

Supporting Information

Structural diversity of alkali-metal (Li, Na, K) alkyl zincates containing bidentate aminopyrrolyl ligand: from molecular complex to coordination polymer

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Experimental

General methods

Unless otherwise noted, all syntheses and manipulations of air-sensitive materials were performed under a purified nitrogen atmosphere using the standard Schlenk techniques. Tetrahydrofuran and diethyl ether were distilled from sodium-benzophenone under nitrogen. Hexane and toluene is dried using sodium potassium alloy and distilled under nitrogen prior to use. nBuLi (2.5M in n-hexane), ZnEt₂ (1.0M in hexane), NaH (60% dispersion in mineral oil) and KH (30% dispersion in mineral oil) were purchased from Aldrich and used as received. N,N,N',N'-tetramethylethylenediamine (TMEDA) was purchased from Aldrich, dried by heating to reflux over calcium hydride and stored with molecular sieves under nitrogen prior to use. The aminopyrrolyl ligand [C₄H₃NH(2-CH₂NH^tBu)] was synthesized according to the literature procedure ^[1]. ¹H NMR (600 MHz), ¹³C NMR (150.9 MHz) and ⁷Li NMR (233.2 MHz) spectra of the compounds were recorded on a BRUKER AVANCE III 600MHz instrument in C₆D₆ and C₅D₅N at 298 K and referenced internally to the residual solvent resonances (¹H, ¹³C) or externally (⁷Li). Elemental analyses were performed on a Vario EL-III instrument. Melting points were determined on a STUART SMP10 melting point apparatus and uncorrected. The IR spectra were determined on Thermo Scientific Nicolet iS50 (ATR-FTIR) spectrophotometer. And the UV spectra are obtained on SHIMADZU UV-2650 spectrophotometer.

Syntheses and characterization of complexes (1-4)

ⁿBuLi (3.0 mmol, 2.2 M in hexane) was added to a solution of [C₄H₃NH(2-CH₂NH^tBu)] (0.457 g, 3.0 mmol) in toluene (20 mL) at 0 °C under nitrogen. After the reaction mixture was stirred at room temperature for 2 h, immediately followed by addition of a solution of ZnEt₂ (3.0 mmol, 1.0 M in hexane). The resulting suspension was heated for 1 hour at 100 °C, affording a clear solution. Then the TMEDA (0.45 mL, 3 mmol) was introduced via syringe, the solution was filtered and concentrated to a small amount and recrystallized to generate **1** (1.50g, 68.6% yield). ¹H NMR (C₆D₆+C₅D₅N): 6.99 (s, 2H, C₄H₃N), 6.72 (s, 2H, C₄H₃N), 6.32 (s, 2H, C₄H₃N), 4.36 (s, 4H, CH₂NBu^t), 1.87 (s, 24H, N(CH₃)₂), 1.71 (s, 8H, CH₂), 1.59 (br, 6H, ZnCH₂CH₃), 1.21 (s, 18H, CH₂NBu^t), 0.62 (br, 4H, ZnCH₂CH₃); ¹³C NMR (C₆D₆+C₅D₅N): 146.7 (C₄H₃N), 135.8 (C₄H₃N), 106.0 (C₄H₃N), 96.4 (C₄H₃N), 57.1 (TMEDA), 51.7 (C(CH₃)₃), 46.2 (CH₂NBu^t), 45.5 (TMEDA), 32.3 (C(CH₃)₃), 15.3 (ZnCH₂CH₃), 5.6 (ZnCH₂CH₃); ⁷Li NMR (C₆D₆+C₅D₅N): 0.98, -11.56; Anal. Calcd for C₃₄H₆₄Li₂N₈Zn₂: C, 55.97; H, 18.84; N, 15.36. Found: C, 55.67; H, 17.99; N, 15.04. IR (cm⁻¹): 2953.3, 2872.8, 2832.7, 2794.8, 1589.2, 1469.7, 1456.1, 1380.6, 1355.6, 1335.9, 1288.6, 1239.6, 1195.6, 1166.5, 1052.4, 1022.8, 946.1, 900.9, 788.4, 773.0, 674.9.

A solution of [C₄H₃NH(2-CH₂NH^tBu)] (0.457 g, 3.0 mmol) in toluene (15 mL) was added slowly to a suspension of NaH (0.072 g, 3.0 mmol) in toluene (15 mL) at -78 °C. The reaction was warmed to room temperature and stirred for 3 h, immediately followed by addition of a solution of ZnEt₂ (3.0 mmol, 1.0 M in hexane).

The resulting suspension was heated for 1 hour at 100 °C, affording a clear solution. Then the TMEDA (0.45 mL, 3 mmol) was introduced via syringe, the solution was filtered and concentrated, the residue was recrystallized from a saturated Et₂O/toluene solution to yield colorless crystals of **2** (1.03g, 53.3% yield). ¹H NMR (C₆D₆+C₅D₅N): 7.06 (s, 2H, C₄H₃N), 6.27 (s, 2H, C₄H₃N), 5.84 (s, 2H, C₄H₃N), 4.38 (s, 4H, CH₂NBu^t), 2.06 (s, 8H, CH₂), 1.93 (s, 24H, N(CH₃)₂), 1.74 (br, 6H, ZnCH₂CH₃), 1.68(s, 18H, CH₂NBu^t), 0.62 (br, 4H, ZnCH₂CH₃); ¹³C NMR (C₆D₆+C₅D₅N): 147.7 (C₄H₃N), 137.5 (C₄H₃N), 106.1 (C₄H₃N), 95.6(C₄H₃N), 57.7 (TMEDA), 56.9 (C(CH₃)₃), 48.8(CH₂NBu^t), 45.7 (TMEDA), 31.3 (C(CH₃)₃), 15.2 (ZnCH₂CH₃), 5.5 (ZnCH₂CH₃). IR (cm⁻¹): 2953.6, 2868.4, 2825.6, 1595.4, 1464.3, 1382.4, 1357.0, 1338.7, 1291.5, 1234.5, 1192.2, 1156.4, 1129.2, 1050.5, 1019.8, 978.6, 948.9, 906.9, 886.8, 785.7, 768.3, 746.3, 731.6, 694.7, 671.9.

A solution of [C₄H₃NH(2-CH₂NH^tBu)] (0.457 g, 3.0 mmol) in toluene (15 mL) was added slowly to a suspension of NaH (0.12 g, 3.0 mmol) in toluene (15 mL) at -78 °C. The reaction was warmed to room temperature and stirred for 3 h, followed by addition of a solution of ZnEt₂ (3.0 mmol, 1.0 M in hexane). The resulting suspension was heated for 1 hour at 100 °C, affording a clear solution. Then a small amount of THF was introduced via syringe, the solution was filtered and concentrated to a small amount and recrystallized to generate **3** (1.16g, 57.2% yield). ¹H NMR (C₆D₆+C₅D₅N): 7.01 (s, 2H, C₄H₃N), 6.28 (s, 2H, C₄H₃N), 5.83 (s, 2H, C₄H₃N), 4.36 (s, 4H, CH₂NBu^t), 3.43 (br, 8H, THF), 2.09 (br, 6H, ZnCH₂CH₃), 1.65(s, 18H, CH₂NBu^t), 1.43 (br, 8H, THF), 0.63 (br, 4H, ZnCH₂CH₃); ¹³C NMR (C₆D₆+C₅D₅N):

147.9 (C_4H_3N), 135.7 (C_4H_3N), 106.0 (C_4H_3N), 95.5(C_4H_3N), 67.5 (THF), 55.7 ($C(CH_3)_3$), 48.8(CH_2NBU^t), 31.3 ($C(CH_3)_3$), 25.5(THF), 15.2 ($ZnCH_2CH_3$), 5.5 ($ZnCH_2CH_3$). IR (cm^{-1}): 2950.7, 2875.1, 1596.2, 1436.4, 1382.8, 1337.7, 1234.9, 1194.4, 1166.1, 1087.7, 1049.5, 1020.8, 978.8, 957.2, 893.0, 749.2, 669.8.

A solution of [$C_4H_3NH(2-CH_2NH^tBu)$] (0.457 g, 3.0 mmol) in toluene (15 mL) was added slowly to a suspension of KH (0.40 g, 3.0 mmol) in toluene (15 mL) at -78 °C; The reaction was warmed to room temperature and stirred for 3 h, followed by addition of a solution of $ZnEt_2$ (3.0 mmol, 1.0 M in hexane). The resulting suspension was heated for 1 hour at 100 °C, affording a clear solution. Then the THF was introduced via syringe, the solution was filtered and concentrated to a small amount and recrystallized to generate **4** (1.36g, 64.1% yield). 1H NMR (C_4D_8O): 6.54 (s, 2H, C_4H_3N), 5.79 (s, 2H, C_4H_3N), 5.47 (s, 2H, C_4H_3N), 4.33 (s, 4H, CH_2NBU^t), 3.61 (br, 8H, THF), 1.22 (br, 6H, $ZnCH_2CH_3$), 1.10(s, 18H, CH_2NBU^t), 1.76 (br, 8H, THF), 0.17 (br, 4H, $ZnCH_2CH_3$); ^{13}C NMR ($C_6D_6+C_5D_5N$): 147.0 (C_4H_3N), 123.5 (C_4H_3N), 106.1 (C_4H_3N), 96.9(C_4H_3N), 67.3 (THF), 55.4 ($C(CH_3)_3$), 47.9(CH_2NBU^t), 30.2($C(CH_3)_3$), 24.8(THF), 13.9 ($ZnCH_2CH_3$), 5.2 ($ZnCH_2CH_3$). IR (cm^{-1}): 2963.1, 2868.3, 1595.8, 1473.7, 1462.9, 1438.2, 1388.9, 1362.6, 1338.3, 1309.8, 1229.9, 1210.3, 1162.7, 1102.7, 1033.3, 1020.7, 977.3, 958.7, 884.9, 814.4, 733.7, 664.4.

X-ray crystallography

Single X-ray diffraction data of the compounds were collected on a Bruker Smart Apex CCD diffractometer using monochromated Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å. A total of N reflections were collected by using ω scan mode. Corrections were applied

for Lorentz and polarization effects as well as absorption using multi-scans (SADABS) [2]. Each structure was solved by direct method and refined on F^2 by full matrix least squares (SHELX97)[3] using all unique data. Then the remaining non-hydrogen atoms were obtained from the successive difference Fourier map. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas the hydrogen atoms were constrained to parent sites, using a riding mode (SHELXTL) [4]. Details of the modelling of disorder in the crystals can be found in their CIF files.

UV-vis absorption spectra

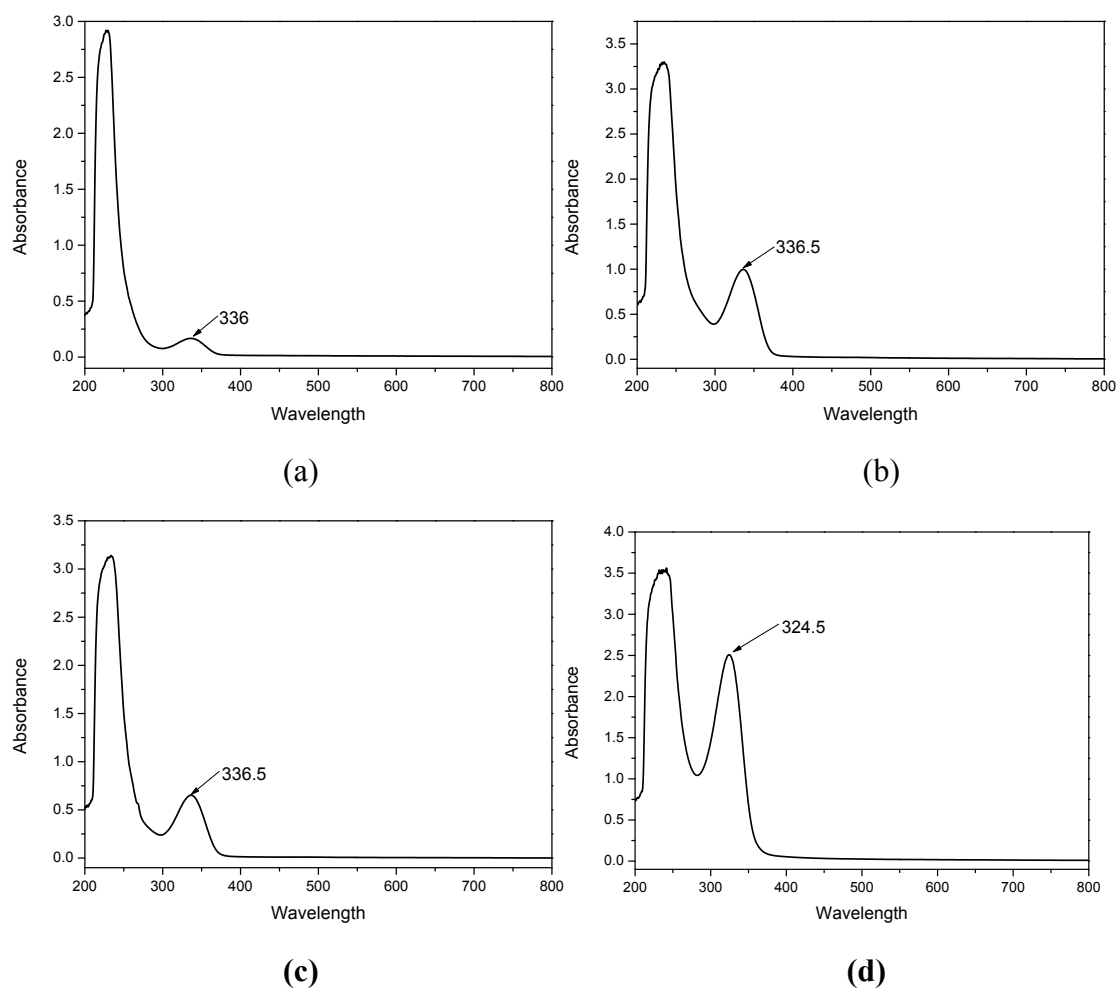


Fig. 1. UV-vis absorption spectra of complexes 1-4 in THF.

Notes and references

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3 Sheldrick, G. M. *Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, **1997**.

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