



Synthesis and Crystal Structure of Tetranuclear Nickel Complex Derived from a N-(3-Methoxy-2-hydroxybenzyl)glycine Ligand

BO-WEN WANG, YU-QIN MA*, YING-GAO, GUI-MIAO YU, HUI-YU WANG and YUN-HUI LI

Changchun University of Science and Technology, Changchun 130022, P.R. China

*Corresponding author: Fax: +86 0431-85308866; Tel: +86 0431-85308866; E-mail: myq9393@sina.com

(Received: 7 March 2013;

Accepted: 7 June 2013)

AJC-13613

A tetranuclear nickel(II) complex featuring defective double-cubane of formula, $[\text{Ni}_4(\text{L})_2(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{CH}_3\text{O})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (**1**), where H_2L is N-(3-methoxy-2-hydroxybenzyl)glycine has been prepared and structurally characterized. The structure of complex **1** consists of one $[\text{Ni}_4(\text{L})_2(\text{C}_{12}\text{H}_8\text{N}_2)_2(\text{CH}_3\text{O})_2(\text{H}_2\text{O})_2]^{2+}$ cation and two perchlorate anions. The vertices of the two face-sharing defective cubanes are occupied by alternating nickel and oxygen ions and the four Ni(II) ions in the cluster are held together by two bridging $\mu_3\text{-CH}_2\text{O}^-$ ions and four $\mu_2\text{-O}^-$ ions from two L^{2-} ligands, forming a planar Ni_4 parallelogram. The complex **1** is further stabilized *via* intramolecular hydrogen bonds, generating a dimeric unit.

Key Words: Nickel complex, Crystal structure, Tetranuclear.

INTRODUCTION

The design and synthesis of metal-organic coordination polymers have received considerable attention because of their fascinating self-assembled structures and potential applications in magnetic¹ and enzyme catalytic processes². The recent development of self-assembled supramolecular chemistry can rationally design and synthesize metal-organic coordination polymers depending on the ligand geometry and coordination propensity of the metal ion. Organic ligands formed by reaction between the amino acids and aldehydes are good candidates to construct metal clusters. More and more geometrically intriguing supramolecular structures derived from such ligands, for example, capsules³, helices⁴ and polynuclear clusters with different numbers of metal ions^{5,6} have been successfully obtained.

Structural studies on the amino acid Schiff bases reveal that they can act as tridentate moiety, coordinating to metal centers through the phenolato-O, imine-N and carboxyl-O with suitable relative positions⁷. The stability of the Schiff base products isolated depends on factors such as the amino acid side chain polarity⁸, the metal, temperature⁹, *etc.* However, Casella Gullotti⁸ found that Schiff bases between amino acids with nonpolar side chains were unstable upon coordination to some transition metal. The problems with ligand instability can be overcome by reduction of the Schiff base to give an amine, because of greater flexibility arising from reduction of the azo methylene ($-\text{CH}=\text{N}-$) group, appear to serve as better

models in this respect^{10,11}. Though the flexibility to the ligand skeleton is offered by the $-\text{CH}_2\text{-NH}-$ moiety, the formation of the final basic structure is guided by the flexibility introduced by the methylene moiety in the side chain of the ligands^{12,13}. This prompted us to investigate the role of a simple side chain such as $-\text{CH}_2\text{COOH}$ in reduced Schiff base ligand on the self-assembly of coordination polymers.

In this communication, we have investigated a new reduced Schiff base ligand derived from *o*-vanillin and glycine, *i.e.* N-(3-methoxy-2-hydroxybenzyl)glycine (H_2L). The reaction of this ligand with $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in presence of the 1,10-phenanthroline in methanol produces a novel tetranuclear Ni(II) complex with defective double-cubane core, representing the first structurally characterized metal complex of this versatile ligand.

EXPERIMENTAL

All the reagents and solvents employed were commercially available and used as received without further purification. The H_2L ligand is prepared in a similar manner according to the reported procedures¹⁴. Elemental analysis for C, N and H were performed with a Perkin-Elmer 2400 II analyzer.

Preparation of complex 1: The reduced Schiff base ligand (H_2L) derived from *o*-vanillin and glycine was prepared in a similar manner according to the reported procedures^{10,15}.

To a solution of glycine (10 mmol) in water (10 mL) containing NaOH (0.40 g, 10 mmol) was added *o*-vanillin (1.55 g, 10 mmol) in ethanol (10 mL). The yellow solution was stirred

for 1 h at room temperature prior to cooling in an ice bath. The intermediate Schiff base that had formed was reduced with an excess of sodium borohydride (0.46 g, 12 mmol) in water (5 mL) containing a few drops of sodium hydroxide solution. The yellow colour was slowly discharged and after 10 min the solution was acidified with concentrated hydrogen chloride to a pH of 5-6. The resulting white solid was filtered off, washed with dry methanol and then diethyl ether, dried and recrystallized from water/ethanol (1:1). Yield was 1.62 g (53 %).

The title complex was synthesized by adding Ni(ClO₄)₂·6H₂O (36.5 mg, 0.1 mmol) and 1,10-phenanthroline monohydrate (9.9 mg, 0.05 mmol) to a solution of H₂L (21.1 mg, 0.1 mmol) and LiOH (0.20 mmol) in 10 mL of methanol. The resulting mixture was stirred for 5 h at room temperature to afford a 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 three weeks. Yield was 8.1 mg (24.7 % based on metal salt).

X-Ray crystallography: Crystallographic data were collected on a Bruker Apex II CCD diffractometer with graphite monochromated Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$) at a temperature of 185 K, for **1**. Data processing was accomplished with the SAINT processing program. These structures were solved by the direct methods and refined on F² by full-matrix least squares using SHELXTL97^{16,17}. The location of Ni 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 data and refinement details of **1** are listed in Table-1. CCDC-922289 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].

RESULTS AND DISCUSSION

The molecular structure of title complex **1** is illustrated in Fig. 1. Selected bond distances and angles are given in Table-2. The asymmetric unit consists of one [Ni₄(L)₂(C₁₂H₈N₂)₂(CH₃O)₂(H₂O)₂]²⁺ cation and two perchlorate anions. The four Ni(II) ions in the cluster are held together by two bridging μ_3 -CH₃O⁻ ions (O9 and O10) and four μ_2 -O⁻ ions (O1, O3, O5 and O7) from two L²⁻ ligands forming a planar Ni₄ parallelogram. The maximum displacements from the least-squares plane through Ni1, Ni2, Ni3 and Ni4 are -0.0507(6) and -0.0512(6) Å for atoms Ni2 and Ni3, respectively. Two μ_3 -CH₃O⁻ ligands bridge the four Ni²⁺ ions displaced above 1.0610(28) and below -1.3062(28) Å the Ni₄ plane. The Ni...Ni distances are in the range 3.1287(8)-3.2036(9) Å, like that observed in reported similar tetranuclear nickel clusters¹⁸. The Ni2 and Ni3 exhibit the same N₃O₃ coordination sphere, which was completed by a chelating L²⁻ ligand (terminal acetate O atom, phenolate O atom and the secondary amino N atom), 1,10-phenanthroline (two N atoms) and μ_3 -CH₃O⁻ ions. The coordination spheres of the Ni1 and

TABLE-1
CRYSTALLOGRAPHIC DATA FOR COMPOUND **1**

Complex	1
Formula	C ₄₆ H ₄₈ N ₆ Ni ₄ O ₂₀ Cl ₂
Mr	1310.64
Cryst size [mm]	0.19 × 0.17 × 0.15
Colour	green blocks
Cryst. syst.	Triclinic
Space group	P $\bar{1}$
T [K]	185(2)
a [Å]	13.26(9)
b [Å]	13.31(10)
c [Å]	16.12(12)
α [deg]	80.66°(10)
β [deg]	87.68°(10)
γ [deg]	68.11°(10)
V [Å ³]	2595.5(3)
Z	2
D _{calcd} [g cm ⁻³]	1.677
μ (Mo K α) [mm ⁻¹]	1.615
F(000)	1344
Reflns collected	14409
Unique reflns	10102
R _{int}	0.0258
Parameters/restraints	707 / 0
GOF	1.040
R1 [I > 2 σ (I)]	0.0525
wR2 (all data)	0.1443
Largest diff. peak/hole [e Å ⁻³]	1.160 and -0.599

$$^a R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)} \right]^{1/2}$$

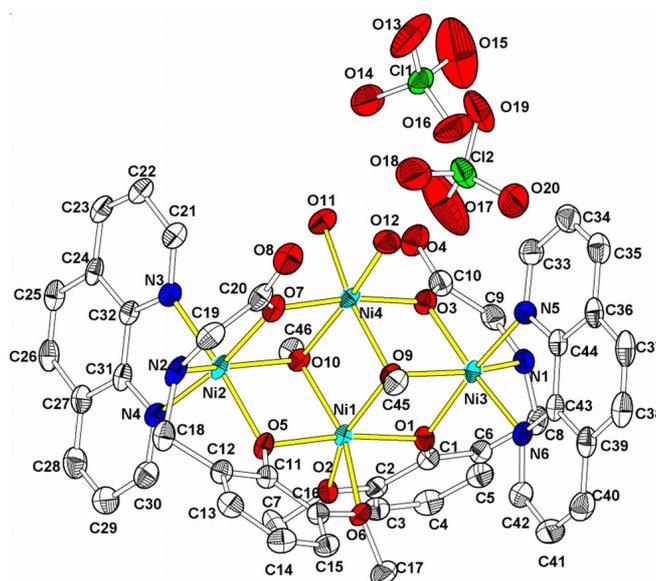


Fig. 1. A view of the complex **1**, showing the atomic numbering scheme. Hydrogen atoms have been removed for clarity. Thermal ellipsoids are at 30 % probability level

Ni4 are completed by two methoxy group of L²⁻ ligands (O1 and O6) for Ni1 and two water molecules for Ni4, respectively, generating six-coordinate centres with a distorted octahedral environment.

The successful reduction of the imine is evident from the N1-C8 and N2-C18 (1.475(6), 1.496(7) Å) distances when compared with the distance seen for related glycine-*o*-vanillin complex (1.241(7) Å)¹⁹. Further, the distances for N1-C9,

TABLE-2
SELECTED BOND LENGTHS (Å) AND
ANGLES (°) FOR COMPLEX 1

Ni1–O1	1.967(3)	Ni2–O5	2.008(3)
Ni1–O5	1.980(3)	Ni2–O7	2.029(3)
Ni1–O10	2.048(3)	Ni2–O10	2.144(3)
Ni1–O9	2.054(3)	Ni2–N3	2.008(4)
Ni1–O6	2.173(3)	Ni2–N4	2.093(4)
Ni1–O2	2.202(3)	Ni2–N2	2.103(4)
Ni3–O1	2.009(3)	Ni4–O3	2.039(3)
Ni3–O9	2.122(3)	Ni4–O7	2.043(4)
Ni3–O3	2.010(3)	Ni4–O9	2.055(3)
Ni3–N1	2.093(4)	Ni4–O10	2.069(3)
Ni3–N5	2.090(4)	Ni4–O11	2.088(3)
Ni3–N6	2.072(4)	Ni4–O12	2.091(3)
O1–Ni1–O5	171.44(13)	O5–Ni1–O6	77.45(12)
O1–Ni1–O10	107.14(13)	O10–Ni1–O6	157.85(12)
O5–Ni1–O10	81.00(13)	O9–Ni1–O6	95.05(12)
O1–Ni1–O9	80.06(12)	O1–Ni1–O2	75.89(12)
O5–Ni1–O9	103.68(13)	O5–Ni1–O2	101.17(12)
O9–Ni1–O10	85.04(13)	O10–Ni1–O2	94.88(12)
O1–Ni1–O6	94.65(13)	O9–Ni1–O2	154.80(12)
O6–Ni1–O2	94.28(12)	O1–Ni3–O3	96.20(13)
O5–Ni2–O7	99.46(13)	O1–Ni3–N6	92.21(15)
O5–Ni2–N3	167.35(14)	O3–Ni3–N6	169.94(15)
O7–Ni2–N3	90.86(14)	O1–Ni3–N5	170.66(15)
O5–Ni2–N4	89.86(14)	O3–Ni3–N5	92.11(15)
O7–Ni2–N4	170.65(14)	N6–Ni3–N5	79.12(16)
N3–Ni2–N4	79.80(16)	O1–Ni3–N1	89.02(14)
O5–Ni2–N2	90.11(14)	O3–Ni3–N1	81.33(15)
O7–Ni2–N2	80.16(15)	N6–Ni3–N1	104.38(16)
N3–Ni2–N2	98.89(15)	N5–Ni3–N1	96.44(16)
N4–Ni2–N2	100.65(17)	O1–Ni3–O9	77.50(12)
O5–Ni2–O10	78.05(12)	O3–Ni3–O9	79.47(12)
O7–Ni2–O10	77.92(12)	N6–Ni3–O9	97.06(14)
N3–Ni2–O10	97.19(13)	N5–Ni3–O9	99.94(14)
N4–Ni2–O10	103.59(13)	N1–Ni3–O9	155.10(14)
N2–Ni2–O10	152.89(14)	O3–Ni4–O7	171.40(13)
O9–Ni4–O10	84.47(12)	O3–Ni4–O9	80.40(12)
O3–Ni4–O11	87.13(14)	O7–Ni4–O9	92.47(12)
O7–Ni4–O11	99.81(14)	O3–Ni4–O10	95.07(13)
O9–Ni4–O11	167.43(13)	O7–Ni4–O10	79.35(12)
O3–Ni4–O12	96.88(14)	O10–Ni4–O11	95.12(13)

C6–C8, N2–C19 and C12–C18 (1.471(6), 1.504(7), 1.464(6) and 1.501(7) Å, respectively) are typical of single bonds, being significantly longer than those of imine complex and indicating the loss of conjugation. The angles centered about N1 and N2 are consistent with an sp^3 tetrahedral N and are similar to those for this general class of N-(*o*-hydroxybenzyl)-glycine ligand in $[\text{Cu}_2(\text{C}_9\text{H}_9\text{O}_3\text{N})_2(\text{H}_2\text{O})]_n \cdot n\text{H}_2\text{O}^{20}$ and $[\text{Cu}(\text{C}_9\text{H}_{10}\text{O}_3\text{N})(\text{C}_{10}\text{H}_8\text{N}_2)]_n \text{Cl}_n \cdot n\text{H}_2\text{O}^{21}$ complexes.

In the crystal structure of complex **1**, the uncoordinated perchlorate anions are involved in forming intermolecular hydrogen bonds. Two adjacent nickel clusters participate in complementary O11–H11B \cdots O14, O12–H12B \cdots O16 and N2i–H2A \cdots O13 hydrogen bonds forming a dimeric structure [symmetry code: (i) 1 - x, 2 - y, 1 - z] (Fig. 2 and Table-3). In addition, there are intramolecular O11–H11A \cdots O4 and O12–H12A \cdots O8 hydrogen bonds in complex **1** between the water molecules and carboxylate groups of the ligands.

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

D–H \cdots A	d(D–H)	d(H \cdots A)	d(D \cdots A)	\angle (DHA)
N2 ⁱ –H2A \cdots O13	0.91	2.19	3.057(6)	159.1
O11–H11A \cdots O4	0.85	1.91	2.756(6)	171.0
O11–H11B \cdots O14	0.85	2.12	2.967(6)	171.3
O12–H12A \cdots O8	0.85	1.89	2.728(6)	167.1
O12–H12B \cdots O16	0.85	2.06	2.896(7)	167.4

Symmetry codes: (i) 1 - x, 2 - y, 1 - z

Conclusion

To summarize, a novel Ni_4 complex featuring defective double-cubane has been prepared by using the reduced Schiff base ligand (H_2L). The reduction of the ligand increases donor strength of the internal nitrogen donors and also generates the methylene with an increased torsional strain, which further increases ligand flexibility. Both chelating and bridging capacities of this quadridentate Schiff-base ligand consolidate this Ni_4 cluster.

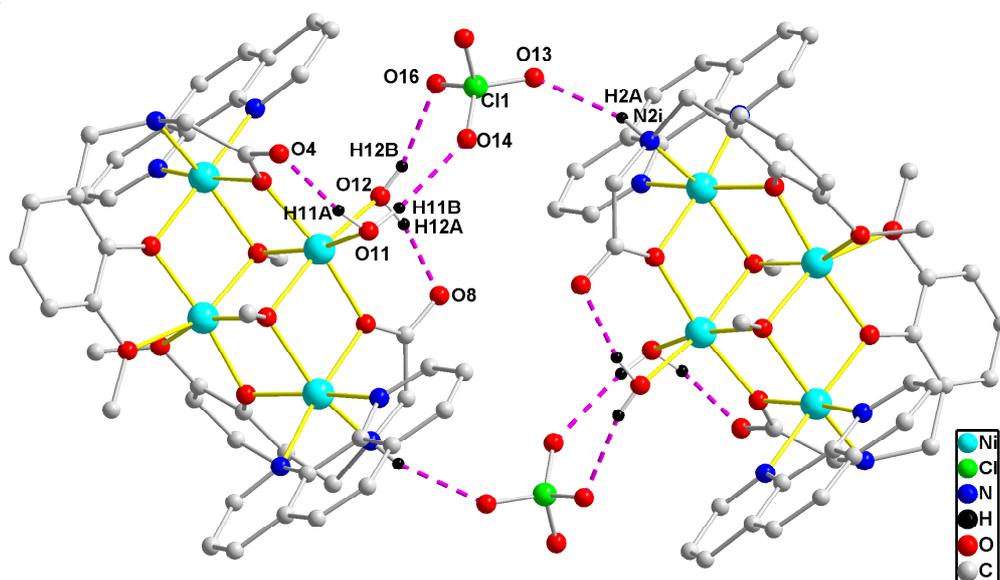


Fig. 2. The dimeric structure of the complex **1**, with hydrogen bonds shown as dashed lines

ACKNOWLEDGEMENTS

The authors thank the project supported by the Development and Reform Commission of Jilin Province, the Science and Technology Bureau of Changchun City, the Science and Technology Department of Jilin Province, China (2011174) and Changchun University of Science and Technology for their financial support.

REFERENCES

1. E.C. Yang, W. Wernsdorfer, S. Hill, R.S. Edwards, M. Nakano, S. Maccagnano, L.N. Zakharov and D.N. Hendrickson, *Polyhedron*, **22**, 1727 (2003).
2. H. Carlsson, M. Haukka, A. Bousseksou, J.M. Latour and E. Nordlander, *Inorg. Chem.*, **43**, 8252 (2004).
3. M.A. Alam, M. Nethaji and M. Ray, *Angew. Chem. Int. Ed.*, **42**, 1940 (2003).
4. B. Sreenivasulu and J.J. Vittal, *Angew. Chem. Int. Ed.*, **43**, 5769 (2004).
5. A. Das, F.J. Klinke, S. Demeshko, S. Meyer, S. Dechert and F. Meyer, *Inorg. Chem.*, **51**, 8141 (2012).
6. S.Y. Zhang, W.Q. Chen, B. Hu, Y.M. Chen, W. Li and Y.H. Li, *Inorg. Chem. Commun.*, **16**, 74 (2012).
7. B. Baruah, S. Das and A. Chakravorty, *Inorg. Chem.*, **41**, 4502 (2002).
8. L. Casella and M. Gullotti, *Inorg. Chem.*, **22**, 2259 (1983).
9. R. Wagner and F. A. Walker, *Inorg. Chem.*, **22**, 3021 (1983).
10. L.L. Koh, J.O. Ranford, W.T. Robinson, J.O. Svensson, A.L.C. Tan and D.Q. Wu, *Inorg. Chem.*, **35**, 6466 (1996).
11. S. Bandyopadhyay, G.N. Mukherjee and M.G.B. Drew, *Inorg. Chim. Acta*, **359**, 3243 (2006).
12. M. Nagarathinam, K. Saravanan, W.L. Leong, P. Balaya and J.J. Vittal, *Cryst. Growth Des.*, **9**, 4461 (2009).
13. X.D. Yang, J.D. Ranford and J.J. Vittal, *Cryst. Growth Des.*, **4**, 781 (2004).
14. O. Pouralimardan, A.C. Chamayou, C. Janiak and M.H. Hosseini, *Inorg. Chim. Acta*, **360**, 1599 (2007).
15. C.T. Yang, M. Vetrichelvan, X.D. Yang, B. Moubaraki, K.S. Murray and J.J. Vittal, *J. Chem. Soc., Dalton Trans.*, 113 (2004).
16. G.M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Germany (1997).
17. G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany (1997).
18. P. King, R. Clerac, W. Wernsdorfer, C.E. Anson and A.K. Powell, *Dalton Trans.*, 2670 (2004).
19. X.G. Cui, H.J. Sun, D.X. Liu, X.Y. Li and S.L. Li, *Acta Chim. Sin.*, **51**, 346 (1993).
20. X.D. Yang, D.Q. Wu, J.D. Ranford and J.J. Vittal, *Cryst. Growth Des.*, **5**, 41 (2005).
21. Z.L. Lu, D.Q. Zhang, S. Gao and D.B. Zhu, *Inorg. Chem. Commun.*, **8**, 746 (2005).