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# Synthesis And Crystal Structure Of Nickel Complex: $Ni[(DMF)_4(H_2O)_2]\cdot Br_2$

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**ABSTRACT**

One nickel complex $Ni[(DMF)_4(H_2O)_2]\cdot Br_2$ (DMF=N,N-dimethylformamide) was prepared and structurally characterized. Single crystal X-ray diffraction analysis revealed that the Ni(II) is six-coordinate by six oxygen atoms of four DMF and two water molecules, the complex molecular is further assembled into a one-dimension super molecular chain through weak H–Br–H interaction. Crystal data: monoclinic, space group P2(1), a=8.359(12)Å, b=8.359(12)Å, c=8.835(13)Å, $\alpha=\gamma=91^0$, $\beta=93.411(16)^0$, V=616.0(15)Å$^3$, Z=2, D=1.453 Mg·m$^{-3}$. 

**KEYWORDS**

Nickel;
Single crystal;
One-dimension chain

## INTRODUCTION

Late transition metal catalyzed olefin polymerization has attracted a great deal of interest during the past decade, because of their tolerance toward polar substrates[1]. In 1995, A revolutionary system was reported by Brookhart and co-workers, in which nickel(II) and palladium(II) complexes containing bulky α-diimine ligands were capable of polymerizing ethylene to give high-molecular-weight polymers[2-3]. Moreover, in 1998, Brookhart's[4] and Gibson's[5] groups independently reported highly active cationic iron and cobalt olefin polymerization catalysts with bulky pyridinyldiimine ligands, and their catalytic activities were up to $10^7$g PE/(mol Feh). Grubbs group reported new neutral Ni(II) salicylaldiminato complexes as catalyst for the polymerization of ethylene under moderate conditions[6]. We were also interested in exploring new nickel ethylene oligomerization catalysts[7-8]. Here we describe

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the synthesis and crystal structure of $Ni[(DMF)_4(H_2O)_2]\cdot Br_2$, it shows ethylene oligomerization activity with MAO as co-catalyst.

## EXPERIMENTAL

### Preparation of $Ni[(DMF)_4(H_2O)_2]\cdot Br_2$

$NiBr_2$(0.5mmol) was added to a mixture of DMF(9ml) and $H_2O$(2ml), after it was stirred for about 4 hours, the solution was filtered and the filtrate was kept at room temperature for about four weeks, blue single crystal was founded, yield about 30%.

### Structure determination

X-ray single-crystal diffraction data for the nickel complex was collected on a Bruker Smart 1000 CCD diffractometer at 293(2) K with Mo-KR radiation ($\lambda$=0.71073Å) by $\omega$ scan mode. The program SAINT[9] was used for integration of the diffraction profiles. Semi empirical absorption corrections were applied using SADABS program. All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL[10]. Metal atoms in each complex were located from the E-maps and other non-hydrogen atoms were located in successive difference fourier syntheses and refined with anisotropic thermal parameters on $F^2$. Hydrogen atoms of carbon were included in calculated positions and refined with fixed thermal parameters riding on their parent atoms. Crystallographic data and experimental details for structural analysis are summarized in TABLE 1. Selected bond lengths and angles are listed in TABLE 2.

## RESULTS AND DISCUSSION

The title compound exists as an air-stable blue solid and is a potentially useful starting reagent for the synthesis of Ni(II) complexes. Figure 1 shows the independent $[Ni(DMF)_4(H_2O)_2]^{2+}$ cations(DMF is N,N-dimethylformamide), which have the expected octahedral geometry, with each DMF and $H_2O$ molecule acting as a monodentate ligand via its O atom donor. Ni---O distances range from 1.969(10) to

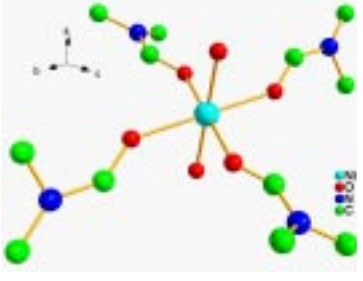

**Figure 1: View of the coordination environment of Ni(II) ions in the complex**

**TABLE 1: Crystallographic data and structure refinement summary for the complexes**

| Complex | $Ni[(DMF)_4(H_2O)_2]\cdot Br_2$ | | |
|---|---|---|---|
| Chemical formula | $C_6H_{12}Br_1N_2NiO_3$ | $\gamma$/deg | 91.00 |
| Formula weight | 300.78 | V/Å$^3$ | 616.0(15) |
| Crystal system | Monoclinic | Z | 2 |
| Space group | P2(1) | D/g cm$^{-3}$ | 1.453 |
| A(Å) | 8.359(12) | $\mu$/mm$^{-1}$ | 4.058 |
| B(Å) | 8.359(12) | T/K | 293(2) |
| C(Å) | 8.835(13) | $R^a$/$wR^b$ | 0.0712/ 01495 |
| $\alpha$/deg | 91.00 | Total/unique/$R_{int}$ | 1021/ 897/ 0.0483 |
| $\beta$/deg | 93.411(16) | - | - |

**TABLE 2: Selected bond distances(Å) and angles(deg) for the complexes**

| | | | |
|---|---|---|---|
| Ni(1)-O(1) | 2.382(9) | Ni(1)-O(2) | 2.137(9) |
| Ni(1)-O(3) | 1.969(10) | O(3)-Ni(1)-O(2) | 79.6(4) |
| O(3)#1-Ni(1)-O(2) | 100.4(4) | O(3)-Ni(1)-O(1)#1 | 103.9(4) |
| O(3)#1-Ni(1)-O(1)#176.1(4) | - | O(2)#1-Ni(1)-O(1)#1 | 81.0(4) |

Symmetry code: -x,-y+2,-z+1

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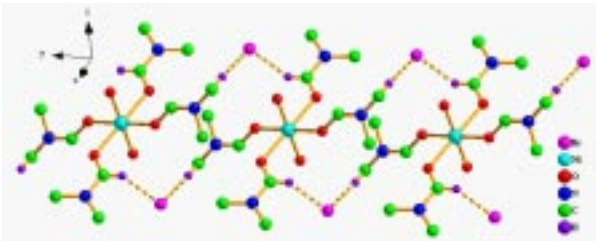

**Figure 2: View of 1D polymeric chain in the complex**

2.382(9)Å, and the Ni---O---C angles are in the range 79.6(4)-180.0$^0$. The uncoordinated $Br^-$ anions serving as counter anions, however the cationic complex can be assembled in to a one-dimension supermolecular chain through weak H---Br---H interaction (Figure 2). Upon treatment with MAO, it shows ethylene oligomerzation activity

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