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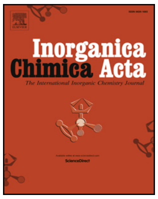

Research paper

(S)-N-[(2-hydroxynaphthalen-1-yl)methylidene]valine – A valuable ligand for the preparation of chiral complexes

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ABSTRACT

The reaction of (S)-N-[(2-hydroxynaphthalen-1-yl)methylidene]valine (H_2L), **1**, with organoelement halides from group 4 and 14 leads to different hypercoordinated complexes depending on the substitution of the starting material. The dianion of **1** therein acts as tridentate ligand in κ^3O,N,O' coordination mode. Complexes with silicon, germanium, tin, and titanium have been prepared in that way and are presented here as proof of concept. With one exception diorganoelement chlorides R_2ECl_2 yield pentacoordinate complexes LER_2. Element tetrachlorides yield hexacoordinate complexes L_2E. The prepared compounds were characterized via NMR, IR and UV/Vis spectroscopy, elemental and X-ray structure analysis. Furthermore solid state NMR measurements and chemical shift tensor analysis with the help of quantum chemical methods were used to investigate the electron density distribution around the central atoms of several products. This study demonstrates the ability of **1** to form chiral hypercoordinate complexes with different elements.

1. Introduction

Schiff bases in general are versatile ligands [1–3]. Silicon and tin Schiff base complexes are a fast developing field of research [4] which is due to their various possible applications. These complexes can exhibit fungicidal [5,6], bactericidal [7,8], antimicrobial [9] or bacteriostatic [10] properties. In some cases it was shown that they are potent antitumor reagents [6]. Therefore the large number of recently published reports regarding silicon and tin complexes with tridentate O,N,O'-ligands is not surprising [11–20]. (S)-N-[(2-hydroxynaphthalen-1-yl)methylidene]valine (H_2L), **1**, has shown to be a good coordination partner for various metals. Complexes of the dianion of **1** with zirconium [21], vanadium [22–26], chromium, manganese [27], iron, cobalt, nickel [28–33], copper [34–40], zink, cadmium [41,42], lanthanum, cerium [43,44], silicon [9], and tin [45–47] have been reported. Coordination of metal atoms usually proceeds via the phenolic oxygen atom, the imine nitrogen atom and one of the carboxylic oxygen atoms of **1** (see Scheme 1). Double deprotonation accompanies this reaction.

We are interested in chiral complexes of group 14 elements. For that purpose we explored several chiral ligand types [15,16,48,49] and have already published a tin complex with the dianion of **1** [47]. Herein, we report about the synthesis and characterization of a number of complexes of group 14 elements as central atom with the dianion of **1** as chiral chelating ligand. For comparison with group 14 elements, one derivative of titanium has been prepared as well. In addition, solid state NMR spectra are recorded for selected substances to determine the silicon and tin NMR chemical shift tensors.

2. Experimental

2.1. General considerations

All chemicals obtained from commercial suppliers were used as received. Since both the educts and the synthesized complexes are sensitive to moisture, preparation was performed in Schlenk tubes under argon atmosphere using anhydrous and air-free solvents.

Melting points were determined with a Polytherm A from Wagner & Munz using samples in sealed capillaries.

Standard ^1H, ^{13}C, ^{119}Sn, and ^{29}Si solution NMR spectra were recorded on a Bruker DPX 400 spectrometer at 293 K [^1H (400.13 MHz), ^{13}C (100.61 MHz), ^{29}Si (79.49 MHz), ^{119}Sn (149.17 MHz)] or on a Bruker Avance 500 spectrometer at 293 K [^1H (500.13 MHz), ^{13}C (125.76 MHz), ^{29}Si (99.36 MHz). ^1H, ^{13}C, ^{29}Si chemical shifts are reported relative to tetramethylsilane, ^{119}Sn chemical shifts relative to tetramethyltin as external reference. Used solvents are specified below.

Solid state NMR spectra were recorded with a Bruker Avance 400 WB spectrometer operating at 79.52 MHz (^{29}Si) and 149.24 MHz

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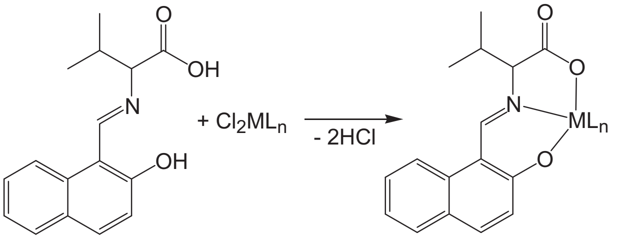

Scheme 1. Formation of complexes with (S)-N-[(2-hydroxynaphthalen-1-yl) methylidene]valine (H_2L) **1**.

(^{119}Sn), respectively. ^{29}Si spectra were recorded using a 7 mm DVT/MAS probe, applying cross polarization with 5 ms contact time and a spinning frequency of 4 kHz, if not noted otherwise. For chemical shift tensor measurement the sample was placed into the middle third of the rotor using teflon inserts. The chemical shift scale was referenced with Q_8M_8 (strongest shielded Q^4-group at −109 ppm relative to TMS). ^{119}Sn solid state NMR spectra were obtained using a 4 mm DVT/MAS probe, a spinning frequency of up to 15 kHz and single pulse excitation applying 30° pulses and repetition times of 30 s. Tppm15 decoupling was applied for all measurements. The chemical shift was referenced with SnO_2 (−603 ppm relative to tetramethyltin) [50]. Principal components of the chemical shift tensor were calculated from spinning side band spectra using DMFIT [51] and HBA [52].

IR spectra were recorded in the range 400–4000 cm^{-1} at room temperature with a Nicolet 380 FT-IR spectrometer. The samples (KBr pellets) were prepared under N_2 atmosphere. Elemental analyses were performed with a Vario Micro CHNS.

Optical rotation measurements were carried out with a digital polarimeter model 241 MC of Perkin Elmer at 293 K and a wavelength of 589 nm (sodium vapor lamp). All values were determined from the average of 2–3 measurements with c = 1 g/100 mL in $CHCl_3$.

UV/Vis spectra were measured on a Jasco V-650. Determination of the extinction coefficients are based on the Beer-Lambert law.

(S)-N-[(2-hydroxynaphthalen-1-yl)methylidene]valine, **1**, was prepared from L-valine and 2-hydroxy-1-naphthaldehyde according to a literature method [53].

2.2. General procedure for the synthesis of the complexes 2–13

(S)-N-[(2-hydroxynaphthalen-1-yl)methylidene]valine, **1**, was dissolved in tetrahydrofuran and triethylamine was added slowly via syringe. The yellow solution was then cooled down to 273 K. The corresponding element chloride, dissolved in tetrahydrofuran, was added dropwise to the solution. Immediately, a white precipitate was formed. After 30 min the mixture was warmed up to room temperature and stirred for several days at room temperature. Triethylamine hydrochloride was collected via suction filtration, washed with tetrahydrofuran three times (à 10 mL) and the solvent was removed completely under reduced pressure. The residue was solved in chloroform. For crystallisation *n*-hexane was added, the crystals collected via suction filtration and dried in vacuum.

2: **1** (1.20 g, 4.42 mmol) in THF (30 mL), triethylamine (1.16 g, 11.46 mmol) and dichlorodiethylsilane (0.70 g, 4.45 mmol) in THF (15 mL) yield yellow crystals (0.73 g, 46.5%), m.p. 418 K (decomposition). *Anal. Calc.* for the complex $LSiEt_2$ with $C_{20}H_{25}NO_3Si$ (355.510 g/mol): C, 67.57; H, 7.09; N, 3.94; for the complex $(LSiEt_2)_2{*}CHCl_3$ according to the complex found in the X-ray structure with $C_{41}H_{51}N_2O_6Cl_3Si_2$ (830.398 g/mol): C, 59.30; H, 6.19; N, 3.37. Found: C, 59.55; H, 6.13; N, 3.37%; ^{29}Si NMR ($CDCl_3$): $\delta = -67.3$ ppm; ^{29}Si NMR (CP/MAS): $\delta = -69.1$; ^{1}H NMR ($CDCl_3$): $\delta = 0.73$ (q, 4H, $Si{-}CH_2$); 0.84 (t, 6H, $Si{-}CH_2{-}CH_3$); 1.15 (d, 6H, $CH(CH_3)_2$); 2.35 (m, 1H, $CH(CH_3)_2$); 4.03 (d, 1H, $CH{-}COO$, $^3J_{HH} = 5.5$ Hz); 7.02–8.01 (m, 6H, H_{ar}); 8.99 (s, 1H, $HC{=}N$) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 8.5$, 9.1, 9.8, 13.4 (2 $CH_2{-}CH_3$); 18.7, 18.8 ($CH(CH_3)_2$); 34.0 ($CH(CH_3)_2$); 73.4 ($CH{-}COO$); 108.9 ($C_{ar}{-}CH{=}N$); 118.4, 122.4, 124.9, 127.4, 129.6, 129.9, 132.3, 141.9 (8 C_{ar}); 164.0 ($CH{=}N$); 169.6 ($C_{ar}{-}O$); 170.6 (COO) ppm. IR: $\nu = 3064.7$, 3047.9, 2960.4, 2931.2, 2873.5, 1708.6, 1624.8, 1605.9, 1587.1, 1549.9, 1496.9, 1469.0, 1434.6, 1425.2, 1406.7, 1377.3, 1344.1, 1314.7, 1264.3, 1168.7, 1142.7, 1105.1, 1087.7, 1013.8, 961.0, 878.9, 834.0, 808.9, 763.2, 750.9, 735.1, 573.9, 520.8, 509.0, 490.5, 420.3 cm^{-1}. $[\alpha]_D^{20} = -339.3°$. UV–Vis (c = 0.0963 mmol/l in $CHCl_3$): λ_{max} (ε, 1 mol^{-1} cm^{-1}) = 414 (14173), 341 (16607), 306 (5566), 292 (4908), 253 (34070) nm.

3: **1** (0.77 g, 2.84 mmol) in THF (20 mL), triethylamine (0.63 g, 6.25 mmol) and Dichlorodiphenylsilane (0.74 g, 2.92 mmol) in THF (10 mL) yield yellow crystals (0.78 g, 60.9%), m.p. 383 K. *Anal. Calc.* for the complex $LSiPh_2$ with $C_{28}H_{25}NO_3Si$ (451.598 g/mol): C, 74.47; H, 5.58; N, 3.10; for the complex $LSiPh_2{*}CHCl_3$ according to the complex found in the X-ray structure with $C_{29}H_{26}NO_3Cl_3Si$ (570.976 g/mol): C, 61.00; H, 4.59; N, 2.45. Found: C, 60.91; H, 4.67; N, 2.26%; ^{29}Si NMR ($CDCl_3$): $\delta = -99.1$ ppm; ^{29}Si NMR (CP/MAS): $\delta = -97.1$ ppm; ^{1}H NMR ($CDCl_3$): $\delta = 1.02$, 1.04 (2d, 6H, $2CH_3$); 2.31 (m, 1H, $CH(CH_3)_2$); 4.24 (d, 1H, $CH{-}COO$, $^3J_{HH} = 4.1$ Hz); 7.19–8.12 (mm, 16H, H_{ar}); 7.26 (s, 1H, $CHCl_3$); 9.17 (s, 1H, $HC{=}N$) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 18.5$, 18.9 ($CH(CH_3)_2$); 34.3 ($CH(CH_3)_2$); 73.2 ($CH{-}COO$); 109.2 ($C_{ar}{-}CH{=}N$); 118.6, 122.0, 125.1, 127.4, 127.5, 127.7; 129.4, 129.5, 129.8, 129.8, 132.1, 136.3, 137.5, 137.8, 139.7, 142.5 (16 C_{ar}); 164.6 ($CH{=}N$); 168.8 ($C_{ar}{-}O$); 170.4 (COO) ppm. IR: $\nu = 3072.1$, 3007.4, 2963.9, 1721.7, 1645.7, 1621.9, 1602.3, 1584.9, 1576.0, 1569.4, 1548.1, 1484.5, 1476.0 1461.2, 1428.9, 1397.0, 1369.2, 1343.4, 1331.4, 1317.8, 1206.2, 1192.6, 1143.7, 1114.6, 1102.7, 1055.7, 1036.0, 997.2, 975.9, 965.5, 840.2, 803.9, 782.0, 767.6, 757.2, 749.6, 743.2, 730.9, 716.9, 701.0, 681.5, 594.7, 546.1, 529.4, 522.2, 515.5, 464.8, 457.9, 422.8, 418.8 cm^{-1}. $[\alpha]_D^{20} = -590.0°$. UV–Vis (c = 0.3100 mmol/l in $CHCl_3$): λ_{max} (ε, 1 mol^{-1} cm^{-1}) = 411 (6957), 347 (9459), 301 (3059), 289 (3062), 258 (15316) nm.

4: **1** (1.11 g, 4.09 mmol) in THF (25 mL), triethylamine (0.91 g, 9.00 mmol) and Dichlorosilacyclopropane (0.58 g, 4.09 mmol) in THF (10 mL) yield yellow crystals (0.89 g, 64.1%), m.p. 437 K. *Anal. Calc.* for the complex $LSi[CH_2]_3$ with $C_{19}H_{21}NO_3Si$ (339.467 g/mol): C, 67.23; H, 6.24; N, 4.13. Found: C, 67.12; H, 6.18; N, 4.10%; ^{29}Si NMR ($CDCl_3$): $\delta = -80.3$ ppm; ^{29}Si NMR (CP/MAS): $\delta = -81.8$, -82.8 ppm; ^{1}H NMR ($CDCl_3$): $\delta = 1.17$ (d, 3H, CH_3, $^3J_{HH} = 7.0$ Hz); 1.24 (d, 3H, CH_3, $^3J_{HH} = 7.0$ Hz); 1.36–1.70 (mm, 6H, CH_2); 2.38 (m, 1H, $CH(CH_3)_2$); 3.86 (d, 1H, $CH{-}COO$, $^3J_{HH} = 8.0$ Hz); 7.23–8.02 (mm, 6H, H_{ar}); 8.79 (s, 1H, $HC{=}N$) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 13.0$ ($CH_2{-}CH_2{-}CH_2$); 19.0, 19.4 ($CH(CH_3)_2$); 28.0, 28.8 ($CH_2{-}CH_2{-}CH_2$); 32.3 ($CH(CH_3)_2$); 72.5 ($CH{-}COO$); 111.2 ($C_{ar}{-}CH{=}N$); 120.0, 122.2, 125.1, 128.5, 129.0, 129.4, 131.5, 138.3 (8 C_{ar}); 158.8 ($CH{=}N$); 160.9 ($C_{ar}{-}O$); 170.0 (COO) ppm. IR: $\nu = 3092.7$, 3061.3, 2963.1, 2926.1, 2874.9, 1744.8, 1631.6, 1561.7, 1519.5, 1461.9, 1387.3, 1365.8, 1343.6, 1294.7, 1257.8, 1197.8, 1140.8, 1124.5, 1109.0, 1091.3, 990.6, 975.3, 946.7, 879.9, 848.9, 825.7, 783.2, 753.4, 698.5, 661.2, 630.5, 594.3, 565.0, 520.8 cm^{-1}. $[\alpha]_D^{20} = 0°$. UV–Vis (c = 0.2060 mmol/l in $CHCl_3$): λ_{max} (ε, 1 mol^{-1} cm^{-1}) = 393 (6628), 343 (7847), 255 (13279) nm.

5: **1** (1.08 g, 3.98 mmol) in THF (20 mL), triethylamine (0.89 g, 8.76 mmol) and Dichlorosilacyclopentane (0.67 g, 3.98 mmol) in THF (10 mL) yield yellow crystals (0.42 g, 28.7%), m.p. 438 K. *Anal. Calc.* for the complex $LSi[CH_2]_5$ with $C_{21}H_{25}NO_3Si$ (367.521 g/mol): C, 68.63; H, 6.86; N, 3.81. Found: C, 68.63; H, 6.89; N, 3.90%; ^{29}Si NMR ($CDCl_3$): $\delta = -71.3$ ppm; ^{29}Si NMR (CP/MAS): $\delta = -72.2$ ppm; ^{1}H NMR ($CDCl_3$): $\delta = 0.64$–2.03 (mm, 10H, CH_2); 1.08, 1.09 (2d, 6H, $2CH_3$); 2.36 (m, 1H, $CH(CH_3)_2$); 4.06 (d, 1H, $CH{-}COO$); 7.11–8.04 (mm, 6H, H_{ar}); 8.94 (s, 1H, $HC{=}N$) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 14.6$, 20.7, 24.6, 25.9, 29.3 (5 CH_2); 18.0, 18.5 ($CH(CH_3)_2$); 33.7 ($CH(CH_3)_2$); 73.2 ($CH{-}COO$); 109.7 ($C_{ar}{-}CH{=}N$); 118.7, 122.4, 125.0, 127.6, 129.6, 129.8, 132.2, 141.6 (8 C_{ar}); 163.4 ($CH{=}N$); 169.0 ($C_{ar}{-}O$); 170.9 (COO) ppm. IR: $\nu = 3062.8$, 3043.8, 2977.5, 2929.1, 2850.7,