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Structural diversity of alkylzinc complexes with pyrrole-based *N*,*O*-ligands: from molecular complexes to coordination polymers†

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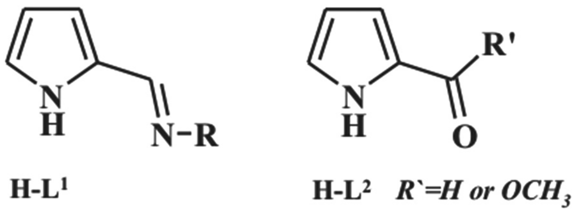
The equimolar reaction of R$_2$Zn (where R = Et or ^{t}Bu) with pyrrole-based *N*,*O*-proligands afforded a series of alkylzinc compounds with a variety of intriguing structures including a hexanuclear macrocyclic complex and 1D coordination polymers with versatile intramolecular or intermolecular bonding modes.

The variety of chemistries displayed by organozinc complexes supported by ligand systems that incorporate a pyrrolide anion and terminal N′-donor sites is well documented. The combination of the pyrrolyl skeleton and N-donor sites renders *N*,*N*′- and *N*′,*N*,*N*′-multifunctional ligands with versatile intramolecular or intermolecular bonding modes to zinc centers.[1–3] It is also pertinent to note that multidentate ligands with pyrrolic units in combination with Zn(II) ions have appeared as an interesting building block for the supramolecular architecture through self-assembly.[4,5] Moreover, alkylzinc complexes with these versatile ligands show remarkable reactivity in a variety of metal-mediated transformations.[2a,b,6,7] Our previous studies show that *N*,*N*′-pyrroles (**H-L^1**, Scheme 1) are versatile supporting proligands. For example, the controlled oxygenation of [RZn(*N*,*N*′)] complexes (where *N*,*N*′ = 2,2′-(1′-pyrrolinyl)-pyrrole) provided a novel zinc alkyl peroxide or zinc oxo-encapsulated cluster, the formation of which was mediated by the nature of zinc-bonded alkyl substituents.[6b] Strikingly, in the case of a [EtZn(*N*′,*N*,*N*′)] complex (where *N*′,*N*,*N*′ = deprotonated 2,5-bis[(2,6-diisopropylphenyl)-aldimino]-pyrrole) the oxygenation of the Et–Zn subunit led to the formation of zinc acetate species.[6c] This particular ligand set is also able to promote the catalytic activity of both zinc alkoxides in the ring-opening polymerization of cyclic esters,[8] or zinc alkylperoxides in the asymmetric epoxidations of enones.[9] Surprisingly, the related ligand systems incorporating a pyrrolide anion and a terminal carbonyl O-donor site still remain poorly explored in the field of organozinc chemistry. As a part of our ongoing interest in the development of new reaction systems based on zinc complexes supported by multidentate pyrrole-based ligands, herein we have focused on the versatile bonding modes of monoanionic pyrrolate ligands derived from 1*H*-pyrrole-2-carboxylate (H–PyrC(O)OMe) and 1*H*-pyrrole-2-carboxaldehyde (H–PyrC(O)H) as model proligands (**H-L^2**, Scheme 1).



Scheme 1 Representation of pyrrole-based *N*,*O*-proligands.

The equimolar reaction of R$_2$Zn (where R = Et or ^{t}Bu) with 1 equiv. of methyl 1*H*-pyrrole-2-carboxylate (H–PyrC(O)OMe) in a non-coordinating solvent at −78 °C afforded the alkylzinc complexes of general formula [RZn(PyrC(O)OMe)]$_n$, where R = Et ($\mathbf{1}_n$) and ^{t}Bu (**2**), respectively (Scheme 2). The single crystals of 1n suitable for the X-ray diffraction studies were isolated from a toluene solution. Despite numerous attempts, the isolation of single crystals of **2** suitable for X-ray diffraction studies was unsuccessful due to its good solubility, thus complex **2** was characterized spectroscopically (for details see the ESI†).

Complex $\mathbf{1}_n$ crystallized as colorless needles in the $P2_1/m$ space group. The monomeric basic unit of $\mathbf{1}_n$ consists of the three-coordinated zinc center supported by one pyrrolide PyrC(O)OMe ligand (Fig. 1a). The coordination sphere of the zinc atom is completed with the ethyl group. The central five-membered ring formed by the *N*,*O*-ligand and the metal center is planar (the torsion angle between C6–C7–O1–Zn1 is 0.00° with the ethyl group located in the same plane). The Zn1–N1$_{\text{pyrrole}}$ and Zn1–O1$_{\text{carbonyl}}$ bond lengths are 1.930(3) Å and

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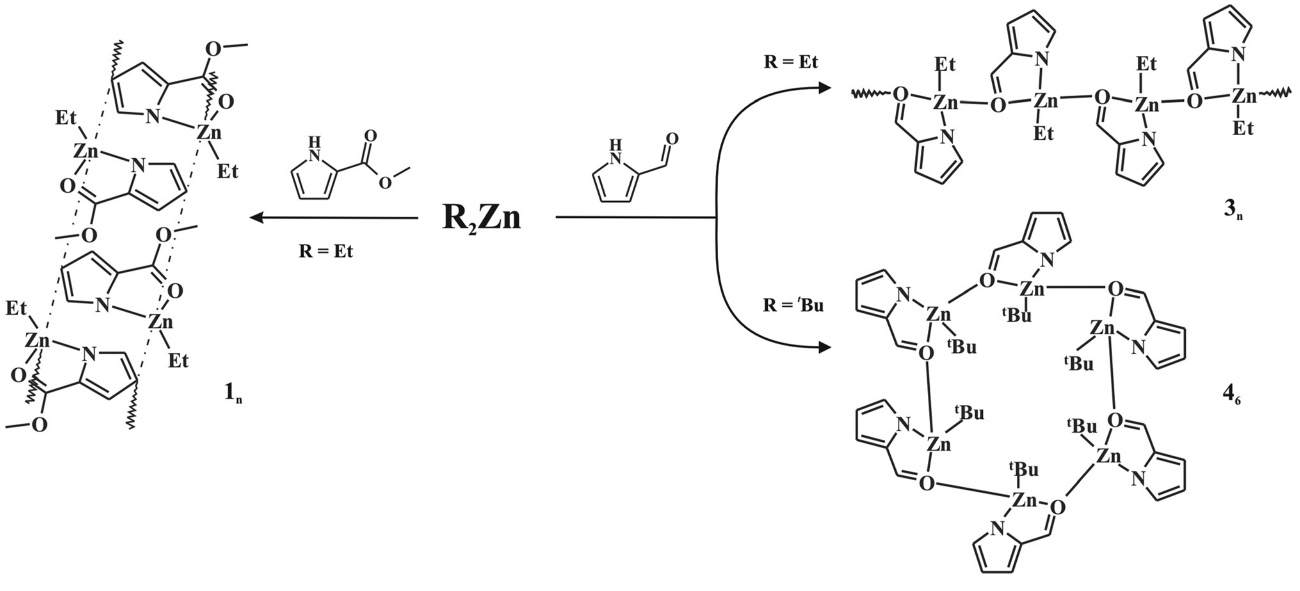
† Electronic supplementary information (ESI) available: All experimental details and characterization data. CCDC 1453366–1453368. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt00674d



Scheme 2 The solid state structures of $\mathbf{1}_n$, $\mathbf{3}_n$ and $\mathbf{4}_6$.

2.185(3) Å, respectively. The crystal structure analysis revealed that the molecules of **1** form a 1D coordination polymer from the alternating molecular units. The adjacent molecules of **1** are connected by a network of intermolecular Zn⋯π interactions between the coordinatively unsaturated metal centers and the C(4) carbon atoms of the pyrrolide ring (with the Zn1⋯π(C4′) and Zn1⋯π(C4″) distances of 3.119(2) Å, dotted lines in Fig. 1b). Similar Zn⋯π interactions were observed previously for a dimeric $[^t\mathrm{BuZn(PyrPri)}]_2$ complex supported by a bifunctional *N*,*N*-pyrrolylaldiminato ligand.[1e,7] We note that in contrast to **1**, the related low-alkyl zinc complexes incorporating pyrrolylaldiminato ligands were unstable and the formation of bis(pyrrolylaldiminato) compounds was only observed.[1a,b,f,g,3c]

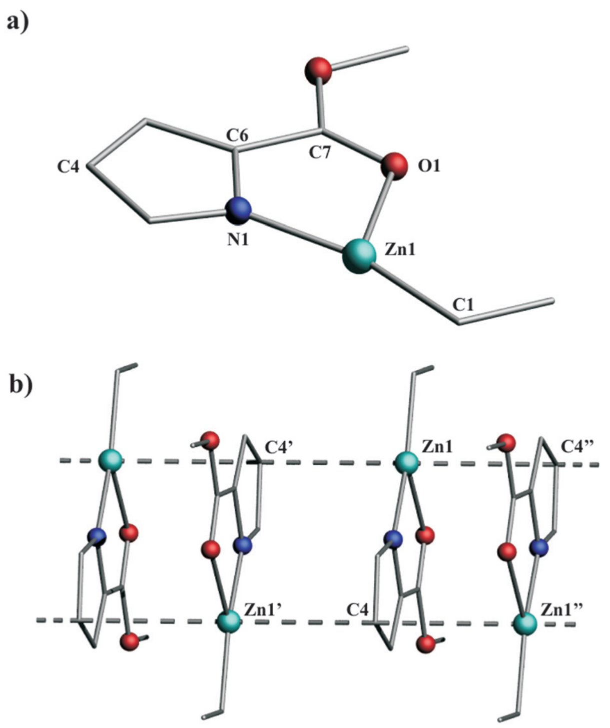


Fig. 1 (a) The molecular structure of **1** and (b) its polymeric form, created through Zn⋯π interactions. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zn1–N1 1.930(3), Zn1–O1 2.185(3), Zn1–C1 1.935(4), Zn1–C4′ 3.119(2); N1–Zn1–C1 161.4(2), O1–Zn1–C1 116.9(1), N1–Zn1–O1 81.7(1).

To understand more in depth the factors which determine the structure and stability of alkylzinc complexes supported by *N*,*O*-pyrrole based monoanionic ligands, we investigated the reactivity of 1*H*-pyrrole-2-carboxaldehyde (H–PyrC(O)H) towards R_2Zn species (where R = Et or ᵗBu). The equimolar reaction between H–PyrC(O)H and R_2Zn at −78 °C afforded two alkylzinc complexes of the general formula $[\mathrm{RZn(PyrC(O)H)}]_n$, where R = Et ($\mathbf{3}_n$) and ᵗBu ($\mathbf{4}_6$), respectively (Scheme 2). In both cases colorless needle-like crystals suitable for X-ray diffraction measurements were isolated from a toluene solution at room temperature. Compound $\mathbf{3}_n$ crystallizes in the monoclinic space group $P2_1/c$ as a 1D zig-zag coordination polymer (Fig. 2). The molecular unit **3** consists of a three-coordinate ethylzinc species supported by a chelating monoanionic *N*,*O*-pyrrole-2-carboxaldehyde ligand. The carbonyl oxygen atom O1 bridges the adjacent units of **3** with a μ_2-*O* mode and fulfills the coordination sphere of the metal center. Each [EtZn(PyrC(O)H)] unit is nearly planar (the torsion angle between C6–C7–O1–Zn1 is 0.9(4)°). The analysis of Zn1–O bond lengths clearly indicates the stronger coordination of the zinc center to the O1′ carbonyl oxygen atom from the adjacent unit when compared to the O1 atom (the $\mathrm{Zn–O_{carbonyl}}$ bond distances fall in the range of 2.091–2.189 Å, and the C–O dis-

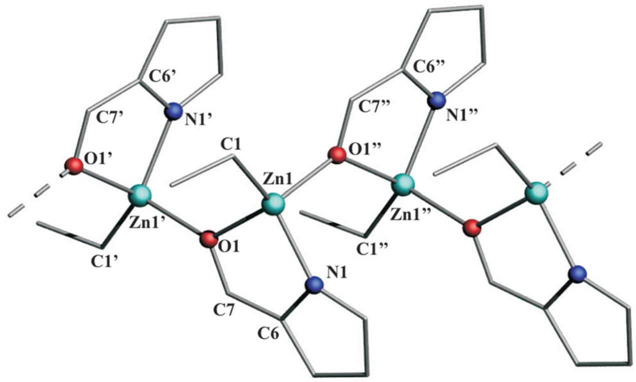


Fig. 2 The molecular structure of $\mathbf{3}_n$. Selected bond lengths (Å) and angles (°): Zn1–C1 1.964(4), Zn1–N1 1.994(3), Zn1–O1 2.189(3), Zn1–O1′ 2.091(3); C7–O1 1.292(5); N1–Zn1–C1 141.7(2), O1–Zn1–C1 115.6(2), C6–N1–Zn1 112.4(3), C7–O1–Zn1 108.1(2), O1–Zn1–O1″ 99.2(5).

tance is 1.292(5) Å). The supramolecular structure of $\mathbf{3}_n$ consists of repeating monomeric units [EtZn(PyrC(O)H)] rotated relative to one another by *ca.* 72°.

Compound $\mathbf{4}_6$ crystallizes in the $P\bar{1}$ space group from a toluene solution at room temperature.‡ The single-crystal X-ray diffraction analysis demonstrated that in the solid state complex $\mathbf{4}_6$ exists as a hexanuclear macrocyclic cluster [^{t}BuZn(PyrC(O)H)]$_6$. The molecular structure of $\mathbf{4}_6$ consists of six discrete monomeric units bridged by the oxygen atom of the aldehyde group with a μ$_2$-*O* mode (Fig. 3). The geometry of the zinc atoms in $\mathbf{4}_6$ is a distorted tetrahedral with angles in the range of 80.2° to 142.3°. The bond distance between the zinc center and the oxygen atoms is between 2.084 and 2.240 Å, while the Zn–N$_{\text{pyrrole}}$ distance varies from 1.976 to 1.996 Å (the average C–O distance is 1.280 Å). Similarly as observed in $\mathbf{3}_n$, the analysis of Zn–O$_{\text{carbonyl}}$ bond lengths in $\mathbf{4}_6$ confirmed the stronger binding affinity of the Zn atom to the carbonyl oxygen atom from the adjacent [^{t}BuZn(PyrC(O)H)] unit. We note that the average Zn–O$_{\text{carbonyl}}$ bond distances in $\mathbf{3}_n$ and $\mathbf{4}_6$ are significantly longer than that observed in dinuclear zinc complexes incorporating the bridging μ-*O*-enolate ligand (the corresponding Zn–O bond lengths fall around 2.0 Å)[10] as well as in a dimeric ethylzinc complex incorporating the μ-*O*,*N*-enolate chelating ligand, [EtZn(μ-*O*(Me)═(H)CN(Et)^{t}Bu)]$_2$ (average Zn–O bond distance is 2.067 Å).[11] Moreover, the 12-membered ring of $\mathbf{4}_6$ comprises six zinc atoms that are linked *via* O$_{\text{carbonyl}}$ atoms in the μ-*O* bridging fashion (Fig. 3). The Zn$_6$(μ-*O*)$_6$ central ring is non-planar around which the pyrrole ligands self-organize in an alternating "up and down" manner. All of the ^{t}Bu groups are directed outside of this macrocyclic ring. Thus, the structural analyses of $\mathbf{3}_n$ and $\mathbf{4}_6$ revealed that the presence of a more bulky ^{t}Bu group favors the formation of a hexanuclear macrocycle. Notably, in $\mathbf{3}_n$ and $\mathbf{4}_6$ the coordination mode of pyrrole ligands through the O$_{\text{carbonyl}}$ atom is unusual compared with the reported pyrrole-based complexes, which commonly appear as dimeric species joined by π or δ interactions between the metal center and the nitrogen atom from the pyrrole ring.

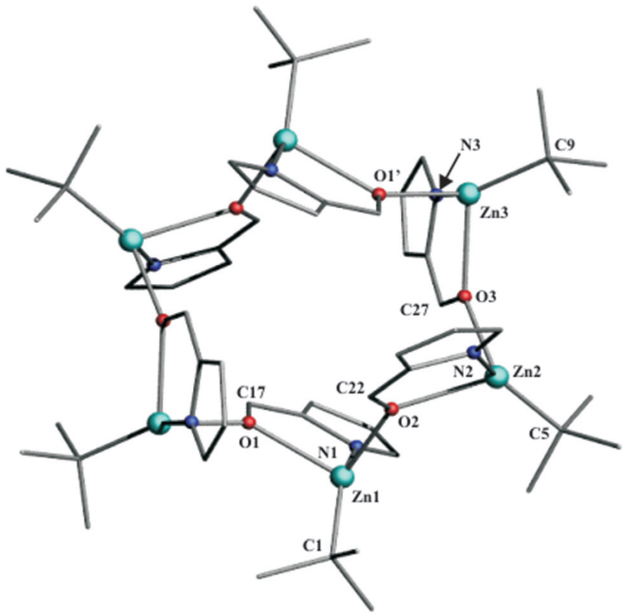


Fig. 3 The molecular structure of $\mathbf{4}_6$. Hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles (°): Zn1–C1 1.990(2), Zn1–N1 1.996(2), Zn1–O1 2.246(2), Zn1–O2 2.124(2), C17–O1 1.286(3), Zn2–C5 1.984(3), Zn2–N2 1.976(2), Zn2–O2 2.240(2), Zn2–O3 2.120(2), C22–O2 1.278(3), Zn3–C9 1.986(2), Zn3–N3 1.992(2), Zn3–O3 2.236(2), Zn3–O1′ 2.084(2), C27–O3 1.278(3); N1–Zn1–C1 138.9(1), O1–Zn1–C1 115.5(9), O1–Zn1–O2 96.39(7).

Conclusions

In conclusion, we demonstrated the diversity in bonding modes of pyrrole-based *N*,*O*-bifunctional monoanionic ligands in the solid state which resulted in the formation of a series of novel alkylzinc complexes. We isolated and characterized for the first time the non-covalent coordination polymers connected through Zn–π interactions. Moreover, we demonstrated a new type of connectivity in the alkylzinc pyrrole based complexes, through the Zn–O$_{\text{carbonyl}}$ interactions. These new types of interactions shed a new light on pyrrole-based complexes and could provide useful tools in the field of molecular engineering. Further studies on the factors controlling the structure and reactivity of the alkylzinc complexes supported by multifunctional *N*,*O*-pyrrole ligands are in progress.

Acknowledgements

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Notes and references

‡ Crystal data for $\mathbf{1}_n$; [C$_8$H$_{11}$NO$_2$Zn]$_n$: *M* = 218.55, crystal dimensions 0.30 × 0.15 × 0.08 mm^3, monoclinic, space group $P2_1/m$ (no. 11), *a* = 8.5170(6) Å, *b* = 6.2320(3) Å,

c = 8.7800(6) Å, β = 112.358(3)°, U = 430.99(5) Å^3, Z = 2, F(000) = 224, D_c = 1.684 g cm^{-3}, T = 100(2) K, μ(Mo-Kα) = 2.804 mm^{-1}, Nonius Kappa-CCD diffractometer, θ_{max} = 27.60°, R_1 = 0.0488, wR_2 = 0.0899 for all data, R_1 = 0.0398, wR_2 = 0.0847 for 932 reflections with $I_o > 2\sigma(I_o)$. The residual electron density = +0.45/−1.35 e Å^{-3}. CCDC 1453366.

Crystal data for **3$_n$**; [(C$_7$H$_9$NOZn)·0.5(C$_7$H$_8$]$_n$: M = 234.59, crystal dimensions 0.28 × 0.14 × 0.10 mm^3, monoclinic, space group $P2_1/c$ (no. 14), a = 9.3370(9) Å, b = 5.4990(4) Å, c = 20.667(2) Å, β = 100.267(3)°, U = 1044.14(16) Å^3, Z = 2, F(000) = 484, D_c = 1.492 g cm^{-3}, T = 100(2) K, μ(Mo-Kα) = 2.314 mm^{-1}, Nonius Kappa-CCD diffractometer, θ_{max} = 27.482°, R_1 = 0.0652, wR_2 = 0.1064 for all data, R_1 = 0.0508, wR_2 = 0.1007 for 1880 reflections with $I_o > 2\sigma(I_o)$. The residual electron density = +0.70/−0.61 e Å^{-3}. CCDC 1453367.

Crystal data for **4$_6$**; $C_{54}H_{78}N_6O_6Zn_6$: M = 1299.44, crystal dimensions 0.37 × 0.24 × 0.12 mm^3, triclinic, space group $P\bar{1}$ (no. 2), a = 11.3230(3) Å, b = 12.2960(6) Å, c = 12.9120(5) Å, α = 64.145(2)°, β = 68.888(2)°, γ = 86.131(3)°, U = 1500.55(11) Å^3, Z = 1, F(000) = 672, D_c = 1.438 g cm^{-3}, T = 100(2) K, μ(Mo-Kα) = 2.409 mm^{-1}, Nonius Kappa-CCD diffractometer, θ_{max} = 27.47°, R_1 = 0.0518, wR_2 = 0.1002 for all data, R_1 = 0.0383, wR_2 = 0.0954 for 5499 reflections with $I_o > 2\sigma(I_o)$. The residual electron density = +1.11/−0.76 e Å^{-3}. CCDC 1453368.

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