Lab. Scan, Reachim and VEB Jano-pharm Labochem Apolda, respectively. The remaining materials were p.a. from POCh-Gliwice. An aqueous solution of manganese(II) monochloroacetate was prepared by adding 20 cm^3 of 2 mol/dm^{-3} monochloroacetic acid to freshly precipitated manganese(II) carbonate in *ca.* stoichiometric quantities. The reaction mixture contained 2 cm^3 of 10% v/v hydroxyloamine to prevent oxidation of Mn(II).

Preparation of the Complex

A solution of 2-bpy (12.8 mmol) in 96% ethanol (31.3 cm^3) was added to a fresh solution of manganese(II) monochloroacetate (4.3 mmol) in water (8.7 cm^3) at room temperature. Over a period of several days a crystalline complex, [Mn(2-bpy)$_2$ (mcac-O)$_2$]$\cdot 2H_2O$, was obtained. The light-yellow product was collected by filtration, washed with cold EtOH and Et_2O, and dried at room temperature. Anal. calcd. for $Mn(H_2O)_2(ClCH_2COO)_2(C_{10}N_2H_8)_2$(%): Mn, 9.31; C, 48.83; H, 4.10; N, 9.49. Found: Mn, 9.47; C, 48.09; H, 4.07; N, 9.58.

Crystal Structure Determination

A yellow rectangular prismatic crystal was mounted on a KM-4-CCD automatic diffractometer equipped with a CCD detector and used for data collection. X-ray intensity data were collected with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293.0(2) K with the ω scan mode. A 44-s exposure time was used and a whole Ewald sphere was collected up to $2\theta = 50.21°$. Unit cell parameters were determined from least-squares refinement of the setting angles of the 4560 strongest reflections. Details concerning crystal data and refinement are given in Table I. Examination of two reference frames monitored after each 20 frames measured showed 32.7% loss of intensity. During the data reduction the above decay correction was taken into account. Lorentz, polarization and absorption [16] corrections were applied. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically using the full-matrix least-squares technique on F^2. All hydrogen atoms were found from difference Fourier syntheses after four cycles of anisotropic refinement, and refined as "riding" on adjacent atoms with individual isotropic temperature factors equal to 1.2 times the value of the equivalent temperature factor of the parent atom. SHELXS97 [17], SHELXL97 [18] and SHELXTL [19] programs were used for all calculations. Atomic scattering factors were those incorporated in the computer programs. Interatomic bond distances and angles are listed in Table II. Atomic coordinates and equivalent isotropic displacement parameters for non-H atoms are listed in Table III.

TABLE I Crystal data and structure refinement details for the complex

Empirical formula	$C_{24}H_{24}Cl_2MnN_4O_6$
Formula weight	590.31
Temperature (K)	293.0(2)
Wavelength (Å)	$\lambda(\text{Mo K}\alpha) = 0.71073$
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions (Å, °)	$a = 10.7069(7)$ $b = 13.1766(10)$ $c = 18.8878(13)$ $\beta = 95.024(6)$
Volume (Å^3)	2654.5(3)
Z, Calculated density (Mg m^{-3})	4, 1.477
Absorption coefficient (mm^{-1})	0.744
$F(000)$	1212
Crystal size (mm)	0.069 × 0.125 × 0.139
θ range for data collection	3.09 to 25.11
Index ranges	$-12 \leq h \leq 12$, $-15 \leq k \leq 15$, $-22 \leq l \leq 22$
Reflections collected/unique	27 828/4732 [$R_{(\text{int})} = 0.0456$]
Completeness to $2\theta = 25.11°$	95.3%
Refinement method	Full-matrix least-squares on F^2
Max. and min. transmission	0.894 and 0.966
Data/restraints/parameters	4732/0/334
Goodness-of-fit on F^2	1.004
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0386$, $wR2 = 0.0837$
R indices (all data)	$R1 = 0.0745$, $wR2 = 0.0962$
Largest diff. peak and hole (e Å^{-3})	0.594 and −0.566

Other Measurements

Elemental analyses were carried out using a Carlo-Erba instrument, Mn(II) was determined chelatometrically after decomposition of the complex in dilute HNO_3. IR spectra were obtained using KBr pellets on a Shimadzu spectrophotometer (4000–400 cm^{-1}). Conductivity measurements were performed on an OK-102/1 conductivity meter equipped with an OK 902 electrode at 298.14 ± 0.05 K. Molar conductivity (Λ_M) of the complex was measured using 10^{-3} M solutions in MeOH, DMF and DMSO. 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 [20]. Thermal decomposition studies were carried out on a Q-1500 derivatograph over the temperature range 293–1273 K at a heating rate of 10 K min^{-3}, in static air. The sample mass was 100 mg; α-Al_2O_3 served as the reference. Thermal decomposition products were confirmed by recording IR spectra of sinters prepared by heating samples to fixed temperatures. The final solid product of decomposition was verified by X-ray powder diffraction [21]. The TG-MS system used to monitor CO_2 produced during pyrolysis consisted of a TG/DTA (SETSYS-16/18) coupled to a mass spectrometer (QMS-422; ThermoStar Balzers Instruments) with a platinum crucible (100 mm^3). Dynamic measurements were carried out in air at a flow rate of 1 dm^3 h^{-1}. The carbon dioxide detector proved to be an important tool in the study of the decomposition of the complex.

RESULTS AND DISCUSSION

The complex is air stable at room temperature; its solubility in water is 5.0×10^{-2} M at 294 K. The room temperature effective magnetic moment, 5.89 BM, is characteristic of

TABLE II Selected structural data for the complex, distances in Å, angles in degrees

Mn(1)–O(31)	2.106(2)	N(11)–C(11)	1.340(3)
Mn(1)–O(21)	2.1327(19)	C(11)–C(12)	1.376(4)
Mn(1)–N(2)	2.255(2)	C(12)–C(13)	1.353(5)
Mn(1)–N(11)	2.261(2)	C(13)–C(14)	1.371(5)
Mn(1)–N(12)	2.282(2)	C(14)–C(15)	1.390(4)
Mn(1)–N(1)	2.312(2)	C(15)–C(16)	1.480(4)
N(1)–C(1)	1.333(3)	C(16)–N(12)	1.344(3)
N(1)–C(5)	1.346(3)	C(16)–C(17)	1.381(4)
C(1)–C(2)	1.374(4)	C(17)–C(18)	1.373(5)
C(2)–C(3)	1.365(4)	C(18)–C(19)	1.359(5)
C(3)–C(4)	1.377(4)	C(19)–C(20)	1.373(5)
C(4)–C(5)	1.380(3)	C(20)–N(12)	1.332(4)
C(5)–C(6)	1.487(3)	O(21)–C(21)	1.270(3)
C(6)–N(2)	1.348(3)	O(22)–C(21)	1.220(3)
C(6)–C(7)	1.379(4)	C(21)–C(22)	1.515(4)
C(7)–C(8)	1.378(4)	C(22)–Cl(21)	1.769(3)
C(8)–C(9)	1.367(4)	O(31)–C(31)	1.247(3)
C(9)–C(10)	1.366(4)	O(32)–C(31)	1.220(3)
C(10)–N(2)	1.337(3)	C(31)–C(32)	1.511(4)
N(11)–C(15)	1.338(3)	C(32)–Cl(31)	1.757(3)
O(31)–Mn(1)–O(21)	89.94(8)	C(10)–N(2)–Mn(1)	123.45(18)
O(31)–Mn(1)–N(2)	94.86(8)	C(6)–N(2)–Mn(1)	118.67(16)
O(21)–Mn(1)–N(2)	98.20(8)	C(15)–N(11)–C(11)	118.7(2)
O(31)–Mn(1)–N(11)	94.69(9)	C(15)–N(11)–Mn(1)	118.20(19)
O(21)–Mn(1)–N(11)	96.32(8)	C(11)–N(11)–Mn(1)	123.09(19)
N(2)–Mn(1)–N(11)	162.60(8)	N(11)–C(11)–C(12)	123.1(3)
O(31)–Mn(1)–N(12)	162.90(9)	C(13)–C(12)–C(11)	117.8(3)
O(21)–Mn(1)–N(12)	101.81(8)	C(12)–C(13)–C(14)	120.5(3)
N(2)–Mn(1)–N(12)	95.69(8)	C(13)–C(14)–C(15)	119.1(3)
N(11)–Mn(1)–N(12)	71.90(8)	N(11)–C(15)–C(14)	120.7(3)
O(31)–Mn(1)–N(1)	84.61(8)	N(11)–C(15)–C(16)	116.2(2)
O(21)–Mn(1)–N(1)	168.11(8)	C(14)–C(15)–C(16)	123.1(3)
N(2)–Mn(1)–N(1)	71.82(8)	N(12)–C(16)–C(17)	120.9(3)
N(11)–Mn(1)–N(1)	94.66(8)	N(12)–C(16)–C(15)	116.3(2)
N(12)–Mn(1)–N(1)	85.94(8)	C(17)–C(16)–C(15)	122.7(3)
C(1)–N(1)–C(5)	117.7(2)	C(18)–C(17)–C(16)	119.4(4)
C(1)–N(1)–Mn(1)	124.98(19)	C(19)–C(18)–C(17)	119.8(4)
C(5)–N(1)–Mn(1)	116.68(16)	C(18)–C(19)–C(20)	118.1(4)
N(1)–C(1)–C(2)	123.9(3)	N(12)–C(20)–C(19)	123.3(3)
C(3)–C(2)–C(1)	118.1(3)	C(20)–N(12)–C(16)	118.5(3)
C(2)–C(3)–C(4)	119.4(3)	C(20)–N(12)–Mn(1)	124.2(2)
C(3)–C(4)–C(5)	119.4(3)	C(16)–N(12)–Mn(1)	117.04(19)
N(1)–C(5)–C(4)	121.5(2)	C(21)–O(21)–Mn(1)	126.08(18)
N(1)–C(5)–C(6)	116.1(2)	O(22)–C(21)–O(21)	125.1(3)
C(4)–C(5)–C(6)	122.4(2)	O(22)–C(21)–C(22)	121.9(3)
N(2)–C(6)–C(7)	121.2(2)	O(21)–C(21)–C(22)	113.0(3)
N(2)–C(6)–C(5)	116.3(2)	C(21)–C(22)–Cl(21)	113.3(2)
C(7)–C(6)–C(5)	122.5(2)	C(31)–O(31)–Mn(1)	162.1(2)
C(8)–C(7)–C(6)	119.7(3)	O(32)–C(31)–O(31)	126.7(3)
C(9)–C(8)–C(7)	119.0(3)	O(32)–C(31)–C(32)	120.3(3)
C(10)–C(9)–C(8)	118.5(3)	O(31)–C(31)–C(32)	112.9(3)
N(2)–C(10)–C(9)	123.6(3)	C(31)–C(32)–Cl(31)	115.5(2)
C(10)–N(2)–C(6)	117.9(2)		

the singlet states [22] (similarly for $[Mn(H_2O)_2(CH_3COO)_2(2,4'\text{-bpy})_2]$ $\mu_{\text{eff}} = 5.82$ BM [22]). The complex dissociates partially in solution. Molar conductance ($\Omega^{-1}\,cm^2\,mol^{-1}$) in MeOH (68.5), DMF (15.4) and DMSO (36.6) indicates behaviour intermediate between non- and 1 : 1 electrolytes [23].

TABLE III Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for the non-H atoms

	x	*y*	*z*	*U*(*eq*)
Mn(1)	3397(1)	1849(1)	1441(1)	35(1)
N(1)	1718(2)	1094(2)	1925(1)	39(1)
C(1)	1767(3)	216(2)	2278(2)	52(1)
C(2)	810(3)	−148(2)	2647(2)	56(1)
C(3)	−250(3)	426(3)	2655(2)	55(1)
C(4)	−324(3)	1340(2)	2300(2)	48(1)
C(5)	666(2)	1652(2)	1932(1)	35(1)
C(6)	656(2)	2633(2)	1543(1)	34(1)
C(7)	−395(3)	3240(2)	1450(2)	50(1)
C(8)	−330(3)	4161(2)	1109(2)	56(1)
C(9)	776(3)	4444(2)	856(2)	51(1)
C(10)	1772(3)	3794(2)	943(2)	47(1)
N(2)	1737(2)	2902(2)	1278(1)	38(1)
N(11)	4605(2)	439(2)	1518(1)	42(1)
C(11)	5516(3)	287(2)	2039(2)	52(1)
C(12)	6247(3)	−574(3)	2088(2)	65(1)
C(13)	6018(4)	−1298(3)	1586(2)	79(1)
C(14)	5092(4)	−1166(2)	1045(2)	69(1)
C(15)	4397(3)	−274(2)	1016(2)	45(1)
C(16)	3411(3)	−46(2)	440(2)	47(1)
C(17)	3079(4)	−715(3)	−107(2)	79(1)
C(18)	2153(4)	−450(4)	−623(2)	96(1)
C(19)	1585(4)	470(3)	−595(2)	82(1)
C(20)	1979(3)	1114(3)	−49(2)	61(1)
N(12)	2863(2)	871(2)	463(1)	45(1)
O(21)	4778(2)	2830(2)	1064(1)	51(1)
O(22)	3961(2)	3047(2)	−41(1)	60(1)
C(21)	4800(3)	3157(2)	433(2)	40(1)
C(22)	6002(3)	3713(2)	313(2)	52(1)
Cl(21)	6068(1)	4124(1)	−575(1)	74(1)
O(31)	3916(2)	2325(2)	2490(1)	63(1)
O(32)	5542(2)	2351(2)	3291(1)	83(1)
C(31)	4421(3)	2359(2)	3110(2)	48(1)
C(32)	3483(3)	2463(3)	3659(2)	77(1)
Cl(31)	4104(1)	2359(1)	4548(1)	88(1)
O(98)	6864(2)	2783(2)	2078(1)	75(1)
O(99)	2549(2)	3988(2)	−1213(1)	89(1)

$U_{(\text{eq})}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

A perspective view of the structure together with the atom numbering scheme is shown in Fig. 1; displacement ellipsoids are plotted with 50% probability. All atoms lie in general positions. The manganese atom adopts a significantly distorted square bipyramidal coordination geometry (Fig. 2). All least-squares planes of the manganese polyhedron are *trans*-distorted. The maximum deviation, 0.243(1) Å, occurs for atom O(31) for the plane calculated through N(1)–N(12)–O(21)–O(31), and the smallest (0.0141(9) Å) for N(2) of the N(11)–N(12)–N(2)–O(31) plane. The dihedral angle between these planes is 83.44(5)°, and for these planes and that of N(1)–N(2)–N(11)–O(21) are respectively 82.39(6) and 86.06(5)°. Manganese deviates from these planes by 0.032(1), 0.247(1) and 0.047(1) Å, respectively.

In the literature only two compounds with a similar arrangement of bipyridine and acetate groups, *cis*-bis(2,2′-bipyridyl)-bis(trifluoroacetato-O) manganese(II) [24] and bis(2,2′-bipyridine-*N*,*N*′)bis(dichloroacetato-O) manganese(II) [25], are described. Bond valences were computed as $v_{ij} = \exp[(R_{ij} - d_{ij})/0.37]$ [26,27], where R_{ij} is the

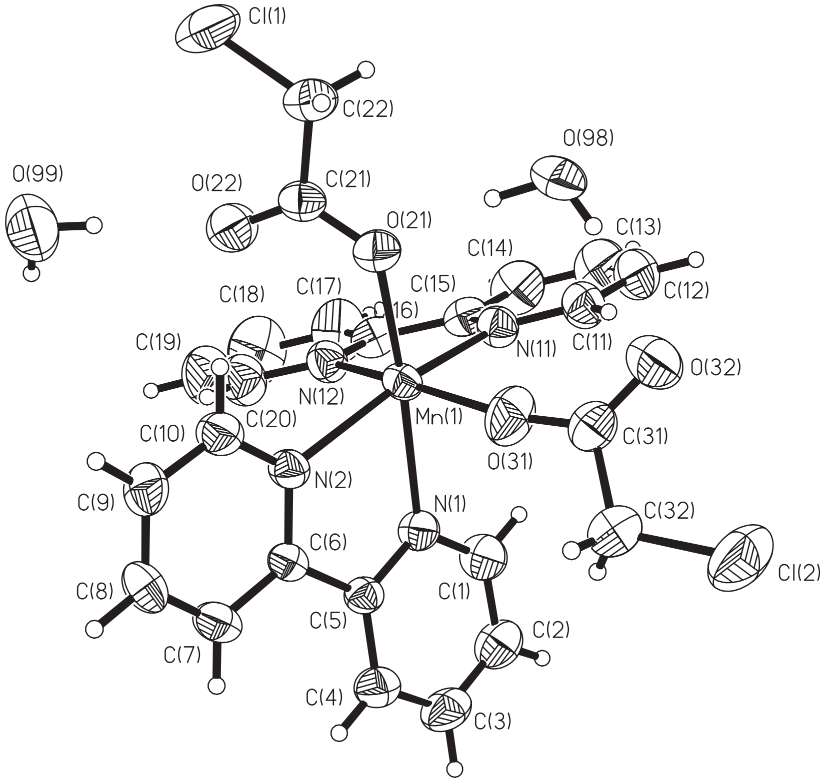

FIGURE 1 The molecular conformation of the complex with the atom numbering, plotted with 50% probability displacement ellipsoids.

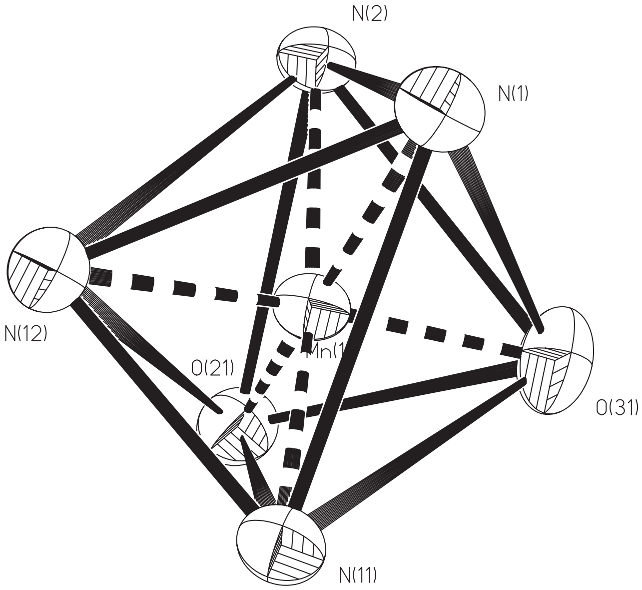

FIGURE 2 The manganese coordination polyhedron.

bond-valence parameter (in the formal sense R_{ij} is the single bond length between i and j atoms) [28]. $R_{\mathrm{Mn–O}}$ and $R_{\mathrm{Mn–N}}$ were taken as 1.790 and 1.87 [29], respectively. The computed bond valences are $\nu_{\mathrm{Mn(1)–O(21)}} = 0.396$, $\nu_{\mathrm{Mn(1)–O(31)}} = 0.426$, $\nu_{\mathrm{Mn(1)–N(1)}} = 0.303$, $\nu_{\mathrm{Mn(1)–N(2)}} = 0.354$, $\nu_{\mathrm{Mn(1)–N(11)}} = 0.348$, $\nu_{\mathrm{Mn(1)–N(12)}} = 0.328$ valence units, and thus the computed valence of Mn(1) atom is 2.15 v.u. The deviation from the valence sum rule can be explained by steric restraints of the relatively rigid 2,2′-bipyridine ligands. Mn–O bonds are distinctly stronger than Mn–N bonds, but monochloroacetato substituents are bonded more weakly (bipyridine bonding valence is 0.657 and 0.676 v.u., respectively for substituents indicated by N(1) and N(11) atoms). Each bipyridine substituent has one Mn–N bond weaker than the other. The planar (within experimental error) pyridine rings are inclined at 7.1(1)° (indicated by N(1) and N(2) atoms), and 3.1(2)° (indicated by N(11) and N(12) atoms). Chloroacetate groups are close to planarity.

Molecules of the complex are linked by strong hydrogen bonds [O(99)–H···O(acetate)] to form infinite hydrogen-bonded chains along the *ac* diagonal (for details see Table IV). In the structure O(98)–H···O(acetate) hydrogen bonds and weak C(10)–H(10)···O(22) hydrogen bonds [30] also exist (Table IV), providing additional conformational stability to the chloroacetate substituents. The hydrogen-bonded chains are assembled via weak C–H···O hydrogen bonds (Table IV) to give a three-dimensional infinite net structure.

IR spectra of the complex exhibit several absorption bands characteristic of 2-bpy and OCO groups. The spectrum of free 2-bpy undergoes a change upon coordination with manganese(II). The characteristic ring stretching vibration modes ν(CC), ν(CN), $\nu(\mathrm{CC})_{\mathrm{inter\ ring}}$ (A_1 symmetry) ν(CC), ν(CN) (B_1 symmetry) appear at 1579 and 1553 cm^{-1} in the free ligand [31]. In spectra of the complex, they are observed at 1650.0, 1593.7 (A_1 symmetry) and 1575.7 cm^{-1} (B_1 symmetry), respectively. The ring "breathing" mode is shifted by 23.5 cm^{-1} towards higher frequencies in comparison to unbonded 2-bpy. The characteristic aromatic out-of-plane hydrogen deformation modes in unbonded 2-bpy are observed at 753 and 736 (satellite) cm^{-1}. The complex exhibits very strong absorption at 769.5 cm^{-1}; the satellite of this band at 738 cm^{-1} gains intensity and is clearly split. Thus, the obtained complex contains 2,2′-bipyridine acting as a chelating ligand [32]. The absorption bands at 1685.7, 1647.1 are identified as OCO asymmetric and at 1367.4 cm^{-1} as OCO symmetric stretching modes. Comparison of these bands with those of sodium monochloroacetate shows that ν_s(OCO) is shifted to lower and ν_{as}(OCO) is shifted to higher frequencies. The separations $\Delta\nu = \nu_{as}(\mathrm{OCO}) - \nu_s(\mathrm{OCO})$

TABLE IV Hydrogen bonds for the complex, distances in Å, angles in degrees

D–H···A	*d(D–H)*	*d(H···A)*	*d(D···A)*	*∠(DHA)*
O(98)–H(98O)···O(32)	0.82	2.05	2.854(3)	168.5
O(98)–H(98P)···O(21)	0.98	1.84	2.812(3)	172.9
O(99)–H(99O)···O(22)	0.88	1.97	2.853(3)	175.7
O(99)–H(99P)···O(32)$^{\#1}$	0.97	1.94	2.874(4)	159.4
C(7)–H(7)···O(98)$^{\#2}$	0.93	2.39	3.315(3)	170.3
C(8)–H(8)···O(99)$^{\#3}$	0.93	2.53	3.423(4)	162.3
C(10)–H(10)···O(22)	0.93	2.57	3.267(3)	132.2
C(12)–H(12)···O(98)$^{\#4}$	0.93	2.57	3.271(4)	132.2
C(14)–H(14)···O(22)$^{\#5}$	0.93	2.56	3.333(4)	141.3

Symmetry transformations used to generate equivalent atoms:
$^{\#1}x-1/2,\ -y+1/2,\ z-1/2$; $^{\#2}x-1,\ y,\ z$; $^{\#3}-x,\ -y+1,\ -z$; $^{\#4}-x+3/2,\ y-1/2,\ -z+1/2$; $^{\#5}-x+1,\ -y,\ -z$.

are greater (318.3, 279.7 cm^{-1}) than $\Delta\nu$ of sodium salts ($\Delta\nu = 185\,\mathrm{cm}^{-1}$) [33], caused by terminal carboxylate groups [34–36]. The ν_s(OCO) absorption band is split, owing to the non-equivalence of bonds between manganese(II) and carboxylate groups. The complex exhibits a broad band in the water stretching region at *ca.* 3400 cm^{-1}. H_2O wagging vibrations for coordinated water were not observed. Spectra are entirely consistent with the X-ray structure.

Thermal decomposition of $[\mathrm{Mn(2\text{-}bpy)_2(mcac\text{-}O)_2}]\cdot 2H_2O$ in air is a multi-stage process. The complex is stable to 333 K. The first mass loss can be assigned to water evolution in a two-step process in the temperature range 343–393 K. With increasing temperature, decomposition of monochloroacetates takes place and the stepwise release of 2-bpy begins. These processes are accompanied by liberation of CO_2 with maxima of ion current at 440.3, 544.3, 623.9, 698.5, 833.0 and 916.6 K. During these processes, intermediate species $\mathrm{Mn(2\text{-}bpy)Cl_2}$ and $\mathrm{Mn(2\text{-}bpy)_{0.5}Cl_2}$ are probably formed. In the sinter of the complex only absorption bands for 2-bpy and chlorine ions were evident. Formation of Mn_3O_4 (via Mn_2O_3) occurs above 1173 K (calcd. 12.92%, found 12.00%). Pyrolysis of the investigated complex is accompanied by several exo- and endothermic effects in the DTA curve (given in the scheme below).

$$[\mathrm{Mn(2\text{-}bpy)_2(mcac)_2}]\cdot 2H_2O \xrightarrow[343-393\,\mathrm{K}]{393\,\mathrm{K\ endo}} [\mathrm{Mn(2\text{-}bpy)_2(mcac)_2}] \xrightarrow[393-633\,\mathrm{K}]{493\,\mathrm{K\ endo},\ 591\,\mathrm{K\ exo}}$$

$$[\mathrm{Mn(2\text{-}bpy)Cl_2}] \xrightarrow[633-733\,\mathrm{K}]{693\,\mathrm{K\ exo}} [\mathrm{Mn(2\text{-}bpy)_{0.5}Cl_2}] \xrightarrow[733-973\,\mathrm{K}]{913\,\mathrm{K\ exo}}$$

$$Mn_2O_3 \xrightarrow[>1173\,\mathrm{K}]{} Mn_3O_4$$

The stabilities of mixed-ligand complexes of manganese(II) containing 2,4′-bpy and CH_3COO^- [1] or 2-bpy and $ClCH_2COO^-$ are very similar. However, anhydrous complexes decompose in various ways.

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Supplementary Data

Tables of crystal data and structure refinement, anisotropic displacement coefficients, atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms, H-atom coordinates and isotropic displacement parameters, bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre, No. CCDC224142.

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