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研究简报

以 Schiff 碱 *N*- 丁酰基水杨酰肼为配体的三核镍(Ⅱ)配合物的合成与结构

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Synthesis and Crystal Structure of the Trinuclear Nickel (Ⅱ) Complex with Schiff Base Ligand *N*-butylsalicylhydrazide

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The trinuclear nickel (Ⅱ) complex $Ni_3(C_{11}H_{11}N_2O_3)_2(C_5H_5N)_4$ was prepared by the reaction of $Ni(OAc)_2 \cdot 4H_2O$ with *N*-butylsalicylhydrazide Schiff base ligand and characterized by X-ray crystallography. The crystal belongs to triclinic, $M_r = 930.91$, space group $P\bar{1}$ with cell parameters $a = 9.8489(2)$ Å, $b = 12.3110(2)$ Å, $c = 18.4035(3)$ Å, $\alpha = 71.353(2)°$, $\beta = 76.638(2)°$, $\gamma = 84.815(2)°$, $V = 2056.72(6)$ Å^3, $Z = 2$, $D_c = 1.503$ g·cm^{-3}, $\mu(Mo K\alpha) = 1.417$ mm^{-1}, $F(000) = 964$, $R = 0.0317$, $wR = 0.0868$. A total of 5393 independent reflections were collected, of which 4448 reflections with $I \geqslant 2\sigma(I)$ were observed. There are two centrosymmetrical trinuclear molecules in a unit cell, each molecule exhibits a linear trinuclear metal arrangement with the Ni···Ni···Ni angle of 180°. The interatomic distances between the nickel atoms on the two sides are 9.2030(8) Å and 9.1876(9) Å for the two molecules, respectively. The central nickel atom adopts an axially elongated octahedral geometry whereas the nickel atoms on the two sides have square-planar coordination environment. CCDC: 194083.

Keywords: Schiff base nickel complex hydrazone crystal structure

0 Introduction

Nickel Schiff base complexes have been of great interest for inorganic and bioinorganic chemistry[1~12]. These complexes exhibit the higher antitumor[6~9], antibacterial activities[8], and the stronger scavenging O_2 ability as compared with the free ligand[9]. They have also been extensively used in catalysis, because of their high activity and selectivity[2~4, 11, 12]. A series of Mn (Ⅲ), Fe (Ⅲ) and Co (Ⅲ) metallomacrocyles with the

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Schiff base *N*-alkylsalicylhydrazide ligands have been reported[13~15] . As an extension of our work on the chelating properties of the *N*-alkylalicylhydrazide ligands, we report the synthesis and crystal structure of a trinuclear nickel (Ⅱ) complex with *N*-butylsalicylhydrazide ligand, $Ni_3(C_{11}H_{11}N_2O_3)_2(C_5H_5N)_4$.

1 Experimental

1.1 Preparation of *N*-butylsalicylhydrazidate

4.66mL (33.4mmol) of benzyl chloride and 3.91 mL (33.4mmol) of triethylamine were added dropwise to 65mL of chloroform solution of 5.082g (33.4mmol) of butyric acid at 0℃. After warming to room temperature, 4.238g (27.9mmol) of salicylhydrizde was added to the reaction mixture and stirred till a large amount of white precipitate appeared and then staying for overnight at refrigerator. The resulting white precipitate was filtered and rinsed with chloroform and diethyl ether. m. p.: 194 ~ 196℃

1.2 Preparation of Complex

0.055g (0.25mmol) of *N*-butylsalicylhydrazidate was dissolved in 5 mL of DMF, and 0.062g (0.25 mmol) of nickelous acetate tetrahydrate was dissolved in 5mL of pyridine in another flask. The two solutions were mixed and filtered after stirring for ten minutes. The mixed solution was allowed to stand for 5d and the red block crystals were obtained from the filrate. Anal. Calcd. for $Ni_3(C_{11}H_{11}N_2O_3)_2(C_5H_5N)_4$/(%): C, 54.19; H, 4.55; N, 12.04; Found/(%): C, 55.74; H, 4.89; N, 11.79. IR data (cm^{-1}, KBr): 2930.50m, 1602.07s, 1564.29s, 1375.42m, 1334.42m, 1523.09s, 1467.15s, 1266.40m, 573.62w, 541.93w, 417.48w.

1.3 Data Collection and Structure Determination

A red crystal with dimensions of 0.19mm × 0.23mm × 0.27mm was mounted on a glass fiber. Data collection were performed on a Rigaku Weissenberg IP diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$Å), the scan mode being ω. A total of 5393 independent reflections were collected in the range of $3.50° \leqslant 2\theta \leqslant 46.00°$, of which 4448 observed reflections with $I \geqslant 2\sigma(I)$ were used in the succeeding structure determination and refinement. The intensity data were corrected for Lorentz-polarization effects and Ψ absorption. The structure was solved by direct methods. All hydrogen atoms were found from the difference Fourier syntheses and geometrical calculation. The refinement by full-matrix least-squares on F^2 based on 537 variables gave the final $R = 0.0317$ and $wR = 0.0868$, where $w = [\sigma^2(F_o^2) + (0.0602P)^2 + 0.070P]^{-1}$, $P = (F_o^2 + 2F_c^2)/3$. $\Delta/\sigma_{max} = 0.000$, $S = 1.063$. The maximum peak and minimum peak in the final difference Fourier map are 0.318e · Å^{-3} and −0.403e · Å^{-3}, respectively.

2 Results and Discussion

The molecular structure of the title compound is shown in Fig. 1. Selected bond lengths and angles are

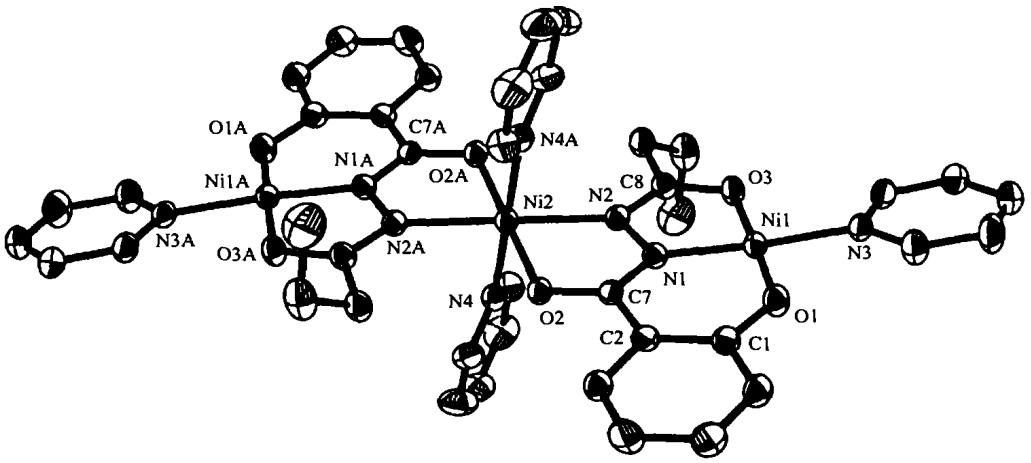

Fig. 1 Molecular structure of complex **1** showing the atom numbering and 30% probability displacement ellipsoids

given in Tables 1 and 2, respectively.

There are two trinuclear molecules in a unit cell, i. e. the molecule **a** containing Ni(1), Ni(2) and Ni (1A) and the molecule **b** containing Ni(3), Ni(4) and Ni(3B). The two molecules are of centrosymmetrical trinuclear structure type with Ni(2) at (0, 0, 1/2) and Ni(4) at (0, 1/2, 0), respectively. The nickel atoms on the center (Ni(2) and Ni(4)) have an axially elongated octahedral coordination with Ni(ON) (ON) (N)(N) type.

The bond distances of Ni-O(carbonyl) and Ni-N (hydrazide) on the equatorial plane are 2.026(2) Å, 2.073(3) Å for molecule **a**, and 2.029(2) Å, 2.068 (3) Å for molecule **b**, respectively. The axial bond distances of Ni-N(py) are 2.149(3) Å for molecule **a** and 2.148(3) Å for molecule **b**, which are longer than the corresponding values of 2.107(2) Å and 2.115(2) Å in some Ni (Ⅱ) complexes[16].

The nickel (Ⅱ) ions on the sides (Ni(1), Ni(1A), Ni(3), Ni(3B)) adopt square-planar geometry with Ni (ONO) (N) type. The bond distances of Ni-O(phenolic) are 1.816(2) Å in molecule **a** and 1.822(3) Å in molecule **b**. The Ni-O(acyloxy) distances are 1.843 (2) Å and 1.847(3) Å for molecules **a** and **b**, respectively, which are close to corresponding bond lengths (1.859(2)Å, 1.850(2)Å) reported[17]. Ni-N(hydrazine) bond lengths (1.825(3) Å and 1.826(3) Å) are comparable with the value(1.815 ~ 1.910Å) found in several Ni (Ⅱ) complexes[17~21]. The Ni-N(py) distances in the square-planar coordination configuration

Table 1　Selected Bond Lengths(Å)

bond	dist.	bond	dist.	bond	dist.	bond	dist.
Ni(1)-O(1)	1.816(2)	Ni(1)-N(1)	1.825(3)	Ni(1)-O(3)	1.843(2)	Ni(1)-N(3)	1.942(3)
Ni(2)-O(2A)	2.026(2)	Ni(2)-O(2)	2.026(2)	Ni(2)-N(2A)	2.073(3)	Ni(2)-N(2)	2.073(3)
Ni(2)-N(4A)	2.149(3)	Ni(2)-N(4)	2.149(3)	O(1)-C(1)	1.326(4)	O(2)-C(7)	1.280(4)
O(3)-C(8)	1.304(4)	N(1)-C(7)	1.323(4)	N(1)-N(2)	1.416(4)	N(2)-C(8)	1.297(4)
Ni(3)-O(4)	1.822(3)	Ni(3)-N(5)	1.826(3)	Ni(3)-O(6)	1.847(3)	Ni(3)-N(7)	1.941(3)
Ni(4)-O(5B)	2.029(2)	Ni(4)-O(5)	2.029(2)	Ni(4)-N(6)	2.068(3)	Ni(4)-N(6B)	2.068(3)
Ni(4)-N(8B)	2.148(3)	Ni(4)-N(8)	2.148(3)	O(4)-C(22)	1.325(5)	O(5)-C(28)	1.269(4)
O(6)-C(29)	1.298(4)	N(5)-C(28)	1.334(4)	N(5)-N(6)	1.408(4)	N(6)-C(29)	1.301(5)

Symmetry codes: A: $-x, -y, 1-z$; B: $-x, 1-y, -z$.

Table 2　Selected Bond Angles(°)

angle	(°)	angle	(°)	angle	(°)
O(1)-Ni(1)-N(1)	94.8(1)	O(1)-Ni(1)-O(3)	177.8(1)	N(1)-Ni(1)-O(3)	83.9(1)
O(1)-Ni(1)-N(3)	90.4(1)	N(1)-Ni(1)-N(3)	174.7(1)	O(3)-Ni(1)-N(3)	90.9(1)
O(2A)-Ni(2)-O(2)	180.000(1)	O(2A)-Ni(2)-N(2A)	78.8(1)	O(2)-Ni(2)-N(2A)	101.2(1)
O(2A)-Ni(2)-N(2)	101.2(1)	O(2)-Ni(2)-N(2)	78.8(1)	N(2A)-Ni(2)-N(2)	180.0
O(2A)-Ni(2)-N(4A)	90.7(1)	O(2)-Ni(2)-N(4A)	89.3(1)	N(2A)-Ni(2)-N(4A)	93.2(1)
N(2)-Ni(2)-N(4A)	86.8(1)	O(2)-Ni(2)-N(4)	89.3(1)	O(2)-Ni(2)-N(4)	90.7(1)
N(2A)-Ni(2)-N(4)	86.8(1)	N(2)-Ni(2)-N(4)	93.2(1)	N(4A)-Ni(2)-N(4)	180.00(8)
C(1)-O(1)-Ni(1)	126.6(2)	C(7)-O(2)-Ni(2)	113.4(2)	C(8)-O(3)-Ni(1)	111.7(2)
C(7)-N(1)-N(2)	115.0(3)	C(7)-N(1)-Ni(1)	131.2(2)	N(2)-N(1)-Ni(1)	113.8(2)
C(8)-N(2)-N(1)	109.4(3)	C(8)-N(2)-Ni(2)	139.7(2)	N(1)-N(2)-Ni(2)	109.9(2)
O(4)-Ni(3)-N(5)	94.5(1)	O(4)-Ni(3)-O(6)	178.3(1)	N(5)-Ni(3)-O(6)	83.7(1)
O(4)-Ni(3)-N(7)	90.7(1)	N(5)-Ni(3)-N(7)	174.4(1)	O(6)-Ni(3)-N(7)	91.1(1)
O(5B)-Ni(4)-O(5)	180.0(1)	O(5B)-Ni(4)-N(6)	101.5(1)	O(5)-Ni(4)-N(6)	78.6(1)
O(5B)-Ni(4)-N(6B)	78.6(1)	O(5)-Ni(4)-N(6B)	101.5(1)	N(6)-Ni(4)-N(6B)	180.0(2)
O(5B)-Ni(4)-N(8B)	88.8(1)	O(5)-Ni(4)-N(8B)	91.2(1)	N(6)-Ni(4)-N(8B)	93.3(1)
N(6B)-Ni(4)-N(8B)	86.7(1)	O(5B)-Ni(4)-N(8)	91.2(1)	O(5)-Ni(4)-N(8)	88.8(1)
N(6)-Ni(4)-N(8)	86.7(1)	N(6B)-Ni(4)-N(8)	93.3(1)	N(8B)-Ni(4)-N(8)	180.000(1)
C(22)-O(4)-Ni(3)	127.0(2)	C(28)-O(5)-Ni(4)	112.4(2)	C(29)-O(6)-Ni(3)	111.6(2)
C(28)-N(5)-N(6)	114.2(3)	C(28)-N(5)-Ni(3)	131.8(2)	N(6)-N(5)-Ni(3)	114.0(2)
C(29)-N(6)-N(5)	109.4(3)	C(29)-N(6)-Ni(4)	139.4(2)	N(5)-N(6)-Ni(4)	109.9(2)

are 1.942(3)Å and 1.941(3)Å, which are ~0.204Å shorter than those in octahedral coordination environments.

All atoms of salicylhydrazide in the trianionic pentadentate ligand *N*-butylsalicylhydrazide are planar. The average deviations from plane are 0.0827Å and 0.0378Å in molecules **a** and **b**, respectively. The two molecules exhibit a linear trinuclear arrangement with the Ni···Ni···Ni angle of 180°. The interatomic distances between the nickel atoms on the two sides are 9.2030(8)Å and 9.1876(9)Å for molecules **a** and **b**, respectively.

3 Supplementary Material

Lists of the CIF files for the title compound has been deposited at the Cambridge Structural Database (CCDC: 194083). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336033; E-mail: deposit@ ccdc. cam. ac. uk or http: //www. ccdc. cam. ac. uk).

References

[1] Halcow M. A., Christou G. *Chem. Rev.*, **1994**, **94**, 2421.

[2] Debabrata C., Sanghamitra M., Anannya M. *J. Mol. Catal. A: Chemical*, **2000**, **154**, 5.

[3] Debabrata C., Anannya M. *J. Mol. Catal. A: Chemical*, **1999**, **144**, 363.

[4] Kureshy R. I., Khan N. H., Abdi S. H. R., Patel S. T., Iyer P., Suresh E., Dastider P. *J. Mol. Catal. A: Chemical*, **2000**, **160**, 217.

[5] Ferrari M. B., Capacchi S., Reffo G., Pelosi G., Tarasconi P., Albertini R., Pinelli S., Lunghi P. *J. Inorg. Biochem.*, **2000**, **81**, 89.

[6] YANG Gao-Wen(杨高文), XIA Xiao-Ping(夏小平), TU Huan(涂 欢), YUE Cheng-Xue(越成学) *Huaxue Yanjiu Yu Yingyong*(*Chemical Research and Application*), **1995**, **7**(1), 41.

[7] XU Chun(许 纯), REN You-Xian(任友贤), CHEN Yun-Sheng(陈运生), MO Jian(莫 简) HUANG Yin-Qiao(黄荫乔) *Huaxue Yanjiu Yu Yingyong*(*Chemical Research and Application*), **1993**, **5**(2), 40.

[8] WANG Gang(王 刚), TANG Ning(唐 宁), TAN Min-Yu(谭民裕) *Huaxue Yanjiu Yu Yingyong*(*Chemical Research and Application*), **1996**, **8**(4), 493.

[9] YANG Gao-Wen(杨高文), XIA Xiao-Ping(夏小平), TU Huan(涂 欢), YUE Cheng-Xue(越成学) *Yingyong Huaxue*(*Chinese J. Applied Chemistry*), **1995**, **12**(2), 13.

[10] SHI Wei-Liang(史卫良), CHEN De-Yu(陈德余), CHEN Shi-Ming(陈士明), YAN Xiao-Min(严小敏) *Wuji Huaxue Xuebao*(*Chinese J. Inorg. Chem.*), **2001**, **17**(2), 241.

[11] WANG Hai-Ping(王海平), XI Zu-Wei(奚祖威), CAO Guo-Ying(曹国英) *Fenzi Cuihua*(*J. Mol. Catal.* (*China*)), **1998**, **12**(1), 19.

[12] YIN Guo-Chuan(尹国川), XI Zu-Wei(奚祖威), CAO Guo-Ying(曹国英) *Cuihua Xuebao*(*Chinese J. Catal.*), **1996**, **17**(1), 79.

[13] (a) LIU Shi-Xiong, LIN Shen, LIN Bi-Zhou, LIN Chi-Chang *Angew. Chem. Int. Ed. Engl.*, **2001**, **40**, 1084;
(b) LIN Shen, LIU Shi-Xiong, LIN Bi-Zhou *Inorg. Chim. Acta*, **2002**, **328**, 69;
(c) LIN Shen, LIU Shi-Xiong, HUANG Jian-Quan, LIN Chi-Chang *J. Chem. Soc., Dalton Trans.*, **2002**, 1595.

[14] Kwak B., Rhee H., Lah M. S. *Polyhedron*, **2000**, **19**, 1985.

[15] Kim I., Kwak B., Lah M. S. *Inorg. Chim. Acta*, **2001**, **317**, 12.

[16] SUN Ming(孙 命), WANG Jin-Ling(王瑾玲), DUAN Yue-Qin(段月琴), MIAO Fang-Ming(缪方明), WENG Lin-Hong(翁林红), LENG Xue-Bing(冷雪冰) *Jiegou Huaxue*(*Chinese J. Struct. Chem.*), **2001**, **20**(1), 8.

[17] YIN Hua(尹 华), LIU Shi-Xiong(刘世雄) *Wuji Huaxue Xuebao*(*Chinese J. Inorg. Chem.*), **2002**, **18**(3), 269.

[18] Arion V., Wieghardt K., Weyhermueller T., Bill E., Leovac V., Rufinska A. *Inorg. Chem.*, **1997**, **36**, 661.

[19] Gabel J., Hasemann V., Henriksen H., Larsen E., Larsen S. *Inorg. Chem.*, **1979**, **18**, 1088.

[20] Bogdanović G. A., Biré A. S., Leovac V. M., Češljević V. I. *Acta Cryst.*, **1999**, **C55**, 1656.

[21] Bogdanović G. A., Biré A. S., Prelesnik B. V., Leovac V. M. *Acta Cryst.*, **1998**, **C54**, 766.

[22] Bacchi A., Carcelli M., Pelagatti P., Pelizzi C., Pelizzi G., Salati C., Sgarabotto P. *Inorg. Chim. Acta*, **1999**, **295**, 171.

[23] Kaminsky W., Jasinski J. P., Woudenberg R., Goldberg K. I., Xest D. *J. Mol. Struct*, **2002**, **608**, 135.