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Synthesis and X-ray Crystal Structures of Multinuclear Zinc Amidinate Complexes

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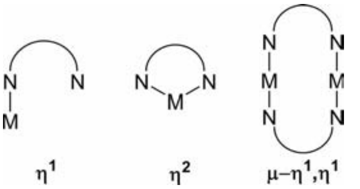
The reactions of Me_2Zn with carbodiimides RN=C=NR (R = Et, Ph) yielded the polynuclear zinc amidinate complexes $\{[MeZn]_4[C(RNCNR)_4]\}$ [R = Et (**1**), Ph (**3**)] and $\{[MeZn]_2[C(EtNCNEt)_2(C_2(NEt)_3)]\}$ (**2**). In addition, the reaction of $\{[ClZn]_4[C(i\text{Pr}NCNi\text{Pr})_4]\}$ with MCl_3 gave the corresponding Lewis acid–base adducts $\{[MCl_3]_2[ClZn]_4[C(i\text{Pr}NCNi\text{Pr})_4]\}$ [M = Al (**4**), Ga (**5**)]. Compounds **1**–**5** were characterized by multinuclear NMR (^1H, ^{13}C) and IR spectroscopy, elemental analyses and single-crystal X-ray diffraction.

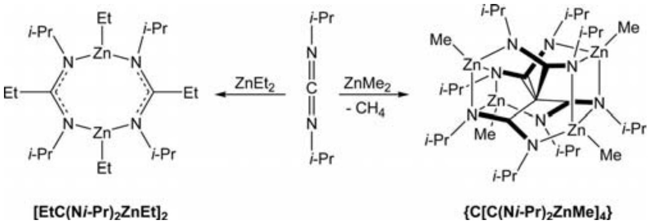
Introduction

N,*N′*-Chelating organic ligands such as β-diketiminate,[1] guanidinate,[2] and amidinate anions[3] are well known in coordination chemistry of s-, p-, d-, and f-block metals.[4] Their flexible binding modes (monodentate η^1, chelating η^2, bridging monodentate μ-η^1-η^1, Scheme 1) and tunable steric and electronic properties render them promising candidates for the synthesis of *tailor-made* complexes with potential technical applications in catalysis[5] and in the material sciences (i.e. CVD precursors).[6]



Scheme 1. Typical binding modes of *N*,*N′*-chelating ligands.

Considering the long history of metal amidinate complexes in main group and transition-metal chemistry, it came to us as a surprise that zinc amidinate complexes have been structurally characterized to a far lesser extent.[7] In contrast, guanidinate complexes[8] and β-diketiminate complexes,[9] which have been used in the ROP polymerization of lactide and the copolymerization of epoxides and carbon dioxide, have been studied in more detail. We therefore became interested in this specific class of compounds and reported on the synthesis of mono- and bisamidinate complexes of the type LZnX and L_2Zn (L = amidinate), which were obtained from salt elimination reactions between ZnX_2 and the corresponding lithium amidinate complex.[10] Moreover, reactions of carbodiimides RN=C=NR with ZnR'_2, which were expected to proceed with insertion of the carbodiimide into the zinc–carbon bond and formation of the corresponding amidinate complexes $[R'ZnNRC(R')NR]_x$,[11] were investigated. While the reaction of $ZnEt_2$ with bis(isopropyl)carbodiimide gave the expected dimeric amidinate complex $[EtC(Ni\text{Pr})_2ZnEt]_2$,[12] in which the amidinate units serve as μ-η^1,η^1-bridging moieties, multinuclear zinc amidinate complexes such as $\{[MeZn]_4[C(RNCNR)_4]\}$ (R = *i*Pr,[13] Cy[14]) were unexpectedly formed in the reaction with $ZnMe_2$ (Scheme 2). No reactions were observed with sterically hindered carbodiimides (R = *t*Bu, $SiMe_3$, Dipp).



Scheme 2. Synthesis of zinc amidinate complexes by carbodiimide insertion reaction.

These reactions, which proceeded with C–H activation and C–C bond formation, are without precedent in carbodiimide chemistry. In order to further clarify the role of the N-bonded substituent R′ of the carbodiimide and to verify both steric and electronic influences, we studied reactions of $ZnMe_2$ with carbodiimides R′N=C=NR′ in more detail. Herein, we report on the reactions of $ZnMe_2$ with bis(ethyl)carbodiimide and bis(phenyl)carbodiimide, which yield the polynuclear zinc amidinate complexes $\{[MeZn]_4[C(RNCNR)_4]\}$ [R = Et (**1**), Ph (**3**)] and $\{[MeZn]_2[C(EtNCNEt)_2(C_2(NEt)_3)]\}$ (**2**), respectively. Moreover, re-

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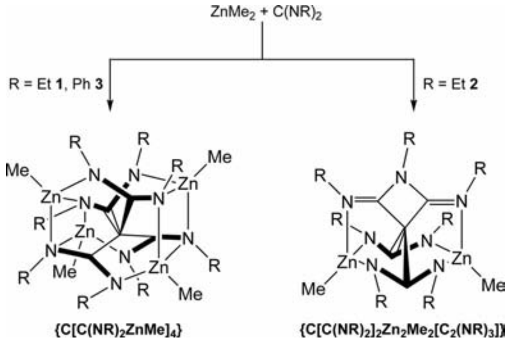
actions of the Cl-substituted tetranuclear complex $\{[ClZn]_4[C(i\text{Pr}NCN i\text{Pr})_4]\}$ with MCl_3 (M = Al, Ga) resulted in the formation of the Lewis acid–base adducts $\{[MCl_3]_2[ClZn]_4[C(i\text{Pr}NCN i\text{Pr})_4]\}$ [M = Al (**4**), Ga (**5**)].

Results and Discussion

Equimolar amounts of $ZnMe_2$ and RN=C=NR (R = Et, Ph) were stirred at 90 °C for 48 h, yielding colorless crystalline solids (Scheme 3). The reaction with $C(NEt)_2$ gave a mixture of $\{[MeZn]_4[C(EtNCNEt)_4]\}$ (**1**) and $\{[MeZn]_2[C(EtNCNEt)_2(C_2(NEt)_3)]\}$ (**2**), as was observed for the reactions with $C(Ni\text{Pr})_2$ and $C(NCy)_2$, respectively, whereas the reaction with $C(NPh)_2$ exclusively gave $\{[MeZn]_4[C(PhNCNPh)_4]\}$ (**3**) in almost quantitative yield. Compounds **1** and **2** were separated by fractional crystallization from toluene.



Scheme 3. Synthesis of **1**–**3**.

Even though the reactions of $ZnMe_2$ and $C(NEt)_2$ generally yielded a product mixture of **1** and **2** as was shown by ^1H NMR spectroscopy, the relative amounts of **1** and **2** within this mixture can be controlled to some extent by variation of the reaction temperature, reaction time and the $ZnMe_2/C(NEt)_2$ molar ratio. Compound **1** is preferably formed at 90 °C and with a molar ratio of 1:1 in about 80% yield according to the ^1H NMR spectrum of the raw product and 56% yield (isolated crystals) after re-crystallization, whereas an excess of the carbodiimide gave **2** in larger amounts (65% raw product; 47% after re-crystallization). Analogous trends have been previously observed for the reaction of $ZnMe_2$ with $C(Ni\text{Pr})_2$ and $C(NCy)_2$, respectively.[14]

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **1** and **3** each show a single resonance for the Zn–Me group. The ^1H NMR spectrum of **1** also shows two triplets and two quartets for the nonequivalent Et groups with equal relative intensities, whereas for **3** only one additional multiplet is observed. In addition, for **2**, a relative intensity for the Zn–Me and Et groups of 2:7 is observed.

Single crystals of **1**, **2**, and **3** were obtained from solutions in pentane (**1**), *n*-hexane (**2**) and toluene (**3**) after storage at –30 °C. Compounds **1** and **3** each contain a central, sp^3-hybridized C atom (C1), which is tetrahedrally coordinated by four C atoms of adjacent amidinate groups, which results in the formation of a tetraamidinate ligand system. Each amidinate group coordinates to the Zn atoms in a μ-η^1,η^1-bridging fashion. The cluster-type structures are therefore best described as two eight-membered $Zn_2(NCN)_2$ rings (top and bottom half of the cluster in Figures 1 and 3, respectively), which are connected by the central carbon atom (C1). Each Zn atom also binds to a methyl group and is intramolecularly coordinated by an additional N atom of the adjacent eight-membered ring, which results in tetrahedral coordination geometries (Figures 1, 2, and 3).

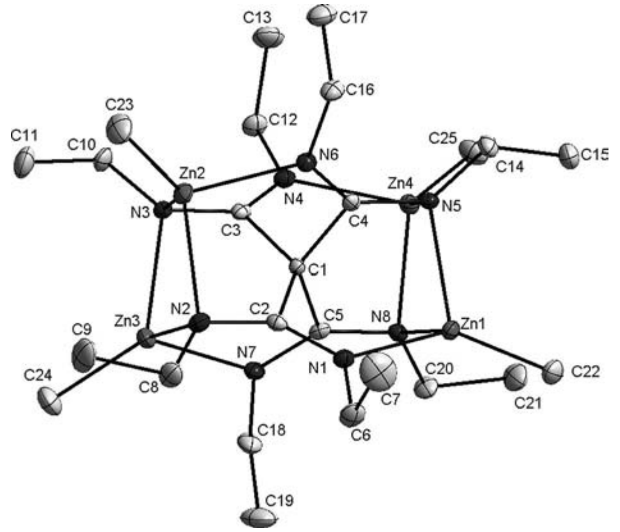


Figure 1. Solid-state structure of **1** (thermal ellipsoids are shown at the 50% probability level); H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1–N1 2.1241(11), Zn1–N8 2.1285(11), Zn1–N5 2.1783(10), Zn2–N2 2.1541(11), Zn2–N3 2.1749(11), Zn2–N6 2.1195(11), Zn3–N2 2.1596(12), Zn3–N3 2.1457(11), Zn3–N7 2.1242(11), Zn4–N4 2.1220(11), Zn4–N5 2.1383(10), Zn4–N8 2.1666(11), Zn1–C22 1.9650(14), N1–C2 1.3087(16), N2–C2 1.3558(16), N3–C3 1.3525(16), N4–C3 1.3056(16), C1–C2 1.5503(17), C1–C3 1.5495(17), C1–C4 1.5473(18), C1–C5 1.5504(17); N1–Zn1–N8 95.84(4), N1–Zn1–N5 97.22(4), N5–Zn1–N8 82.31(4), N2–Zn2–N6 96.98(4), N3–Zn2–N6 96.47(4), N2–Zn2–N3 81.96(4), N1–C2–N2 137.02(12), N3–C3–N4 136.32(12), C2–C1–C3 129.46(10), C2–C1–C4 101.16(9), C3–C1–C4 100.60(9), C2–C1–C5 99.95(9), C3–C1–C5 100.30(9).

The equal C–C bond lengths within the central CC_4 moieties [average values: **1** 1.549(2) Å, **3** 1.544(2) Å] clearly prove the formation of C–C single bonds. The Zn–N bond lengths in **1** [2.1195(11)–2.1783(10) Å] are comparable to those of the isopropyl- [2.108(2)–2.134(2) Å] and cyclohexyl-substituted complexes [2.141(3)–2.180(3) Å], whereas the range observed for **3** [2.1332(17)–2.2339(17) Å] is much larger; in particular, the Zn2a–N4 bond length of 2.2339(17) Å is significantly elongated. The N–C bond lengths of the threefold-coordinated N atoms [**1**: N1–C2 1.3087(16), N4–C3 1.3056(16), N6–C4 1.3066(16), N7–C5 1.3042(17); **3**: N1–C2 1.314(3), N3–C3 1.312(2) Å] within the amidinate NCN backbone are slightly shorter than those of the fourfold-coordinated N atoms [**1**: N2–C2 1.3558(16), N3–C3 1.3525(16), N5–C4 1.3565(16), N8–C5 1.3573(16); **3**: N2–C2 1.340(3), N4–C3 1.341(3) Å], which indicates that the π-electron systems are not perfectly delocalized. The Zn–C bond lengths of **1** [1.9650(14),

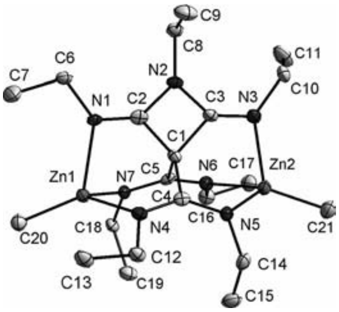


Figure 2. Solid-state structure of complex **2** (thermal ellipsoids are shown at the 50% probability level); H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1–N1 2.165(3), Zn1–N4 2.075(3), Zn1–N7 2.115(3), Zn2–N3 2.135(3), Zn2–N5 2.094(3), Zn2–N6 2.099(3), N1–C2 1.259(4), N2–C2 1.398(4), N2–C3 1.399(4), N3–C3 1.256(4), N4–C4 1.335(4), N5–C4 1.311(4), N6–C5 1.300(4), N7–C5 1.338(4), C1–C2 1.515(5), C1–C3 1.532(5), C1–C4 1.532(5), C1–C5 1.542(5); N1–Zn1–N4 90.62(11), N4–Zn1–N7 95.55(10), N1–Zn1–N7 90.87(10), N5–Zn2–N6 94.42(11), N3–Zn2–N5 91.72(11), N3–Zn2–N6 89.69(11), N1–C2–N2 138.0(3), N2–C3–N3 139.4(3), N4–C4–N5 138.2(3), N6–C5–N7 137.2(3), C2–C1–C3 83.4(2), C2–C1–C4 118.9(3), C3–C1–C4 117.7(3), C2–C1–C5 117.2(3), C3–C1–C5 116.2(3).

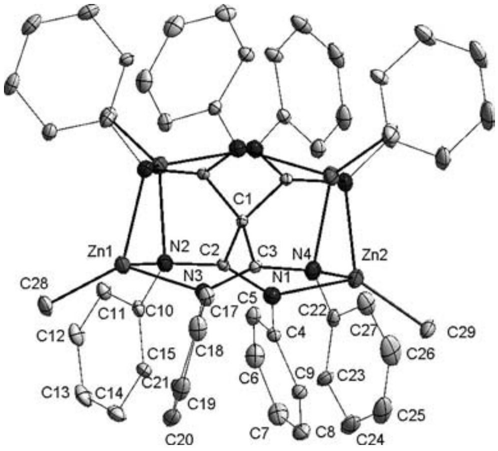


Figure 3. Solid-state structure of **3** (thermal ellipsoids are shown at the 50% probability level); H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1–N2 2.1735(16), Zn1–N3 2.1433(17), Zn1–N2a 2.1886(16), Zn2–N1 2.1509(17), Zn2–N4 2.1332(17), Zn2–N4a 2.2338(17), N1–C2 1.314(3), N2–C2 1.340(3), N3–C3 1.312(2), N4–C3 1.341(3), C1–C2 1.544(2), C1–C3 1.544(2); N2–Zn1–N3 95.76(6), N2a–Zn1–N3 94.36(6), N2–Zn1–N2a 80.59(7), N1–Zn2–N4 95.02(6), N1–Zn2–N4a 95.08(6), N4–Zn2–N4a 81.67(7), N1–C2–N2 136.07(18), N3–C3–N4 135.32(18), C2–C1–C3 100.22(9), C2–C1–C3a 100.93(9), C3–C1–C3a 129.4(2), C2–C1–C2a 129.1(2). a: –*x* + 1, *y*, –*z* + 1/2.

1.9681(15), 1.9658(15), 1.9649(13) Å] and **3** [1.951(2), 1.946(2) Å] are within the typical range observed for Zn–Me bonds.

Compound **2** crystallizes with two molecules in the asymmetric unit with nearly identical structaral parameters of the central core. The central C1 atom binds to two sp^2-hybridized C atoms (C4, C5) of adjacent amidinate moieties and two carbon atoms of a NCNCN unit (C2, C3) in a tetrahedral coordination mode as was previously observed for $\{[MeZn]_2[C(i\text{Pr}NCNi\text{Pr})_2(C_2(Ni\text{Pr})_3)]\}$.[13] The C–C bond lengths in **2** [1.524(2)–1.547(2) Å] are comparable to those previously observed for multinuclear complexes of this type. The two amidinate groups adopt μ-η^1,η^1-bridging positions between the two Zn atoms, hence an eight-membered $[Zn_2(\mu\text{-NCN})_2]$ heterocycle is formed. The N–C bond lengths within the NCNCN unit, which is most likely formed via intermediate formation of a guanidinate unit and elimination of $RN(ZnMe)_2$ as was described previously,[14] significantly differ. The bond lengths of the terminal C–N bonds [N1–C2 1.259(4), N3–C3 1.256(4) Å] are typical for a C=N double bond, whereas those of the inner C–N–C unit [N2–C2 1.398(4), N2–C3 1.399(4) Å] are in the range typically observed for C–N single bonds. These distances clearly show that the π-electrons within the N=C–N–C=N moiety are fully localized. In contrast, the C–N bond lengths within the eight-membered $[Zn_2(\mu\text{-NCN})_2]$ ring of **2** [N4–C4 1.335(4), N5–C4 1.311(4), N6–C5 1.300(4), N7–C5 1.338(4) Å] are similar, which indicates a delocalized π-electron system. Comparable findings have been reported for $\{[MeZn]_2[C(i\text{Pr}NCNi\text{Pr})_2(C_2(Ni\text{Pr})_3)]\}$.[13]

The formation of **1** and **3** clearly prove that multinuclear zinc amidinate complexes can generally be prepared by reaction of $ZnMe_2$ with sterically less-demanding carbodiimides. In order to clarify whether the presence of electron-withdrawing groups bound to the N atoms more selectively yield tetranuclear zinc amidinate complexes $\{[MeZn]_4[C(RNCNR)_4]\}$ (as observed for the reaction of $ZnMe_2$ with PhN=C=NPh, in which **3** was obtained in almost quantitative yield without the formation of any by-products as typically observed in reactions with bis(alkyl)carbodiimides), the reactions have to be extended to other carbodiimides containing perfluorated substituents such as CF_3 and C_6F_5.

Reactions of tetranuclear complexes $\{[MeZn]_4[C(RNCNR)_4]\}$ (R = *i*Pr, Et, Ph) with O–H and N–H acidic alcohols and amines failed to give the expected alkoxides and amides, respectively. These findings clearly reveal that the nucleophilicity of the Me group is rather low. We therefore became interested in halide-substituted complexes of the general type $\{[XZn]_4[C(RNCNR)_4]\}$, which were expected to be promising starting reagents for salt metathesis reactions.[15] Moreover, (multi)cationic complexes may be accessible as well. However, while $\{[MeZn]_4[C(i\text{Pr}NCNi\text{Pr})_4]\}$ was found to react cleanly with aluminum halides AlX_3 (X = Cl, Br, I) with the formation of $\{[XZn]_4[C(i\text{Pr}NCNi\text{Pr})_4]\}$,[16] reactions of **1** and **3** with AlX_3 failed to give the expected complexes $\{[XZn]_4[C(RNCNR)_4]\}$ (R = Et, Ph; X = Cl, Br, I). We therefore investigated reactions of $\{[ClZn]_4[C(i\text{Pr}NCNi\text{Pr})_4]\}$ with halide abstraction reagents such as $AgPF_6$ and AgOTf (Tf = OSO_2CF_3), but these only yielded insoluble precipitates, which could not be characterized in more detail, to date. In contrast, reactions of $\{[ClZn]_4[C(i\text{Pr}NCNi\text{Pr})_4]\}$ with two equivalents of $AlCl_3$ and $GaCl_3$ yielded the corresponding Lewis acid–base adducts $\{[MCl_3]_2[ClZn]_4[C(i\text{Pr}NCNi\text{Pr})_4]\}$ [M = Al (**4**), Ga (**5**)].

Single crystals of **4** and **5** suitable for single-crystal X-ray diffraction studies were obtained from solutions in toluene (Figures 4 and 5). Both complexes are isostructural and crystallize in the orthorhombic space group *Pbcn*. The central structural parameters such as Zn–N, C–N, and C–C bond lengths as well as N–C–N, C–C–C, and N–Zn–N bond angles are almost unchanged relative to the starting complex $\{[\text{ClZn}]_4[\text{C}(i\text{PrNCN}i\text{Pr})_4]\}$. In contrast, the Zn–Cl bond lengths differ significantly from each other. While those of the terminally bonded Cl2 atoms [2.1571(5) Å **4**; 2.1564(6) Å **5**] are comparable to the Zn–Cl bond length reported for $\{(\text{ClZn})_4[\text{C}(i\text{PrNCN}i\text{Pr})_4]\}$ (av. value 2.172 Å),[15] the bridging Cl1 atoms show both significantly longer Zn–Cl (2.2732(5) Å **4**; 2.2643(6) Å **5**) and M–Cl bond lengths [Al(1)–Cl(1) 2.2814(9) Å **4**; Ga(1)–Cl(1) 2.3389(6) Å **5**] than the average value of the remaining three terminal M–Cl bond lengths [Al–$\text{Cl}_{\text{term.}}$ 2.1013(6) Å **4**; Ga–$\text{Cl}_{\text{term.}}$ 2.1342(7) Å **5**]. A similar bond length difference between terminal and bridging M–Cl bonds was previously reported for $\{[(\text{Me}_3\text{Si})\text{NCH}_2\text{CH}_2]\text{N}(\text{Me}_3\text{Si})\}\text{VCl}_2\text{AlCl}_3$ [V–$\text{Cl}_{\text{term.}}$ 2.244(1) Å, V–$\text{Cl}_{\text{bridg.}}$ 2.4649(1)][17] and $\text{Cp}_2\text{ZrCl}(\text{AlCl}_4)$ [Zr–$\text{Cl}_{\text{term.}}$ 2.406(3) Å, Zr–$\text{Cl}_{\text{bridg.}}$ 2.605(2) Å],[18] in which the AlCl_3 moieties were considered as $[\text{AlCl}_4]^-$ anions, which loosely coordinate to the cationic metal moiety. However, **4** and **5** rather form donor–acceptor complexes since the bridging M–Cl bond lengths (M = Al, Ga) are significantly elongated relative to M–Cl distances typically observed for tetrachloroaluminates (Al–Cl 2.069–2.149 Å) and –gallanates (Ga–Cl 2.121–2.195 Å).[19] Moreover, the Cl–M–Cl angles as observed in **4** and **5** also differ significantly from ideal tetrahedral geometry as would be expected for MCl_4^- anions (**4**: av. $\text{Cl}_{\text{term.}}$–Al–$\text{Cl}_{\text{bridg.}}$ 103.8°, $\text{Cl}_{\text{term.}}$–Al–$\text{Cl}_{\text{term.}}$ 114.5°; **5**: Cl–Ga–$\text{Cl}_{\text{bridg.}}$ 103.1°, $\text{Cl}_{\text{term.}}$–Ga–$\text{Cl}_{\text{term.}}$ 115.0°).

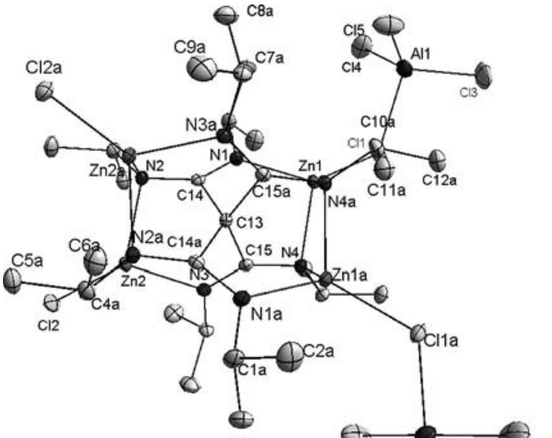


Figure 4. Solid-state structure of **4** (thermal ellipsoids are shown at the 50% probability level); H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1–Cl1 2.2732(5), Zn2–Cl2 2.1571(5), Zn1–N1 2.0523(17), Zn1–N4 2.0968(18), Zn1–N4a 2.1052(18), Zn2–N3 2.1009(17), Zn2–N2a 2.1494(18), Zn2–N2 2.1060(17), Al1–Cl1 2.2814(9), Al1–Cl3 2.0978(10), N4–C14 1.309(3), C13-C14a 1.570(2), C13–C15 1.573(2); N1–Zn1–N4a 104.43(7), N1–Zn1–N4 98.92(7), Cl1–Al1–Cl3 101.32(4), Cl3–Al1–Cl5 115.40(2), N2–C14–N1 136.90(19), C14–C13–C15 98.25(10), C14a-C13-C15 101.78(10), C15–C13–C15a 130.8(2), C14–C13–C14a 130.7(2). a: –*x* + 1,*y*, –*z* + 3/2.

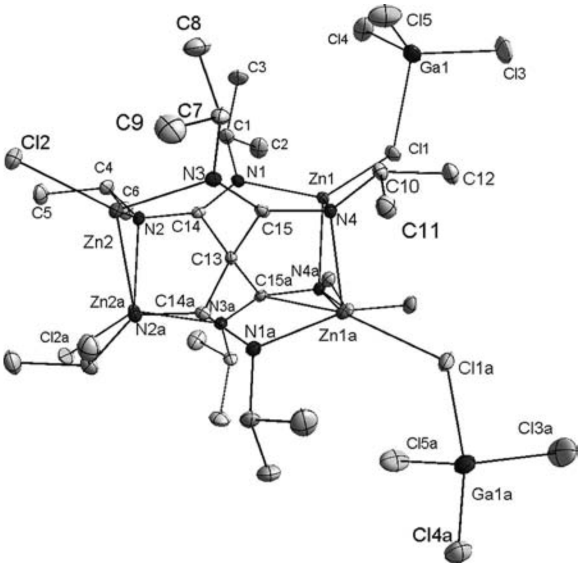


Figure 5. Solid-state structure of **5** (thermal ellipsoids are shown at the 50% probability level); H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1–Cl1 2.2643(6), Zn2–Cl2 2.1564(6), Zn1–N1 2.0521(18), Zn1–N4 2.0984(18), Zn1–N4a 2.1055(17), Zn2–N3 2.0972(18), Zn2–N2a 2.1454(17), Zn2–N2 2.1066(18), Ga1–Cl1 2.3389(6), Ga1–Cl3 2.1322(7), C13–C14 1.567(2), C13–C15 1.571(2); N1–Zn1–N4a 104.14(7), N1–Zn1–N4 98.88(7), Cl1–Ga1–Cl3 100.60(3), Cl3–Ga1–Cl4 114.57(3), N2–C14–N1 136.81(19), C14–C13–C15 98.47(10), C14a-C13-C15 101.50(10), C15–C13–C15a 130.7(2), C14a–C13–C14 130.9(2). a: –*x* + 1,y, –*z* + 3/2.

According to these structural findings, **4** and **5** are best described as Lewis acid–base adducts, which still show significant attractive interactions between the Zn and the Cl atoms. Several attempts to coordinate additional MX_3 Lewis acids to the two terminally bonded Cl atoms failed. In these reactions, which were performed with up to a five-fold excess of MX_3, colorless solids precipitated. These solids were completely insoluble in non-coordinating organic solvents as well as in 1,2-difluorobenzene.

Conclusions

Cluster-type zinc amidinate complexes **1**–**3** were obtained from reactions of ZnMe_2 and the corresponding carbodiimides. These reactions were found to be strongly favored by small organic substituents bound to the N atoms of the carbodiimide. Moreover, carbodiimides containing electron-withdrawing groups at the N atoms more selectively form the tetranuclear complex in even shorter reaction times, as was observed for the synthesis of **3**. Unfortunately, complexes **1** and **3** failed to react with aluminum trihalides with the formation of halide-substituted complexes $\{[\text{ClZn}]_4[\text{C}(\text{RNCNR})_4]\}$. Complexes of this type are promising starting reagents for the synthesis of cationic complexes, as was shown in reactions of {$[ClZn]_4[C(i\text{PrNCN}i\text{Pr})_4]$} with $AlCl_3$ and $GaCl_3$ to yield Lewis acid–base adducts of the type {$[MCl_3]_2[ClZn]_4[C(i\text{PrNCN}i\text{Pr})_4]$} [M = Al (**4**), Ga (**5**)]. Further reactions with regard to the synthesis of cationic zinc complexes are currently under investigation.

Experimental Section

General Procedures: All manipulations were performed under an Ar atmosphere. Solvents were carefully dried with Na/K and degassed prior to use. $ZnMe_2$ (1.2 M in toluene) was purchased from Acros and used as received, and EtN=C=NEt,[20] PhN=C=NPh[21] and {$[ClZn]_4[C(i\text{PrNCN}i\text{Pr})_4]$}[16] were prepared according to literature methods. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker DMX 300 spectrometer and are referenced to internal C_6D_5H (^1H: δ = 7.154; ^{13}C: δ = 128.0 ppm). IR spectra were recorded on an ALPHA-T FTIR spectrometer equipped with a single-reflection ATR sampling module. Melting points were measured in sealed capillaries and were not corrected. Elemental analyses were performed at the Elementaranalyse Labor of the University of Essen.

{$[MeZn]_4[C(EtNCNEt)_4]$} (1): $ZnMe_2$ (0.48 g, 5 mmol) and $C(NEt)_2$-(1.03 g, 5 mmol) were stirred for 2 d at 90 °C to yield a colorless solid, which was suspended in *n*-pentane (30 mL) and filtered. The filtrate was stored at –30 °C, and colorless **1** was obtained within 12 h. The pentane-insoluble residue was dissolved in toluene and stored at –30 °C to yield colorless **2** over 24 h. Yield (isolated crystals) 0.51 g (56%). Melting point: >220 °C. $C_{25}H_{52}N_8Zn_4$ (726.23 g/mol): calcd. C 41.3, H 7.2, N 15.4; found C 41.3, H 7.2, N 15.3. ^1H NMR (500 MHz, C_6D_6, 25 °C): δ = –0.23 (s, 3 H, Zn*Me*), 0.89 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, CH_3), 1.36 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, CH_3), 3.29 (q, $^3J_{HH}$ = 7.2 Hz, 2 H, CH_2), 3.30 (q, $^3J_{HH}$ = 7.2 Hz, 2 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 25 °C): δ = –14.3 (s, Zn*Me*), 17.0 (CH_3), 18.1 (CH_3), 41.9 (CH_2), 43.4 (CH_2), 172.3 (NCN) ppm. IR: $\tilde{\nu}$ = 2966, 2928, 2862, 2829, 583, 1548, 1478, 1446, 1377, 1329, 1296, 1263, 1133, 1102, 1040, 984, 901, 863, 818, 771, 669, 648, 524, 493, 434 cm^{-1}.

{$[MeZn]_2[C(EtNCNEt)_2(C_2(NEt)_3)]$} (2): $ZnMe_2$ (4.2 mL, 1.2 M in toluene, 5 mmol) and purified $(EtN)_2C$ (2.06 g, 10 mmol) were stirred for 5 d at 110 °C. All volatiles were removed at reduced pressure, and the resulting solid was dissolved in hexane (30 mL) and stored at 0 °C. Colorless crystals of **2** were formed over 24 h and were isolated by filtration. Yield (isolated crystals) 0.61 g (47%). Melting point: 118 °C. $C_{21}H_{41}N_7Zn_2$ (522.35 g/mol): calcd. C 48.29, H 7.91, N 18.77; found C 48.56, H 8.13, N 18.23. ^1H NMR (500 MHz, C_6D_6, 25 °C): δ = –0.07 (s, 6 H, Zn*Me*), 0.32 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, CH_2CH_3), 1.23 (t, $^3J_{HH}$ = 7.2 Hz, 6 H, CH_2CH_3), 1.30 (t, $^3J_{HH}$ = 7.2 Hz, 12 H, CH_2CH_3), 2.40 (q, $^3J_{HH}$ = 7.2 Hz, 2 H, CH_2CH_3), 3.03 (q, $^3J_{HH}$ = 7.2 Hz, 4 H, CH_2CH_3), 3.64 (q, $^3J_{HH}$ = 7.2 Hz, 8 H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 25 °C): δ = –14.8 (Zn*Me*), 16.2 (CH_2CH_3), 17.1 (CH_2CH_3), 19.3 (CH_2CH_3), 30.5 (CH_2CH_3), 41.8 (CH_2CH_3), 42.9 (CH_2CH_3) ppm. Resonances of the NCN unit were not observed because of the limited solubility of **2** in organic solvents. ATR-IR: $\tilde{\nu}$ = 2963, 2925, 2890, 2822, 1694, 1572, 1474, 1443, 1376, 1320, 1261, 1155, 1099, 1031, 967, 801, 637, 609, 518, 436 cm^{-1}.

{$[MeZn]_4[C(PhNCNPh)_4]$} (3): $ZnMe_2$ (0.48 g, 5 mmol) and $C(NPh)_2$ (0.97 g, 5 mmol) were stirred for 2 d at 90 °C. The resulting solid was dissolved in toluene (30 mL) and stored at –30 °C to yield colorless crystals of **3** over 12 h. Yield 1.33 g (96%). Melting point: >220 °C. $C_{57}H_{52}N_8Zn_4$ (1110.58 g/mol): calcd. C 61.6, H 4.7, N 10.1; found C 61.6, H 4.6, N 10.1. ^1H NMR (500 MHz, C_6D_6, 25 °C): δ = –0.29 (s, 12 H, Zn*Me*), 6.56–7.15 (m, 40 H, *Ph*) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 25 °C): δ = –14.5 (Zn*Me*), 123.7 (*Ph*), 123.7 (*Ph*), 124.3 (*Ph*), 128.5 (*Ph*), 128.5 (*Ph*), 144.4 (*Ph*), 144.7 (*Ph*), 169.5 (s, NCN) ppm. IR: $\tilde{\nu}$ = 3068, 3028, 2962, 2906, 2844, 1594, 1554, 1519 1485, 1449, 1330, 1259, 1071, 1021, 925, 797, 755, 728, 686, 595, 542, 512, 463, 417, 404 cm^{-1}.

{$[MCl_3]_2[ClZn]_4[C(i\text{PrNCN}i\text{Pr})_4]$} [M = Al (4), Ga (5)]: {$[ClZn]_4$-$[C(i\text{PrNCN}i\text{Pr})_4]$} (0.5 g, 0.54 mmol) and MCl_3 (0.14 g M = Al, 0.32 g M = Ga; 1.08 mmol) were dissolved in toluene (15 mL) and stirred for 1 h at 100 °C. Colorless crystals of **4** and **5** formed within 24 h upon slow cooling to room temperature.

{$[AlCl_3]_2[ClZn]_4[C(i\text{PrNCN}i\text{Pr})_4]$} (4): Yield (isolated crystals): 0.56 g (87%). Melting point: >250 °C. $C_{29}H_{56}Al_2Cl_{10}N_8Zn_4$ (1186.94 g/mol): calcd. C 29.34, H 4.75, N 9.44; found C 29.12, H 4.63, N 9.21. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 1.15 [d, $^3J_{HH}$ = 6.4 Hz, 24 H, $CH(CH_3)_2$], 1.24 [d, $^3J_{HH}$ = 6.4 Hz, 24 H, $CH(CH_3)_2$], 3.72 [sept, $^3J_{HH}$ = 6.4 Hz, 4 H, $CH(CH_3)_2$], 3.93 [sept, $^3J_{HH}$ = 6.4 Hz, 4 H, $CH(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (200 MHz, C_6D_6, 25 °C): δ = 23.9 [$CH(CH_3)_2$], 24.4 [$CH(CH_3)_2$], 49.5 [$CH(CH_3)_2$], 50.6 [$CH(CH_3)_2$], 71.8 (CC4), 169.4 (NCN) ppm. ATR-IR: $\tilde{\nu}$ = 2967, 2932, 2905, 2875, 1562, 1533, 1451, 1391, 1372, 1327, 1305, 1255, 1235, 1121, 1083, 1017, 871, 786, 732, 694, 669, 538, 526, 472 cm^{-1}.

{$[GaCl_3]_2[ClZn]_4[C(i\text{PrNCN}i\text{Pr})_4]$} (5): Yield (isolated crystals): 0.51 g (74%). Melting point: >250 °C (dec.). $C_{29}H_{56}Cl_{10}Ga_2N_8Zn_4$ (1272.27 g/mol): calcd. C 27.38, H 4.44, N 8.81; found C 26.68, H 4.38, N 8.64. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 1.16 [d, $^3J_{HH}$ = 6.4 Hz, 24 H, $CH(CH_3)_2$], 1.30 [d, $^3J_{HH}$ = 6.4 Hz, 24 H, $CH(CH_3)_2$], 3.71 [sept, $^3J_{HH}$ = 6.4 Hz, 4 H, $CH(CH_3)_2$], 3.96 [sept, $^3J_{HH}$ = 6.4 Hz, 4 H, $CH(CH_3)_2$] ppm. $^{13}C\{^1H\}$ NMR (200 MHz, C_6D_6, 25 °C): δ = 23.8 [$CH(CH_3)_2$], 24.4 [$CH(CH_3)_2$], 49.3 [$CH(CH_3)_2$], 50.6 [$CH(CH_3)_2$], 71.9 (CC4), 169.5 (NCN) ppm. ATR-IR: $\tilde{\nu}$ = 2974, 2932, 2875, 1558, 1530, 1511, 1451, 1391, 1372, 1267, 1229, 1121, 1071, 931, 890, 868, 814, 732, 694, 647, 583, 520, 463, 409 cm^{-1}.

Single-Crystal X-ray Analyses: Crystallographic data of **1**–**5**, which were collected on a Bruker AXS D8 Kappa diffractometer (Mo-K_α radiation, λ = 0.71073 Å), are summarized in Table 1. Figures 1–5 show diagrams of the solid-state structures of **1**–**5**. The structures were solved by direct methods (SHELXS-97)[22] and refined by full-matrix least-squares on F^2. Absorption corrections were performed semi-empirically from equivalent reflections on the basis of multiscans (Bruker AXS APEX2). All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97)[23] on idealized geometries with the 1.2 fold (1.5 fold for methyl groups) isotropic displacement parameters of the equivalent U_{ij} of the corresponding carbon atom. The crystal of **2** was racemically twinned and refined accordingly. Complex **3** contained a toluene molecule disordered over two positions. The phenyl rings were constrained to regular hexagons. Complexes **4** und **5** contained 1.5 toluene molecules severely disordered over a twofold axis. The half-occupied one was constrained to a regular hexagon and refined with fixed U and without hydrogen atoms. The methyl hydrogen atoms of the fully occupied toluene were refined as idealized disorder with two positions rotated from each other by 60°.

CCDC-794409 (**1**), CCDC-794408 (**2**), CCDC-794412 (**3**), CCDC-826704 (**4**), CCDC-826705 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystallographic data for **1**–**5**.

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{25}H_{52}N_8Zn_4$	$C_{21}H_{41}N_7Zn_2$	$C_{57}H_{52}N_8Zn_4\cdot[C_7H_8]$	$C_{29}H_{56}Al_2Cl_{10}N_8Zn_4\cdot1.5[C_7H_8]$	$C_{29}H_{56}Ga_2Cl_{10}N_8Zn_4\cdot1.5[C_7H_8]$
Molecular mass	726.23	522.35	1202.68	1326.93	1412.41
Crystal system	triclinic	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	$P\bar{1}$	$P2_1$	*C*2/*c*	*Pbcn*	*Pbcn*
a [Å]	11.7097(4)	10.7283(6)	22.1716(8)	14.3298(9)	14.3175(9)
b [Å]	11.7102(4)	21.1976(12)	15.6427(5)	19.3470(12)	19.3167(12)
c [Å]	11.8034(4)	11.6755(7)	17.4266(6)	19.7439(12)	19.7752(13)
α [°]	93.757(2)	90	90	90	90
β [°]	92.321(2)	106.564(3)	110.926(2)	90	90
γ [°]	96.337(2)	90	90	90	90
V [Å^3]	1603.31(9)	2545.0(3)	5645.3(3)	5473.8(6)	5469.2(6)
Z	2	4	4	4	4
T [K]	103(2)	100(1)	103(1)	100(1)	100(1)
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
μ [mm^{-1}]	2.983	1.906	1.727	2.290	3.224
$D_{calcd.}$ [g cm^{-3}]	1.504	1.363	1.415	1.610	1.715
$2\theta_{max}$ [°]	61.2	50.8	60.1	56.6	56.7
Crystal dimension [mm]	0.36 × 0.32 × 0.28	0.27 × 0.13 × 0.10	0.22 × 0.18 × 0.13	0.45 × 0.37 × 0.28	0.34 × 0.25 × 0.22
No. of reflections	25594	20037	33112	46986	57651
No. unique reflections	9582	8629	8231	6713	6788
R_{merg}	0.0231	0.0227	0.0291	0.0234	0.0239
No. of parameters/restraints	334/0	542/1	328/0	254/0	254/0
*R*1[a]	0.0255	0.0284	0.0340	0.0292	0.0276
*wR*2[b]	0.0545	0.0667	0.0968	0.0833	0.0750
Goodness-of-fit[c]	1.043	1.059	1.032	1.048	1.075
Max./min. transmission	0.75/0.56	0.75/0.64	0.75/0.60	0.75/0.63	0.75/0.44
Final max/min. Δ*ρ* [e Å^{-3}]	0.680/–0.344	0.690/–0.263	0.840/–0.581	1.022/–1.002	1.161/–0.888

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ [for $I > 2\sigma(I)$]. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] Goodness-of-fit $= \{\Sigma[w(|F_o^2| - |F_c^2|)^2]/(N_{observns.} - N_{params.})\}^{1/2}$. $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ with $P = [F_o^2 + 2F_c^2]/3$, a and b are constants chosen by the program.

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