Notes

Bull. Korean Chem. Soc. **1994**, Vol. 15, No. 9 803

Synthesis of Heterobimetallic Complexes Containing Ni(II) Complex of N,N'-Dimethyl-N,N'-Bis(β-mercaptoethyl)ethylenediamine and Metal Carbonyls

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There has been much recent interest in the synthesis and characterization of nickel-sulfur complexes.[1] The intensive study of this field stems from the recognition of redox active nickel-sulfur and/or nitrogen cores.[2] Along with the role of metal oxidoreductases by means of nickel complexs with thiolate and amine ligands, these complexes become functional models which are able to react with CO_2, CO or CH_3 groups.[3] Besides the biological role of nickel thiolate amine, nickel complexes with sulfur ligands has led to the widespread use as synthons for heteronuclear transition metal complexes due to the propensity of sulfur to form M (μ-SR) M' bridges.[4] Of particular interest are extensive structural studies of such speceis, especially those involving bent metallocene fragments.[5] The nickel-sulfur bond is dominated by a four-electron repulsive interaction which renders thiolate sulfurs more nucleophilic than in their free form.[6] Heterobi- or polymetallic complexes bridged by nickel thiolate sulfurs readily form. For the design of the synthesis of heterometallic complexes, we chose the ligand N,N'-dimethyl-N,N'-bis(β-mercaptoethyl)ethylenediamine(dsdm).[7] It is interesting to note that the nickel thiolate amine complexe[Ni($N_2H_2S_2$ = 1,2-ethanediamin-N,N'-bis(2-benzenthiolate) was prepared by Sellmann and coworkers.[8] The Ni(II) complexes in a N_2S_2 coordination environment have also been reported.[9]

Following our interest on the synthesis of heterobimetallic complexes,[10] we describe in the article the synthesis of a Ni(II) complex of dsdm ligand and heterobimetallic complexes bridged by sulfur atoms.

Results and Discussion

The nickel-dsdm complex has been prepared according to the Eq. (1).

$$Ni(CH_3COO)_2\text{-}4H_2O + [\text{ligand}] \xrightarrow{\text{toluene}} [\text{complex}] \quad (1)$$

I
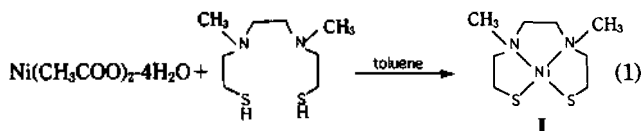
The reaction of $Ni(CH_3COO)_2$-$4H_2O$ with dsdm in toluene at 60°C gave a brown precipitate. The nickel-dsdm complex I was isolated as air-stable reddish brown crystal in 59% yield. The structure of compound I was deduced from its ¹H NMR, IR and mass spectra. The ¹H NMR spectrum of I exhibits resonance of CH_3 at δ 2.90, which is shifted to down field compared with that of dsdm appeared at δ 2.20.
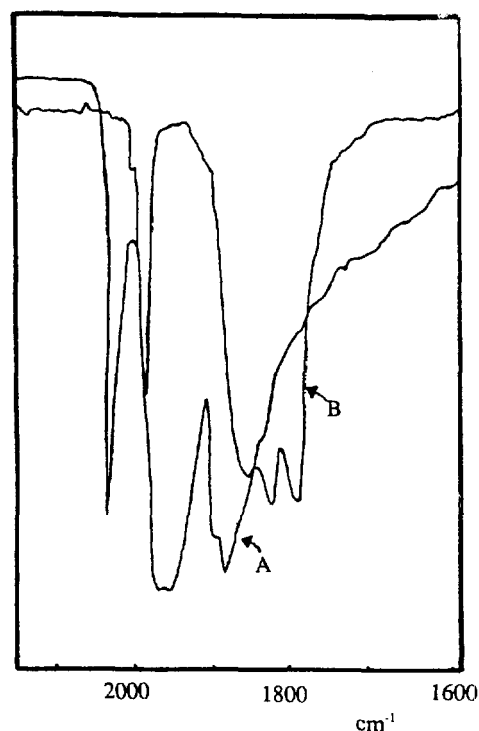

Figure 1. (A) The ν(CO) region of the infrared spectrum of IV on KBr pellet. (B) The ν(CO) region of the infrared spectrum of (NBD)W(CO)₄ on KBr pellet.

It demonstrates that the electron density on nitrogen atoms is shifted to nickel site. In addition to that, there are peaks at δ 3.2-2.2, assigned to methylene hydrogens. The mass spectrum of I gave the molecular ion of m/e (265).

The room temperature reaction of I with (NBD)M(CO)₄ (M=Cr, Mo, W) dissolved in CH_2Cl_2 gave a heterobimetallic complex according to the Eq. (2).

$$[\text{complex}] + (NBD)M(CO)_4 \longrightarrow [\text{complex}] \quad (2)$$
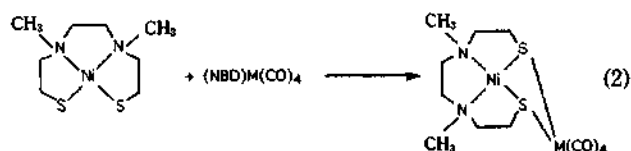
II. M=Cr
III. M=Mo
IV. M=W

The reaction of I with (NBD)W(CO)₄ in CH_2Cl_2 gave a brown precipitate. The nickel-tungsten heterobimetallic complex was isolated as air-stable brown powder in 36% yield. The infrared spectrum of III is shown in Figure 1 along with that of the starting compound (NBD)W(CO)₄, which shows four well-separated bands in the carbonyl region. The CO stretching bands of IV were consistent with a compound of C_{2v} symmetry ($2A_1+B_1+B_2$), assuming the most intense band is a composite of two (1990 (s), 1850 (vs), 1830 (s)). The highest band at 1990 cm⁻¹, assigned to the A_1 vibrational mode is shifted to lower frequency than that of the starting material (2035 cm⁻¹). This indicates that nickel complex containing thiolate ligand is a strong donor than tungsten site. The pattern is quite similar to that of Ni(Ph₂PCH₂CH₂S)₂ Mo(CO)₄.[11] In addition, the compound IV is a stronger donor

804 *Bull. Korean Chem. Soc.* **1994**, Vol. 15, No. 9

Notes
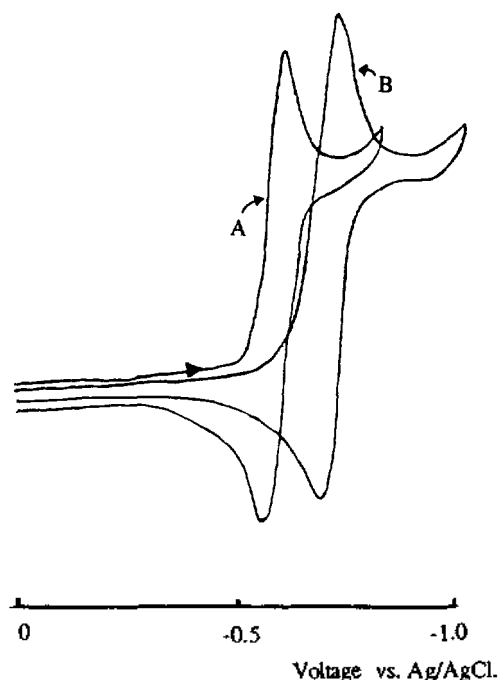
Figure 2. (A) Cyclic voltammogram of IV in 0.1 M (n-Bu₄N)(ClO₄) -DMF electrolyte solution. (B) Cyclic voltammogram of I in 0.1 M (n-Bu₄N)(ClO₄)-DMF electrolyte solution.

Table 1. Electrochemical Data[a]

Compound	Solvent	E_{pa}, V[b]	I_{pa}/I_{pc}
I	DMF	−0.71	0.96
II	DMF	−0.62	0.89
III	DMF	−0.53	0.93
IV	DMF	−0.58	0.96
V	DMF	−0.67	0.87

[a]Measured in 0.1 M[n-Bu₄N][ClO₄]-DMF electrolyte solution *vs.* Ag/AgCl. [b]Scan rate=100 mV/s.

than is Cp₂Ti(SPh).[12] The mass spectrum of IV gave the molecular ion of m/w (561), together with the fragment ion. The cyclic voltammogram of IV (Fig. 2) shows a quasi-reversible wave at −0.58 V *vs.* Ag/AgCl in DMF, assigned to the Ni⁺²/Ni⁺ couple. As the M(CO)₄ group becomes increasingly more electron withdrawing, the reduction potentials become increasingly more positive. The reduction potential for the complex IV is approximately 0.13 V more positive than that of mononuclear complex I, indicating that the complex IV is more easily reduced. Electrochemical data for other complexes is listed in Table 2. Although all the spectroscopic data support their formulation as the heterobimetallic complexes bridged by the sulfur atoms, the correct configuration on sulfur atoms is not certain. It is assumed that metal fragments show either a planar MS₂M' core or a bent core (Chart 1).
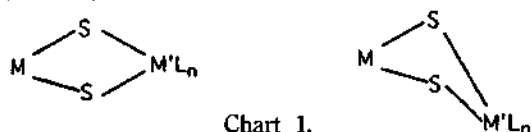

Chart 1.

To get a geometrical information of the complexes, we tried to get a crystallographic data. However, we failed to solve molecular structure due probably to the disorder problem. Viewed from a similar complex Ni(μ-ScH₂CH₂PPh₂)₂Mo (CO)₄, the heterobimetallic complexes II-V are presumed to have a bent core.

Experimental Section

All manipulations of air-sensitive materials were carried out under an argon atmosphere with use of standard Schlenk or vaccum line technique or a Mebraun MB150 glovebox. ¹H NMR spectra were recorded on a Bruker WM-250 spectrometer in CDCl₃ or DMSO-d₆. Chemical shifts are given in parts per million relative to TMS for ¹H NMR spectra. Mass spectra were measured on a high resolution VG70-VSEG Spectrometry. Cyclic voltammetry was carried out with Potentiostat-Galvanostat Model 273 at a glassy-carbon electrode with an Ag/AgCl couple as a reference and tetra-*n*-butyl ammonium perchlorate (TBAP) as an electrolyte in DMF. Elemental analyses were carried out at the Basic Science Center. Tetrahydrofuran, benzene and ether were distilled under argon from sodium-benzophenone ketyl. Metylene chloride and acetonitrile were distilled under argon from P₂O₅. Ethylene sulfide and N,N'-dimethylethylenediamine were purchased from Aldrich Chemical Co.. Cr(CO)₆, Mo (CO)₆ and Cp₂ZrCl₂ were purchased from Strem Chemical Co.. N,N'-Dimethyl-N,N'-bis(2-mercaptoethyl)ethylenediamine(dsdm), Cr(CO)₄(η⁴-NBD)(NBD = norbornadiene),[13] Mo (CO)₄(η⁴-NBD),[13] W(CO)₄(η⁴-NBD)[14] and Cp₂Zr(CO)₂[15] were prepared according to literature methods.

Preparation of [Ni(SCH₂CH₂N(CH₃)CH₂CH₂N(CH₃) CH₂CH₂S)] (I). To a stirred toluene solution (40 m*l*) of Ni(OOCCH₃)₂·4H₂O (0.348 g, 1.4 mmol) was added dsdm (0. 29 g, 1.4 mmol) in toluene (10 m*l*) dropwise. The solution was warmed to 60℃ and was stirred at that temperature for 2 hr. During which time the brown powder was precipitated. The brown solid was filtered and washed with ether. The reddish brown crystals were obtained by recrystallization from CH₃CN. The yield was 0.22 g (59%), mp. 168℃. ¹H NMR (CDCl₃): δ 3.2-2.2 (m, 12H, (H₂), 2.90 (s, 6H, CH₃); IR (on KBr pellet; cm⁻¹) 3000 (w), 2900 (w), 2850 (w), 1460 (m), 1430 (m), 1410 (m), 1290 (s), 1250 (s), 1230 (w), 1190 (m), 1150 (w), 1140 (m), 1100 (w), 1040 (m), 1020 (s), 990 (w), 960 (w), 940 (s), 890 (w), 810 (w), 780 (s), 770 (m); mass spectrum, m/e (relative intensity) 265 (M⁺, 16).

Anal. Calcd. for C₈H₁₈N₂S₂Ni: C, 36.25; H, 6.85; N, 10.57. Found: C, 36.13; H, 6.85; N, 10.55.

Preparation of [Ni(SCH₂CH₂N(CH₃)CH₂CH₂N(CH₃) CH₂CH₂S)]Cr(CO)₄ (II). To a stirred methylene chloride solution (3 m*l*) of I (0.1 g, 0.38 mmol) was added Cr(CO)₄(η⁴-NBD) (0.12 g, 0.47 mmol) dissolved in CH₂Cl₂ (3 m*l*) dropwise. On addition of the solution of Cr(CO)₄(η⁴-NBD), the brown solid was precipitated. The solution was stirred for 8 hr to increase the yield. The brown solid was filtered and washed with 2 m*l* of methylene chloride three times, and then dried in vacuo to give in 63% yield (0.10 g). mp. 182℃. ¹H NMR (DMSO-d₆): δ 4.0-1.8 (m, 12H, CH₂), 2.5 (s, 6H, CH₃); IR (on KBr pellet; cm⁻¹) 3012 (w), 2921 (m), 1980 (s), 1850 (s), 1800 (s), 1450 (w), 1250 (w), 1060 (w), 690 (w), 640 (w); mass spectrum, m/e (relative intensity) 429 (M⁺,

Notes

Bull. Korean Chem. Soc. **1994**, Vol. 15, No. 9   805

22), 401 (M⁺-CO, 43), 373 (M⁺-2CO, 54), 345 (M⁺-3CO, 72), 317 (M⁺-4CO, 58).

Anal. Calcd. for $C_{12}H_{18}N_2S_2O_4CrNi$: C, 33.59; H, 4.19; N, 6.53. Found: C, 33.21; H, 4.02; N, 6.32.

Preparation of [Ni(SCH₂CH₂N(CH₃)CH₂CH₂N(CH₃) CH₂CH₂S)]Mo(CO)₄ (III). The same procedure was taken as described in the preparation of II. The yield was 0.05 g (30%). mp. 185℃. ¹H NMR (DMSO-d_6): δ 3.9-1.9 (m, 12H, CH₂), 2.5 (s, 6H, CH₃); IR (on KBr pellet; cm⁻¹) 3008 (w), 2917 (m), 2000 (s), 1870 (s), 1810 (s), 1450 (w), 1260 (w), 1060 (w), 684 (w), 642 (w); mass spectrum, m/e (relative itnensity) 473 (M⁺, 17), 445 (M⁺-CO, 38), 417 (M⁺-2CO, 54), 389 (M⁺-3CO, 64), 361 (M⁺-4CO, 58).

Anal. Calcd. for $C_{12}H_{18}N_2S_2O_4MoNi$: C, 30.47; H, 3.81; N, 5.92. Found: C, 30.02; H, 3.62; N, 5.72.

Preparation of [Ni(SCH₂CH₂N(CH₃)CH₂CH₂N(CH₃) CH₂CH₂S)]W(CO)₄ (IV). The same procedure was taken as described in the preparation of II. The yield was 0.08 g (36%). mp. 187℃. ¹H NMR (DMSO-d_6): δ 4.0-2.15 (m, 12H, CH₂), 2.75 (s, 6H, CH₃); IR (on KBr pellet; cm⁻¹) 3012 (w), 2910 (m), 1990 (s), 1850 (sh), 1830 (m), 1790 (m), 1460 (m), 1440 (sh), 1430 (sh), 1280 (w), 1260 (w), 1190 (w), 1150 (w), 1060 (w), 1030 (w), 770 (w), 670 (w), 620 (m); mass spectrum, m/e (relative intensity) 561 (M⁺, 18), 533 (M⁺-CO, 38), 505 (M⁺-2CO, 58), 577 (M⁺-3CO, 62), 547 (M⁺-4CO, 42).

Anal. Calcd. for $C_{12}H_{18}N_2S_2O_4WNi$: C, 25.69; H, 3.21; N, 5.00. Found: C, 25.19; H, 3.08; N, 4.83.

Preparation of [Ni(SCH₂CH₂N(CH₃)CH₂CH₂N(CH₃) CH₂CH₂S)]ZrCp₂ (V). To a stirred methylene chloride solution (4 m*l*) of I (0.2 g, 0.8 mmol) was added Cp₂Zr(CO)₂ (0.222 g, 0.8 mmol) dissolved in CH₂Cl₂ (2 m*l*) dropwise. The reaction was continued for 20 hr and the hexane (3 m*l*) was added. The resulting orange solid was filtered. Recrystallization from methylene dichloride/hexane gave yellow crystals. The yield was 0.23 g (60%). mp. 192℃. ¹H NMR (DMSO-d_6): δ 6.4 (s, 5H, Cp), 3.0-1.9 (m, 12H, CH₂), 2.75 (s, 6H, CH₃); IR (on KBr pellet; cm⁻¹) 3014 (w), 2922 (m), 1620 (w), 1460 (m), 1430 (w), 1260 (w), 1230 (w), 1200 (w), 1060 (m), 1040 (w), 1020 (w), 1010 (w), 950 (w), 920 (w), 810 (w), 770 (m), 750 (m); mass spectrum, m/e (relative intensity) 486 (M⁺, 38), 421 (M⁺-C₅H₅, 58).

Anal. Calcd. for $C_{18}H_{28}N_2S_2NiZr$: C, 44.45; H, 5.76; N, 5.76. Found: C, 44.07; H, 5.89; N, 5.38.

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A Three-Dimensional Active Site Model of Carboxypeptidase A

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Carboxypeptidase A (CPA, EC 3.4.17.1) is a much studied prototypic zinc-containing peptidase[1] which preferentially cleaves off the C-terminal amino acid residue having a hydrophobic side chain with L-stereochemisty. Although the X-ray crystallographic structural information of CPA is available[2], the development of empirical, yet functional active site model which portrays the substrate-as well as stereospecificity of the enzyme is highly desirable. Most of the proposed models are two dimensional and thus inadequate for explaining the stereospecificity of the enzymic action. We herein propose a simple three dimensional model of the active site of CPA, which ameliorate the existing models. This three dimensional model enables one to visualize not only the observed stereochemical course of the enzymic reaction[3] but also explains the stereoselective binding of inhibitors.