Crystal Structure of Bis{[μ -*N,N'*-bis(salicylidene)-1,3-pentanediaminato-(μ -acetato)-(*N,N'*-dimethylformamide)nickel(II)}manganese(II)

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The title compound, [C₄₈H₆₀N₆O₁₀Ni₂Mn], crystallizes in the monoclinic space group *P*2₁/*c* with cell parameters *a*=10.965(2) Å, *b*=17.838(4) Å, *c*=13.951(3) Å, β =112.800(10)°, *V*=2515.5(9) Å³, *Z*=2. The structure was refined to a final *R* value of 0.0508 for 2414 reflections [*I*>2 σ (*I*)]. The manganese atom is in an octahedral environment by four oxygen atoms and two acetato oxygen atoms. The phenolic oxygen ions and acetate ions of the two organic ligands coordinate both Ni and Mn atoms, forming a μ -bridge.

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The *N,N'*-bis(salicylidene)-1,3-pentanediamine is an interesting ligand, and has appeared in the coordination chemistry literature for 60 years, and their metal complexes have received considerable attention because of their biological properties.¹⁻³ The complexes formed between this ligand and first row-transition metals tend toward μ -bridging in non-aqueous media with Lewis acids. They can yield mono-, di-, tri- and even polynuclear complexes.^{4,5} The title complex is shown in Fig. 1 and 2.

A solution of *N,N'*-bis(salicylidene)-1,3-pentanediamine (1.560 g, 0.005 mol) was dissolved in 50 ml of hot ethanol. Then, a solution of NiCl₂·6H₂O (1.200 g, 0.005 mol) in 50 ml hot water and 10 ml concentrated ammonia added to it. The dark-red complex [Ni(C₁₉H₂₀N₂O₂)], which precipitated out after a one day, was filtered off and dried in an oven at 303 K; 0.369 g (0.001 mol) of this complex was then dissolved in 50 ml dimethylformamide (DMF). After this solution were heated to 383 K, a solution of Mn(AcO)₂·4H₂O (0.100 g, 0.005 mol) in 20 ml hot methanol was added to it. The resulting mixture was set aside for one day and the dark-red crystals that formed were filtered off and dried in air.

Fig. 1 Chemical diagram of the title compound.

The crystal structure and other experimental details are given in Table 1. The structure was solved by direct methods, and refined on *F*² by full-matrix least-squares procedures. The non-hydrogen atoms were refined anisotropically, and all of the hydrogens were fixed as a riding model over their parent atoms. The final atomic coordinates and bond distances and angles are given Tables 2 and 3.

The complex has the central Mn²⁺ ion located at the inversion centre. The Ni-Mn bridging distance is 3.138(3) Å.

The coordinations around the Ni and Mn atoms are distorted from the ideal octahedral geometry due to constraints imposed by the chelating ligands. The average Ni-O, Mn-O and Ni-N bond lengths are [2.066(3), 2.177(3) and 2.040(4) Å], respectively. The N1-Ni1-N2, O1-Ni1-O2, N1-Ni1-O2 and N2-Ni1-O1 bond angles are [96.01(19), 84.48(12), 173.15(18) and 171.44(15)°], respectively. The bond lengths and angles are in agreement with the values reported previously for Ni(II) complexes.³⁻⁵ The coordination about the nickel ion is not

Fig. 2 Molecular structure of the title compound with the atom numbering scheme. The thermal ellipsoids are drawn at the 30% probability level.

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Table 1 Crystal and experimental data

Formula: C ₄₈ H ₆₀ N ₆ O ₁₀ Ni ₂ Mn
Formula weight = 1053.38
Crystal system: monoclinic
Space group: <i>P</i> 2 ₁ / <i>c</i> <i>Z</i> = 2
<i>a</i> = 10.965(2) Å <i>β</i> = 112.800(10)°
<i>b</i> = 17.838(4) Å
<i>c</i> = 13.951(3) Å
<i>V</i> = 2515.5(9) Å ³
<i>D_s</i> = 1.391 g/cm ³
<i>μ</i> (Mo <i>K</i> _α) = 1.049 mm ⁻¹
<i>T</i> = 300(2) K
Crystal color: prism, dark red
<i>λ</i> (Mo <i>K</i> _α) = 0.71073 Å
<i>R</i> = 0.0508 <i>wR</i> = 0.1128
No. of reflections measured = 4903
No. of reflections used = 2414 [<i>I</i> > 2σ(<i>I</i>)]
No. of parameters = 314
Goodness-of-fit: 0.943
(Δ/ <i>σ</i>) _{max} = 0.010
(Δ <i>ρ</i>) _{max} = 0.424 e Å ⁻³
(Δ <i>ρ</i>) _{min} = -0.360 e Å ⁻³
2θ _{max} = 51.94°
Measurements: Enraf Nonius CAD4
Program system: Stoe-XRED
Structure determination: SHELXS-97
Hydrogen atoms: geometrically located
Refinement: full matrix least-squares on <i>F</i> ²
Deposit number: CCDC 270771

Table 2 Final atomic coordinates and equivalent anisotropic thermal parameters for non-hydrogen atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (Å ²)
Mn	0.0000	1.0000	0.0000	0.0431(3)
Ni	0.2545(6)	0.899(3)	0.0770(6)	0.0486(2)
N1	0.4213(4)	0.8999(2)	0.0461(4)	0.060(11)
N2	0.3193(4)	0.8207(2)	0.1926(3)	0.063(12)
N3	0.0388(4)	0.7196(2)	-0.1025(3)	0.055(10)
O1	0.1656(3)	0.9677(15)	-0.0443(3)	0.0492(8)
O2	0.0735(3)	0.8987(15)	0.0893(2)	0.0477(8)
O3	0.3224(3)	0.9875(18)	0.1773(3)	0.064(10)
O4	0.1401(3)	1.0593(16)	0.1312(3)	0.0548(9)
O5	0.1983(3)	0.8042(17)	-0.0265(3)	0.0586(9)
C1	0.1864(5)	0.9675(2)	-0.1305(5)	0.052(13)
C2	0.0911(6)	0.9922(3)	-0.2233(5)	0.069(15)
C3	0.1107(8)	0.9937(3)	-0.3137(6)	0.086(19)
C4	0.2304(9)	0.9708(3)	-0.3156(6)	0.094(2)
C5	0.3275(7)	0.9456(3)	-0.2260(6)	0.077(18)
C6	0.3094(5)	0.9421(3)	-0.1339(5)	0.063(14)
C7	0.4167(6)	0.9162(3)	-0.0451(6)	0.072(17)
C8	0.5461(5)	0.8743(3)	0.1254(5)	0.081(19)
C9	0.5307(5)	0.8013(3)	0.1746(5)	0.085(2)
C10	0.4632(5)	0.8059(3)	0.2506(5)	0.085(2)
C11	0.2379(5)	0.7752(3)	0.2057(4)	0.067(15)
C12	0.0962(5)	0.7738(2)	0.1567(4)	0.057(13)
C13	0.0301(7)	0.7091(3)	0.1613(5)	0.078(17)
C14	-0.1036(7)	0.7017(3)	0.1168(5)	0.083(19)
C15	-0.1794(6)	0.7625(4)	0.0647(5)	0.082(18)
C16	-0.1199(5)	0.8294(3)	0.0593(4)	0.058(13)
C17	0.0186(4)	0.8371(3)	0.1015(4)	0.049(12)
C18	0.2574(5)	1.0432(3)	0.1867(4)	0.059(14)
C19	0.3330(6)	1.0974(4)	0.2708(5)	0.113(3)
C20	0.0832(5)	0.7880(3)	-0.0771(4)	0.0505(12)
C21	0.1248(6)	0.6563(3)	-0.0688(5)	0.092(2)
C22	-0.1005(5)	0.7038(3)	-0.1607(4)	0.0788(17)
C23	0.5229(6)	0.8665(5)	0.3315(6)	0.112(3)
C24	0.4645(8)	0.8614(7)	0.4147(7)	0.173(4)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* (a_i \cdot a_j)$$

Table 3 Selected bond distances (Å) and angles (°)

N1-Ni	2.036(4)	O5-Ni	2.157(3)
N2-Ni	2.044(4)	O1-Mn	2.209(3)
O1-Ni	2.006(3)	O2-Mn	2.166(3)
O2-Ni	2.058(3)	O4-Mn	2.157(3)
O3-Ni	2.044(3)		
Ni1-O1-Mn1	96.13(14)	Ni1-O2-Mn1	95.95(12)
O1-Ni1-N1	90.05(17)	O1-Ni1-O3	92.19(13)
N1-Ni1-O3	91.25(15)	O1-Ni1-N2	171.44(15)
N1-Ni1-N2	96.01(19)	O1-Ni1-O2	84.48(12)
N1-Ni1-O2	173.15(18)	O3-Ni1-O2	93.09(13)
N2-Ni1-O2	89.00(15)	O1-Ni1-O5	89.64(13)
O2-Ni1-O5	91.00(12)	O4-Mn1-O2	86.39(11)
O2-Mn1-O1	77.30(11)		
Mn1-O1-Ni1-N1	-165.15(14)	Mn1-O1-Ni1-O3	-73.89(13)
Mn1-O1-Ni1-O5	110.05(12)	Mn1-O2-Ni1-O1	-19.39(12)

completely regular; cis bond angles at Ni(II) atom range from [84.48(12) to 96.01(19)°].

The four-membered ring Ni-O1-O2-Mn is not entirely planar with, for example, Mn 0.159(12) Å out of the plane defined by Ni, O1 and O2. The dihedral angles between the planes of the two chelating moieties, (O1, C1, C6, C7, N1 and O2, C11, C12, C17, N2), has a value of 36.6(2)°.

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