

Synthesis and characterization of semicarbazone metal complexes of Sn(IV) and Zr(IV)

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Three semicarbazonyl ligands were synthesized and used to form six novel organometallic complexes with Ph_2SnCl_2 and Cp_2ZrCl_2 . All these complexes were characterized by IR, ^1H NMR, MS and elemental analysis.

Keywords Semicarbazone, Ph_2SnCl_2 , Cp_2ZrCl_2 , organometallic complexes

Introduction

Since Preiffer carried out creative work on the Schiff base chemistry, a lot of research work on the theory and application of Schiff base chemistry has been done.¹⁻⁵ As a kind of Schiff base, semicarbazone can provide good coordinate atoms, such as O, S, N, and can be used to synthesize organometallic complexes.

It has been found that this kind of complexes has ability of absorbing special wavelength light, which can be used to measure their contents.⁶ Furthermore, they also have ability of anti-cancer⁷ and anti-virus.⁸ Therefore, it is of great value for the research in this field to synthesize new types of Schiff base metal complexes that are characteristic of structure.

In this paper we synthesized a series of new and potential physiological active organometallic complexes. Their anti-cancer and anti-viral activity will be studied further.

Experimental

Reagents

The reagents of bis(cyclopentadienyl)zirconium

dichloride, diphenyltin dichloride and 2-hydroxy-1-naphthaldehyde were purchased from Aldrich Chemical Company, Inc. The ligands were prepared by known methods.^{9,10} The anhydrous inert solvents were distilled after reflux with sodium.

Apparatus

Melting points were measured on RY-1 melting point apparatus and uncorrected. IR spectra were recorded on a Hitachi 260-50 IR spectrometer (KBr disc). ^1H NMR spectra were obtained at 300 MHz on a Bruker DMX-300 NMR apparatus (CDCl_3 as solvent, TMS as internal standard). MS spectra were recorded on a Bruker BIFLEX III apparatus with MALDI-TOF technique, using CCA as matrix. Elemental analyses were conducted using a Perkin-240C elemental analysis apparatus.

Synthesis of RNHCSNHNH_2 (1a—c, thiocarbazide)⁹

PhCH_2NH_2 (10.7 g, 0.1 mol) and 25% ammonia liquor (19.1 g, 0.28 mol) were mixed thoroughly. Then carbon disulfide (9.14 g, 0.12 mol) was added dropwise with stirring at the temperature 10—15°C. The reaction mixture was heterogeneous. The mixture was stirred for 1 h at the room temperature and for 1.5 h at the temperature 25—30°C. The mixture became homogeneous. The reaction was completed.

50% Hydrazine hydrate (11.0 g, 0.11 mol) was added dropwise and the resulting mixture was refluxed for 3 h at the temperature of about 85°C. Then the mix-

ture was cooled to room temperature or further cooled in ice-salt bath if necessary. The crude products were filtered and recrystallized in H₂O. 13.0 g (yield: 71.8%) of pure product **1a** was obtained. mp 126—127°C. Anal. C₈H₁₁N₃S. Calcd: C, 53.01; H, 6.12; N, 23.18. Found: C, 52.77; H, 5.97; N, 22.88.

1b and **1c** were prepared by the same procedure as that for **1a**.

1b Yield: 78.1%. mp 77—79°C. Anal. C₃H₉N₃S. Calcd: C, 30.25; H, 7.56; N, 35.29. Found: C, 30.60; H, 7.93; N, 35.73.

1c Yield: 73.6%. mp 61—63°C. Anal. C₄H₁₁N₃S. Calcd: C, 36.09; H, 8.27; N, 31.58. Found: C, 36.20; H, 8.58; N, 31.71.

Synthesis of thiosemicarbazones (**2a—c**)¹⁰

2-Hydroxy-1-naphthaldehyde (1.72 g, 0.01 mol), PhCH₂NHCSNHNH₂ (1.81 g, 0.01 mol) and ethanol (15 mL) were added to 50 mL flask. The mixture was heated to about 35°C with stirring. After the solids were dissolved completely, 2 drops of acetic acid (glacial) were added. The reaction temperature was kept at the temperature of about 35°C for 0.5 h to complete the reaction. The crude products were filtered and recrystallized in ethanol. 2.78 g (yield: 82.6%) of pure product **2a** was obtained. mp 196—197°C. ν_{\max} (KBr): 3370, 3150, 1620($\nu_{C=N}$), 1225($\nu_{C=S}$) cm⁻¹. Anal. C₁₉H₁₇ON₃S. Calcd: C, 68.03; H, 5.11; N, 12.53. Found: C, 67.87; H, 5.00; N, 12.16.

2b and **2c** were prepared by the same procedure as that for **2a**.

2b Yield: 84.0%. mp 195—196°C. ν_{\max} (KBr): 3398, 3130, 1618($\nu_{C=N}$), 1240($\nu_{C=S}$) cm⁻¹. Anal. C₁₄H₁₅ON₃S. Calcd: C, 61.47; H, 5.53; N, 15.36. Found: C, 61.72; H, 5.39; N, 14.96.

2c Yield: 83.5%. mp 190—191°C. ν_{\max} (KBr): 3390, 3130, 1623($\nu_{C=N}$), 1230($\nu_{C=S}$) cm⁻¹. Anal. C₁₅H₁₇ON₃S. Calcd: C, 62.69; H, 5.96; N, 15.36. Found: C, 62.88; H, 5.93; N, 15.33.

Synthesis of thiosemicarbazone metal complexes (**3a—f**)¹¹

Under moisture-free and oxygen-free conditions, thoroughly dried **2a** (0.353 g, 1 mmol) and diphenyltin

dichloride (0.344 g, 1 mmol) were dissolved in 50 mL of toluene. Triethylamine (0.8 mL) was added to catalyze the reaction. The mixture was stirred at room temperature for 4 h. The crude products obtained after removing the solvent was recrystallized in chloroform-petroleum ether. 0.562 g (yield: 90.0%) of pure product **3a** was obtained. mp 107—109°C. ν_{\max} (KBr): 3370, 1615, 1598, 625(ν_{C-S}), 572(ν_{Sn-O}), 458(ν_{Sn-N}) cm⁻¹. δ_H (CDCl₃): 4.69(d, $J = 5.34$ Hz, 2H), 5.17(t, $J = 5.34$ Hz, 1H), 7.23—7.42(m, 15H), 7.69—7.96(m, 6H), 9.47(s, 1H). m/z : 608.09 (M⁺). Anal. C₃₁H₂₅ON₃SSn. Calcd: C, 61.40; H, 4.16; N, 6.93. Found: C, 61.73; H, 4.05; N, 6.75.

3b—f were prepared by the same procedure as that for **3a**.

3b Yield: 85.5%. mp 130—131°C. ν_{\max} (KBr): 3398, 1613, 1595, 620(ν_{C-S}), 565(ν_{Sn-O}), 459(ν_{Sn-N}) cm⁻¹. δ_H (CDCl₃): 1.27(t, $J = 7.20$ Hz, 3H), 3.48—3.54(m, 2H), 4.90(t, $J = 5.16$ Hz, 1H), 7.23—7.54(m, 10H), 7.68—7.95(m, 6H), 9.47(s, 1H). Anal. C₂₆H₂₃ON₃SSn. Calcd: C, 57.37; H, 4.27; N, 7.72. Found: C, 57.72; H, 4.34; N, 7.32.

3c Yield: 82.0%. mp 151—153°C. ν_{\max} (KBr): 3390, 1620, 1598, 623(ν_{C-S}), 550(ν_{Sn-O}), 470(ν_{Sn-N}) cm⁻¹. δ_H (CDCl₃): 0.98(t, $J = 7.38$ Hz, 3H), 2.32—2.45(m, 2H), 3.37—3.47(m, 2H), 4.85—4.89(t, $J = 5.17$ Hz, 1H), 7.23—7.50(m, 10H), 7.67—7.95(m, 6H), 9.45(s, 1H). Anal. C₂₇H₂₅ON₃SSn. Calcd: C, 58.08; H, 4.52; N, 7.53. Found: C, 58.20; H, 4.62; N, 7.49.

3d Yield: 64.0%. mp > 300°C. ν_{\max} (KBr): 3360, 1618, 1590, 750(ν_{Zr-O}), 625(ν_{C-S}), 480(ν_{Zr-N}) cm⁻¹. δ_H (CDCl₃): 4.66(d, $J = 4.32$ Hz, 2H), 4.99(t, $J = 4.31$ Hz, 1H), 6.13(s, 10H), 7.21—7.39(m, 5H), 7.60—7.92(m, 6H), 9.35(s, 1H). m/z : 491.06(M⁺). Anal. C₂₉H₂₅ON₃SZr. Calcd: C, 62.77; H, 4.55; N, 7.58. Found: C, 62.73; H, 4.05; N, 7.50.

3e Yield: 76.5%. mp > 300°C. ν_{\max} (KBr): 3350, 1618, 1595, 748(ν_{Zr-O}), 618(ν_{C-S}), 500(ν_{Zr-N}) cm⁻¹. δ_H (CDCl₃): 1.25(t, $J = 7.36$ Hz, 3H), 3.47—3.55(m, 2H), 4.87—4.93(t, $J = 4.36$ Hz, 1H), 6.10(s, 10H), 7.62—7.98(m, 6H), 9.37(s, 1H). Anal. C₂₄H₂₃ON₃SZr. Calcd: C, 58.49; H,

4.71; N, 8.53. Found: C, 58.10; H, 4.31; N, 8.59.

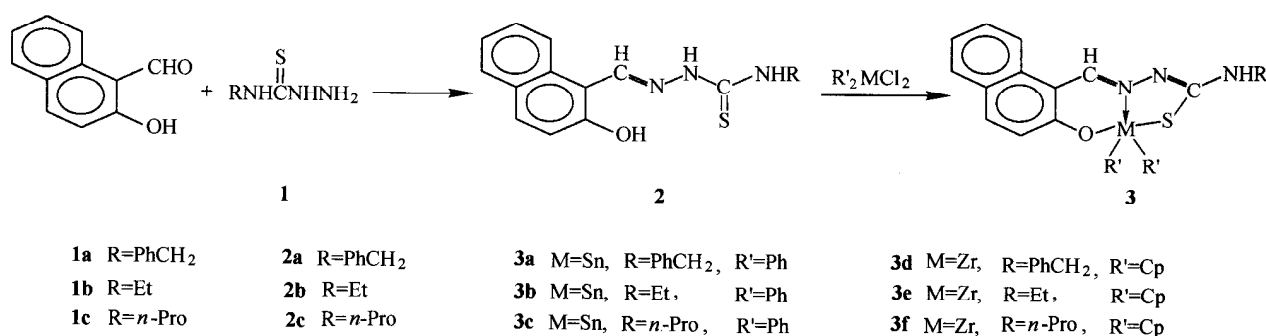
3f Yield: 70.0%. mp > 300°C. ν_{\max} (KBr): 3355, 1620, 1598, 752 ($\nu_{\text{Zr-O}}$), 628 ($\nu_{\text{C-S}}$), 470 ($\nu_{\text{Zr-N}}$) cm^{-1} . δ_{H} (CDCl_3): 0.99 (t, $J = 7.40$ Hz, 3H), 2.30–2.40 (m, 2H), 3.36–3.46 (m, 2H), 4.87 (t, $J = 4.38$ Hz, 1H), 6.11 (s, 10H), 6.90–8.01 (m, 6H), 9.15 (s, 1H). Anal. $\text{C}_{25}\text{H}_{25}\text{ON}_3\text{SZr}$.

Calcd: C, 59.24; H, 4.98; N, 8.29. Found: C, 58.92; H, 4.75; N, 8.86.

Results and discussion

The synthesis and structure of the metal complexes studied in this paper are shown in Scheme 1.

Scheme 1 Synthesis and chemical structures of the metal complexes **3**



It is likely that thiosemicarbazone coordinated with tin(IV) and zirconium(IV) in thioenol form and hydrochloride was eliminated.

The reaction was carried out at room temperature. Triethylamine was used to absorb hydrochloride in order to increase the yield. The organometallic complexes are white or orange solids. They are stable in the air. They are very soluble in benzene and chloroform, insoluble in petroleum ether.

A remarkable difference of the IR spectra between the ligands and those of the corresponding complexes is that the stretching vibration bands of O—H and C = S disappear from the spectra of the complexes. The disappearance of the bands assigned to thiocarbonyls unambiguously confirms that the ligands coordinated with the metal are in the thioenol form. The characteristic absorptions at 1613–1620 cm^{-1} and 1590–1598 cm^{-1} in the spectra of these complexes indicate the presence of C = N and C = N—N = C groups.¹² A peak at 620–640 cm^{-1} is characteristic of the C—S group. In the IR spectra of tin complexes two new IR bands at 560–570 cm^{-1} and 440–460 cm^{-1} are characteristic of Sn—O and Sn—N groups, while in the IR spectra of zirconium complexes the Zr—O and Zr—N stretching vibration bands also appear.

The analysis results, especially the MS data, proved that the ligands complexed with the metal substrates in the molar ratio of 1:1. The products are mononuclear pentacoordinate complexes. The coordinate atoms and metal atoms form stable five-membered rings and six-membered rings.

In the ¹H NMR spectra of the ligands, the chemical shifts of the proton at the position alpha to the naphthalene ring are around δ 8.95–9.0. In ¹H NMR spectra of the complexes, the ¹H signals of the hydrogen of the aromatic rings and cyclopentadiene occur at δ 6.90–8.10 and δ 6.10–6.15. The chemical shifts of the proton at the position alpha to the naphthalene ring are around δ 9.10–9.50. It shifts to downfield more than 0.2. The reason is that the coordination of N and metal atom leads to larger deshielding effect.

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