Dalton Transactions

COMMUNICATION



Cite this: Dalton Trans., 2016, 45, 7240

Received 19th February 2016, Accepted 24th March 2016 DOI: 10.1039/c6dt00674d

www.rsc.org/dalton

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_2Zn (where R = Et or ^tBu) with pyrrolebased *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**-L¹, Scheme 1) are versatile supporting proligands. For example, the controlled oxygenation of [RZn(N,N'] complexes (where N,N' = 2,2'-(1'-pyrrolinyl)-pyrrole)



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

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 2,5bis[(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 1H-pyrrole-2carboxylate (H-PyrC(O)OMe) and 1H-pyrrole-2-carboxaldehyde (H-PyrC(O)H) as model proligands (H-L², Scheme 1).

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The equimolar reaction of R_2Zn (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 (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_{pyrrole} and Zn1–O1_{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 1_n , 3_n and 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**



Fig. 1 (a) The molecular structure of 1 and (b) its polymeric form, created through $Zn \cdots \pi$ 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).

are connected by a network of intermolecular $\text{Zn}\cdots\pi$ interactions between the coordinatively unsaturated metal centers and the C(4) carbon atoms of the pyrrolide ring (with the Zn $1\cdots\pi$ (C4') and Zn $1\cdots\pi$ (C4") distances of 3.119(2) Å, dotted lines in Fig. 1b). Similar Zn $\cdots\pi$ interactions were observed previously for a dimeric [^tBuZn(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}

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 R2Zn at -78 °C afforded two alkylzinc complexes of the general formula $[RZn(PyrC(O)H)]_n$, where R = Et (3_n) and ^tBu (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 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 Zn-Ocarbonyl bond distances fall in the range of 2.091-2.189 Å, and the C-O dis-



Fig. 2 The molecular structure of **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 3_n consists of repeating monomeric units [EtZn(PyrC(O)H)] rotated relative to one another by *ca*. 72°.

Compound 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 4_6 exists as a hexanuclear macrocyclic cluster [^tBuZn(PyrC(O)H)]_6. The molecular structure of 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



Fig. 3 The molecular structure of **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).

the zinc atoms in 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_{pyrrole} distance varies from 1.976 to 1.996 Å (the average C–O distance is 1.280 Å). Similarly as observed in 3_n , the analysis of Zn-O_{carbonyl} bond lengths in 46 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 $Zn-O_{carbonyl}$ bond distances in 3_n and 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)^tBu)]₂ (average Zn-O bond distance is 2.067 Å).¹¹ Moreover, the 12-membered ring of 4_6 comprises six zinc atoms that are linked *via* O_{carbonyl} atoms in the μ -O bridging fashion (Fig. 3). The $Zn_6(\mu$ -O)₆ central ring is non-planar around which the pyrrole ligands self-organize in an alternating "up and down" manner. All of the ^tBu groups are directed outside of this macrocyclic ring. Thus, the structural analyses of 3_n and 4_6 revealed that the presence of a more bulky ^tBu group favors the formation of a hexanuclear macrocycle. Notably, in 3_n and 4_6 the coordination mode of pyrrole ligands through the Ocarbonyl 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.

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 $Zn-\pi$ interactions. Moreover, we demonstrated a new type of connectivity in the alkylzinc pyrrole based complexes, through the $Zn-O_{carbonyl}$ 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

The authors would like to acknowledge the National Science Centre, Grant Maestro DEC-2012/04/A/ST5/00595, for financial support.

Notes and references

Crystal data for**1**_n; [C₈H₁₁NO₂Zn]_n: <math>M = 218.55, crystal dimensions $0.30 \times 0.15 \times 0.08 \text{ mm}^3$, 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) Å³, 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°, R₁ = 0.0488, wR₂ = 0.0899 for all data, R₁ = 0.0398, wR₂ = 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*}; [(C₇H₉NOZn)·0.5(C₇H₈]_{*n*}: M = 234.59, crystal dimensions 0.28 × 0.14 × 0.10 mm³, monoclinic, space group $P2_1/c$ (no. 14), a = 9.3370(9) Å, b = 5.4990(4) Å, c = 20.667(2) Å, $\beta = 100.267(3)^\circ$, U = 1044.14(16) Å³, Z = 2, F(000) = 484, $D_c = 1.492$ g cm⁻³, T = 100(2) K, μ (Mo-K α) = 2.314 mm⁻¹, Nonius Kappa-CCD diffractometer, $\theta_{max} = 27.482^\circ$, $R_1 = 0.0652$, $wR_2 = 0.1064$ 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 4₆; C₅₄H₇₈N₆O₆Zn₆: M = 1299.44, crystal dimensions 0.37 × 0.24 × 0.12 mm³, triclinic, space group $P\bar{1}$ (no. 2), a = 11.3230(3) Å, b = 12.2960(6) Å, c = 12.9120(5) Å, $a = 64.145(2)^{\circ}$, $\beta = 68.888(2)^{\circ}$, $\gamma = 86.131(3)^{\circ}$, U = 1500.55(11) Å³, Z = 1, F(000) = 672, $D_c = 1.438$ g cm⁻³, T = 100(2) K, μ (Mo-K α) = 2.409 mm⁻¹, Nonius Kappa-CCD diffractometer, $\theta_{max} = 27.47^{\circ}$, $R_1 = 0.0518$, w $R_2 = 0.1002$ for all data, $R_1 = 0.0383$, w $R_2 = 0.0954$ for 5499 reflections with $I_0 > 2\sigma(I_0)$. The residual electron density = +1.11/-0.76 e Å⁻³. CCDC 1453368.

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