

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)
$$U_{eq} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

| | x | y | z | <i>U</i> _{eq} |
|-----|---------------|---------------|---------------|------------------------|
| Ba1 | 0.383679 (14) | 0.000292 (11) | 0.214799 (8) | 0.01764 (4) |
| S1 | 0.12012 (8) | 0.33320 (6) | 0.35348 (4) | 0.03023 (11) |
| O1 | 0.5357 (2) | 0.1509 (2) | 0.27214 (14) | 0.0351 (4) |
| O2 | -0.0002 (3) | 0.4130 (2) | 0.2886 (2) | 0.0439 (5) |
| O3 | 0.0499 (3) | 0.2870 (2) | 0.4441 (2) | 0.0482 (5) |
| N1 | 0.2534 (3) | 0.2194 (2) | 0.3100 (2) | 0.0308 (4) |
| C1 | 0.2670 (3) | 0.4096 (2) | 0.3645 (2) | 0.0289 (4) |
| C2 | 0.2472 (4) | 0.5155 (3) | 0.3999 (2) | 0.0424 (6) |
| C3 | 0.3920 (5) | 0.5510 (3) | 0.3982 (2) | 0.0498 (8) |
| C4 | 0.5481 (5) | 0.4832 (3) | 0.3649 (2) | 0.0462 (7) |
| C5 | 0.5665 (4) | 0.3758 (2) | 0.3314 (2) | 0.0337 (5) |
| C6 | 0.4225 (3) | 0.3407 (2) | 0.33174 (14) | 0.0256 (4) |
| C7 | 0.4106 (3) | 0.2286 (2) | 0.3013 (2) | 0.0264 (4) |
| S2 | 0.54351 (6) | 0.17306 (5) | 0.02100 (3) | 0.01965 (8) |
| O4 | 0.6980 (3) | 0.2292 (2) | -0.22147 (11) | 0.0329 (4) |
| O5 | 0.6417 (2) | 0.06171 (15) | 0.08081 (10) | 0.0241 (3) |
| O6 | 0.3676 (2) | 0.2105 (2) | 0.05516 (12) | 0.0272 (3) |
| N2 | 0.5690 (3) | 0.1554 (2) | -0.08385 (12) | 0.0250 (3) |
| C11 | 0.6325 (3) | 0.2978 (2) | 0.00359 (14) | 0.0205 (3) |
| C12 | 0.6501 (3) | 0.3649 (2) | 0.0656 (2) | 0.0251 (4) |
| C13 | 0.7304 (3) | 0.4578 (2) | 0.0306 (2) | 0.0307 (4) |
| C14 | 0.7899 (3) | 0.4805 (2) | -0.0620 (2) | 0.0319 (5) |
| C15 | 0.7707 (3) | 0.4117 (2) | -0.1231 (2) | 0.0273 (4) |
| C16 | 0.6908 (3) | 0.3193 (2) | -0.08868 (14) | 0.0217 (3) |
| C17 | 0.6546 (3) | 0.2325 (2) | -0.13926 (14) | 0.0240 (4) |
| O7 | 0.6926 (2) | -0.1701 (2) | 0.27442 (12) | 0.0293 (3) |
| O8 | 0.4163 (2) | -0.1405 (2) | 0.39619 (11) | 0.0273 (3) |
| O9 | 0.0946 (2) | -0.0056 (2) | 0.33593 (11) | 0.0256 (3) |
| O10 | 0.0781 (2) | 0.0620 (2) | 0.14379 (12) | 0.0313 (3) |
| C21 | 0.8110 (4) | -0.2443 (3) | 0.2153 (2) | 0.0435 (6) |
| C22 | 0.7099 (3) | -0.2252 (2) | 0.3698 (2) | 0.0309 (4) |
| C23 | 0.5724 (3) | -0.1454 (3) | 0.4255 (2) | 0.0304 (4) |
| C24 | 0.2729 (3) | -0.0999 (3) | 0.4583 (2) | 0.0322 (5) |
| C25 | 0.1216 (3) | -0.1018 (2) | 0.4171 (2) | 0.0301 (4) |
| C26 | -0.0493 (3) | 0.0011 (3) | 0.2927 (2) | 0.0357 (5) |
| C27 | -0.0668 (3) | 0.1009 (3) | 0.2060 (2) | 0.0353 (5) |
| C28 | 0.0520 (3) | 0.1254 (3) | 0.0501 (2) | 0.0341 (5) |

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTLPC (Sheldrick, 1990). Software used to prepare material for publication: SHELXL93 CIFTAB.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1065). Services for accessing these data are described at the back of the journal.

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Table 2. Selected geometric parameters (Å, °)

| | | | |
|----------|-------------|------------|-------------|
| Ba1—O10 | 2.741 (2) | S1—C1 | 1.772 (3) |
| Ba1—O1 | 2.787 (2) | O1—C7 | 1.239 (3) |
| Ba1—O8 | 2.807 (2) | N1—C7 | 1.343 (3) |
| Ba1—O9 | 2.814 (2) | S2—O6 | 1.450 (2) |
| Ba1—O7 | 2.823 (2) | S2—O5 | 1.453 (2) |
| Ba1—O5 | 2.867 (2) | S2—N2 | 1.598 (2) |
| Ba1—O6 | 2.945 (2) | S2—C11 | 1.766 (2) |
| Ba1—N1 | 2.995 (2) | O4—C17 | 1.232 (3) |
| S1—O2 | 1.441 (2) | O4—Ba1' | 2.898 (2) |
| S1—O3 | 1.442 (2) | N2—C17 | 1.365 (3) |
| S1—N1 | 1.620 (2) | N2—Ba1' | 2.848 (2) |
| O2—S1—O3 | 115.73 (14) | O6—S2—O5 | 112.08 (10) |
| O2—S1—N1 | 111.41 (13) | O6—S2—N2 | 112.80 (11) |
| O3—S1—N1 | 111.21 (13) | O5—S2—N2 | 111.14 (10) |
| O2—S1—C1 | 110.59 (12) | O6—S2—C11 | 111.52 (10) |
| O3—S1—C1 | 109.48 (13) | O5—S2—C11 | 110.98 (10) |
| N1—S1—C1 | 96.81 (11) | N2—S2—C11 | 97.49 (10) |
| C7—N1—S1 | 111.3 (2) | C17—N2—S2 | 111.61 (15) |
| C6—C1—S1 | 106.8 (2) | C16—C11—S2 | 106.86 (15) |
| C2—C1—S1 | 131.4 (2) | C12—C11—S2 | 130.3 (2) |
| O1—C7—N1 | 123.7 (2) | O4—C17—N2 | 122.9 (2) |
| O1—C7—C6 | 122.4 (2) | O4—C17—C16 | 124.4 (2) |
| N1—C7—C6 | 113.9 (2) | N2—C17—C16 | 112.7 (2) |

Symmetry code: (i) 1 - x, -y, -z.

All H atoms were positioned in idealized geometry and refined with individual isotropic displacement parameters using the riding model, with phenyl C—H 0.93, methylene C—H 0.97 and methyl C—H 0.96 Å.

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Bis(μ-bicyclo[2.2.1]hept-5-ene-2-*exo*,3-*exo*-dicarboxylato-κ²O,O':κ²O'',O''')bis-[aqua(2,2'-bipyridine-*N,N'*)manganese(II)] Monohydrate

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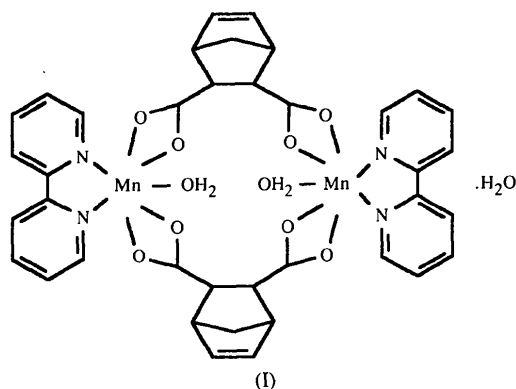
Abstract

The title compound, [Mn(μ-C₉H₈O₄)(C₁₀H₈N₂)(H₂O)]₂·H₂O, exists in the crystal as a cyclic dimer about an inversion centre. Two Mn²⁺ ions are double bridged by two bicyclic dianions which act as tetradentate ligands.

The sevenfold coordination around the Mn^{2+} ion is completed by the two bipyridine N atoms and the O atom of a water molecule. The uncoordinated water molecules are positionally disordered and connect the dimers through hydrogen bonding into chains.

Comment

The synthesis and structural characterization of 3d-metal complexes with bicyclo[2.2.1]hept-5-ene-2-*endo*,3-*endo*-dicarboxylic acid (*endo*- H_2L) and N,N' -donor ligands such as 2,2'-bipyridine (bpy) have been reported previously (Hartung, Baumeister, Kaplonek & Fechtel, 1993). In $[Mn(\textit{endo-L})bpy(H_2O)_3] \cdot 2.5H_2O$, Mn^{II} is octahedrally coordinated by two N amine atoms, three water molecules and, surprisingly, only one carboxylic O atom of the potentially tetradentate bicyclic ligand. But the exchange of *endo*- H_2L for the isomeric 2-*exo*,3-*exo*-dicarboxylic acid (*exo*- H_2L) resulted in the title compound, (I), which has an entirely different structure from the *endo* complex.



The molecular structure of (I) and the atomic numbering scheme are shown in Fig. 1. In (I), the bicyclic ligand is indeed tetradentate, with all four O atoms participating in coordination. The complex is a centrosymmetric dimer and each Mn^{2+} ion is coordinated by two halves of the two different dianions through four O atoms, two N atoms of the amine ligand and the O atom of one water molecule. The coordination geometry is highly irregular, presumably associated with the steric constraints arising from the shapes of the polydentate ligands; perhaps the best approximation is that of a pentagonal bipyramid with N1 and O1W in the axial positions. The bpy ligand is nearly planar; the r.m.s. deviation of the atoms from the least-squares plane is 0.029 Å, indicating that the two pyridine rings do not twist significantly.

The two Mn—N bond lengths are nearly the same (see Table 1). Each of the two chelating carboxylate groups shows considerable differences between its two Mn—O distances [0.128 (2) and 0.177 (2) Å], whereas all C—O bond lengths are similar. The *exo* position

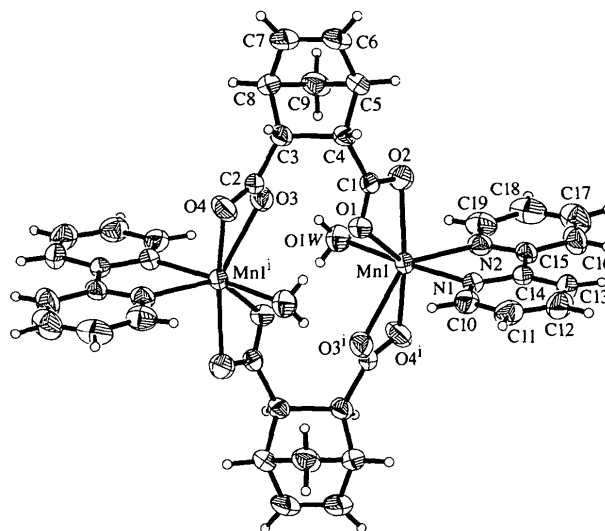


Fig. 1. Molecular structure and atomic numbering of the title compound. The displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

of the carboxylic groups and their *cis* conformation are evident from the torsion angles C1—C4—C5—C6 $-171.5(1)$, C2—C3—C8—C7 $163.7(1)$ and C1—C4—C3—C2 $5.0(2)^\circ$. The rigidity of the norborn-5-ene skeleton is manifested by the good agreement of its geometric parameters in (I) with those observed in the above-mentioned *endo* complex (Hartung *et al.*, 1993), in bicyclo[2.2.1]hept-5-ene-2-*exo*,3-*exo*-dicarboxylic anhydride (Ermer, Bell & Mason, 1989; Filippini, Gramaccioli, Rovere & Simonetta, 1972) and in other related compounds.

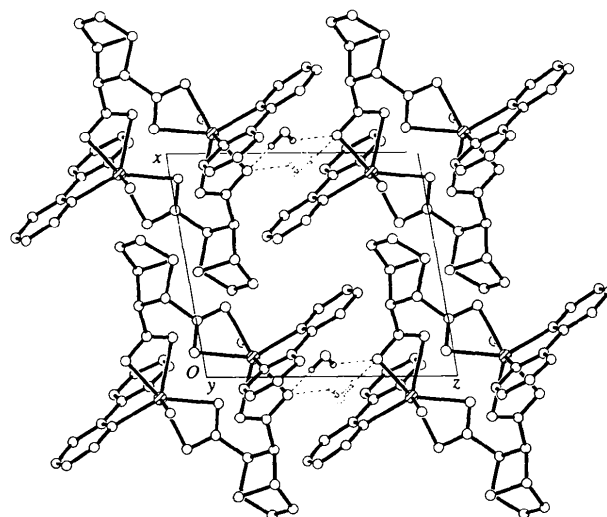


Fig. 2. Projection of the crystal packing of the title compound along [010] showing the disorder of the crystal water molecules and the hydrogen bonding (H atoms except those of the disordered crystal water molecules have been omitted for clarity).

The uncoordinated water molecule shows disorder of position about an inversion centre, the two centrosymmetrically related sites requiring an occupancy factor of 0.5. This water molecule is involved in two intermolecular hydrogen bonds bridging two dimers in this way. The complexes are thus connected into a chain parallel to the *c* axis. Details of the hydrogen-bonding geometry are given in Table 2 and Fig. 2 shows the crystal packing.

Experimental

The title compound, (I), was synthesized by the same procedure reported for the *endo* complex (Hartung *et al.*, 1993) except for the replacement of the bicyclo[2.2.1]hept-5-ene-2-*endo*,3-*endo*-dicarboxylic anhydride by its *exo* isomer. Suitable crystals were grown by slow evaporation from an aqueous solution at room temperature.

Crystal data

| | |
|--|---|
| [Mn ₂ (C ₉ H ₈ O ₄) ₂ (C ₁₀ H ₈ N ₂) ₂ (H ₂ O) ₂].H ₂ O | Mo K α radiation |
| $M_r = 836.60$ | $\lambda = 0.71073 \text{ \AA}$ |
| Triclinic | Cell parameters from 60 reflections |
| $P\bar{1}$ | $\theta = 10.0\text{--}17.2^\circ$ |
| $a = 9.534(2) \text{ \AA}$ | $\mu = 0.759 \text{ mm}^{-1}$ |
| $b = 10.486(2) \text{ \AA}$ | $T = 293(2) \text{ K}$ |
| $c = 10.486(2) \text{ \AA}$ | Prism |
| $\alpha = 109.05(1)^\circ$ | $0.38 \times 0.28 \times 0.20 \text{ mm}$ |
| $\beta = 92.00(1)^\circ$ | Yellow |
| $\gamma = 110.64(1)^\circ$ | |
| $V = 913.9(3) \text{ \AA}^3$ | |
| $Z = 1$ | |
| $D_x = 1.520 \text{ Mg m}^{-3}$ | |
| D_m not measured | |

Data collection

| | |
|--|-------------------------------|
| Stoe Stadi-4 diffractometer | $\theta_{\max} = 29.97^\circ$ |
| $\omega/2\theta$ scans | $h = -13 \rightarrow 13$ |
| Absorption correction: none | $k = -14 \rightarrow 14$ |
| 10 617 measured reflections | $l = -14 \rightarrow 14$ |
| 5315 independent reflections | 3 standard reflections |
| 3866 reflections with $I > 2\sigma(I)$ | frequency: 60 min |
| $R_{\text{int}} = 0.023$ | intensity decay: 4.3% |

Refinement

| | |
|---|---|
| Refinement on F^2 | $(\Delta/\sigma)_{\max} < 0.001$ |
| $R[F^2 > 2\sigma(F^2)] = 0.032$ | $\Delta\rho_{\max} = 0.271 \text{ e \AA}^{-3}$ |
| $wR(F^2) = 0.084$ | $\Delta\rho_{\min} = -0.223 \text{ e \AA}^{-3}$ |
| $S = 1.006$ | Extinction correction: none |
| 5315 reflections | Scattering factors from |
| 259 parameters | <i>International Tables for</i> |
| H atoms: see below | <i>Crystallography</i> (Vol. C) |
| $w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 0.0847P]$ | |
| where $P = (F_o^2 + 2F_c^2)/3$ | |

Table 1. Selected geometric parameters (\AA , $^\circ$)

| | | | |
|-------------|-------------|-------------|-------------|
| Mn1—O1W | 2.2081 (13) | Mn1—O3' | 2.4338 (13) |
| Mn1—N1 | 2.2221 (13) | O1—C1 | 1.256 (2) |
| Mn1—O4' | 2.2573 (13) | O2—C1 | 1.252 (2) |
| Mn1—N2 | 2.2682 (13) | O3—C2 | 1.249 (2) |
| Mn1—O2 | 2.2690 (12) | O4—C2 | 1.259 (2) |
| Mn1—O1 | 2.3971 (13) | C6—C7 | 1.315 (3) |
| O1W—Mn1—N1 | 176.51 (5) | N1—Mn1—O1 | 88.37 (4) |
| O1W—Mn1—O4' | 80.22 (5) | O4'—Mn1—O1 | 138.42 (4) |
| N1—Mn1—O4' | 101.92 (5) | N2—Mn1—O1 | 135.21 (4) |
| O1W—Mn1—N2 | 105.12 (5) | O2—Mn1—O1 | 55.68 (4) |
| N1—Mn1—N2 | 72.42 (5) | O1W—Mn1—O3' | 93.86 (5) |
| O4'—Mn1—N2 | 85.88 (5) | N1—Mn1—O3' | 89.63 (4) |
| O1W—Mn1—O2 | 80.05 (5) | O4'—Mn1—O3' | 55.17 (4) |
| N1—Mn1—O2 | 97.21 (5) | N2—Mn1—O3' | 133.07 (4) |
| O4'—Mn1—O2 | 156.07 (5) | O2—Mn1—O3' | 139.79 (4) |
| N2—Mn1—O2 | 86.34 (5) | O1—Mn1—O3' | 85.16 (4) |
| O1W—Mn1—O1 | 91.83 (5) | | |

Symmetry code: (i) $-x, -y, -z$.

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

| D—H...A | D—H | H...A | D...A | D—H...A |
|-----------------|-------|-------|-----------|---------|
| O2W—H2W1...O4' | 0.828 | 2.160 | 2.833 (4) | 139 |
| O2W—H2W2...O4'' | 0.850 | 2.084 | 2.871 (5) | 154 |

Symmetry codes: (i) $x, y, 1+z$; (ii) $-x, -y, -z$.

H-atom positions at C atoms were calculated by geometrical considerations and treated according to the riding model. All water H atoms were located by a difference Fourier synthesis and those of the disordered crystal water molecule were also treated as riding with site-occupancy factors of 0.5 on the corresponding O atoms during refinement. The positional parameters of the H atoms of the water molecule coordinated at Mn were refined.

Data collection: *DIF4* (Stoe & Cie, 1991a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1991b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XPIPC* (Siemens, 1990). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1202). Services for accessing these data are described at the back of the journal.

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