



Synthesis and Crystal Structures of Nickel(II) and Cobalt(II) Complexes with 3-Methoxysalicylaldehyde Benzoylhydrazide

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(Received: 18 June 2011;

Accepted: 3 February 2012)

AJC-11031

Two isostructural mononuclear complexes, $[\text{Ni}(\text{HL})(\text{H}_2\text{L})]\cdot\text{ClO}_4\cdot 1.5\text{CH}_3\text{OH}$ (**1**) and $[\text{Co}(\text{HL})(\text{H}_2\text{L})]\cdot\text{ClO}_4\cdot\text{CH}_3\text{CN}\cdot 2\text{H}_2\text{O}$ (**2**), have been synthesized (H_2L = 3-methoxysalicylaldehyde benzoylhydrazide). In complexes **1** and **2**, each metal atom is coordinated by four O atoms and two N atoms from two H_2L ligands, forming a distorted octahedral coordination configuration. Additionally, in complex **1**, the two neighboring molecules are found to form a centrosymmetric dimer through N (hydrazine)-H \cdots O (phenolate/methoxyl) hydrogen bonds and the π - π stacking interactions between the two phenyl rings. The dimers are further constructed into an extended one dimensional chain structure through hydrogen bands. Unlike complex **1**, complex **2** does not form dimer/chain but is rather a simple, discrete complex.

Key Words: Nickel complex, Cobalt complex, Crystal structure, Isostructural, 3-Methoxysalicylaldehyde benzoylhydrazide.

INTRODUCTION

During recent years coordination complexes of acylhydrazone ligands have received much attention^{1,2} as a result of which not only play important roles in the development of coordination chemistry related to catalysis³, enzymatic reactions^{4,5}, magnetism and molecular architecture², but also exhibit variety of pharmacological applications^{6,7}.

From the structural point of view, 3-methoxysalicylaldehyde benzoylhydrazide (H_2L) is a good choice to synthesize coordination polymers with defined geometry⁸⁻¹¹, due to presence of several nitrogen/oxygen donor atoms with suitable relative positions to coordinate metal centers. Furthermore, the vanillin group displays a variety of bonding geometries, such as chelating, monodentate/bidentate bridging and chelating bridging^{12,13}, although the coordination ability of the vanillin group is not strong in some cases¹⁴. We report in this paper the synthesis, crystal structures of two isostructural mononuclear nickel(II) and cobalt(II) complexes with 3-methoxy-salicylaldehyde benzoylhydrazide (H_2L) ligand, $[\text{Ni}(\text{HL})(\text{H}_2\text{L})]\cdot\text{ClO}_4\cdot 1.5\text{CH}_3\text{OH}$ (**1**) and $[\text{Co}(\text{HL})(\text{H}_2\text{L})]\cdot\text{ClO}_4\cdot\text{CH}_3\text{CN}\cdot 2\text{H}_2\text{O}$ (**2**).

EXPERIMENTAL

All the reagents and solvents employed were commercially available and used as received without further purification. The 3-methoxysalicylaldehyde benzoylhydrazide (H_2L) ligand

is prepared by reported procedure¹⁵. Elemental analysis for C, N and H were performed with a Perkin-Elmer 2400 II analyzer.

Caution! although we did not experience any problem during the work, perchlorate salts in presence of organic materials are potentially explosive. They should be used in small quantities and handled with extreme care.

Preparation of complex 1: The complex **1** was synthesized by adding $\text{Ni}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ (36.6 mg, 0.10 mmol) to a solution of H_2L (27.3 mg, 0.10 mmol) in methanol-acetonitrile (1:2 v/v, 15 mL). The resulting mixture was stirred for 3 h at room temperature to afford green solution, which was left unperturbed to allow the slow evaporation of the solvent. Green single crystals suitable for X-ray diffraction analysis were formed after about two weeks. Yield: 21 % (based on Ni). Elemental anal. (%) calcd. for $\text{C}_{31.5}\text{H}_{33}\text{N}_4\text{O}_{11.5}\text{ClNi}$: C, 50.73; H, 4.46; N, 7.51; found C, 50.60; H, 4.42; N, 7.37.

Preparation of complex 2: Complex **2** was obtained by a similar procedure to that for **1**, but using $\text{Co}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ in place of $\text{Ni}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$. Brown crystals formed after two weeks yield: 28.0 % (based on Co). Elemental analysis (%) calcd. for $\text{C}_{32}\text{H}_{34}\text{N}_5\text{O}_{12}\text{ClCo}$: C, 49.59; H, 4.42; N, 9.03; found C, 49.47; H, 4.40; N, 8.83.

X-ray crystallography: Crystallographic data were collected on a Bruker Apex II CCD diffractometer with graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at a temperature of 185 (2) K, for **1** and **2**. Data processing was accomplished

with the SAINT processing program. These structures were solved by the direct methods and refined on F^2 by full-matrix least squares using SHELXTL97^{16,17}. The location of Ni/Co atom was easily determined and O, N and C atoms were subsequently determined from the difference Fourier maps. All non-hydrogen atoms were refined with anisotropic thermal parameters. Crystallographic and refinement details of **1** and **2** are listed in Table-1. CCDC-785033 (**1**) and 785034 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge crystallographic data centre *via* www.ccdc.cam.ac.uk/data_request/cif. [or from the Cambridge crystallographic data centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: (44) 1223-336033; email: deposit@ccdc.cam.ac.uk].

TABLE-1
CRYSTALLOGRAPHIC DATA FOR COMPLEXES **1** AND **2**

Complex	[Ni(HL)(H ₂ L)]·ClO ₄ ·1.5CH ₃ OH (1)	[Co(HL)(H ₂ L)]·ClO ₄ ·CH ₃ CN·2H ₂ O (2)
Formula	C _{31.5} H ₃₃ N ₄ O _{11.5} ClNi	C ₃₂ H ₃₄ N ₅ O ₁₂ ClCo
Formula weight	745.78	775.02
Crystal system	Triclinic	Triclinic
Space group	P $\bar{1}$	P $\bar{1}$
Colour	Green	Brown
a (Å)	12.343(2)	12.1802(11)
b (Å)	12.644(2)	12.3512(12)
c (Å)	13.519(2)	13.3951(13)
α (°)	116.513(2)	112.7540(10)
β (°)	95.487(2)	100.270(2)
γ (°)	108.753(2)	93.843(2)
V(Å ³)	1715.00(4)	1807.9(3)
Z	2	2
D _{calc} /g cm ⁻³	1.444	1.424
μ (mm ⁻¹)	0.709	0.616
F(000)	774	802
Max and min transmission	0.9324 and 0.8770	0.9410 and 0.8973
Range of h, k, l	-15 ≤ h ≤ 15, -15 ≤ k ≤ 8, -16 ≤ l ≤ 16	-11 ≤ h ≤ 15, -15 ≤ k ≤ 14, -16 ≤ l ≤ 16
GOF	1.024	1.085
Data/restraints/parameters	6722 / 1 / 455	7228 / 1 / 472
R ₁ , wR ₂ [I > 2σ(I)] ^{a,b}	R ₁ = 0.0612, wR ₂ = 0.1308	R ₁ = 0.0672, wR ₂ = 0.2023
R indices (all data)	R ₁ = 0.1160, wR ₂ = 0.1582	R ₁ = 0.0812, wR ₂ = 0.2164
Largest diff. peak and hole (eÅ ⁻³)	0.617 and -0.463	1.390 and -1.546

^aR = $\sum ||F_o| - |F_c|| / \sum |F_o|$; ^bwR₂ = $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$

RESULTS AND DISCUSSION

The reactions of Co(II)/Ni(II) perchlorate with H₂L in a mixture of methanol and acetonitrile in a 1:2 ratio produce the mononuclear complexes of general formula [M(HL)(H₂L)]·ClO₄ solvent, where M = Ni, solvent = CH₃OH for **1** and M = Co, solvent = CH₃CN·H₂O for **2**. Selected bond distances and angles are listed in Table-2. Single-crystal X-ray analysis revealed that both Ni and Co complexes are isostructural and hence only the details of **1** is given in the ensuing discussion.

The molecular structure **1** is shown in Fig. 1. Ni(II) center exhibits a distorted octahedral geometry comprising two

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°) OF COMPLEXES **1** AND **2**

Complex 1		Complex 2	
Ni1—O1	2.049 (3)	Co1—O1	2.115 (2)
Ni1—O2	2.109 (3)	Co1—O3	2.108 (3)
Ni1—O4	2.073 (3)	Co1—O4	1.983 (3)
Ni1—O5	2.000 (3)	Co1—O6	2.104 (3)
Ni1—N2	2.006 (4)	Co1—N1	2.053 (3)
Ni1—N4	1.982 (3)	Co1—N3	2.035 (3)
O1—Ni1—O2	164.13 (11)	O3—Co1—O1	161.05 (11)
O5—Ni1—O4	169.06 (12)	O4—Co1—O6	164.10 (11)
N2—Ni1—O1	79.37 (13)	O4—Co1—N3	88.60 (12)
N2—Ni1—O2	85.21 (12)	N1—Co1—O1	84.72 (11)
N2—Ni1—O4	87.65 (13)	N1—Co1—O3	76.82 (11)
N4—Ni1—O4	79.27 (13)	N3—Co1—O6	76.72 (11)
N4—Ni1—N2	165.29 (14)	N3—Co1—N1	161.42 (12)

inequivalence Schiff base ligands (H₂L), which positioned very nearly perpendicularly to each other. Several mononuclear complexes with similar structures have been reported previously^{18,19}. Each of ligand acts as a tridentate mode through the hydrazine N, phenolate O and carbonyl O, form two chelate rings (5 and 6-membered). In one ligand, the angles for the equatorial donor atoms [79.37(13)° for O1-Ni1-N2 and 85.21(12)° for N2-Ni1-O2] correspond with the more constrained five-membered chelate ring Ni1-O1-C7-N1-N2 and the less constrained six-membered ring Ni1-O2-C10-C9-C8-N2, respectively. The distorted octahedral symmetry is indicated by the angles N4-Ni1-N2 for 165.29(14)°, O1-Ni1-O2 for 164.13(11)° and O5-Ni1-O4 for 169.06(12)°, which are deviate from the ideal value of 180°. The charge balance requires that two H₂L ligands adopt different deprotonated fashions. The phenolic hydroxyl group of one ligand adopts in its deprotonated form (O⁻), which strongly coordinated to the metal center with shorter Ni1-O5 bond (2.000(3) Å); whereas another ligand binds to the metal ion without losing its proton, which exhibits a longer Ni1-O2 bond (2.109(3) Å)¹⁸. In complex **2**, the molecular structure and coordination geometry is similar to that in complex **1** (Fig. 2).

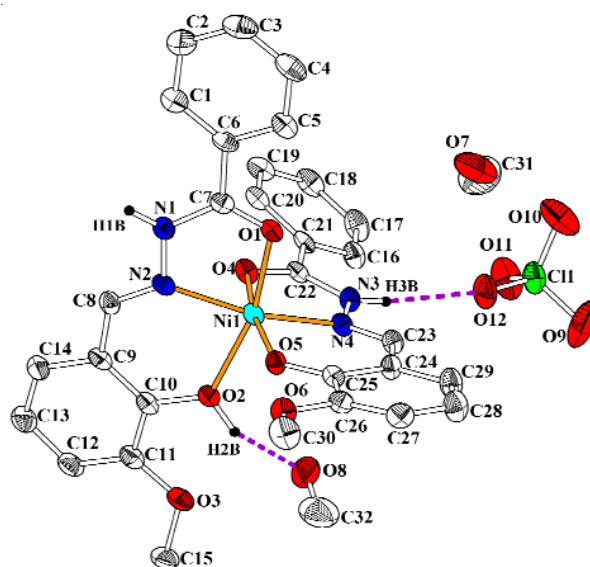


Fig. 1. A view of the complex **1**, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 40 % probability level

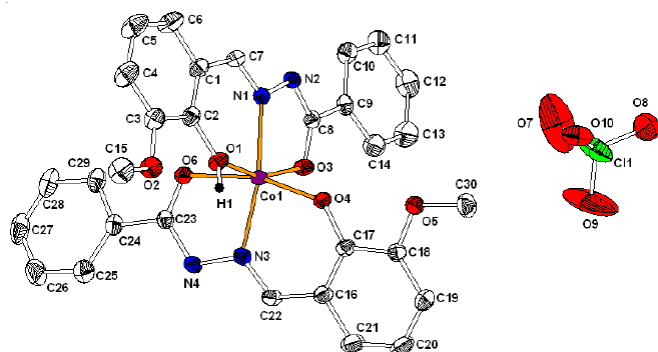


Fig. 2. Molecular structure of **2** with the atom numbering at the 40 % probability level scheme, solvent molecules are omitted for clarity

In the crystal structure of **1**, two adjacent nickel molecules participate in complementary N(hydrazine)-H...O (phenolate/methoxy) hydrogen bonds and the π - π stacking interactions between the (C1-C6) phenyl ring and the phenyl ring (C9-C14), forming a dimeric structure (Fig. 3). And the dimers are further constructed into an extended one dimensional chain structure through O2-H2B...O8, O8-H8B...O9 and N3-H3B...O12 hydrogen bonds (Fig. 4, Table-3). Unlike complex **1**, complex **2** does not form dimer but is rather a simple, discrete complex. Different solvent molecules in complexes may affect the intra- and intermolecular bonding interaction.

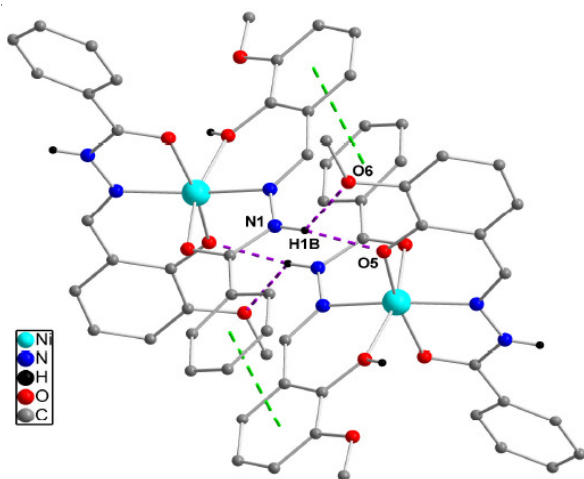


Fig. 3. Dimeric structure of the complex **1**, with hydrogen bonds shown as violet dashed lines and π - π stacking shown as green dashed lines

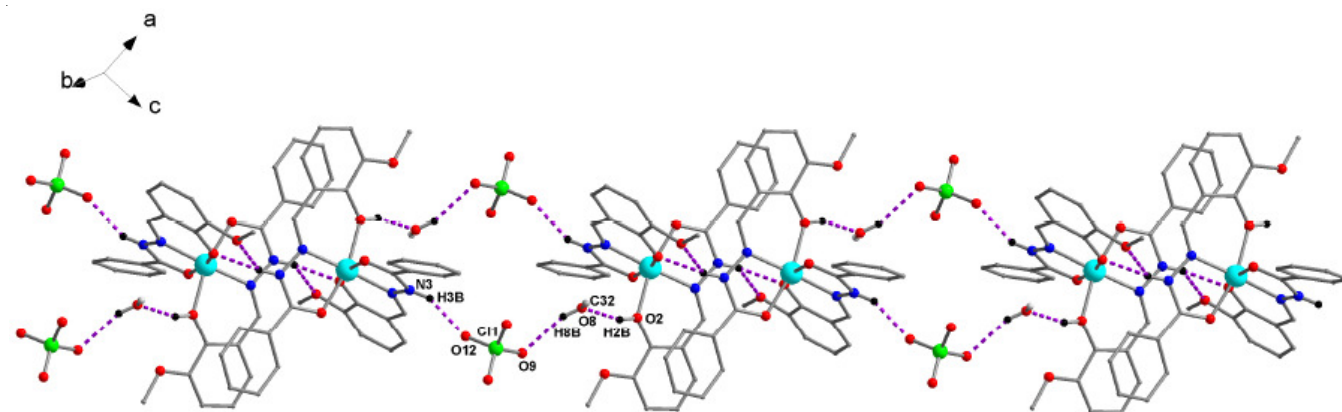


Fig. 4. One-dimensional chain structure of the complex **1**. Hydrogen bonds are shown as violet dashed lines

TABLE-3
INTRA- AND INTERMOLECULAR HYDROGEN
BONDS FOR COMPLEX **1**

D—H...A	d (D—H)	d (H...A)	d (D...A)	<(DHA)
N1—H1B...O5 ^a	0.88	1.97	2.745(4)	146.6
N1—H1B...O6 ^a	0.88	2.26	2.923(5)	131.6
O2—H2B...O8	0.95	1.70	2.595(5)	154.6
O8—H8B...O9 ^a	0.84	2.19	3.002(7)	162.4
N3—H3B...O12 ^b	0.88	2.06	2.871(5)	152.4

Symmetry codes: (a) $-x+1, -y+1, -z+1$; (b) $x+1, y, z+1$

Conclusion

Reactions of a multidentate 3-methoxysalicylaldehyde benzoylhydrazone ligand (H_2L) with $Ni(ClO_4)_2 \cdot 6H_2O$ or $Co(ClO_4)_2 \cdot 6H_2O$ in a mixed solvent of methanol and acetonitrile results in the formation of two isostructural complexes, $[Ni(HL)(H_2L)] \cdot ClO_4 \cdot 1.5CH_3OH$ (**1**) and $[Co(HL)(H_2L)] \cdot ClO_4 \cdot CH_3CN \cdot 2H_2O$ (**2**). Both complexes are characterized by elemental analysis and crystal structure analysis. The metal centers of complexes **1** and **2** have exhibit a distorted octahedral geometry, but different solvent molecules in complexes may be affect the intra- and intermolecular bonding interaction.

ACKNOWLEDGEMENTS

The authors thank the project supported by the Science and Technology Department of Jilin Province, China (201105051) and Changchun University of Science and Technology for their financial support.

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