Crystal Structure of Trinuclear Complex, Bis[μ-*N*,*N*′-bis(salicylidene)-1,3-propanediaminato(dimethylformamide)-(μ-nitrito-*N*)nickel(II)]cobalt(II)

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Oxygen bridged polynuclear complexes transition elements are of interest bacause of their magnetic properties.[1,2] The synthesis and structural properites of trinuclear linear complexes based in Schiff base ligands have been the subject of considerable interest in our laboratories.[3-5] We reported here a new hetero metallic trinuclear complex, $[Ni_2Co(NO_2)_2(C_{17}H_{16}N_2O_2)_2C_3H_7(NO)_2]$.

To synthesize the complex; to a solution of *N*,*N*′-bis(salicylidene)-1,3-propandiamine 0.282 g (0.001 mol) in 50 ml hot methanol, 10 ml, 20% ammonia was added. After mixing this solution, a solution of 0.238 g (0.001 mol) $NiCl_2 \cdot 6H_2O$ in 30 ml hot water was added. After 2 h, light-green nickel complex was filtered and dried at 125 – 130˚C for 3 – 4 h in an oven. From this complex 0.339 g (0.001 mol) was then dissolved in 50 ml hot dimethylformamide. A solution of 0.119 g (0.0005 mol) $CoCl_2 \cdot 6H_2O$ in 20 ml of hot methanol and a solution of 0.069 g $NaNO_2$ (0.001 mol) in 10 ml of hot water were added. The resulting mixture was set aside for 2 – 3 d. The precipitated crystals were filtered and dried in air.

The structure was solved using the program SIMPEL, while for full matrix refinement the program LSFM was used; both were incorporated in the MolEN package. All non-H atoms were refined with anisotropic displacement parameters. The H atoms were placed geometrically 0.95 Å from their parent C atoms with $U_{ISO}(H)=1.3U_{eq}(C)$. A riding model was subsequently used for all H atoms.

The unit cell contains two molecules of the hetero-trinuclear complex. The coordination around the central Co ion as well as the terminal Ni ions are distorted octahedral (Fig. 2). The Co-Ni pairs are each triply bridged, involving the O atoms of the ligand and O and N atoms of a nitrite group. The central Co ion occupying the inversion center at (0 0 0) has six O atoms as nearest neighbors: two from each ligand and one from each bridging nitrite group.

Inversion related terminal Ni ions are coordinated by the two O and two N atoms of a ligand and one N atom from a nitrite and O atom from a dimethylformamide. The DMF and nitrite groups are mutually *trans* about the Ni ion. The coordination in the title compound is very similar to those observed in the literature cited above.

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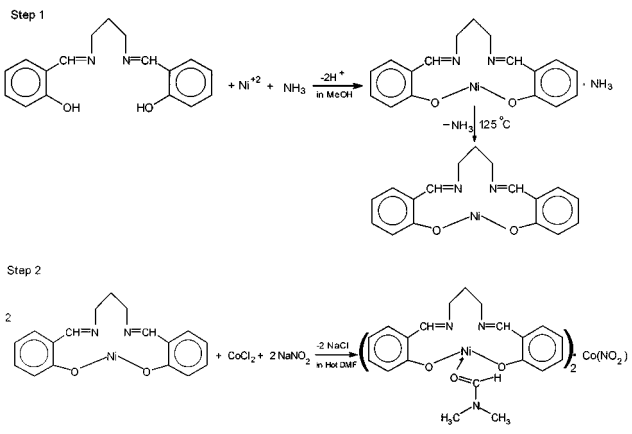

Fig. 1 Synthesis and chemical structure.

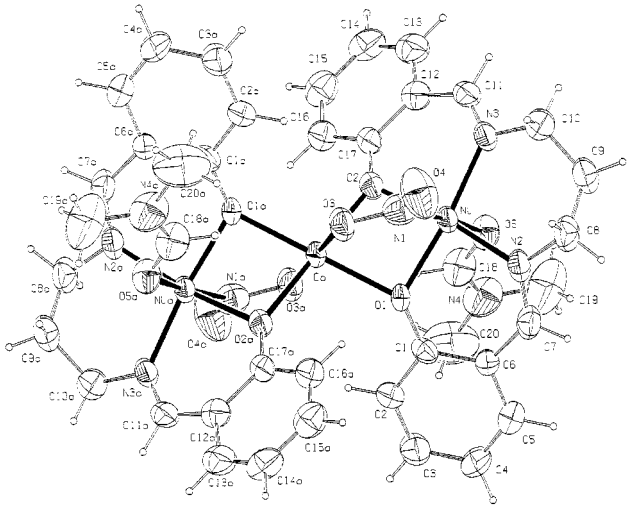

Fig. 2 The ORTEP drawing of the title compound with atom labeling.

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Table 1 Crystal and experimental data

Formula: $C_{40}H_{46}CoNi_2N_8O_{10}$
Formula weight: 975.213
Crystal system: monoclinic
Space group: *P*21/*c* *Z*=2
a=10.4243(14)Å
b=16.1182(11)Å
c=14.0950(12)Å
β=109.816(6)˚
V=2225.57(39)Å^3
D_x=1.4552 g/cm^3
μ(Mo K$_\alpha$)=1.269 mm^{-1}
T=295 K
Red
F(0 0 0)=1010
Crystal size: 0.40×0.15×0.10 mm
Radiation=Mo K$_\alpha$
R=0.0732
Rw=0.0708
$2\theta_{max}$=54.1˚
$(\Delta/\sigma)_{max}$=0.00006
$(\Delta\rho)_{max}$=1.25 eÅ^{-3}
$(\Delta\rho)_{min}$=–0.24 eÅ^{-3}
No. of reflections used=2386
No. of parameters=277
Goodness-of-fit=1.02
Measurement: Enraf Nonius CAD-4 diffractometer
Program system: CAD-4 EXPRESS Software
Structure determination: MolEN
Treatment of hydrogen atoms: geometric calculation
Refinement: full matrix least-squares (MolEN)

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

Atom	*x*	*y*	*z*	B_{eq}/Å^2
Ni	0.2252(1)	-0.11655(6)	0.10783(8)	2.75(2)
Co	0.000	0.000	0.000	2.71(3)
O1	0.0242(5)	-0.1096(3)	0.0827(4)	3.2(1)
O2	0.1745(5)	-0.0463(3)	-0.0161(4)	3.0(1)
O3	0.1336(6)	0.0501(4)	0.1369(4)	3.9(1)
O4	0.3102(8)	0.0185(5)	0.2616(6)	7.1(2)
O5	0.1974(6)	-0.2276(4)	0.0146(4)	3.8(1)
N1	0.2310(7)	-0.0028(5)	0.1830(5)	4.1(2)
N2	0.2457(7)	-0.1919(4)	0.2260(5)	3.4(2)
N3	0.4209(6)	-0.1173(4)	0.1146(5)	3.5(2)
N4	0.0336(9)	-0.3143(5)	-0.0833(6)	5.8(2)
C1	-0.0515(7)	-0.1725(5)	0.0944(6)	2.8(2)
C2	-0.1898(8)	-0.1785(6)	0.0373(7)	3.9(2)
C3	-0.2670(9)	-0.2434(6)	0.0486(7)	4.5(2)
C4	-0.211(1)	-0.3072(6)	0.1163(8)	5.5(3)
C5	-0.074(1)	-0.3032(6)	0.1720(8)	5.0(3)
C6	0.0078(8)	-0.2375(5)	0.1631(6)	3.4(2)
C7	0.1471(9)	-0.2400(6)	0.2297(7)	3.9(2)
C8	0.3797(9)	-0.2026(6)	0.3040(7)	4.3(2)
C9	0.4895(9)	-0.2174(6)	0.2571(7)	4.7(3)
C10	0.5283(9)	-0.1417(6)	0.2101(7)	4.6(3)
C11	0.4555(8)	-0.1019(5)	0.0382(6)	3.6(2)
C12	0.3690(8)	-0.0783(5)	-0.0615(6)	3.2(2)
C13	0.4264(9)	-0.0815(6)	-0.1371(7)	4.3(2)
C14	0.3554(9)	-0.0619(6)	-0.2352(7)	4.5(2)
C15	0.222(1)	-0.0345(6)	-0.2585(7)	4.6(2)
C16	0.1614(9)	-0.0283(6)	-0.1858(6)	3.8(2)
C17	0.2318(8)	-0.0502(5)	-0.0860(6)	3.1(2)
C18	0.084(1)	-0.2418(6)	-0.0460(7)	4.4(2)
C19	0.121(2)	-0.3853(8)	-0.052(1)	9.3(5)
C20	-0.107(1)	-0.3264(9)	-0.1452(9)	8.8(4)

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

Table 3 Bond distances (Å) and angles (˚)

Ni - O1	2.006(5)	O5 - C18	1.22(1)
Ni - O2	1.995(5)	N2 - C7	1.30(1)
Ni - O5	2.179(6)	N2 - C8	1.47(1)
Ni - N1	2.107(8)	N3 - C10	1.48(1)
Ni - N2	2.011(7)	N3 - C11	1.27(1)
Ni - N3	2.010(7)	N4 - C18	1.32(1)
Co - O1	2.083(6)	N4 - C19	1.44(2)
Co - O2	2.048(6)	N4 - C20	1.45(1)
Co - O3	2.118(5)	C6 - C7	1.44(1)
O1 - C1	1.33(1)	C8 - C9	1.52(2)
O2 - C17	1.31(1)	C9 - C10	1.51(1)
O3 - N1	1.317(9)	C11 - C12	1.44(1)
O4 - N1	1.185(9)		
O1 - Ni - O2	82.1(2)	C8 - C9 - C10	114.6(8)
O1 - Ni - O5	91.2(2)	O2 - C17 - C12	120.5(7)
O1 - Ni - N1	83.7(3)	O2 - C17 - C16	121.7(7)
O1 - Ni - N2	89.5(3)	O5 - C18 - N4	127.5(9)
O1 - Ni - N3	172.4(3)	Ni - O2 - C17	125.1(5)
O2 - Ni - O5	89.9(2)	Co - O2 - C17	138.3(4)
O2 - Ni - N1	84.2(3)	Co - O3 - N1	111.2(5)
O2 - Ni - N2	171.2(2)	Ni - O5 - C18	118.4(6)
O2 - Ni - N3	90.5(3)	Ni - N1 - O3	115.4(5)
O5 - Ni - N1	172.7(2)	Ni - N1 - O4	127.9(6)
O5 - Ni - N2	87.6(3)	O3 - N1 - O4	116.7(8)
O5 - Ni - N3	87.1(3)	Ni - N2 - C7	121.9(5)
N1 - Ni - N2	97.6(3)	Ni - N2 - C8	119.9(6)
N1 - Ni - N3	97.2(3)	C7 - N2 - C8	117.6(7)
N2 - Ni - N3	97.8(3)	Ni - N3 - C10	119.1(6)
O1 - Co - O2	79.0(2)	Ni - N3 - C11	122.3(5)
O1 - Co - O3	84.1(2)	C10 - N3 - C11	118.5(7)
O2 - Co - O3	84.5(2)	C18 - N4 - C19	117.1(9)
Ni - O1 - Co	93.9(2)	C18 - N4 - C20	123(1)
Ni - O1 - C1	124.3(5)	C19 - N4 - C20	119(1)
Co - O1 - C1	138.7(4)	O1 - C1 - C2	121.5(7)
Ni - O2 - Co	95.3(3)	O1 - C1 - C6	120.5(6)
C1 - C6 - C7	125.3(8)	N3 - C10 - C9	112.4(7)
C5 - C6 - C7	115.8(8)	N3 - C11 - C12	127.9(8)
N2 - C7 - C6	126.3(8)	C11 - C12 - C13	116.6(8)
N2 - C8 - C9	111.1(8)	C11 - C12 - C17	124.4(9)

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