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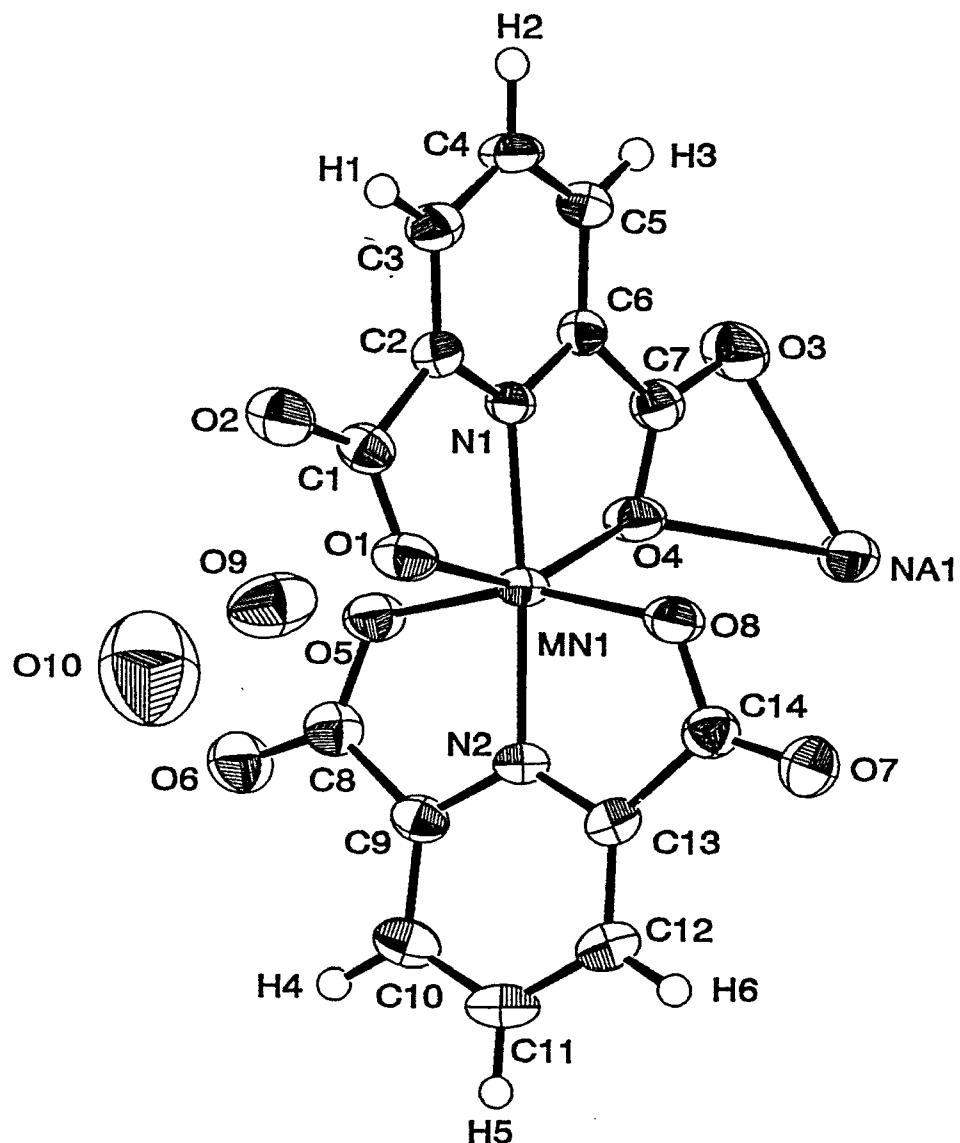
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S1

## Supplementary material.

**Synthesis and characterization of  $\text{Na}[\text{Mn}(\text{dpa})_2] \cdot 2\text{H}_2\text{O}$ .** To a stirring solution of  $[(\text{bpy})_2\text{MnOOMn}(\text{bpy})_2](\text{ClO}_4)_3$ , prepared by the method of Cooper et al (*J. Am. Chem. Soc.* 1977, 99, 6623), (0.29 mmol) in acetonitrile (2.5 ml) was added solid dipicolinic acid (2.2 mmol) and solid NaOH (2.3 mmol). After stirring for ten min at 25°C the green solution had turned brown. At this time two drops of water were added and the solution stirred for a further two hr. Filtration isolated a lilac precipitate (0.466 g) which was washed with 2 ml acetonitrile, two 5 ml potions of ethyl ether, and four 5 ml portions of hexanes. The precipitate was dissolved in 10 ml hot methanol to give a red solution which was refrigerated. After two days a brown precipitate had formed which was removed by filtration and the remaining red solution was left to evaporate at room temperature. Hexagonal red crystals of  $[\text{Mn}(\text{dpa})_2]\text{Na}$  formed overnight (yield = 25% based on bpy-dimer). A suitable crystal was taken for X-ray analysis.  $^1\text{H}$  NMR ( $d_4\text{-MeOH}$ , 350 MHz)  $\delta$  16.7 (s, 2H), -63.8 (s, 1H). IR (KBr pellet) 1682, 1659, 1646, 1600  $\text{cm}^{-1}$ .

**Solution chemistry of  $[\text{Mn}(\text{dpa})_2]^-$ .** Chandra et al.<sup>14</sup> isolated and solved the crystal structure of a red manganese-dpa complex that was formulated as  $[(\text{Mn}(\text{dpa})_2)^- (\text{Mn}(\text{dpaH}_2)(\text{dpa}))^+].5\text{H}_2\text{O}$ . However, we found that their synthesis initially produced a violet powder that had different spectroscopic characteristics when compared to the red  $\text{Na}[\text{Mn}(\text{dpa})_2] \cdot 2\text{H}_2\text{O}$ . The  $^1\text{H}$  NMR of the violet complex in methanol showed broad singlets at +18 ppm (2 H) and -33 ppm (1 H) with a UV/Vis band at  $\lambda_{\text{max}} = 520$  nm. On dissolution in water the violet complex gave a red solution showing singlets at +14 ppm (2 H) and -66 ppm (1 H) with a UV/Vis band at  $\lambda_{\text{max}} = 495$  nm. Subsequent isolation of this red complex with excess tetraphenylphosphonium bromide gave a crystalline precipitate which was identified as  $(\text{PPh}_4)[\text{Mn}(\text{dpa})_2]$  by comparison to the sodium salt. Redissolution in methanol gave a red solution with singlets at +15 and -66 ppm. The IR of  $(\text{PPh}_4)[\text{Mn}(\text{dpa})_2]$  (KBr pellet) has bands at 1688, 1660 and 1653  $\text{cm}^{-1}$ . The violet solid (KBr pellet) has IR bands at 1722, 1699, 1691, 1663 and 1648  $\text{cm}^{-1}$ . In the present study the complex was added to the oxone solutions in methanol as the violet form, but on addition to water it immediately converted to a red solution of the structurally characterized  $[\text{Mn}(\text{dpa})_2]^-$ .



**Figure S1.** ORTEP diagram of  $\text{Na}[\text{Mn}(\text{dpa})_2] \cdot 2\text{H}_2\text{O}$  with thermal ellipsoids at 50% probability.

## YALE CHEMICAL INSTRUMENTATION CENTER

### X-RAY STRUCTURE REPORT

Reference Number: SRH293 BRUDVIG  
1-DEC-1995

#### DATA COLLECTION

A deep purple crystal of  $C_{14}H_8O_{10}N_2MnNa$  having approximate dimensions of 0.097 X 0.36 X 0.45 mm was mounted on a glass fiber. All measurements were made on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo K $\alpha$  radiation.

Cell constants and an orientation matrix for data collection obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range  $10.60 < 2\theta < 18.20^\circ$  corresponded to a monoclinic cell with dimensions:  $a = 8.684 (1)\text{\AA}$ ,  $b = 14.692 (3)\text{\AA}$ ,  $c = 12.419 (2)\text{\AA}$ ,  $\beta = 91.98 (1)^\circ$  and  $V = 1583.5 (8)\text{\AA}^3$ . For  $Z = 4$  and F.W. = 442.15 the calculated density is 1.855 g/cm $^3$ . Based on the systematic absences of:  $h0l$ :  $h+l = 2n+1$ ;  $0k0$ :  $k = 2n+1$ , and the successful solution and refinement of the structure the space group was determined to be:  $P2_1/n$  (#14).

The data were collected at a temperature of  $23 \pm 1^\circ\text{C}$  using the  $2\theta/\omega$  scan technique to a maximum  $2\theta$  value of  $52.6^\circ$ . Scans of  $(0.63 + 0.50 \tan \theta)^\circ$  were made at speeds ranging from 1.0 to  $16.5^\circ/\text{min}$  (in omega). Moving-crystal moving counter background measurements were made by scanning an additional 25% above and below the scan range. The counter aperture consisted of a variable horizontal slit with a width ranging from 2.0 to 2.5 mm and a vertical slit set to 2.0 mm. The diameter of the incident beam collimator was 0.8 mm and the crystal to detector distance was 21 cm. For intense reflections an attenuator was automatically inserted in front of the detector.

#### DATA REDUCTION

Of the 3556 reflections which were collected 3360 were unique ( $R_{\text{int}} = .014$ ). The intensities of three representative reflections which were measured after every 60 minutes of X-ray exposure time remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied).

The linear absorption coefficient for Mo K $\alpha$  is  $8.9 \text{ cm}^{-1}$ . Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects.

## STRUCTURE SOLUTION AND REFINEMENT

The structure was solved by direct methods<sup>1</sup>. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions except for those on the water molecule which were located in the difference map but not refined. The hydrogen atoms in the second water molecule could not be located in the difference map. The final cycle of full-matrix least-squares refinement<sup>2</sup> was based on 2688 observed reflections ( $I > 3.00\sigma(I)$ ) and 253 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R = \sum |||F_O| - |F_C||| / \sum |F_O| = 0.038$$

$$R_w = [(\sum w (|F_O| - |F_C|)^2 / \sum w F_O^2)]^{1/2} = 0.059$$

The standard deviation of an observation of unit weight<sup>3</sup> was 2.61. The weighting scheme was based on counting statistics and included a factor ( $p = 0.03$ ) to downweight the intense reflections. Plots of  $\sum w (|F_O| - |F_C|)^2$  versus  $|F_O|$ , reflection order in data collection,  $\sin \theta/\lambda$ , and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.34 and -0.70 e-/Å<sup>3</sup> respectively.

Neutral atom scattering factors were taken from Cromer and Waber<sup>4</sup>. Anomalous dispersion effects were included in  $F_{calc}$ <sup>5</sup>; the values for  $\Delta f'$  and  $\Delta f''$  were those of Cromer<sup>6</sup>. All calculations were performed using the TEXSAN<sup>7</sup> crystallographic software package of Molecular Structure Corporation.

## References

### (1) Structure Solution Methods:

#### MITHRIL

Gilmore C.J.; MITHRIL - an integrated direct methods computer program, *J. Appl. Cryst.*, 17, 42-46, University of Glasgow, Scotland (1984).

#### DIRDIF

Beurskens P.T.; DIRDIF: Direct Methods for Difference Structures - an automatic procedure for phase extension and refinement of difference structure factors. Technical Report 1984/1, Crystallography Laboratory, Toernooiveld 6525 Ed Nijmegen, Netherlands.

### (2) Least-Squares:

Function minimized:  $\sum w (|F_O| - |F_C|)^2$

where:  $w = 4F_O^2/\sigma^2(F_O^2)$

$\sigma^2(F_O^2) = [S^2(C+R^2B) + (pF_O^2)^2]/Lp^2$

S = Scan rate

C = Total Integrated Peak Count

R = Ratio of Scan Time to background counting time

B = Total Background Count

L<sub>p</sub> = Lorentz-polarization factor

p = p-factor

(3) Standard deviation of an observation of unit weight:

$$[\sum w(|F_O| - |F_C|)^2 / (N_O - N_V)]^{1/2}$$

where: N<sub>O</sub> = number of observations N<sub>V</sub> = number of variables

(4) Cromer D.T. & Waber J.T.; "International Tables for X-ray Crystallography," Vol. IV, The Kynoch Press, Birmingham England, Table 2.2 A (1974).

(5) Ibers J.A. & Hamilton W.C.; *Acta Crystallogr.*, 17, 781 (1964).

(6) Cromer D.T.; "International Tables for X-ray Crystallography," Vol. IV, The Kynoch Press, Birmingham England, Table 2.3.1 (1974).

(7) TEXSAN - TEXRAY Structure Analysis Package Molecular Structure Corporation (1989).

## EXPERIMENTAL DETAILS

### A. Crystal Data

Empirical Formula	$C_{14}H_8O_{10}N_2MnNa$
Formula Weight	442.15
Crystal Color/Habit	deep purple prism
Crystal Dimensions (mm)	0.097 X 0.36 X 0.45
Crystal System	monoclinic
No. Reflections Used for Unit Cell Determination ( $2\theta$ range)	25 (10.6 - 18.2°)
Lattice Parameters:	$a = 8.684 (1)\text{\AA}$ $b = 14.692 (3)\text{\AA}$ $c = 12.419 (2)\text{\AA}$ $\beta = 91.98 (1)^\circ$  $V = 1583.5 (8)\text{\AA}^3$
Space Group	P2 <sub>1</sub> /n (#14)
Z value	4
Dcalc	1.855 g/cm <sup>3</sup>
F000	888
$\mu(MoK\alpha)$	8.88 cm <sup>-1</sup>

### B. Intensity Measurements

Diffractometer	Enraf-Nonius CAD-4
Radiation	MoK $\alpha$ ( $\lambda = 0.71069 \text{\AA}$ )
Temperature	23°C
Attenuator	Zr foil (factor = 20.4)

Take-off Angle	2.8°
Detector Aperture	2.0-2.5 mm hor./2.0 mm vert.
Crystal to Detector Distance	21 cm
Scan Type	$2\theta/\omega$
Scan Rate	1.0 - 16.5°/min (in omega)
Scan Width	(0.63 + 0.50 tanθ)°
$2\theta_{\text{max}}$	52.6°
No. of Reflections Measured	Total: 3556
Unique:	3360 ( $R_{\text{int}} = .014$ )
Corrections	Lorentz-polarization

### C. Structure Solution and Refinement

Structure Solution	Direct Methods
Refinement	Full-matrix least-squares
Function Minimized	$\sum w ( F_O  -  F_C )^2$
Least-squares Weights	$4F_O^2/\sigma^2(F_O^2)$
p-factor	0.03
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ( $I > 3.00\sigma(I)$ )	2688
No. Variables	253
Reflection/Parameter Ratio	10.62
Residuals:	$R; R_w$ 0.038; 0.059
Goodness of Fit Indicator	2.61
Max Shift/Error in Final Cycle	0.00
Maximum Peak in Final Diff. Map	0.34 e-/Å³
Minimum Peak in Final Diff. Map	-0.70 e-/Å³

## Positional parameters and B(eq) for SRH293 BRUDVIG - LIMBURG

atom	x	y	z	B(eq)
MN1	0.20910(5)	0.25925(3)	0.75026(3)	2.27(2)
NA1	-0.0076(2)	0.51294(8)	0.8484(1)	3.54(5)
O1	0.3765(2)	0.1491(1)	0.7498(2)	3.11(9)
O2	0.4460(3)	0.0252(2)	0.8425(2)	4.0(1)
O3	-0.0056(3)	0.3926(2)	0.9983(2)	4.1(1)
O4	0.0524(2)	0.3465(1)	0.8339(1)	3.04(9)
O5	0.0492(2)	0.1791(1)	0.6901(1)	3.07(9)
O8	0.3658(2)	0.3556(1)	0.7562(2)	3.09(8)
O6	-0.0527(3)	0.1235(2)	0.5355(2)	4.2(1)
O7	0.4759(3)	0.4653(2)	0.6603(2)	4.1(1)
O9	0.7783(3)	0.0145(2)	0.6800(2)	5.6(1)
O10	0.2315(6)	0.0048(3)	0.5960(5)	11.2(3)
N1	0.2213(2)	0.2141(1)	0.9053(2)	2.14(8)
N2	0.2172(2)	0.2914(2)	0.5987(2)	2.27(9)
C1	0.3836(3)	0.0997(2)	0.8343(2)	2.6(1)
C2	0.3078(3)	0.1419(2)	0.9305(2)	2.3(1)
C3	0.3283(3)	0.1133(2)	1.0367(2)	2.9(1)
C4	0.2567(4)	0.1633(2)	1.1156(2)	3.2(1)
C5	0.1663(4)	0.2372(2)	1.0883(2)	2.8(1)
C6	0.1493(3)	0.2613(2)	0.9812(2)	2.2(1)
C7	0.0568(3)	0.3404(2)	0.9360(2)	2.7(1)
C8	0.0360(3)	0.1733(2)	0.5851(2)	2.9(1)
C9	0.1374(3)	0.2394(2)	0.5279(2)	2.5(1)
C10	0.1545(4)	0.2519(2)	0.4190(2)	3.2(1)
C11	0.2525(4)	0.3202(2)	0.3869(2)	3.6(1)
C12	0.3317(4)	0.3751(2)	0.4618(2)	3.2(1)
C13	0.3120(3)	0.3572(2)	0.5694(2)	2.5(1)
C14	0.3925(3)	0.3996(2)	0.6676(2)	2.8(1)

## Positional parameters and B(eq) for SRH293 BRUDVIG - LIMBURG

atom	x	y	z	B(eq)
H1	0.3890	0.0613	1.0546	3.5
H2	0.2704	0.1464	1.1892	3.8
H3	0.1164	0.2710	1.1422	3.3
H4	0.1007	0.2148	0.3676	3.9
H5	0.2661	0.3299	0.3122	4.3
H6	0.3968	0.4230	0.4395	3.8
H7	0.8275	0.0455	0.6303	6.6
H8	0.8496	-0.0084	0.7302	6.6

## Cartesian coordinates

atom	x	y	z
MN1	1.4940	3.8088	9.3121
NA1	-0.4302	7.5358	10.5301
O1	2.9475	2.1909	9.3062
O2	3.5116	0.3706	10.4571
O3	-0.4768	5.7676	12.3902
O4	0.0976	5.0910	10.3497
O5	0.1312	2.6306	8.5649
O8	2.8527	5.2241	9.3858
O6	-0.6877	1.8139	6.6465
O7	3.8497	6.8363	8.1956
O9	6.4666	0.2129	8.4397
O10	1.7543	0.0700	7.3973
N1	1.5338	3.1456	11.2369
N2	1.6294	4.2804	7.4304
C1	2.9735	1.4653	10.3554
C2	2.2736	2.0850	11.5491
C3	2.4059	1.6640	12.8669
C4	1.7509	2.3997	13.8470
C5	0.9772	3.4845	13.5081
C6	0.8753	3.8393	12.1789
C7	0.0919	5.0017	11.6171
C8	0.0618	2.5457	7.2628
C9	0.9671	3.5167	6.5517
C10	1.1623	3.7011	5.2010
C11	2.0268	4.7044	4.8018
C12	2.6824	5.5110	5.7315
C13	2.4648	5.2481	7.0675
C14	3.1219	5.8713	8.2865
H1	2.9255	0.9005	13.0897
H2	1.8385	2.1508	14.7597
H3	0.5209	3.9809	14.1773
H4	0.7168	3.1561	4.5630
H5	2.1772	4.8469	3.8746
H6	3.2572	6.2150	5.4549
H7	6.9156	0.6686	7.8231
H8	7.0647	-0.1237	9.0637

## U values for SRH293 BRUDVIG - LIMBURG

atom	U11	U22	U33	U12	U13	U23
MN1	0.0320(3)	0.0344(3)	0.0198(2)	-0.0006(2)	0.0013(2)	0.0034(1)
NA1	0.0618(8)	0.0392(7)	0.0338(6)	0.0107(6)	0.0068(5)	0.0023(5)
O1	0.042(1)	0.048(1)	0.029(1)	0.009(1)	0.0061(8)	0.0021(9)
O2	0.063(1)	0.049(1)	0.039(1)	0.025(1)	0.002(1)	-0.002(1)
O3	0.071(2)	0.045(1)	0.039(1)	0.022(1)	0.009(1)	-0.005(1)
O4	0.047(1)	0.040(1)	0.028(1)	0.012(1)	0.0029(8)	0.0059(8)
O5	0.039(1)	0.047(1)	0.031(1)	-0.008(1)	0.0011(8)	0.0046(9)
O8	0.044(1)	0.047(1)	0.027(1)	-0.007(1)	-0.0007(8)	0.0014(8)
O6	0.052(1)	0.062(1)	0.045(1)	-0.019(1)	-0.005(1)	-0.002(1)
O7	0.059(1)	0.050(1)	0.048(1)	-0.022(1)	0.004(1)	0.001(1)
O9	0.053(1)	0.097(2)	0.063(2)	-0.016(1)	0.004(1)	0.022(1)
O10	0.125(4)	0.134(4)	0.162(5)	-0.014(3)	-0.019(3)	-0.013(3)
N1	0.030(1)	0.029(1)	0.022(1)	-0.000(1)	0.0008(8)	0.0013(8)
N2	0.028(1)	0.036(1)	0.023(1)	0.001(1)	0.0013(8)	0.005(1)
C1	0.032(1)	0.039(2)	0.030(1)	0.005(1)	-0.002(1)	-0.002(1)
C2	0.032(1)	0.030(1)	0.027(1)	0.000(1)	0.000(1)	0.003(1)
C3	0.043(2)	0.037(1)	0.031(1)	0.004(1)	-0.002(1)	0.007(1)
C4	0.051(2)	0.048(2)	0.021(1)	-0.001(1)	0.001(1)	0.009(1)
C5	0.042(2)	0.039(2)	0.025(1)	-0.001(1)	0.007(1)	-0.001(1)
C6	0.031(1)	0.030(1)	0.026(1)	-0.002(1)	0.003(1)	-0.000(1)
C7	0.038(1)	0.032(1)	0.033(1)	0.004(1)	0.004(1)	-0.001(1)
C8	0.030(1)	0.042(2)	0.037(2)	-0.001(1)	-0.002(1)	0.001(1)
C9	0.029(1)	0.039(1)	0.027(1)	0.005(1)	-0.002(1)	0.000(1)
C10	0.040(2)	0.054(2)	0.028(1)	0.002(1)	-0.005(1)	-0.000(1)
C11	0.048(2)	0.061(2)	0.026(1)	0.005(2)	0.003(1)	0.010(1)
C12	0.041(2)	0.046(2)	0.035(2)	-0.001(1)	0.006(1)	0.011(1)
C13	0.030(1)	0.034(1)	0.031(1)	0.002(1)	0.002(1)	0.006(1)
C14	0.036(1)	0.037(1)	0.034(1)	-0.000(1)	0.005(1)	0.001(1)

## Intramolecular Distances Involving the Nonhydrogen Atoms

atom	atom	distance	atom	atom	distance
MN1	O1	2.175(2)	O6	C8	1.215(4)
MN1	O4	2.161(2)	O7	C14	1.212(4)
MN1	O5	1.950(2)	N1	C2	1.330(3)
MN1	O8	1.963(2)	N1	C6	1.343(3)
MN1	N1	2.036(2)	N2	C9	1.339(4)
MN1	N2	1.945(2)	N2	C13	1.329(4)
NA1	O1	2.624(2)	C1	C2	1.516(4)
NA1	O2	2.455(2)	C2	C3	1.390(4)
NA1	O3	2.567(3)	C3	C4	1.390(4)
NA1	O3	2.356(2)	C4	C5	1.375(4)
NA1	O4	2.508(2)	C5	C6	1.380(4)
NA1	O9	2.364(3)	C6	C7	1.510(4)
NA1	O10	2.476(5)	C8	C9	1.506(4)
O1	C1	1.276(3)	C9	C10	1.377(4)
O2	C1	1.224(4)	C10	C11	1.383(4)
O3	C7	1.228(3)	C11	C12	1.395(5)
O4	C7	1.271(3)	C12	C13	1.379(4)
O5	C8	1.307(3)	C13	C14	1.519(4)
O8	C14	1.304(3)			

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Distances Involving the Hydrogen Atoms

atom	atom	distance	atom	atom	distance
O9	H7	0.889	C5	H3	0.950
O9	H8	0.928	C10	H4	0.950
C3	H1	0.950	C11	H5	0.950
C4	H2	0.950	C12	H6	0.950

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

## Intramolecular Bond Angles Involving the Nonhydrogen Atoms

atom	atom	atom	angle	atom	atom	atom	angle
O1	MN1	O4	150.98(7)	O3	NA1	O3	79.7(1)
O1	MN1	O5	90.95(9)	O3	NA1	O4	52.00(7)
O1	MN1	O8	94.24(9)	O3	NA1	O9	95.5(1)
O1	MN1	N1	75.36(8)	O3	NA1	O10	77.4(1)
O1	MN1	N2	97.54(8)	O3	NA1	O4	128.91(9)
O4	MN1	O5	95.21(9)	O3	NA1	O9	97.8(1)
O4	MN1	O8	90.08(9)	O3	NA1	O10	77.5(1)
O4	MN1	N1	75.64(8)	O4	NA1	O9	101.9(1)
O4	MN1	N2	111.45(8)	O4	NA1	O10	76.8(1)
O5	MN1	O8	158.98(8)	O9	NA1	O10	172.0(2)
O5	MN1	N1	100.31(8)	MN1	O1	NA1	150.40(9)
O5	MN1	N2	79.89(9)	MN1	O1	C1	115.7(2)
O8	MN1	N1	100.71(8)	NA1	O1	C1	86.5(2)
O8	MN1	N2	79.24(9)	NA1	O2	C1	95.5(2)
N1	MN1	N2	172.89(9)	NA1	O3	NA1	100.3(1)
O1	NA1	O2	51.87(7)	NA1	O3	C7	88.0(2)
O1	NA1	O3	150.47(9)	NA1	O3	C7	150.0(2)
O1	NA1	O3	85.21(8)	MN1	O4	NA1	138.5(1)
O1	NA1	O4	127.98(8)	MN1	O4	C7	116.1(2)
O1	NA1	O9	111.6(1)	NA1	O4	C7	89.8(2)
O1	NA1	O10	74.6(1)	MN1	O5	C8	117.3(2)
O2	NA1	O3	138.99(9)	MN1	O8	C14	118.0(2)
O2	NA1	O3	137.0(1)	MN1	N1	C2	119.5(2)
O2	NA1	O4	87.10(8)	MN1	N1	C6	119.0(2)
O2	NA1	O9	95.98(9)	C2	N1	C6	121.3(2)
O2	NA1	O10	91.8(2)	MN1	N2	C9	117.5(2)
MN1	N2	C13	119.0(2)	N2	C13	C12	120.2(3)
C9	N2	C13	123.2(2)	N2	C13	C14	110.6(2)
O1	C1	O2	125.9(3)	C12	C13	C14	129.1(3)
O1	C1	C2	113.9(2)	O8	C14	O7	125.6(3)
O2	C1	C2	120.2(2)	O8	C14	C13	112.6(2)
N1	C2	C1	113.4(2)	O7	C14	C13	121.8(3)
N1	C2	C3	121.1(2)	C1	C2	C3	125.4(2)
C2	C3	C4	117.6(3)	C3	C4	C5	120.6(2)
C4	C5	C6	118.8(3)	N1	C6	C5	120.5(2)
N1	C6	C7	113.0(2)	C5	C6	C7	126.5(2)
O3	C7	O4	125.9(3)	O3	C7	C6	119.1(2)
O4	C7	C6	115.0(2)	O5	C8	O6	125.3(3)
O5	C8	C9	113.4(2)	O6	C8	C9	121.3(3)
N2	C9	C8	110.8(2)	N2	C9	C10	119.8(3)
C8	C9	C10	129.4(3)	C9	C10	C11	118.0(3)
C10	C11	C12	121.4(3)	C11	C12	C13	117.5(3)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

## Intramolecular Bond Angles Involving the Hydrogen Atoms

atom	atom	atom	angle	atom	atom	atom	angle
NA1	O9	H7	113.66	C6	C5	H3	120.59
NA1	O9	H8	137.25	C9	C10	H4	121.02
H7	O9	H8	109.09	C11	C10	H4	121.02
C2	C3	H1	121.19	C10	C11	H5	119.30
C4	C3	H1	121.19	C12	C11	H5	119.30
C3	C4	H2	119.70	C11	C12	H6	121.26
C5	C4	H2	119.70	C13	C12	H6	121.26
C4	C5	H3	120.59				

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

## Torsion or Conformation Angles

(1)	(2)	(3)	(4)	angle	(1)	(2)	(3)	(4)	angle
MN1	O1	NA1	O2	-143.3(2)	NA1	O3	NA1	O4	18.0(1)
MN1	O1	NA1	O9	136.4(2)	NA1	O3	C7	O4	-22.0(3)
MN1	O1	NA1	O10	-38.4(2)	NA1	O3	C7	C6	157.6(2)
MN1	O1	C1	O2	164.8(2)	NA1	O3	NA1	O3	0
MN1	O1	C1	C2	-16.1(3)	NA1	O3	NA1	O4	-162.3(1)
MN1	O4	NA1	O1	0.2(2)	NA1	O3	C7	O4	129.3(4)
MN1	O4	NA1	O2	34.7(1)	NA1	O3	C7	C6	-50.2(6)
MN1	O4	NA1	O3	-142.1(2)	NA1	O4	MN1	O1	131.1(2)
MN1	O4	NA1	O3	-119.4(1)	NA1	O4	MN1	O5	-127.5(1)
MN1	O4	NA1	O9	130.2(1)	NA1	O4	MN1	O8	32.2(1)
MN1	O4	NA1	O10	-57.9(2)	NA1	O4	MN1	N1	133.2(2)
MN1	O4	C7	O3	168.8(3)	NA1	O4	MN1	N2	-46.3(2)
MN1	O4	C7	C6	-10.8(3)	NA1	O4	C7	O3	22.5(3)
MN1	O5	C8	O6	176.5(3)	NA1	O4	C7	C6	-157.1(2)
MN1	O5	C8	C9	-6.7(3)	O1	MN1	O4	C7	7.9(3)
MN1	O8	C14	O7	173.6(2)	O1	MN1	O5	C8	-88.5(2)
MN1	O8	C14	C13	-9.0(3)	O1	MN1	O8	C14	102.7(2)
MN1	N1	C2	C1	-2.2(3)	O1	MN1	N1	C2	-4.4(2)
MN1	N1	C2	C3	175.1(2)	O1	MN1	N1	C6	171.6(2)
MN1	N1	C6	C5	-174.3(2)	O1	MN1	N2	C9	79.8(2)
MN1	N1	C6	C7	4.3(3)	O1	MN1	N2	C13	-93.8(2)
MN1	N2	C9	C8	8.8(3)	O1	NA1	O2	C1	2.7(2)
MN1	N2	C9	C10	-171.8(2)	O1	C1	C2	N1	12.4(3)
MN1	N2	C13	C12	173.4(2)	O1	C1	C2	C3	-164.8(3)
MN1	N2	C13	C14	-3.3(3)	O2	NA1	O1	C1	-2.6(2)
NA1	O3	NA1	O3	0	O2	C1	C2	N1	-168.5(3)
O2	C1	C2	C3	14.4(4)	O5	MN1	N2	C13	176.6(2)
O3	NA1	O3	NA1	0	O5	C8	C9	N2	-1.3(3)
O3	NA1	O3	C7	-104.2(5)	O5	C8	C9	C10	179.4(3)
O3	NA1	O4	C7	-10.8(2)	O8	MN1	O1	C1	111.8(2)
O3	NA1	O3	NA1	0	O8	MN1	O4	C7	-91.0(2)
O3	NA1	O3	C7	151.0(2)	O8	MN1	O5	C8	15.9(4)
O3	NA1	O4	C7	-11.8(2)	O8	MN1	N1	C2	-96.0(2)
O3	C7	C6	N1	-175.0(3)	O8	MN1	N1	C6	80.0(2)
O3	C7	C6	C5	3.6(5)	O8	MN1	N2	C9	172.7(2)
O4	MN1	O1	C1	13.9(3)	O8	MN1	N2	C13	-0.9(2)
O4	MN1	O5	C8	119.9(2)	O8	C14	C13	N2	7.8(3)
O4	MN1	O8	C14	-106.0(2)	O8	C14	C13	C12	-168.5(3)
O4	MN1	N1	C2	176.7(2)	O6	C8	C9	N2	175.6(3)
O4	MN1	N1	C6	-7.3(2)	O6	C8	C9	C10	-3.6(5)
O4	MN1	N2	C9	-101.5(2)	O7	C14	C13	N2	-174.7(3)
O4	MN1	N2	C13	84.9(2)	O7	C14	C13	C12	9.0(5)
O4	NA1	O3	C7	11.2(2)	O9	NA1	O1	C1	-82.9(2)
O4	NA1	O3	C7	-122.1(4)	O9	NA1	O2	C1	115.6(2)
O4	C7	C6	N1	4.6(4)	O10	NA1	O1	C1	102.3(2)
O4	C7	C6	C5	-176.8(3)	O10	NA1	O2	C1	-66.0(2)
O5	MN1	O1	C1	-88.6(2)	N1	MN1	O1	C1	11.8(2)

The sign is positive if when looking from atom 2 to atom 3 a clock-wise motion of atom 1 would superimpose it on atom 4.

## Torsion or Conformation Angles (cont)

(1)	(2)	(3)	(4)	angle	(1)	(2)	(3)	(4)	angle
O5	MN1	O4	C7	109.4(2)	N1	MN1	O4	C7	10.0(2)
O5	MN1	O8	C14	-1.1(4)	N1	MN1	O5	C8	-163.8(2)
O5	MN1	N1	C2	83.9(2)	N1	MN1	O8	C14	178.6(2)
O5	MN1	N1	C6	-100.1(2)	N1	MN1	N2	C9	82.4(7)
O5	MN1	N2	C9	-9.9(2)	N1	MN1	N2	C13	-91.2(7)
N1	C2	C3	C4	-0.7(4)	N1	C6	C5	C4	-0.8(4)
N2	MN1	O1	C1	-168.6(2)	N2	MN1	O4	C7	-169.5(2)
N2	MN1	O5	C8	9.0(2)	N2	MN1	O8	C14	5.9(2)
N2	MN1	N1	C2	-7.1(8)	N2	MN1	N1	C6	168.9(6)
N2	C9	C10	C11	-1.4(4)	N2	C13	C12	C11	-1.8(4)
C1	C2	N1	C6	-178.1(2)	C1	C2	C3	C4	176.2(3)
C2	N1	C6	C5	1.6(4)	C2	N1	C6	C7	-179.8(2)
C2	C3	C4	C5	1.5(5)	C3	C2	N1	C6	-0.8(4)
C3	C4	C5	C6	-0.8(5)	C4	C5	C6	C7	-179.2(3)
C8	C9	N2	C13	-177.9(2)	C8	C9	C10	C11	177.8(3)
C9	N2	C13	C12	0.2(4)	C9	N2	C13	C14	-176.5(2)
C9	C10	C11	C12	-0.1(5)	C10	C9	N2	C13	1.4(4)
C10	C11	C12	C13	1.7(5)	C11	C12	C13	C14	174.3(3)

The sign is positive if when looking from atom 2 to atom 3 a clock-wise motion of atom 1 would superimpose it on atom 4.