PAPER

Synthesis, structure and unique reactivity of the ethylzinc derivative of a bicyclic guanidine†

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An equimolar reaction between $ZnEt_2$ and 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine (hppH) results in the formation of EtZn(hpp) (**1**) which crystallizes as a trinuclear agglomerate with the guanidinate ligands spanning 4-coordinate Zn centers. Exposure of a pre-formed THF solution of **1** to undried air leads to a ZnO-incorporating derivative $\mathbf{1}_4$·ZnO, while an analogous experiment with CH_2Cl_2 as solvent leads to a novel tetranuclear mixed aggregate formulated as [EtOZn(hpp)]$_2$[ClZn(hpp)]$_2$ (**2**). The composition of **2** indicates that its formation proceeds *via* a complex multi-step reaction route that involves not only the oxygenation of ZnEt moieties, but also the activation of CH_2Cl_2, causing the transfer of a chloride anion to the Zn center. Compounds were characterized by ^{1}H NMR spectroscopy and single-crystal X-ray diffraction analysis.

Introduction

Zinc complexes supported by monoanionic *N,N*-bifunctional ligands are currently receiving considerable attention due to their increasing role in a wide variety of stoichiometric and catalytic transformations.[1] In this regard, the search for new ligand systems possessing the desired electronic and steric properties and the investigation of factors influencing the structure and reactivity of the resulting organozinc complexes represents a challenging task for organic and organometallic chemists. Our research groups have a long-standing interest in the synthesis, structural characterization and reactivity of designed alkylzinc complexes supported by a variety of multidentate ligands. This interest arises, in part, from the search for model systems with which to probe such fundamentally intriguing transformations as dioxygen activation[2] and oxide or hydride anion encapsulation.[3] As part of our ongoing efforts to gain a more intimate view of the role of supporting ligands in the reactions of zinc alkyls with O_2 and/or H_2O we turned our attention to guanidine-type ligands as suitable starting materials for further transformations. The choice of this ligand system was based on recent advances in understanding the coordination chemistry of *N,N*-bidentate

guanidinates[4,5] and our previous experience with these highly versatile ligands.[3,6] With regard to the chemistry of zinc guanidinates, recent investigations demonstrated that the equimolar reaction between R_2Zn and acyclic guanidines gives either a cisoid dimer of formulation MeZn(guanidinate)[5b,6a,7] or the homoleptic bis(guanidinate) chelate complex,[7] the selectivity of the reaction being mediated by the identity of the guanidine substrate. Unexpectedly, it was also demonstrated that the analogous reaction involving bicyclic guanidines and $ZnMe_2$ reproducibly gives the trinuclear adduct Zn_3(guanidinate)$_4Me_2$ as the only isolable product.[5f,6a]

We now report experiments involving the reactions of Et_2Zn with a bicyclic guanidine, 1,3,4,6,7,8-hexahydro-2H-pyrimido-[1,2-a]pyrimidine (hppH), that lead to the isolation of a trimer based on the formulation EtZn(hpp) (**1**), and its transformation *via* exposure to undried air into the ZnO-incorporating derivatives $\mathbf{1}_4$·ZnO and novel tetranuclear mixed aggregate [EtOZn(hpp)]$_2$[ClZn(hpp)]$_2$ (**2**) depending on the reaction conditions, as shown in Scheme 1.

Results and discussion

The treatment of a toluene solution of hppH with 1 eq. of diethylzinc, followed by solvent removal and recrystallization from hexane/toluene affords crystalline material which NMR spectroscopy reveals to incorporate ethyl and guanidinate moieties in a 1:1 ratio (Scheme 1). X-Ray diffraction corroborates this view, showing a trimer based on EtZn(hpp) (**1**), in each trinuclear agglomerate the guanidinate ligands span metal centers and render each metal ion tetracoordinate.
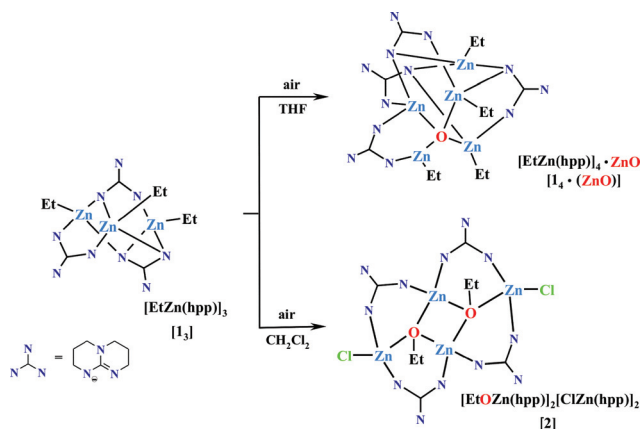
Overall, the trigonal Zn core of $\mathbf{1}_3$ is lipophilically wrapped by [hpp]$^-$ions that exhibit three fundamental types of bridging

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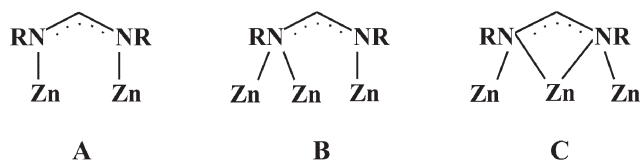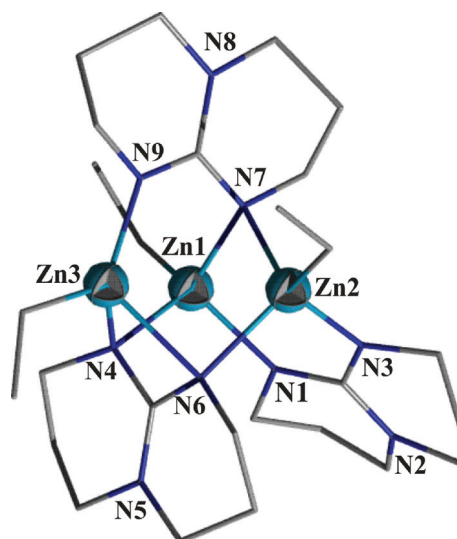
Scheme 1

Fig. 1 Molecular structure of 1_3; H-atoms, minor ligand disorder and lattice solvent omitted. Selected bond lengths (Å) and angles (°): C1–Zn1 2.013(8), C3–Zn2 1.995(8), C5–Zn3 1.983(10), N1–Zn1 1.996(6), N3–Zn2 2.029(6), N7–Zn2 2.111(6), N7–Zn1 2.105(6), N9–Zn3 1.961(8), N6–Zn2 2.107(7), N6–Zn3 2.080(7), N4–Zn1 2.161(6), N4–Zn3 2.290(7), N1–C13–N3 120.1(7), N7–C28–N9 119.5(8), N4–C21–N6 113.0(7). The distance between zinc atoms: Zn1–Zn2 3.084(2), Zn1–Zn3 3.181(7), Zn2–Zn3 3.361(7).

mode: $\kappa^1 N$–$\kappa^2 N'$ (N1–Zn1, N3–Zn2; ligand type **A** in Scheme 2), $\kappa^{1,2} N$–$\kappa^3 N'$ (N7–Zn1/2, N9–Zn3; type **B**), and $\kappa^{1,3} N$–$\kappa^{2,3} N'$ (N6–Zn2/3, N4–Zn1/3; type **C**). The action of ligand types **A** and **B** (Scheme 2 and Fig. 1) in which N1/3/9 each bond to a single metal center renders N1–Zn1, N3–Zn2 and N9–Zn3 relatively short [1.966(6)–2.029(6) Å] whereas the remaining metal coordination (by bridging N-centers in ligand types **B** and **C**) is relatively extended [2.080(7)–2.290(7) Å] and falls into two categories. While N4 and N7 straddle Zn1/3 and Zn1/2, respectively [N–Zn 2.105(6)–2.290(7) Å], N6 interacts more strongly with the metal core [N–Zn 2.080(7), 2.107(7) Å]. The N4/6-containing ligand is also relatively contracted at the guanidinate C-center [N4···C21···N6 113.1(7)° compares with a mean N···C···N of 120.2° in the remaining ligands].

In seeking to investigate the reactivity of **1** towards dioxygen in a number of control experiments a pre-formed THF solution of ethylzinc guanidinate was exposed to a source of O_2 for an extended period of time (*ca.* 2 h) prior to removal of the solvent, its replacement with a 1 : 2 THF/hexane mixture and storage at −15 °C. While it was found that the use of either pure O_2 or of pre-dried air failed to yield isolable products, exposure of the reaction mixture to undried air reproducibly gave a crystalline material. ^{1}H NMR spectroscopic analysis of this product demonstrated both the retention of a 1 : 1 ratio of ethyl and guanidinate moieties and also, through the observation of a multiplet at δ 0.33–0.70 ppm, the passivity of C–Zn bonds in **1** to limited oxygen or air exposure. X-Ray crystallography elucidated this single isolable product as 1_4·ZnO (Scheme 1 and Fig. 2), the structure of which reveals the presence of both type **A** and **B** guanidinate ligands. The above observations reinforce our view that four-coordinate EtZn species, such as are noted in the aggregate 1_3, are essentially resistant to oxygenation[8] and that the encapsulated oxide in 1_4·ZnO can be attributed to the reaction of **1** with H_2O rather than with O_2. To test this hypothesis, a small

amount of degassed water was added to a THF solution of **1**, and following similar reaction time and workup conditions as in the previous case, formation of crystalline 1_4·ZnO was again observed.

The captured oxide dianion in 1_4·ZnO resides at the center of a distorted tetrahedron of Zn centers but is significantly displaced from Zn2 [O···Zn2 3.427(7) Å]. The interaction between the oxide ion and Zn5 is 1.955(7) Å, with this Zn center
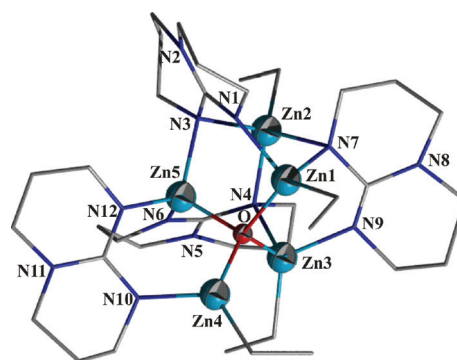

Fig. 2 Molecular structure of 1_4·ZnO; H-atoms and minor disorder omitted. Selected bond lengths (Å): C–Zn 1.996 (average), O14–Zn1 2.000(9), O14–Zn5 1.955(7), O14–Zn3 1.991(8), O14–Zn4 1.883(9), N3–Zn2 2.144(11), N7–Zn2 2.078(12), N4–Zn2 2.158(13), N1–Zn1 2.047(12), N7–Zn1 2.187(12), N4–Zn3 2.152(13), N9–Zn3 1.982(13), N12–Zn5 1.962(10), N6–Zn5 1.996(10), N3–Zn5 2.052(10), N10–Zn4 2.013(11), Zn1–O14–Zn3 108.6(4), Zn1–O14–Zn4 123.6(4), Zn1–O14–Zn5 105.2(4), Zn3–O14–Zn4 108.3(4), Zn3–O14–Zn5 105.7(4). The distance between zinc atoms: Zn1–Zn2 3.339(1), Zn1–Zn3 3.242(1), Zn2–Zn3 3.292(1), Zn1–Zn5 3.143(2), Zn2–Zn5 3.103(2), Zn3–Zn4 3.140(2), Zn3–Zn5 3.145(2), Zn4–Zn5 3.027(2).

Scheme 2

otherwise bonding only to guanidinate ligands and therefore constituting the remainder of an encapsulated fragment of *in situ* formed ZnO. The remaining metal ions each retain one Zn–C(Et) bond, again pointing to the stability of these bonds in aggregates based on **1** under limited air exposure. Overall, therefore, the product can be viewed not merely as a species that incorporates ZnO, but as a 4 : 1 adduct between the organometallic precursor EtZn(hpp) and a pre-organized ZnO unit.

As in **1**$_3$, each guanidinate ligand in **1**$_4$·ZnO spans metal centers. However, in contrast to the former structure, only type **A** (κ^1N–κ^2N′, N12–Zn5, N10–Zn4) and **B** ($\kappa^{1,2}$N–κ^3N′, N3–Zn2/5, N1–Zn1; N7–Zn1/2, N9–Zn3; N4–Zn2/3, N6–Zn5) ligands now present themselves. Within the structural core, three coordination environments can be noted for Zn. Zn1/3/5 are supported by bonds to two different types of N-center; one interacts directly with the Zn (N1/6/9) while the other (N3/4/7) bridges to a second metal ion. For each of Zn1/3/5, the metal bonding sphere is completed by interaction with the oxide core. Tetrahedral coordination of the oxide is itself completed by the final ZnEt moiety (Zn4), which is further complexed by a just single guanidinate N-center (N10). Uniquely, Zn2 interacts with three bridging N-centers (N3/4/7) and fails to interact with O [3.427 (7) Å].

Interestingly, performing analogous experiments using dichloromethane as a solvent strongly affects the reaction outcome. Exposing a pre-formed CH_2Cl_2 solution of **1** to undried air for an extended period of time (6 h) and following the same workup conditions as in the case of the formation of the oxocluster **1**$_4$·ZnO, formation of the new crystalline tetranuclear mixed aggregate [EtOZn(hpp)]$_2$[ClZn(hpp)]$_2$ (**2**) was observed reproducibly (Scheme 1). Single crystals were grown from a THF/hexane solution upon storage at −15 °C. The ^{1}H NMR spectrum of **2** shows resonances due to the O–Et groups (quartet and triplet at δ 3.14 and 1.10 ppm, respectively) and the guanidinate ligand in a 1 : 2 ratio. The composition of **2** indicates that this species forms *via* a complex multi-step reaction route that involves both the oxygenation of ZnEt units, giving [EtOZn(hpp)] moieties, and the independent activation of CH_2Cl_2, involving the transfer of a chloride anion to the Zn center and resulting in the formation of [ClZn(hpp)] moieties. The observations mentioned earlier concerning the oxygenation of **1** in THF solution indicated that the aggregate **1**$_3$ is relatively resistant towards the action of dioxygen. Therefore it is likely that the preliminary formation of [ClZn(hpp)] species, affording a mixed aggregate [EtZn(hpp)]$_x$[ClZn(hpp)]$_y$, precedes the oxygenation events. The mechanism by which CH_2Cl_2 activation occurs is not known; however, a related chloride transfer has been previously observed by ourselves for the reaction of Me$_2$Zn with a bifunctional alcohol in the presence of CH_2Cl_2.[9,10] It is interesting to note that dichloromethane is one of the most commonly used solvents for organic and organometallic reactions involving alkylzinc reagents. However, as far as we are aware, the influence of CH_2Cl_2 on the course or outcome of the reactions of organozinc substrates has never been considered. In this regard, our studies demonstrate that CH_2Cl_2 seems to be a highly undesirable solvent for reactions involving alkylzinc reagents supported by multidentate ligands.

The dimeric structure of **2** is shown in Fig. 3, for which agglomerate there exist two molecules of lattice THF. The
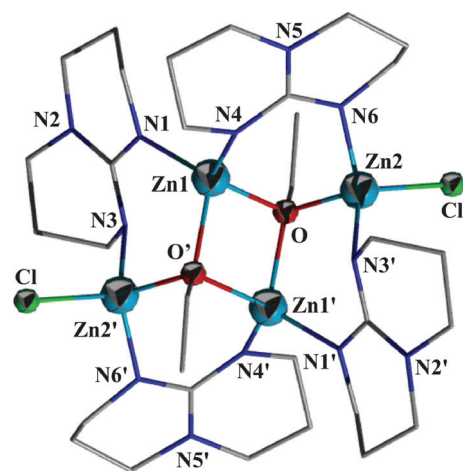

Fig. 3 Molecular structure of **2**; H-atoms, lattice THF and minor disorder omitted. Selected bond lengths (Å) and angles (°): O1–Zn1 2.039 (2), O1–Zn2 2.056(2), O1–Zn2′ 2.029(2), Cl1–Zn1 2.258(8), N1–Zn1 1.981(2), N4–Zn1 1.988(2), N3–Zn2 1.949(2), N6–Zn2′ 1.950(2), O1–C1 1.443(3), Zn1–O1–Zn2 103.05(8), Zn1–O1–Zn2′ 98.67(8), O1–Zn1–Cl1 106.42(6), N1–Zn1–N4 108.19(10), N3–Zn2–N6′ 113.26(10), Cl1–Zn1–O1 106.42(6). The distance between zinc atoms: Zn1–Zn2 3.085(6), Zn1–Zn2′ 3.205 (6).

asymmetric unit contains an [EtOZn$_2$(hpp)$_2$Cl] moiety with the dimer being built around a central Zn$_4$(μ_3-OEt)$_2$ core based on a 4-membered metallocycle [mean Zn–O 2.043 Å], the two oxygen atoms in which each also bind to an exocyclic zinc center [Zn1–O1 2.039(2) Å]. The four guanidinate ligands all exhibit identical type **A** bridging modes and peripherally span Zn centers [mean Zn–N 1.967 Å]. Each of the metal centers adopts a distorted tetrahedral geometry, with the coordination environment of Zn2 and Zn2′ being completed by terminally bonded chloride ligands [Zn1–Cl1 2.258(8) Å].

Conclusions

In conclusion, we have demonstrated that the equimolar reaction of ZnEt$_2$ with 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (hppH) results in the selective formation of EtZn(hpp) (**1**). This contrasts with the analogous reaction involving ZnMe$_2$, which has previously given the trinuclear adduct Zn$_3$(hpp)$_4$Me$_2$ as the only isolable product.[6b] Exposure of a THF solution of **1** to undried air has led to ZnO-incorporating derivative **1**$_4$·ZnO, while the analogous experiment with CH_2Cl_2 as solvent leads to the novel mixed aggregate [EtOZn(hpp)]$_2$[ClZn(hpp)]$_2$ (**2**). The composition of **2** clearly indicates that its formation is preceded by complex multi-step reactions involving both the oxygenation of ZnEt moieties as well as the activation of CH_2Cl_2 and subsequent transfer of a chloride ion to a Zn center. Further studies on the activation of small molecules by alkylzinc complexes supported by guanidinate ligands are currently in progress.

Experimental section

Reactions and manipulations were carried out under an inert atmosphere of dry nitrogen, using standard double manifold and

glove-box techniques. Solvents were distilled off sodium-benzophenone (THF, toluene, hexane) immediately prior to use. 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine (hppH) was purchased from Aldrich and stored under dry nitrogen in a glove-box, whilst Et_2Zn (Aldrich) used as received. NMR data were collected on a Varian Mercury 400 Spectrometer NMR spectrometer at 298 K and chemical shifts are internally referenced to d_6-benzene and calculated relative to TMS. Chemical shifts are expressed in δ (ppm). The following abbreviations are used for NMR spectra: t = triplet, q = quartet, br = broad and m = multiplet.

Synthesis and characterization

1_3: A solution of 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine (hppH) (0.209 g, 1.5 mmol) in toluene (5 ml) was cooled to −78 °C under N_2 and a solution of Et_2Zn (0.185 g, 1.5 mmol) in hexane was added. After warming to room temperature the solution was stirred for 1 h until the evolution of gas could no longer be observed. The resulting compound, EtZn(hpp) **1**, deposited as colorless rectangular crystals from this toluene/hexane solution after 24 h at −15 °C. Yield 0.331 g (95%); elemental analysis (%) calcd for $C_{27}H_{51}N_9Zn_3$: C 46.45, H 7.38, N 18.06; found: C 46.39, H 7.26, N 18.31. ^{1}H NMR (400 MHz, d_6-benzene): δ 3.09 (br, 12H, –CH_2–), 2.72 (br, 12H, –CH_2–), 1.76–1.57 (m, 12H, –CH_2–), 0.78 (m, 9H, CH_3CH_2–), 0.43 (br, 4H, CH_3CH_2–), 0.27 (br, 2H, CH_3CH_2–).

1_4·**ZnO: (a)** A solution of **1** (0.349 g, 1.5 mmol) in THF (4 ml) was exposed to undried air for 2 h with no stirring at ambient temperature. The mixture was concentrated to 1 ml volume, hexane (2 ml) was added, and the solution was left under an inert atmosphere of N_2. The resulting compound, 1_4·ZnO, deposited as colorless hexagonal crystals after two

weeks at −15 °C. Yield 0.212 g (70%). **(b)** A solution of **1** (0.349 g, 1.5 mmol) in THF (4 ml) was cooled to −78 °C under N_2 and a solution of H_2O (5.4 mg, 0.3 mmol) in THF was added. After warming to room temperature the solution was stirred for 1 h until the evolution of gas could no longer be observed. The resulting compound, 1_4·ZnO, deposited as colorless hexagonal crystals after two weeks at −15 °C under an inert atmosphere. Yield 0.188 g (62%); elemental analysis (%) calcd for $C_{36}H_{68}N_{12}Zn_5O$: C 42.72, H 6.79, N 16.61; found: C 42.65, H 6.70, N 16.72. ^{1}H NMR (400 MHz, d_6-benzene): δ 3.43–3.39 (m, 12H, –CH_2–), 2.92–2.89 (m, 12H, –CH_2–), 1.83–1.77 (br, 12H, –CH_2–), 0.88 (t, 12H, CH_3CH_2–), 0.70–0.33 (m, 8H, CH_3CH_2–).

2: A solution of **1** (0.323 g, 1.39 mmol) in CH_2Cl_2 (3 ml) was exposed to undried air for 6 h at ambient temperature without stirring. The solvent was removed *in vacuo* and the residue was dissolved in THF (2 ml) and subsequently hexane (2 ml) was added. The resulting solution was stored at −15 °C, producing yellow crystals after 5 days under an inert atmosphere of N_2. Yield 0.258 g (76%); elemental analysis (%) calcd for $C_{32}H_{58}N_{12}Zn_4O_2Cl_2$: C 39.40, H 6.01, N 17.24; found: C 39.63, H 6.17, N 17.11 (NMR spectroscopy (see below) demonstrates that lattice THF molecules were completely removed during isolation *in vacuo*). ^{1}H NMR (400 MHz, d_8-THF): δ 3.28 (br, 16H, –CH_2–), 3.14 (q, 4H, CH_3CH_2–) 3.11–2.97 (br, 16H, –CH_2–), 1.78–1.65 (br, 16H, –CH_2–), 1.10 (t, 6H, CH_3CH_2–).

X-Ray crystallography

The data were collected at 100(2) K on a Nonius Kappa CCD diffractometer[11] (Table 1) using graphite monochromated Mo–Kα radiation (λ = 0.71073 Å). The crystal was mounted in a nylon loop in a drop of silicon oil to prevent the possibility of

Table 1 Crystallographic data for 1_3, 1_4·ZnO, and **2**·2THF

Compound	1_3	1_4·ZnO	**2**·2THF
Empirical formula	$C_{27}H_{51}N_9Zn_3$	$C_{36}H_{68}N_{12}OZn_5$	$C_{40}H_{74}Cl_2N_{12}O_4Zn_4$
Formula weight	697.94	1011.97	1119.57
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	C 2/c (no. 15)	P n a 21 (no. 33)	P −1 (no. 2)
a (Å)	38.0471(5)	19.9841(4)	9.3691(2)
b (Å)	10.2929(8)	10.5322(10)	10.1339(4)
c (Å)	18.4412(2)	20.1641(10)	13.1572(5)
α (°)			94.3290(10)
β (°)	107.167(4)		105.682(2)
γ (°)			95.588(2)
V (Å^3)	6900.1(6)	4244.1(5)	1190.21(7)
Z	8	4	1
μ (mm^{-1})	1.344	1.584	1.562
T (K)	100	100	100
F(000)	2928	2104	584
θ range, deg	2.06–21.97	2.41–24.10	2.46–27.52
No. of unique data, R_{int}	4189, 0.0306	6162, 0.00	5337, 0.0240
No. of obsd data [$I>2\acute{o}(I)$]	3522	5375	4688
Refined parameters/restraints	363/24	532/53	281/0
R1, wR2 (all data)^a	0.0652, 0.1314	0.0831, 0.1800	0.0453, 0.0837
R1, wR2 (obsd data)^a	0.0544, 0.1268	0.0647, 0.1561	0.0376, 0.0794
GooF (all data)	1.103	1.085	1.033
Largest difference peak, e Å^{-3}	+0.891/−0.745	+0.889/−0.772	+0.983/−0.908

^{a} R1 = $\sum||Fo| - |Fc|/\sum|Fo|$, wR2 = $[\sum w(Fo^2 - Fc^2)^2/\sum w(Fo^4)]^{1/2}$.

decay of the crystal during data collection. The unit cell parameters were determined from ten frames, then refined on all data. The data were processed with DENZO and SCALEPACK (HKL2000 package).[12] The structure was solved by direct methods using the SHELXS-97[13] program and was refined by full matrix least squares on F^2 using the program SHELXL-97.[14] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at geometrically idealized coordinates with a fixed isotropic displacement parameter equal to 1.5 (methyl groups) times the value of the equivalent isotropic displacement parameter of the parent carbon. We applied least squares restraints of the DFIX and SIMU type for structures of compounds 1_3 and 1_4·ZnO in order to provide corresponding geometric parameters for the disordered fragments. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 805379 (1_3), CCDC 805380 (1_4·ZnO) and CCDC 843486 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

Notes and references

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