

Amidinate Ligands in Zinc coordination sphere: Synthesis and structural diversity

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Abstract. A one-pot reaction involving neosilyllithium and three different carbodiimides (RN=C=NR, R = cyclohexyl, isopropyl and *tert*-butyl) in diethyl ether, followed by the addition of anhydrous ZnCl₂, afforded, in high yield, corresponding homoleptic zinc amidinate complexes having the molecular formulae [Zn{CyN=C(CH₂SiMe₃)NCy}₂] (**1**), [Zn{^{*i*}PrN=C(CH₂SiMe₃)N^{*i*}Pr}₂] (**2**) and [Zn{^{*t*}BuN=C(CH₂SiMe₃)N^{*t*}Bu}₂] (**3**), respectively, and amidinato moieties in the zinc coordination sphere. Solid state structures of complexes **1-3** are reported thereafter - all the three complexes are isostructural, and each of them consists of two four-membered metallacycles.

Keywords. Zinc; carbodiimides; amidinate; alkyl migration.

1. Introduction

Zinc is biologically one of the most important metal and an adult human body contains approximately 2 g of it in the form of active site in various enzymes.¹ The remarkable discovery by Frankland of the first organometallic compound ‘diethyl zinc’ from ethyl iodide and zinc metal unearthed the potential of application of organo-zinc compounds in the development of synthetic organic chemistry.^{2,3} There has been significant interest in zinc chemistry in the last decade. Several systems including *N, N'*-chelating organic ligands such as β -diketiminato,⁴ guanidinate⁵ and amidinate anions⁶ have been investigated intensely in both main group and transition metal chemistry.⁷ It has been proven that steric and electronic properties of these *N, N'*-chelating substituents can be easily modified by using the different organic substituents R and R' present on the nitrogen atom, thus allowing fine-tuning of the chemical properties of the resulting metal complexes. Consequently, a large variety of low-coordinate organometallic compounds in low oxidation states have been synthesized and structurally characterized.⁸

In case of organozinc chemistry, interest has been focused on β -diketiminato complexes of the general

type LZnR (L = β -diketiminato)⁹ which were shown to be active catalysts in the metal catalyzed ring-opening polymerization (ROP) of cyclic esters - in particular lactides,¹⁰ and in copolymerization of CO₂ and epoxides, respectively.¹¹ Moreover, low-valent organozinc compounds of the general type LZn-ZnL containing a direct Zn-Zn bond, which were initially prepared by Carmona *et al.*,¹² can be stabilized by using chelating organic substituents, (L-[(2,6-^{*i*}Pr₂C₆H₃)N(Me)C]₂CH),¹³ 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene).¹⁴ There are several reports on zinc guanidinate and amidinate complexes, and their applications in various polymerization of cyclic esters and copolymerization reactions, and in the materials science (*i.e.*, CVD precursors).¹⁵ Very recently, zinc(II) was used as competent metal ion to prepare one and two dimensional coordination polymers using various flexible ligands.¹⁶ In our ongoing work too, we are working with zinc, supported by various mixed N-/O- donors¹⁷ and NHC based ligands.¹⁸ However, to the best of our knowledge, there are no reports on any direct synthesis of zinc amidinate complexes while using one-pot reaction with alkyl migration to the carbodiimide backbone to generate anionic amidinate moiety.

Herein, we report the syntheses of homoleptic zinc amidinate complexes having the molecular formulas [Zn{CyN=C(CH₂SiMe₃)NCy}₂] (**1**), [Zn{^{*i*}PrN=C(CH₂SiMe₃)N^{*i*}Pr}₂] (**2**) and [Zn{^{*t*}BuN=C(CH₂SiMe₃)N^{*t*}Bu}₂] (**3**). Full characterization and structural studies of all the complexes are also presented.

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This work is dedicated to Prof. Dr. Peter W. Roesky on the occasion of his 49th birth anniversary

2. Experimental

2.1 General Information

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame dried Schlenk-type glassware, either on a dual manifold Schlenk line interfaced to a high vacuum (10^{-4} torr) line, or in an argon-filled M. Braun glove box. Diethyl ether was pre-dried over Na wire and distilled under nitrogen from sodium and benzophenone ketyl prior to use. Hydrocarbon solvent (n-pentane) was distilled under nitrogen from LiAlH₄ and stored in the glovebox. ¹H NMR (400 MHz) and ¹³C{¹H}NMR spectra were recorded on a Bruker Avance III-400 spectrometer. Elemental analyses were performed on a Bruker Euro EA at the Indian Institute of Technology Hyderabad. Carbodiimides (RN=C=NR; R = Cy, ^tPr, ^tBu) were purchased from Sigma Aldrich and used as received. LiCH₂SiMe₃ were prepared according to the procedure described in the literature.¹⁹ Anhydrous ZnCl₂ and NMR solvent C₆D₆ were purchased from Sigma Aldrich. C₆D₆ was dried under Na/K alloy prior to use.

2.2 Synthesis of [Zn{CyN=C(CH₂SiMe₃)NCy}₂] (1)

To a solution of N,N'-dicyclohexylcarbodiimide (DCC) (206 mg, 1 mmol) in 5 mL Et₂O, a pre-cooled ethereal solution (5 mL) of LiCH₂SiMe₃ (95 mg, 1 mmol) was added at ambient temperature (25°C) and stirred for 2 h. To this mixture, anhydrous ZnCl₂ (68 mg, 0.5 mmol) was directly added, and the resultant solution was stirred for another 12 h at ambient temperature (25°C). Thereafter, LiCl was removed by filtration, and the filtrate was evaporated to dryness under reduced pressure resulting in a white solid which was re-crystallized from Et₂O at -35°C which therefore yielded colorless crystals after one day. Yield 295 mg (90%). ¹H NMR (400 MHz, C₆D₆, 25°C): δ = 3.9 (m, 4H, Cy-H), 1.91 (s, 4H, CH₂-SiMe₃), 1.84 (m, 16H, Cy-CH₂), 1.56 (m, 4H, Cy-CH₂), 1.40 (m, 20H, Cy-CH₂), 0.18 (s, 18H, SiMe₃) ppm; ¹³C{¹H} NMR (100 MHz, C₆D₆): δ = 171.4 (N=C-N), 53.5 (Cy-C-N), 37.2 (Cy-CH₂), 26.6 (Cy-CH₂), 25.5 (Cy-CH₂), 16.4 (CH₂SiMe₃), -0.3 (SiMe₃) ppm. Elemental Analysis: C₃₄H₆₆N₄Si₂Zn (657.48): Calcd. (%): C 62.59, H 10.20, N 8.59. Found (%): C 62.34, H 9.93, N 8.29.

2.3 Synthesis of [Zn{^tPrN=C(CH₂SiMe₃)N^tPr}₂] (2)

To a solution of N,N'-diisopropylcarbodiimide (126 mg, 1 mmol) in 5 mL Et₂O, a pre-cooled ethereal solution,

(5 mL) LiCH₂SiMe₃ (95 mg, 1 mmol), was added at ambient temperature and stirred for 2 h. To this solution, anhydrous ZnCl₂ (68 mg, 0.5 mmol) was directly added and the solution was allowed to stir for 12 h at ambient temperature (25°C). LiCl was removed by filtration, and the filtrate was evaporated to dryness under reduced pressure. The resultant white solid was re-crystallized from Et₂O at -35°C thus yielding colorless crystals after one day. Yield 226 mg (92%). ¹H NMR (400 MHz, C₆D₆, 25°C): δ = 3.5 (m, 4H, CH), 1.85 (s, 4H, CH₂-SiMe₃), 1.19 (d, *J* = 6.2 Hz, 24H, CH₃), 0.14 (s, 18H, SiMe₃) ppm; ¹³C{¹H} NMR (100 MHz, C₆D₆, 25°C): δ = 173.3 (N=C-N), 45.7 (Me₂CH-N), 26.6 (CH₃), 16.2 (CH₂-SiMe₃), -0.4 (SiMe₃) ppm. Elemental Analysis: C₂₂H₅₀N₄Si₂Zn (492.91): Calcd. (%): C 53.68, H 10.24, N 11.38. Found (%): C 53.43, H 9.92, N 11.02.

2.4 Synthesis of [Zn{^tBuN=C(CH₂SiMe₃)N^tBu}₂] (3)

To a solution of N,N'-di-tert-butylcarbodiimide (154 mg, 1 mmol) in 5 mL Et₂O, a pre-cooled ethereal solution (5 mL) of LiCH₂SiMe₃ (95 mg, 1 mmol) in Et₂O (5 mL) was added at ambient temperature (25°C) and stirred for 2 h. To this solution, anhydrous ZnCl₂ (68 mg, 0.5 mmol) was directly added and the mixture was allowed to stir for another 12 h at ambient temperature. LiCl was removed by filtration and the filtrate was evaporated to dryness under reduced pressure resulting in a white solid which was recrystallized from Et₂O at -35°C to give colorless crystals after one day. Yield 230 mg (84%). ¹H NMR (400 MHz, C₆D₆, 25°C): δ = 2.2 (s, 4H, CH₂-SiMe₃), 1.38 (s, 36H, CH₃), 0.24 (s, 18H, SiMe₃) ppm; ¹³C{¹H}NMR (100 MHz, C₆D₆): δ = 171.9 (N=C-N), 50.6 (Me₃C-N), 33.6 (CH₃), 20.9 (CH₂-SiMe₃), 1.2 (SiMe₃) ppm. Elemental Analysis: C₂₆H₅₈N₄Si₂Zn (548.32): Calcd. (%): C 56.95, H 10.66, N 10.22. Found (%): C 56.68, H 10.39, N 9.81.

2.5 Single-Crystal X-Ray Structure Determinations

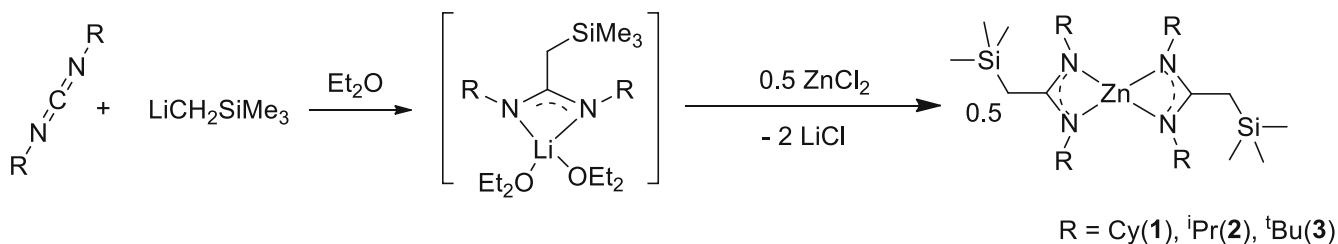
2.5a X-ray Crystallographic Analyses: Single crystals of compounds **1-3** were grown from diethyl ether at -35°C. In each case, a crystal of suitable dimensions was mounted on a CryoLoop (Hampton Research Corp) with a layer of light mineral oil, and placed in a nitrogen stream at 150(2) K. All measurements were made on an Agilent Supernova X-calibur Eos CCD detector with graphite-monochromatic Mo-Kα (0.71069 Å) radiation. Crystal data and structure refinement parameters are summarized in table 1. The structures were solved by direct methods (SIR2004),²⁰ and refined on *F*² by full-matrix least-squares methods using SHELXL-97.²¹

Table 1. Crystallographic details of **1-3**.

Complex	1	2	3
CCDC No.	1455627	1455625	1455626
Empirical formula	C ₃₄ H ₆₆ N ₄ Si ₂ Zn	C ₂₂ H ₅₀ N ₄ Si ₂ Zn	C ₂₆ H ₅₈ N ₄ Si ₂ Zn
Formula weight	652.48	492.21	548.33
<i>T</i> (K)	150	150	150
λ (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	10.8269(7)	17.3685(4)	14.429(2)
<i>b</i> (Å)	10.8986(7)	9.6045(2)	9.3920(4)
<i>c</i> (Å)	17.4171(12)	19.4893(5)	25.500(13)
α (°)	74.661(6)	90	90
β (°)	87.686(5)	114.707(3)	105.24(3)
γ (°)	74.820(5)	90	90
<i>V</i> (Å ³)	1911.9(2)	2953.50(12)	3334.2(17)
<i>Z</i>	2	4	4
<i>D</i> _{calc} g cm ⁻³	1.133	1.107	1.092
μ (mm ⁻¹)	0.731	0.927	0.827
<i>F</i> (000)	712	1072	1200
Theta range for data collection	3.07 to 29.10 deg.	2.95 to 28.89 deg.	2.86 to 29.01 deg.
Limiting indices	-14 ≤ <i>h</i> ≤ 14 -10 ≤ <i>k</i> ≤ 14 -15 ≤ <i>l</i> ≤ 23	-23 ≤ <i>h</i> ≤ 11 -12 ≤ <i>k</i> ≤ 11 -17 ≤ <i>l</i> ≤ 25	-18 ≤ <i>h</i> ≤ 14 -10 ≤ <i>k</i> ≤ 12 -32 ≤ <i>l</i> ≤ 31
Reflections collected / unique	16640 / 8720 [<i>R</i> (int) = 0.0414]	6405 / 3361 [<i>R</i> (int) = 0.0247]	16503 / 7718 [<i>R</i> (int) = 0.0260]
Completeness to theta = 71.25	99.8%	99.8%	99.8%
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Max. and min. transmission	1.000 and 0.99133	1.000 and 0.88467	1.000 and 0.94450
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	8720 / 0 / 376	3361 / 0 / 139	7718 / 0 / 316
Goodness-of-fit on <i>F</i> ²	1.040	1.038	1.034
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0464, <i>wR</i> 2 = 0.0847	<i>R</i> 1 = 0.0320, <i>wR</i> 2 = 0.0684	<i>R</i> 1 = 0.0529, <i>wR</i> 2 = 0.1299
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0669, <i>wR</i> 2 = 0.0971	<i>R</i> 1 = 0.0409, <i>wR</i> 2 = 0.0732	<i>R</i> 1 = 0.0661, <i>wR</i> 2 = 0.1389
Largest diff. peak and hole	0.346 and -0.362 e.Å ⁻³	0.321 and -0.242 e.Å ⁻³	1.082 and -0.679 e.Å ⁻³

Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\sum w(F_o^2 - F_c^2)^2]$ ($w=1/[\sigma^2(F_o^2) + (aP)^2 + bP]$), where $P = (\text{Max}(F_o^2, 0) + 2F_c^2) / 3$ with $\sigma^2(F_o^2)$ was derived from counting statistics. The

function *R*1 and *wR*2 are $(\sum ||F_o| - |F_c||) / \sum |F_o|$ and $[\sum w(F_o^2 - F_c^2)^2 / \sum (wF_o^4)]^{1/2}$, respectively. The ORTEP-3 program²² was used to draw the molecule. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic

**Scheme 1.** Synthesis of zinc complexes **1-3**.

Data Centre as supplementary publication no. CCDC 1455625-1455627. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: + (44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

3. Results and Discussion

3.1 Syntheses of complexes 1-3

Three homoleptic zinc amidinato complexes of molecular formulas $[\text{Zn}\{\text{CyN}=\text{C}(\text{CH}_2\text{SiMe}_3)\text{NCy}\}_2]$ (**1**), $[\text{Zn}\{\text{PrN}=\text{C}(\text{CH}_2\text{SiMe}_3)\text{N}^i\text{Pr}\}_2]$ (**2**) and $[\text{Zn}\{\text{tBuN}=\text{C}(\text{CH}_2\text{SiMe}_3)\text{N}^i\text{Bu}\}_2]$ (**3**) were obtained by one-pot reactions of respective carbodiimides with neosilyllithium ($\text{LiCH}_2\text{SiMe}_3$) followed by the addition of anhydrous ZnCl_2 in a 2:2:1 molar ratio in diethyl ether at room temperature (scheme 1). It is believed that reaction of carbodiimides and neosilyllithium generated lithium amidinates of molecular formula $[(\text{Et}_2\text{O})_2\text{Li}\{\text{RN}=\text{C}(\text{CH}_2\text{SiMe}_3)\text{NR}\}_2]$. The reaction of metal alkyl or metal amides towards carbodiimides have recently been reported by us and others too.²³ Respective zinc amidinate complexes were obtained (scheme 1) following the subsequent reaction of lithium amidinates with anhydrous zinc chloride. All complexes were synthesized in pure form and obtained in good yields through re-crystallization from diethyl ether at -35°C . All the new zinc complexes **1-3** were characterized using standard analytical and spectroscopic techniques. The solid-state structures of all three complexes were established by single-crystal X-ray diffraction analysis.

In the ^1H NMR spectra measured in C_6D_6 , all complexes (**1-3**) exhibited one set of signals in the solution state. A sharp singlet resonance at δ 1.91 (for complex **1**), 1.85 (for complex **2**) and 2.20 ppm (for complex **3**) can be assigned to the methylene protons present in the neosilyl group ($\text{CH}_2\text{-SiMe}_3$) attached to the amidinate ligands. The resonance signals for the corresponding cyclohexyl moieties were in the expected region for complex **1**, and well in agreement with literature values.⁸ A septet signal centred at δ 3.50 ppm, and a doublet signal centered at δ 1.19 were observed for the four isopropyl protons and corresponding eight methyl protons present in complex **2**. However, a sharp singlet in each complex appeared at δ 0.18 (**1**), 0.14 (**2**) and 0.24 (**3**) ppm due to the resonances of SiMe_3 protons. In addition, a sharp singlet resonance at δ 1.38 ppm was observed for the methyl protons of *tert*-butyl group present in complex **3**. In $^{13}\text{C}\{^1\text{H}\}$ NMR, spectra of complexes **1-3** are similar, and the signals at δ 171.4 (for **1**), 173.3 (for **2**) and 171.9 (for **3**) ppm indicate the presence of sp^2 carbon ($-\text{N}-\text{C}(\text{CH}_2\text{SiMe}_3)=\text{N}-$) in all

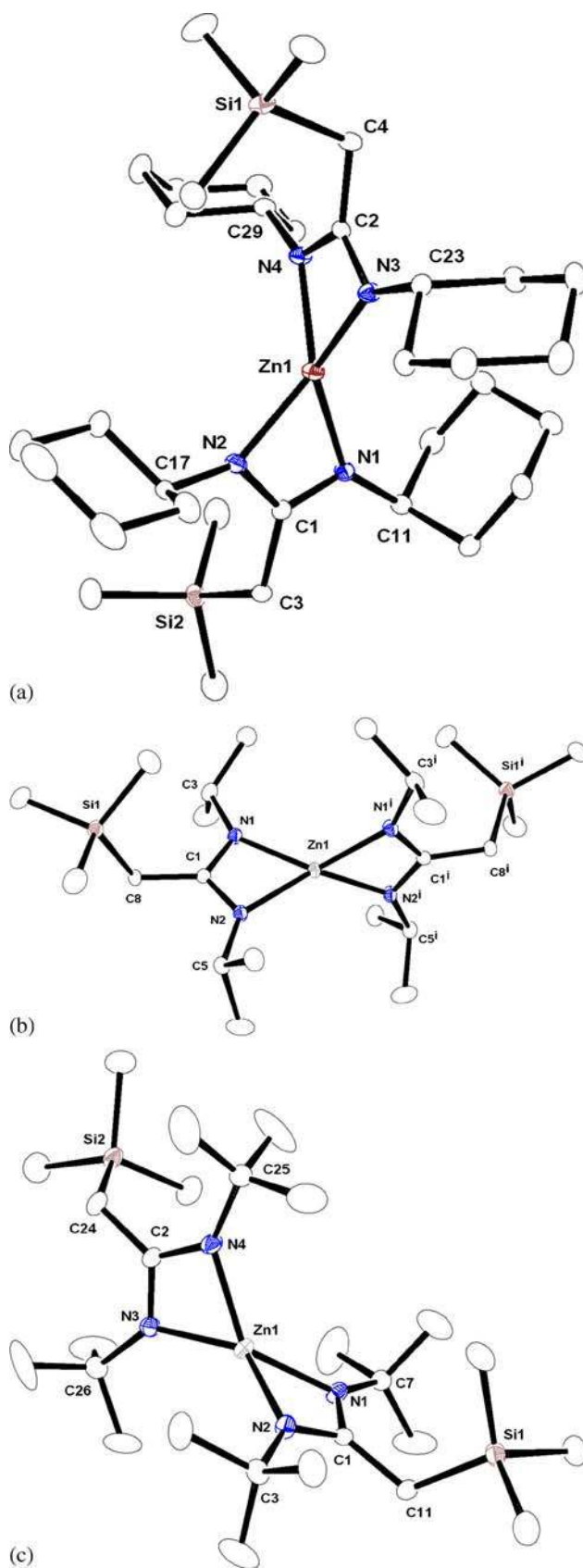


Figure 1. Solid state structures of compound **1** (top), **2** (middle) and **3** (bottom). Ellipsoids are drawn to encompass 30% probability. Selected bond lengths and bond angles are given in table 2.

complexes. Solid state structures of all the complexes (**1-3**) were determined by single crystal X-ray diffraction analysis.

3.2 Molecular Structures of complexes **1-3**

The molecular structures of complexes **1-3** in the solid state confirmed the attachment of amidinate ligand to the zinc ion. It was observed that complex **1** crystallizes in the triclinic space group *P-1* having two independent molecules in the unit cell. In contrast, complexes **2** and **3** crystallize in the monoclinic space group *P2/c* having four individual molecules of **2** and **3** in their respective unit cells. The details of their structural parameters are given in table 1. The solid state structures of complexes **1-3** are presented in figure 1. Selected bond lengths and

bond angles are given in table 2. All the complexes are homoleptic and monomeric in nature, and their structural parameters are similar. All Zn-N bond distances Zn1-N1 2.0215 (2), Zn1-N2 2.0195 (2), Zn1-N3 2.0138 (2) and Zn1-N4 2.0208 (2) for **1**, Zn1-N1 2.0231 (1), Zn1-N2 2.0168 (1), Zn1-N1ⁱ 2.0231 (1) and Zn1-N2ⁱ 2.0168 (1) for **2**, and Zn1-N1 2.018 (2), Zn1-N2 2.011 (2), Zn1-N3 2.012 (2) and Zn1-N4 2.016 (2) for **3** are in the same range, thus indicating complete delocalization of negative charge over the N-C-N skeletons in each complex. This observation is further evidenced by the having comparable N-C bond lengths (in Å), N1-C1 1.335 (3), N2-C1 1.328 (3) for **1**, N1-C1 1.330 (2), N2-C1 1.328 (2) for **2**, and N1-C1 1.337 (3), N2-C1 1.326 (3) for **3**, respectively. In each complex, the geometry of each zinc ion can be best described as dis-

Table 2. Selected bond lengths [Å] and bond angles [°].

1	2	3
Zn1-N1 2.0215(2)	Zn1-N1 2.0231(1)	Zn1-N1 2.018(2)
Zn1-N2 2.0195(2)	Zn1-N2 2.0168(1)	Zn1-N2 2.011(2)
Zn1-N3 2.0138(2)	Zn1-N1 ⁱ 2.0231(1)	Zn1-N3 2.012(2)
Zn1-N4 2.0208(2)	Zn1-N2 ⁱ 2.0168(1)	Zn1-N4 2.016(2)
Zn1-C1 2.440(2)	Zn1-C1 2.4449(2)	Zn1-C1 2.460(3)
Zn1-C2 2.442(2)	Zn1-C1 ⁱ 2.4449(2)	Zn1-C2 2.462(3)
N1-C1 1.335(3)	N1-C1 1.330(2)	N1-C1 1.337(3)
N2-C1 1.328(3)	N2-C1 1.328(2)	N2-C1 1.336(3)
N3-C2 1.337(3)	C1-C8 1.503(2)	N2-C3 1.470(3)
N4-C2 1.331(3)	N2-Zn1-N2 ⁱ 136.44(8)	N3-C2 1.343(3),
C1-C3 1.504(3)	N1-Zn1-N1 ⁱ 135.70(6) N2 ⁱ -	N4-C2 1.338(4)
C2-C4 1.500(3)	Zn1-N1 ⁱ 65.84(5)	C1-C11 1.513(4)
N2-Zn1-N4 134.28(7)	N2-Zn1-N1 65.84(5)	C2-C24 1.513(4)
N3-Zn1-N2 132.47(8)	N2 ⁱ -Zn1-N1 135.70(6) N1 ⁱ -	C3-C4 1.512(5)
N3-Zn1-N4 66.18(7)	Zn1-N1 131.22(8) N2 ⁱ -Zn1-C1	N2-Zn1-N3 137.09(9)
N3-Zn1-N1 135.19(7)	149.30(5) N1 ⁱ -Zn1-C1	N2-Zn1-N4 134.93(1)
N2-Zn1-N1 66.11(8),	144.76(5) N2-Zn1-C1 ⁱ	N3-Zn1-N4 65.92(1)
N4-Zn1-N1 136.38(8)	149.30(5) N1-Zn1-C1 ⁱ	N2-Zn1-N1 65.72(9)
C1-N1-Zn1 90.91(1)	144.76(5) C1-Zn1-C1 ⁱ	N3-Zn1-N1 134.78(1)
C1-N2-Zn1 91.21(1)	176.89(7) C1-N1-C3 125.50(1)	N4-Zn1-N1 132.31(1)
C2-N3-Zn1 91.28(1)	C1-N1-Zn1 91.22(1)	N3-Zn1-C1 149.32(9)
C2-N4-Zn1 91.13(1)	C3-N1-Zn1 143.28(1)	N4-Zn1-C1 144.66(9)
N2-C1-N1 111.73(2)	C1-N2-Zn1 91.57(1)	N2-Zn1-C2 149.15(9)
N2-C1-C3 124.6(2)	C5-N2-Zn1 141.96(1)	N1-Zn1-C1 145.03(9)
N1-C1-C3 123.5(2)	N2-C1-N1 111.37(1)	C1-Zn1-C2 176.85(8)
C3-C1-Zn1 177.85(2)	C8-C1-Zn1 177.68(1).	C1-N1-Zn1 92.06(2)
N4-C2-N3 111.30(2)		C1-N2-Zn1 92.41(2)
N4-C2-C4 125.00(2)		C2-N3-Zn1 92.23(2)
N3-C2-C4 123.47(2)		C2-N4-Zn1 92.17(2)
C4-C2-Zn1 173.05(2)		N2-C1-N1 109.8(2)
		N2-C1-C11 124.1(2)
		N1-C1-C11 126.1(2)
		C11-C1-Zn1 177.36(2)
		N4-C2-N3 109.7(2)
		N4-C2-C24 126.0(2)
		N3-C2-C24 124.3(3).

torted tetrahedral which is commonly observed in zinc chemistry as reported in literature.⁸ In each case, two four-membered zinc metallacycles, Zn1-N1-C1-N2 and Zn1-N3-C2-N4, could be observed due to the bidentate coordination mode of two amidinato ligands to the zinc metal ion in each complex (**1-3**). Two planes having N1, C1, N2, Zn1, and N3, C2, N4 and Zn1 are orthogonal (dihedral angles 89.51° for **1**; 87.59° for **2** and 89.70°) to each other and thereby indicating no influence on amidinato nitrogen atoms from the alkyl substituents.

4. Conclusions

In summary, we have successfully demonstrated a one-pot synthesis and structural characterization of homoleptic zinc amidinate complexes using three different carbodiimides. This method can be used to prepare amidinate moieties from easily available carbodiimides. From their molecular structures in the solid state, we have observed that all the zinc complexes are homoleptic with similar structural parameters, thus resulting in the adoption of a distorted tetrahedral geometry around the zinc ion.

Supplementary Information (SI)

The ¹H and ¹³C{¹H}NMR spectra of complexes **1-3** are given in Supplementary Information, available at www.ias.ac.in/chemsci.

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