Synthesis and Structure Research of Bis[N, N-bis(2-hydroxyethyl)dithiocarbamato-κ²S,S’]nickel(II)

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Abstract. New metal dithiocarbamate complex [(HOC₂H₄)₂NCSS]₂Ni was synthesized by method of One-Pot synthesis and characterized by elemental analysis, IR spectra, melting point. The crystal structure was determined by X-ray single crystal diffraction. Complex [(HOC₂H₄)₂NCSS]₂Ni is monoclinic with space group P2(1)/c. Lattice parameters: a=6.3798(8) Å, b=11.8298(14) Å, c=11.4586(13) Å, β=93.63(0) °. Parameter ratio: a/b=0.5393, b/c=1.0324, c/a=1.7961. The data agreed well with the structure determined by X-ray single crystal diffraction.

1. Introduction
Dithiocarbamate is one type of strong metal-chelating agents [1], which can form stable complexes with many metal ions such as Hg(II) [2], copper(II) [3], Sb (III), Bi (III) [4,5]. Metal dithiocarbamate complexes have been extensively studied due to their wide application, which can be used as chelator for heavy metal ions[6], anticancer drugs[7], friction improvers[8], enzyme inhibitors[9], metal adsorbents[10], plant fungicides[11], surfactants[12], capturing agents[13] and so on. Organic sulfur ligands were widely investigated, and many structure complexes were reported, Monomeric [14,15], dimeric [16], polymeric [17-19]. In this study, Bis[N, N-bis(2-hydroxyethyl)dithiocarbamato-κ²S,S’] nickel (II) was synthesized with One-Pot method [20-22] and characterized with elemental analysis, IR spectra, melting point. The structure was confirmed to be mononuclear by X-ray single crystal diffraction, which is very important to enrich the study of the bonding modes and structure of dithiocarbamate complexes.

2. Experimental

2.1. Synthesis of complex [(HOC₂H₄)₂NCSS]₂Ni
NaOH (1.0mmol, AR), NH(CH₂CH₂OH)₂ (1.0mmol, AR) and CS₂ (1.2mmol, AR) was stirred for 1 h in methanol (25ml, AR) at room temperature. Afterwards, NiCl₂ (0.5mmol, AR) was added. The mixture was stirred for 2 h at room temperature and the precipitate was vacuum filtered. Grass green crystals were obtained via slow evaporation atmosphere. All reagents were used as commercial supplied and without further purification.
2.2. **Elemental analysis**
With Germany elemental analyzer (Vario EL III), elements C, H, N, and S were analyzed with condition of combustion stoves and reduction stoves temperature are specially 1150 °C and 850 °C.

2.3. **Infrared Spectra**
Samples were made into KBr tablet and analyzed using Fourier Transfer Infrared Spectrum (SPECTRUM, American PE Company) in the range of 400-4000cm⁻¹.

2.4. **Melting Point**
X-5 Microscope Melting Point Measuring Instrument, with standard multiple of 80 in the microscope, the enlarged multiple is 20X, the measuring quantity is less than 0.1 mg, the measuring error: ±0.5%, the measuring accuracy: ±1°C±0.1°C.

2.5. **X-ray crystallography**
Crystal samples were select to fit to X-ray single diffraction analysis (Bruker SMART CCD APEXII Area Detector Diffraction) with graphite monochrome Mo-Kα ray (λ=0.71073 Å) as source of diffraction and diffraction point were collected with ω-2θ scan way. The crystal structure was solved by direct methods and refined by full matrix least squares with SHELX98. The non-hydrogen atoms and hydrogen atoms were refined anisotropically and isotropically, respectively [23].

3. **Results and Discussion**

3.1. **Elemental analysis**
The result of elemental analysis (theory values are in the parentheses) are listed as follows:

- C: 28.63% (28.60%), H: 4.65% (4.80%), N: 6.71% (6.68%), S: 30.57% (30.59%).
  
  The measured elemental values agree well with the calculated values.

3.2. **Infrared Spectra**
The bond characteristics of free hydroxyl groups are mostly present at 3643～3630 cm⁻¹, ν O-H at 3315 cm⁻¹ is between 3400～3200 cm⁻¹, which is likely due to the presence of intermolecular hydrogen bond interactions in hydroxyl groups. The strong peak at 975 cm⁻¹ indicates that the formation of complex equalized the formation of two C-S bond. Two S atoms coordinated approximately symmetry in form of bidentate. The strong peak at 1514 cm⁻¹ is attributed to the stretching vibration absorption of C-N bond[24-26], which is just between C-N single bond( 1350～1250 cm⁻¹) and C=N double bond (1690～1640 cm⁻¹), indicating that it has the property of partial double bond[27,28]. (Shown as Figure.1)

![Figure 1. IR Spectrum for [(HOC₂H₄)₂NCSS]₂ Ni](image_url)
3.3. Melting Point
The melting point test result is 179.1 °C ~ 179.4 °C. It showed that the melting process of the complex was shorter, indicating that the purity of the complex was higher.

3.4. Crystal Structure and Analysis
The details of the crystal structure data, data collection and refinement parameters for title complex are summarized in Table 1.

The molecular formula of bis [N, N-bis (2-hydroxyethyl) dithiocarbamato-κ²S, S'] nickel (II) is C_{10}H_{20}N_{2}NiO_{4}S_{4}. Molecular weight is 419.23 g/mol. The complex belongs to monoclinic structure (shown as Figure 2) with space group P2(1)/c. Lattice parameters: a=6.3798(8) Å, b=11.8298(14) Å, c=11.4586(13) Å, β=93.6260(10)º. Parameter ratio: a/b=0.5393, b/c=1.0324, c/a=1.7961. Lattice volume: 863.07(18) Å³, calculated density: 2.39869 g/ cm³ (shown as Table 1).

Table 1. Crystal data, data collection and refinement parameters for [HOC_2H_4NCSS]_2Ni

| Empirical formula | C_{10}H_{20}N_{2}NiO_{4}S_{4} | Crystal size/mm³ | 0.18×0.14×0.12 |
|------------------|-------------------------------|------------------|------------------|
| Formula weight   | 419.23 g/mol                  | GOF              | 1.025            |
| Crystal system   | Monoclinic                    | RI [F_o>2σ(F_o)]| 0.0305           |
| Space group      | P2(1)/c                       | RI (all reflections) | 0.0423           |
| Temperature /K   | 298(2)                        | wRI [F_o>2σ(F_o)]| 0.0679           |
| Wavelength/Å     | 0.71073                       | wRI (all reflections)| 0.0740           |
| a/Å              | 6.3798(8)                     | Scan Range/°     | 2.48 to 27.76   |
| b/Å              | 11.8298(14)                   | Index ranges     | -8≤h≤7          |
| c/Å              | 11.4586(13)                   | -15≤k≤15         |
| α/ (º)           | 90.000                        | Reflections collected / unique | 5246 / 1992 [R(int) = 0.0294] |
| β/ (º)           | 93.6260(10)                   | Calculated density/ Mg/m³ | 2.39869        |
| γ/ (º)           | 90.000                        | Largest diff. peak and hole/ e.A⁻³ | 0.323 and -0.274 |
| Cell volume      | 863.07(18)                    | Absorption coefficient/ mm⁻¹ | 1.621          |
| Z                | 2                             |                   |                  |
| F (000)          | 632                           |                   |                  |

Figure 2. Molecular Structure of Complex [(HOC₂H₄)₂NCSS]₂Ni

According to the title complex structure and data of bond distances (Å) and angles (º) (shown as Table 2), the nickel atom, which has distorted square-planar geometry, was coordinated to four sulfur atoms in the two 2-hydroxyethylthiocarbamate ligands. The Ni-S distances ranged from 1 to 2 Å. This is consistent with the previous literature [29]. The crystal cell stacking diagram is shown in Figure 3.
Table 2. Bond distances (Å) and angles (°) for [HOC\(_2\)H\(_4\)]\(_2\)NCSS\(_2\)Ni

| Atoms 1,2 | d 1,2[Å] | Atoms 1,2 | d 1,2[Å] | Atoms 1,2 | d 1,2[Å] |
|-----------|----------|-----------|----------|-----------|----------|
| C1—N1     | 1.320(3) | C3—O1     | 1.409(3) | Ni1—S2    | 2.1901(6) |
| C1—S2     | 1.717(2) | C4—N1     | 1.475(2) | Ni1—S1i   | 2.2086(6) |
| C1—S1     | 1.721(2) | C4—C5     | 1.507(3) | Ni1—S1    | 2.2086(6) |
| C2—N1     | 1.461(3) | C5—O2     | 1.409(3) | O1—H1     | 0.8200    |
| C2—C3     | 1.504(3) | Ni1—S2\(^i\) | 2.1901(6) | O2—H2     | 0.8200    |

Atoms 1, 2, 3 | Angle 1, 2, 3[°] | Atoms 1, 2, 3 | Angle 1, 2, 3[°]
|-------------|-----------------|-------------|-----------------|
| N1—C1—S2   | 124.37(16)      | C2—N1—C4   | 117.16(17)      |
| N1—C1—S1   | 126.05(15)      | S2—Ni1—S2  | 180.00(3)       |
| S2—C1—S1   | 109.56(11)      | S2\(^i\)—Ni1—S1\(^i\) | 79.37(2) |
| N1—C2—C3   | 111.8(2)        | S2—Ni1—S1\(^i\) | 100.63(2)      |
| O1—C3—C2   | 111.8(2)        | S2—Ni1—S1  | 100.63(2)      |
| N1—C4—C5   | 112.43(18)      | S2—Ni1—S1  | 100.63(2)      |
| O2—C5—C4   | 111.9(2)        | S1\(^i\)—Ni1—S1\(^i\) | 180.00(3) |
| C1—N1—C2   | 121.85(17)      | C1—S1—Ni1  | 85.12(7)       |
| C1—N1—C4   | 120.99(17)      | C1—S2—Ni1  | 85.81(7)       |

Figure 3. Molecular Cell stacking diagram of the complex [(HOC\(_2\)H\(_4\))]\(_2\)Ni

In the title compound [Ni(C\(_5\)H\(_10\)NO\(_2\)S\(_2\))]\(_2\), the Ni(II) cation is chelated with bis (2- hydroxyethyl) dithiocarbamate anions. Molecular Cell are arranged in all directions in the shape of impellers. The hydroxyethyl carbon chain C-C single bond in the ligand can be twisted freely, which helps maintain the dependence of each bond on direction and distance. Intermolecular O—H…O hydrogen bonding was observed between the terminal hydroxy groups in the crystal structure. Due to the existence of hydrogen bonds, the molecules are infinitely connected in space. The bond distances and bond angles of the hydrogen bonds are shown in Table 3.

Table 3. Hydrogen bonding distances (Å) and angles (°) for [HOC\(_2\)H\(_4\)]\(_2\)NCSS\(_2\)Ni

| d O-H[Å] | d O-O[Å] | d H…O[Å] | Angle O-H…O[°] |
|----------|----------|----------|----------------|
| O1-H1    | 0.819    | O1-O2    | 2.726          | H2—O1 1.902 | O1-H1…O2 164.38 |
| O2-H2    | 0.820    | O2-O1    | 2.711          | H1—O2 1.927 | O2-H2…O1 168.83 |
Hydroxyl group is weak in coordinating ability for dithiocarbamate ligand and is not participating coordinating, but can form hydrogen bond between molecules due to the presence of hydroxyl, so this ligand is slightly different to other dithiocarbamate complex. In the course of interaction, 0.001Å difference in the bonding distance between O1-H1 and O2-H2. Bond angles O-H…O with two neighbor molecules were 164.38° and 168.83° respectively. The bond distances and angles of both hydrogen bonds were nearly identical. The molecule is the distorted square-planar structure. The structure can be considered to be comprised of layers holding together primarily by O-H-O interactions in the same plane; successive layers stack parallel to the differ direction to the plane.

4. Conclusion

New complexes Bis [N, N-bis(2-hydroxyethyl) dithiocarbamato-κ²S, S’] nickel (II) has been synthesized, which the bonding characteristics have important theoretical significance to enrich the theory of metal bonding and will have potential application value in many fields.

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