Instrumental Achievements

Crystal Structure of a Symmetrical Heterotrinuclear Ni^{II}-Mn^{II}-Ni^{II} Complex: Bis{(*N*,*N*′-dimethylformamide) (μ-acetato) [μ-*N*,*N*′-bis(salicylidene)-2-hydroxy-1,3-propanediamine]nickel(II)}manganese(II)

Orhan ATAKOL,*† Hasan NAZIR,* Zehra DURMUS,* Ingrid SVOBODA, and Hartmut FUESS****

**Department of Chemistry, Faculty of Science, Ankara University, Tandogan 06100 Ankara, Turkey*
***Strukturforschung, FB Materialwissenschaft, Technische Hochschule Darmstadt Petersenstrasse 23, D-64287 Darmstadt, Germany*

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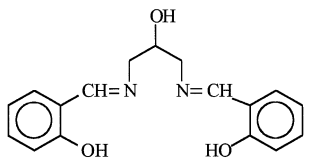
N,*N*′-Bis(salicylidene)-1,3-propanediamine[1,2] and its 2-hydroxy derivative[3-6] (**1**) have been reported to have a greater tendency to yield polynuclear complexes. This communication presents the X-ray structure of the Ni–Mn–Ni complex (**2**) prepared using ligand **1** (Fig. 1). The title complex was prepared in two steps. Step 1: After the ligand (0.01 mol, 2.98 g) was dissolved in hot EtOH (50 mL), a solution of $NiCl_2 \cdot 6H_2O$ (0.01 mol, 2.37 g) in hot water (30 mL) and ammonia (10 mL) was then added. The resulting solution was thoroughly mixed and set aside for 2 h. The precipitated crystals were filtered and dried at 363 K. Step 2: Filtered crystals were dissolved in hot DMF and mixed with a hot MeOH (20 mL) solution of $Mn(AcO)_2 \cdot 4H_2O$ (0.0005 mol, 0.123 g). The resulting solution was set aside for 24 h. The precipitated crystals were filtered, dried in air and used for X-ray data collection with graphite-monochromatized Mo K_α (λ = 0.71093 Å) radiation. The crystal and experimental data are presented in Table 1 and an ORTEP[7] plot of the titled complex is shown in Fig. 2. Table 2 gives the final atomic coordinates, while the bond distances and angles are given in Table 3.

Each Ni atom is coordinated by 4 oxygen and 2 nitrogen atoms. The Mn atom is located on a center of inversion, and is coordinated by 6 oxygen atoms. The distance Ni–Mn is 3.1299(6)Å and the Ni–Mn–Ni bond angle is 180°. The methylene-bonded OH group was expected to form intermolecular interactions, but instead formed intramolecular H-bonding to the O(1) atom of the coordinated dimethylformamide group, such that the O6–H6···O1: O6–H6 distance is 1.11(4)Å; the H6···O1 distance is 1.87(4)Å and the O6–H6···O1 angle is 175(4)°.



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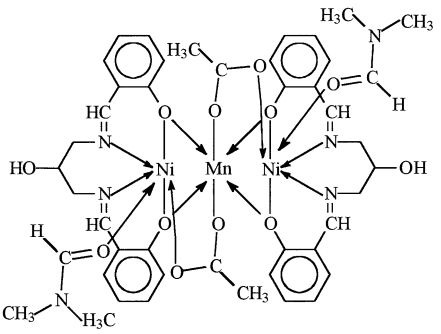

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Fig. 1 Structural chemical diagram.

† To whom correspondence should be adressed.

Table 1 Crystal and experimental data

Formula: $C_{44}H_{52}MnN_6Ni_2O_{12}$	
Formula weight = 1029.38	
Crystal system: triclinic	
Space group: $P\bar{1}$	$Z = 1$
a = 9.466(1)Å	α = 67.167(8)°
b = 10.652(1)Å	β = 80.169(9)°
c = 12.605(1)Å	γ = 89.610(10)°
V = 1151.7(2)Å^3	
D_x = 1.484g/cm^3	
μ = 1.08mm^{-1}	
θ_{max} = 25.98°	
K = 295	
Trans. factors (T_{min}, T_{max}) = 0.750, 0.827	
F(0 0 0) = 535	
Reflns. meas. = 5235	
Reflns with $I \geq 2\sigma(I)$ = 2868	
Reflns unique, R_{int} = 4518, 0.023	
R = 0.037	Rw = 0.086
S = 1.01	
Crystal size = 0.10 × 0.20 × 0.20 mm	
Diffractometer: Enraf-Nonius CAD-4	
Weighting scheme: $w = 1/[\sigma^2(F_0^2) + (0.0469P)^2 + 0.2935P$ where $P = (F_0^2 + 2F_c^2)/3$	
$(\Delta\rho)_{max}$ = 0.38 eÅ^{-3}	
$(\Delta\rho)_{min}$ = –0.31 eÅ^{-3}	
Program used: WinGX[8], SHELXS-97[9], SHELXL-97[10], Platon[7]	

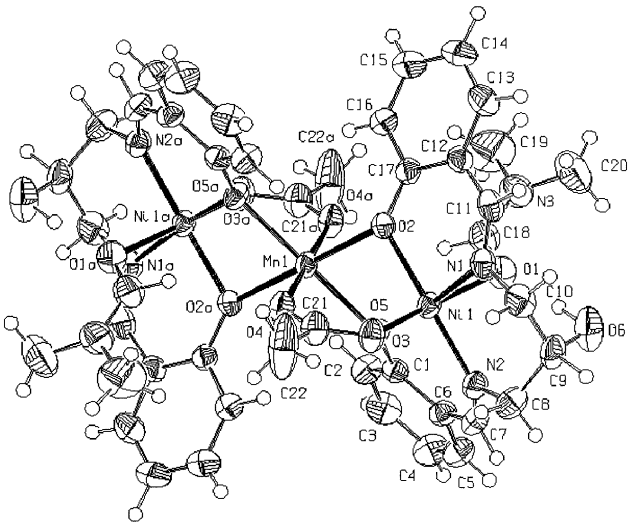

Fig. 2 ORTEP[7] plot of the title complex. The displacement ellipsoids are drawn at the 50% probability level and the H atoms are shown as small circles of arbitrary radii.

Acknowledgements

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References

1. C. Fukuhara, K. Tsuneyoshi, N. Matsumoto, S. Kida, M. Mikuriya, and M. Mori, *J. Chem. Soc. Dalton Trans*., **1990**, 3473.
2. A. Gerli, K. S. Hagen, and L. G. Marzilli, *Inorg. Chem*., **1991**, *30*, 4673.
3. S. Uhlenbrock, R. Wegner, and B. Krebs, *J. Chem. Soc. Dalton Trans*., **1996**, 3731.
4. H. Aneetha, K. Panneerselvam, T. F. Liao, T. H. Lu, and C. S. Chung, *J. Chem. Soc. Dalton Trans*., **1999**, 2689.
5. M. Mikuriya, N. Tsuru, S. Ikemi, and S. Ikenove, *Chem. Lett*., **1998**, 879.
6. M. Mikuriya, K. Nakadera, and T. Kotera, *Chem. Lett*., **1993**, 637.
7. L. Spek, PLATON, A Multipurpose Crystallographic Tool, **2000**, Utrecht University, Utrecht, The Netherlands.
8. L. J. Farrugia, *J. Appl. Cryst*., **1999**, *32*, 837.
9. G. M. Sheldrick, SHELXS97, Program for the Solution of Crystal Structures, University of Göttingen, Germany, **1997**a.
10. G. M. Sheldrick, SHELXL97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, **1997**b.

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

Atom	*x*	*y*	*z*	B_{eq}
C1	-0.0813(4)	0.2527(3)	-0.0729(3)	0.0319(8)
C2	-0.2287(4)	0.2583(4)	-0.0367(3)	0.0412(9)
C3	-0.3275(5)	0.1697(4)	-0.0430(4)	0.0513(11)
C4	-0.2859(5)	0.0703(4)	-0.0858(4)	0.0524(11)
C5	-0.1418(5)	0.0621(4)	-0.1196(4)	0.0476(10)
C6	-0.0377(4)	0.1513(3)	-0.1159(3)	0.0350(8)
C7	0.1108(4)	0.1300(4)	-0.1523(3)	0.0400(9)
C8	0.3609(4)	0.1654(4)	-0.2090(4)	0.0480(10)
C9	0.4444(5)	0.2742(4)	-0.3180(4)	0.0484(10)
C10	0.5075(4)	0.3924(5)	-0.2984(4)	0.0507(11)
C11	0.4181(4)	0.6086(4)	-0.3365(3)	0.0410(9)
C12	0.3262(4)	0.7153(3)	-0.3307(3)	0.0360(8)
C13	0.3596(5)	0.8441(4)	-0.4202(4)	0.0569(12)
C14	0.2777(6)	0.9523(4)	-0.4255(4)	0.0638(13)
C15	0.1610(6)	0.9333(4)	-0.3384(4)	0.0603(13)
C16	0.1258(5)	0.8088(4)	-0.2476(3)	0.0465(10)
C17	0.2055(4)	0.6955(3)	-0.2408(3)	0.0343(8)
C18	0.0227(5)	0.5394(4)	-0.3347(4)	0.0499(10)
C19	-0.1082(7)	0.7316(6)	-0.4333(5)	0.099(2)
C20	0.1079(6)	0.6740(6)	-0.5394(4)	0.0839(16)
C21	0.2820(4)	0.3551(4)	0.0665(3)	0.0453(9)
C22	0.3888(6)	0.3183(8)	0.1475(5)	0.110(2)
N1	0.3969(3)	0.4805(3)	-0.2758(2)	0.0376(7)
N2	0.2213(3)	0.2093(3)	-0.1727(2)	0.0356(7)
N3	0.0049(4)	0.6395(3)	-0.4327(3)	0.0553(9)
O1	0.1189(3)	0.4600(3)	-0.3263(2)	0.0480(7)
O2	0.1686(3)	0.5771(2)	-0.15356(19)	0.0365(6)
O3	0.0115(2)	0.3384(2)	-0.0647(2)	0.0338(6)
O4	0.1697(3)	0.4054(3)	0.0960(2)	0.0428(6)
O5	0.3161(3)	0.3327(3)	-0.0247(2)	0.0428(6)
O6	0.3606(4)	0.3211(4)	-0.4088(3)	0.0751(10)
Ni1	0.21077(5)	0.39383(5)	-0.16194(4)	0.03113(14)
Mn1	0.0000	0.5000	0.0000	0.03038(19)

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (\boldsymbol{a}_i \cdot \boldsymbol{a}_j)$.

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

Ni1-N1	2.036(3)	Ni1-O3	2.018(2)
Ni1-N2	2.023(3)	Ni1-O5	2.029(3)
Ni1-O2	2.029(2)		

O3 Ni1 N2	90.12(10)	O5 Ni1 O2	94.00(10)
O3 Ni1 O5	95.98(10)	O3 Ni1 N1	170.02(11)
N2 Ni1 O5	92.05(11)	N2 Ni1 N1	96.80(12)
O3 Ni1 O2	83.08(9)	O5 Ni1 N1	90.97(11)
N2 Ni1 O2	171.33(11)	O2 Ni1 N1	89.31(11)