Journal of Molecular Catalysis A: Chemical 316 (2010) 139–145

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

New insights into the lactide polymerisation with neutral N-donor stabilised zinc complexes: Comparison of imidazolin-2-imine vs. guanidine complexes

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ARTICLE INFO

Article history:
Received 20 August 2009
Accepted 7 October 2009
Available online 12 November 2009

Keywords:
Biodegradable biopolymers
Zinc
Lactide
Ring-opening polymerisation
Density functional calculations

ABSTRACT

Two imidazolin-2-imine zinc complexes [Zn(8MeBL)Cl_2] (**1**) and [Zn(8MeBL)$(OAc)_2$] (**2**) were synthesised, completely characterised and investigated for their activity in the solvent-free ring-opening polymerisation of D,L-lactide. It could be shown that these compounds are able to act as efficient initiators for lactide polymerisation, and polylactides with molecular weights (M_w) of around 23,000–55,000 g/mol could be obtained with relatively narrow polydispersities. **1** and **2** exhibit an advantageous combination of robustness towards humidity and high activity in the polymer melt. A comparative DFT study on **1** and **2** and their guanidine counterparts revealed that the two complex series possess a strikingly similar electronic structure. Although the imidazolin-2-imine is more basic, its zinc complexes have only a slightly greater positive charge on the zinc atom in comparison to the corresponding guanidine complexes. Accordingly, their activity in the initiation of the ring-opening polymerisation is increased which is directly related to the Lewis acidity of the zinc atom. These findings allow more insights into the mechanism of the lactide polymerisation with neutral N-donor stabilised zinc complexes.

1. Introduction

Modern approaches towards green and sustainable chemistry focus on the substitution of petrochemical-based plastics with biorenewable and biodegradable materials. With regard to this perspective, the biodegradable poly-lactide (PLA) represents one of the most auspicious candidates for the substitution of several petrochemical-based polymers like PET or polystyrene. PLA is produced from lactide by ring-opening polymerisation (ROP) or from lactic acid by polycondensation. Both starting materials are produced in large scale from glucose syrup which originates from annually renewing sources like corn, sugar beets or agricultural by-products [1]. Moreover, PLA offers advantageous material properties which makes it a versatile material for numerous applications in modern technology [2]. The most efficient way for the production of PLA is the ring-opening polymerisation of lactide, the cyclic diester of lactic acid (Scheme 1) [1].

Recent developments for the ROP of lactide show that a vast multiplicity of metal centres of group 2, 3 and 4 metals and lanthanides shows activity through a coordination-insertion mechanism [3–13]. This mechanism is proposed to be active for most Lewis acidic metal centres with anionic ligands, e.g. alkoxides, amides [1,3,4]. During this mechanism, the lactide molecule coordinates to the metal centre which facilitates the nucleophilic ring-opening attack of the alkoxide to the lactide. Usually, the anionic component ends up as polymer endgroup [1,3,4]. With regard to the biotoxicity of some metals remaining in the polymer [3c,4], recent efforts have been directed towards the investigation of active zinc initiators. In this context, a great variety of highly active zinc complexes has been prepared [13a,14–17]. Mostly, the reported complexes are sensitive to air and moisture. For industrial purposes, there is an exigent need for initiators which tolerate air and moisture and small impurities in the monomer. This problematic sensitivity can be ascribed to the anionic nature of the coordinating ligand systems which stabilise almost all of these complexes. Up to now, only few systems using neutral ligands have been described. They make use of strong donors such as guanidines [18,19] and phosphinimines [20]. Especially, the guanidine systems gain their unique properties from the ability to effectively delocalise a positive charge over the CN_3 core moiety [21–25]. By this

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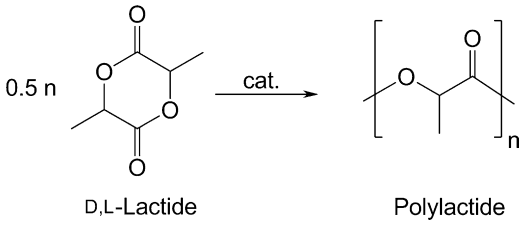
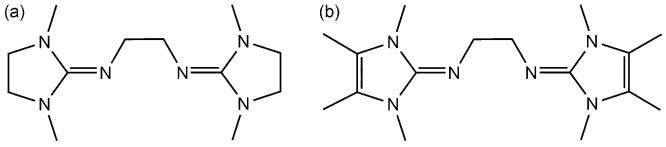
doi:10.1016/j.molcata.2009.10.012



Scheme 1. Ring-opening polymerisation of D,L-lactide.



Scheme 2. (a) Bis(guanidine) ligand $DMEG_2e$ [18] and (b) bis(imidazolin-2-imine) ligand 8MeBL [26b].

intra-guanidine delocalisation, the resulting compounds possess a considerably enhanced basicity and N-nucleophilicity. The basicity is important for inducing a high Lewis acidity on the zinc atom. For the lactide ROP with zinc guanidine systems, the correlation was found that complexes with greater positive charge on the zinc atom exhibit a greater catalytic activity [19].

Targeting a controlled activity of robust initiators in the ROP of D,L-lactide, we extended our research towards other neutral guanidine-related ligand classes like the imidazolin-2-imines [26]. This intriguing ligand family is typically regarded to be a slightly stronger donor compared to guanidines [27]. Furthermore, this ligand class has shown to be able to coordinate a great variety of metals in several coordination modes [26,28]. For a direct comparison of their zinc chemistry and the polymerisation activity of the corresponding zinc complexes, we have chosen the two bis-chelating ligands $DMEG_2e$ [18] and 8MeBL [26b] for our studies because of their structural similarity (Scheme 2). This similarity allows the electronic attributes that promote lactide polymerisation by neutral N-donor stabilised zinc complexes to be elucidated.

Herein, we present the synthesis and characterisation of the first zinc imidazolin-2-imine complexes. An extensive DFT based comparative discussion concentrates on their structural and electronic similarities and differences to their zinc guanidine counterparts. The zinc imidazolin-2-imine complexes proved to be active initiators in D,L-lactide bulk polymerisation, and polylactides with molecular weights (M_w) up to 54,800 g mol^{-1} and polydispersities (M_w/M_n) around 2 could be obtained.

2. Experimental

2.1. Materials and methods

All manipulations were performed under nitrogen (99.996%) dried with P_4O_{10} granulate using Schlenk techniques. Solvents were purified according to literature procedures and also kept under nitrogen. Zinc chloride (99.99%, Acros), zinc acetate (99.99%, Acros) and D,L-lactide (3,6-dimethyl-1,4-dioxane-2,5-dione, Purac) were used as purchased. The ligand 8MeBL was prepared according to literature procedures [26b].

2.2. Physical measurements

Spectra were recorded with the following spectrometers: NMR: Bruker Avance 500. The NMR signals were calibrated to the residual signals of the deuterated solvents (CD_3CN δ_H = 1.94 ppm). Samples for homonuclear decoupling were prepared by dissolving 10 mg of the polymer in 1 ml of $CDCl_3$ (Aldrich) and the samples were left for 2 h to ensure full dissolution [29]. The ^{1}H homonuclear decoupled spectra were recorded on a Bruker Avance 400 MHz spectrometer and referenced to residual solvent peaks. The parameter P_r (probability of heterotactic enchainment) was determined via analysis of the respective integrals of the tetrads, using $P_r^2 = 2[sis]$ [30]. – IR: Nicolet P510. – MS (EI, 70 eV): Finnigan MAT 95. – Elemental analyses: elementar vario MICRO cube.

Table 1
Crystallographic data for the compounds **1** and **2**.

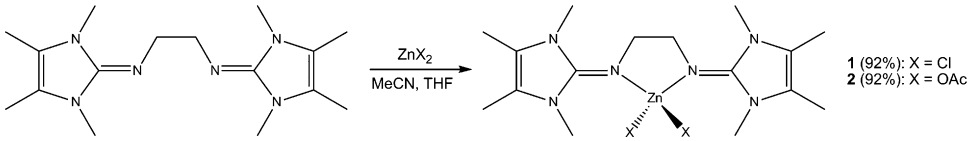
	1	**2**
Empirical formula	$C_{16}H_{28}Cl_2N_6Zn$	$C_{20}H_{34}N_6O_4Zn$
Molecular mass	440.71	487.9
Crystal system	Monoclinic	Monoclinic
Space group	$P2^1/c$	$P2^1/c$
a/Å	8.0823(11)	9.3327(17)
b/Å	8.4648(12)	14.683(3)
c/Å	29.116(4)	16.554(3)
β/°	92.187(3)	92.010(4)
V/Å^3	1990.5(5)	2267.0(7)
Z	4	4
D_{calc}/g cm^{-3}	1.471	1.429
μ/mm^{-1}	1.514	1.122
Temperature/K	120(2)	120(2)
Θ_{max}/°	1.40–27.88	1.85–27.88
Reflections collected	16787	19542
Independent reflections	4747	5409
R1 [$I \geq 2\sigma(I)$]	0.0252	0.0242
wR2 (all data)	0.0635	0.0706
Largest diff. peak, hole/e Å^{-3}	0.381, −0.215	0.318, −0.308

2.2.1. Crystal structure analyses

Crystal data for compounds **1** and **2** are presented in Table 1. Data were collected with a Bruker-AXS SMART [31] APEX CCD, using Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator; data reduction and absorption correction with SAINT and SADABS [31]. The structures were solved by direct and conventional Fourier methods and all non-hydrogen atoms refined anisotropically with full-matrix least squares based on F^2 (SHELXTL [31]). Hydrogen atoms were derived from difference Fourier maps and placed at idealized positions, riding on their parent C atoms, with isotropic displacement parameters Uiso(H) = 1.2 Ueq(C) and 1.5 Ueq(C methyl). All methyl groups were allowed to rotate but not to tip. Full crystallographic data (excluding structure factors) for **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre as supplementary no. CCDC-739147 (1) and -739148 (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.

2.2.2. Gel permeation chromatography

The molecular weight and molecular weight distribution of obtained polylactide samples were determined by gel permeation chromatography (GPC) in THF as mobile phase at a flow rate of 1 mL/min. A combination of PSS SDV columns with porosities of 10^5 and 10^3 Å were used together with a HPLC pump (L6200, Merck Hitachi) and a refractive index detector (Smartline RI Detector 2300, Knauer) detector. Universal calibration was applied to evaluate the chromatographic results. Kuhn–Mark–Houwink (KMH) parameters for the polystyrene standards (K_{PS} = 0.011 ml/g, a_{PS} = 0.725) were taken from literature [32]. Previous GPC measurements utilizing online viscosimetry detection revealed the KMH parameters for polylactide (K_{PLa} = 0.053 ml/g, a_{PLa} = 0.610) [19].



Scheme 3. Synthesis of the imidazolin-2-imine stabilised zinc complexes **1** and **2**.

2.3. Computational details

Density functional theory (DFT) calculations were performed with the program suite Gaussian 03 [33]. The geometries of the complexes were optimised using the B3LYP hybrid DFT functional [34] or the M05-2X functional [35] in combination with the 6-31g(d) basis set implemented in Gaussian on all atoms. Tight conversion criteria were applied. The starting geometries of the complexes **1**, **2**, $\mathbf{1^{gua}}$ and $\mathbf{2^{gua}}$ were generated from their crystal structures. Frequency calculations confirmed the stationary points to be minima. The Mulliken charge of each atom was calculated by a Mulliken population analysis. The NBO charge of each atom was calculated by a natural bond orbital analysis [36]. The coordinates of the optimised structures can be found in Supporting Information.

2.4. Preparation of compounds

[Zn(8MeBL)Cl_2] (**1**): To a suspension of 0.5 mmol of zinc(II) chloride in dry MeCN, a solution of the ligand **1** (0.55 mmol) in MeCN was added under stirring. The resulting reaction mixture was stirred for 20 min. Due to the precipitation of the corresponding complex, the reaction mixture was slowly heated under reflux. Dry MeCN was added to give a clear light yellow solution. Colourless crystals suitable for X-ray diffraction could be obtained by slowly cooling to room temperature (m.p. 261 °C); yield: 92% (0.20 g). ^{1}H NMR (500 MHz, CD_3CN, 25 °C): δ = 2.03 (s, 12H, CH_3), 3.45 (s, 12H, CH_3), 3.62 (s, 4H, CH_2) ppm. ^{13}C NMR (125 MHz, CD_3CN, 25 °C): δ = 8.0 (CH_3), 31.0 (CH_3), 50.7 (CH_2), 153.3 (C), 155.1 (C_{imin}) ppm. IR (KBr) $\tilde{\nu}$ = 2981 [w, ν(C-$H_{aliph.}$)], 2937 [m, ν(C-$H_{aliph.}$)], 2916 [m, ν(C-$H_{aliph.}$)], 2848 [m, ν(C-$H_{aliph.}$)], 1577 [vs, ν(C=N)], 1477 (m), 1444 (m), 1425 (m), 1402 (m), 1363 (m), 1350 (m), 1333 (m), 1261 (w), 1213 (w), 1124 (m), 1084 (w), 1028 (w), 987 (vw), 949 (w), 883 (w), 846 (vw), 822 (vw), 717 (w), 690 (w), 669 (w), 611 (w), 602 (w), 563 (w) cm^{-1}. EI-MS: *m*/*z* (%) = 442 (11) [M^+: $C_{16}H_{28}{}^{35}Cl_2N_6{}^{64}Zn$], 440 (17) [$M^+$: $C_{16}H_{28}{}^{35}Cl_2N_6{}^{66}Zn$, $C_{16}H_{28}{}^{35}Cl^{37}ClN_6{}^{64}Zn$], 438 (14) [$M^+$: $C_{16}H_{28}{}^{35}Cl^{37}ClN_6{}^{66}Zn$, $C_{16}H_{28}{}^{37}Cl_2N_6{}^{64}Zn$, $C_{16}H_{28}{}^{35}Cl_2N_6{}^{68}Zn$], 407 (11) [$M^+$−Cl], 405 (19) [$M^+$−Cl], 403 (17) [$M^+$−Cl], 303 (17) [$C_{16}H_{28}N_6{}^+$ −H], 165 (11) [$C_9H_{16}N_3{}^+$ −H], 153 (69) [$C_8H_{14}N_3{}^+$ +H], 152 (100) [$C_8H_{14}N_3{}^+$], 124 (27) [$C_7H_{12}N_2{}^+$], 56 (24) [$NCH_2CH_2N^+$]. $C_{16}H_{28}Cl_2N_6Zn$ (440,74): calcd. C 43.56, H 6.35, N 19.06; found C 43.58, H 6.37, N 18.92.

[Zn(8MeBL)$(CH_3COO)_2$] (**2**): To a suspension of 0.2 mmol of zinc(II) acetate in dry THF, a solution of the ligand **1** (0.21 mmol) in THF was added under stirring. The resulting solution was stirred for 2 h while a colourless precipitate formed. The reaction mixture was slowly heated under reflux. Dry MeCN was added to give a clear light yellow solution. Colourless crystals suitable for X-ray diffraction could be obtained by slowly cooling to room temperature (m.p. 162 °C); yield: 92% (0.09 g). ^{1}H NMR (500 MHz, CD_3CN, 25 °C): δ = 1.73 (s, 6H, CH_3), 2.01 (s, 12H, CH_3), 3.36 (s, 12H, CH_3), 3.59 (s, 4H, CH_2) ppm. ^{13}C NMR (125 MHz, CD_3CN, 25 °C): δ = 8.0 (CH_3), 22.8 (CH_3), 30.1 (CH_3), 50.9 (CH_2), 153.7 (C), 175.4 (C_{imin}), 199.9 (C_{ac}) ppm. IR (KBr): $\tilde{\nu}$ = 3138 (m), 3053 (m), 2999 [m, ν(C-$H_{aliph.}$)], 2978 [m, ν(C-$H_{aliph.}$)], 2949 [m, ν(C-$H_{aliph.}$)], 1599 [vs, ν(C=N)], 1581 [vs, ν(C=N)], 1491 (m), 1444 (m), 1446 (m), 1421 (m), 1404 (m), 1267 (m), 1246 (m), 1223 (w), 1128 (w), 1113 (w), 1072 (m), 1020 (w), 991 (w), 955 (vw), 918 (w), 897 (w), 847 (w), 766 (m), 735 (m), 725 (m), 706 (m), 648 (m), 619 (m), 596 (m), 561 (m) cm^{-1}. EI-MS: *m*/*z* (%) = 486 (2) [M^+], 425 (45) [M^+−CH_3COO −2H], 266 (17), 198 (7) [$C_8H_{18}N_6{}^+$], 184 (7) [$C_7H_{16}N_6{}^+$], 165 (8) [$C_9H_{16}N_3{}^+$ −H], 153 (10) [$C_8H_{14}N_3{}^+$ +H], 152 (100) [$C_8H_{14}N_3{}^+$], 124 (6) [$C_7H_{12}N_2{}^+$], 113 (15) [$C_6H_{13}N_2{}^+$]. $C_{20}H_{34}N_6O_4Zn$ (487.91): calcd. C 49.19, H 6.97, N 17.22; found C 48.63, H 7.03, N 16.94.

2.5. General procedure for D,L-lactide polymerisation

D,L-Lactide (3.603 g, 25 mmol) and the initiator (*I*/*M* ratio 1/500) were weighed into a 50 mL flask, which was closed with a glass stopper. The D,L-lactide was used as purchased from Purac without further purification steps. The reaction vessel was then heated at 150 °C. After the reaction time of 24 or 48 h the polymer melt was allowed to cool to room temperature and then dissolved in 25 mL of dichloromethane. The PLA was precipitated in 350 mL of ice-cooled ethanol und dried under vacuum at 50 °C.

3. Results and discussion

3.1. Complex syntheses

The imidazolin-2-imine ligand 8MeBL was synthesised by reaction of the imidazolin-2-imine [27] imine^{Me} with 1,2-ethyleneditosylate and subsequent deprotonation with KO*t*Bu in high yields [26b]. The reaction with the zinc salts $ZnCl_2$ and $Zn(CH_3COO)_2$ in a dry, aprotic solvent (MeCN, THF) resulted straightforwardly in the formation of the imidazolin-2-imine stabilised zinc complexes [Zn(8MeBL)Cl_2] (**1**) and [Zn(8MeBL)$(OAc)_2$] (**2**) (Scheme 3). They could both be isolated as colourless crystals in good yields of 92%. Single crystals of the complexes were obtained by cooling the saturated solution slowly to room temperature. The isolated crystalline solids are stable towards moisture and air. They can be handled and stored in air for several days, whereas the corresponding imidazolin-2-imine ligands and zinc salts are sensitive towards hydrolysis or rather hygroscopic.

The molecular structures of the compounds **1** and **2** (Figs. 1 and 2) were determined by X-ray crystallography. In these complexes, the zinc atom is fourfold coordinated by the two N-donor atoms of the imidazolin-2-imine ligand and two chlorine ions or two acetate ions, respectively. In order to compare the structural properties of the zinc complexes stabilised by imidazolin-2-imine ligands, these complexes are discussed together with their guanidine counterparts [Zn(DMEG$_2$e)Cl_2] ($\mathbf{1^{gua}}$)

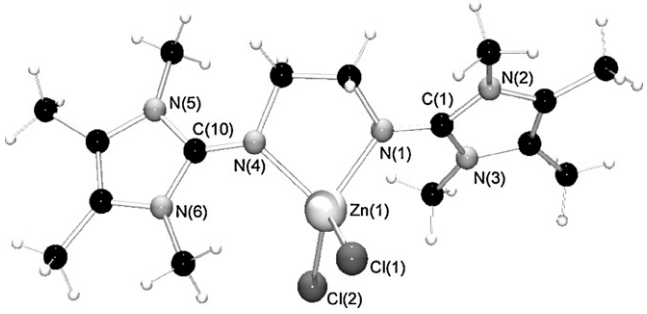


Fig. 1. Molecular structure of [Zn(8MeBL)Cl_2] (**1**) as determined at 120 K.

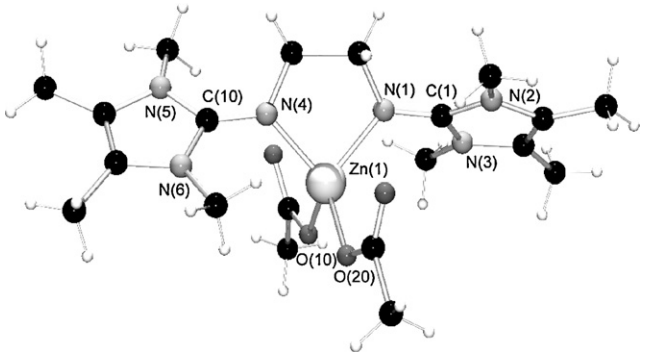


Fig. 2. Molecular structure of [Zn(8MeBL)$(OAc)_2$] (**2**) as determined at 120 K.

and [Zn($DMEG_2e$)$(OAc)_2$] (**2**^{gua}) which are already described in the literature [18].

3.2. Comparative discussion of the molecular structures

The molecular structures of all four zinc complexes are very similar. Selected bond lengths and angles of the compounds are collected in Table 2. In all the complexes the zinc atom is four-fold coordinated, whereby two coordination sites are occupied in a chelating manner by the N-donor atoms of the ligands to form a five-membered heterocycle. The distances between the zinc atom and the N-donor atoms do not differ very much. Their values are ranging from 2.005(1) to 2.038(2) Å. In **1**^{gua} the Zn–Cl distances are equal in length (2.260(1) Å) due to symmetry. In **1** one Zn–Cl bond is longer than the other. The longer bond measures 2.277(1) Å and the shorter 2.241(1) Å and thus their averaged value fits very well with the Zn–Cl distance of **1**^{gua}. In the diacetato complexes the distances of the Zn atom and the coordinated O atom are equal within the limits of significance (av. 1.961 Å). The different electronic character of the imidazolin-2-imine and the guanidine ligands is reflected in the C_{imine}–N_{imine} or C_{gua}–N_{gua} distances, respectively. In the imidazolin-2-imine zinc complexes **1** and **2**, the positive charge is delocalised in the N_2C_3-heterocycle leading to longer C_{imine}–N_{imine} bonds (av. 1.320 Å) whereas in the bisguanidine zinc complexes **1**^{gua} and **2**^{gua} the positive charge is delocalised over the guanidine CN_3 backbone resulting in slightly shorter C_{imine}–N_{imine} distances (av. 1.307 Å). This different delocalisation behaviour is also observed by the angles between the $C_{imine}N_3$ and the $N_{ring}C_3$ planes. Whereas those values of **1** and **2** are with av. 5.6 and 6.3° quite small indicating the planarity of the N_2C_3-heterocycle caused by the high delocalisation of the positive charge, the values of **1**^{gua} and **2**^{gua} are with av. 15.5 and 14.9° significantly higher. This shows the stronger deviation of the heterocycle atoms from the ring plane and therefore the tendency of guanidine systems not to delocalise the positive charge over the heterocycle but over the guanidine moiety.

In all four complexes the coordination geometry of the zinc centre is dictated by the bite angles of the chelating ligands which possess an averaged value of 85.9° and therefore differ considerably from the angle expected for an ideal tetrahedron (109.47°). This leads to a distorted tetrahedral coordination geometry which is also reflected in the dihedral angle between the ZnX_2 (X = Cl, OAc) and the ZnN_2 planes. In ideal tetrahedral coordination geometry it is 90°, but in the imidazolin-2-imine stabilised complexes described here these angles are with 82.1(1) (**1**) and 84.9(1)° (**2**) slightly smaller. However, in the guanidine zinc complexes **1**^{gua} and **2**^{gua} these dihedral angles are with 74.5(1) and 76.6(1)° even smaller than in the imidazolin-2-imine complexes.

3.3. DFT calculations

The structural trends described above are discussed under consideration of gas phase DFT calculations. The electronic structures of the zinc complexes **1**, **2** and their guanidine counterparts **1**^{gua} and **2**^{gua} have been examined using the B3LYP hybrid DFT functional [34] or the M05-2X functional [35] in combination with the 6-31g(d) basis set, implemented by the Gaussian 03 suite of programs [33]. Geometry optimisations were performed using the coordinates from X-ray data as starting points. The results of the optimisations are presented in Tables 3 and 4.

For both functionals, the computed complex structures are in good agreement with their solid-state structures. By trend, the Zn–N distances are predicted 0.01–0.03 Å too long. This tendency has been observed quite frequently for such systems [19,37,38]. The Zn–Cl distances are better described by the M05-2X functional in comparison to the solid-state structure. The Zn–O distances in **2** and **2**^{gua} are predicted too short by both functionals. Remarkably, the B3LYP functional describes the C=N bonds of all four complexes more accurately than the M05-2X functional. For B3LYP, the deviation from the solid-state data averages to 0.003 Å whereas for M05-2X the corresponding values deviate about 0.008 Å.

The tetrahedral coordination environments and the ligand bite angles in **1**, **2**, **1**^{gua} and **2**^{gua} are correctly described by both functionals. It has to be noted that the B3LYP functional describes the angles between the ZnN_2 and the ZnX_2 planes slightly better for the four complexes than the M05-2X functional compared to those found in the solid state. The coordination of the acetate ions in the complexes **2** and **2**^{gua} is in good agreement as well. The calculated values for the twist of the NC_3 unit against the ZnX_2 plane gives an ambiguous picture: for **1**, both functionals describe the difference between the "sides" of the complex qualitatively correct, in contrast to **1**^{gua}, where the twist is predicted considerably too high (22° in solid-state, 34 and 52° for B3LYP, 50° for M05-2X). For **2** and **2**^{gua}, the twist is described reasonably. It might be that this twist is also influenced by packing forces in the crystal. Notably, the accordance between theory and experiment for the angles between the $C_{imine}N_3$ and the $N_{ring}C_3$ planes in the four complexes is very good for both functionals.

For a more detailed analysis of the electronic structure the Mulliken charges and the NBO charges have been determined [36]. The resulting charges are summarized in Tables 5 and 6. These charges

Table 2
Selected bond lengths (Å) and bond angles (°) of 1, 2 and their guanidine counterparts **1**^{gua} and **2**^{gua} [18].

	1	**1**^{gua}	**2**	**2**^{gua}
Zn–N	2.019(1), 2.032(1)	2.038(2)	2.005(1), 2.006(1)	2.011(2), 2.038(2)
Zn–X (X = Cl^-, OAc^-)	2.241(1), 2.277(1)	2.260(1)	1.955(1), 1.965(1)	1.956(2), 1.969(2)
C_{imine}–N_{imine}	1.321(2), 1.318(2)	1.309(3)	1.323(2), 1.318(2)	1.308(2), 1.305(2)
C_{imine}–N_{ring}	1.367(2), 1.362(2), 1.373(2), 1.366(2)	1.381(3), 1.354(3)	1.362(2), 1.364(2), 1.360(2), 1.367(2)	1.367(3), 1.371(3), 1.364(3), 1.368(3)
N–Zn–N	85.4(1)	86.2(1)	85.9(1)	86.2(1)
∠(ZnX_2, ZnN_2)	82.1(1)	74.5(1)	84.9(1)	76.3(1)
∠($C_{imine}N_3$, ZnN_2)	56.4(1), 26.5(1)	22.4(1)	87.7(1), 24.8(1)	39.8(1), 28.1(1)
∠($C_{imine}N_3$, $N_{ring}C_3$) (av.)	5.6	15.5	6.3	14.9

Table 3
Summary of key geometric parameters of the calculated structures of **1** and **1^{gua}** (bond lengths in Å and angles in°).

	1		**1^{gua}**	
	B3LYP/6-31g(d)	M05-2X/6-31g(d)	B3LYP/6-31g(d)	M05-2X/6-31g(d)
Zn–Cl	2.302; 2.259	2.252; 2.285	2.322; 2.354	2.270
Zn–N_{imine}	2.041	2.033; 2.038	2.029; 2.031	2.045
C_{imine}–N_{imine}	1.322; 1.317	1.311; 1.318	1.308; 1.306	1.301
C_{imine}–N_{ring}	1.376; 1.384	1.371; 1.366	1.384; 1.364	1.359
	1.369; 1.371	1.359	1.389; 1.365	1.376
N–Zn–N	84.7	84.2	84.6	83.5
O–Zn–O	117.6	118.7	119.3	120.0
<(ZnO_2, ZnN_2)	79.3	76.7	74.0	69.3
<($C_{imine}N_3$, ZnN_2)	68.0; 30.4	64.3; 33.9	52.2; 34.6	49.9; 49.9
<($C_{imine}N_3$, $N_{ring}C_3$)	6.0	6.0	14.0	15.7

Table 4
Summary of key geometric parameters of the calculated structures of **2** and **2^{gua}** (bond lengths in Å and angles in°).

	2		**2^{gua}**	
	B3LYP/6-31g(d)	M05-2X/6-31g(d)	B3LYP/6-31g(d)	M05-2X/6-31g(d)
Zn–O	1.947	1.955	1.939	1.941
Zn–N_{imine}	2.025	2.027	2.046	2.036
C_{imine}–N_{imine}	1.315	1.309	1.302	1.297
C_{imine}–N_{ring}	1.372, 1.377	1.365, 1.369	1.384, 1.388	1.367, 1.383
N–Zn–N	85.8	85.3	86.5	85.4
O–Zn–O	78.9	100.9	76.8	99.3
<(ZnO_2, ZnN_2)	78.8	62.7	81.0	69.1
<($C_{imine}N_3$, ZnN_2)	51.9, 52.1	49.4; 49.4	37.2; 37.2	36.0; 36.1
<($C_{imine}N_3$, $N_{ring}C_3$)	6.2	5.0	15.0	12.6

Table 5
Mulliken and NBO charges in electron units (charge of electron is equal to −1) of **1** and **1^{gua}** (basis set: 6-31g(d)).

	1				**1^{gua}**			
	Mulliken		NBO		Mulliken		NBO	
	B3LYP	M05-2X	B3LYP	M05-2X	B3LYP	M05-2X	B3LYP	M05-2X
Zn	+0.677	+0.638	+1.529	+1.019	+0.669	+0.609	+1.526	+1.014
Cl	−0.556	−0.543	−0.815	−0.664	−0.545	−0.535	−0.807	−0.657
	−0.540	−0.535	−0.823	−0.649	−0.545	−0.535	−0.810	−0.657
N_{imine}	−0.698	−0.710	−0.838	−0.810	−0.670	−0.688	−0.800	−0.763
	−0.688	−0.713	−0.851	−0.791	−0.664	−0.688	−0.809	−0.763
C_{gua}	+0.801	+0.832	+0.656	+0.692	+0.820	+0.817	+0.697	+0.724
	+0.818	+0.814	+0.657	+0.690	+0.822	+0.817	+0.693	+0.724
N	−0.526	−0.554	−0.387	−0.397	−0.477	−0.491	−0.492	−0.499
	−0.508	−0.576	−0.424	−0.420	−0.455	−0.491	−0.450	−0.466
	−0.538	−0.551	−0.415	−0.399	−0.481	−0.516	−0.488	−0.499
	−0.514	−0.564	−0.388	−0.430	−0.455	−0.516	−0.449	−0.466

do not represent absolute charges but the trends among the complexes give an impression of electronic effects. The advantage of NBO charges over Mulliken charges lies in their greater independence of the basis sets [39].

In comparison of the imidazolin-2-imine stabilised complexes **1** and **2** with the guanidine complexes **1^{gua}** and **2^{gua}**, the charges of the imine N atom of the imidazolin-2-imines are predicted to be in average 0.025 (Mulliken charge) or 0.045 (NBO charge) more nega-

Table 6
Mulliken and NBO charges in electron units (charge of electron is equal to −1) of **2** and **2^{gua}** (basis set: 6-31g(d)).

	2				**2^{gua}**			
	Mulliken		NBO		Mulliken		NBO	
	B3LYP	M05-2X	B3LYP	M05-2X	B3LYP	M05-2X	B3LYP	M05-2X
Zn	+0.854	+0.859	+1.627	+1.288	+0.816	+0.838	+1.631	+1.289
Cl	−0.610	−0.627	−0.890	−0.853	−0.616	−0.630	−0.908	−0.860
	−0.610	−0.627	−0.890	−0.853	−0.616	−0.630	−0.908	−0.860
N_{imine}	−0.699	−0.702	−0.845	−0.805	−0.671	−0.689	−0.787	−0.762
	−0.700	−0.702	−0.845	−0.805	−0.671	−0.689	−0.787	−0.762
C_{gua}	+0.791	+0.797	+0.666	+0.683	+0.828	+0.832	+0.692	+0.719
	+0.791	+0.797	+0.666	+0.683	+0.828	+0.832	+0.692	+0.719
N	−0.528	−0.574	−0.398	−0.425	−0.485	−0.497	−0.461	−0.494
	−0.509	−0.574	−0.419	−0.403	−0.454	−0.497	−0.479	−0.473
	−0.528	−0.543	−0.398	−0.425	−0.485	−0.521	−0.461	−0.494
	−0.509	−0.543	−0.419	−0.403	−0.454	−0.521	−0.479	−0.473

Table 7
Polymerisation of D,L-lactide in the presence of the imidazolin-2-imine zinc complexes **1** and **2**, as well as the guanidine zinc complexes $\mathbf{1}^{gua}$ and $\mathbf{2}^{gua}$ [18].

Initiator		Time [h]	Yield [%]	M_w[a] [g/mol]	PD[b]	P_r[c]
[Zn(8MeBL)Cl_2]	(**1**)	24	85	50,700	2.0	0.53
[Zn(8MeBL)Cl_2]	(**1**)	48	89	54,800	1.9	
[Zn($DMEG_2$e)Cl_2]	($\mathbf{1}^{gua}$)	24	79	38,000	1.7	0.50
[Zn($DMEG_2$e)Cl_2]	($\mathbf{1}^{gua}$)	48	67	32,900	1.6	
[Zn(8MeBL)($CH_3COO)_2$]	(**2**)	24	88	24,000	2.0	0.50
[Zn(8MeBL)($CH_3COO)_2$]	(**2**)	48	85	22,500	2.1	
[Zn($DMEG_2$e)($CH_3COO)_2$]	($\mathbf{2}^{gua}$)	24	69	24,300	1.6	0.50
[Zn($DMEG_2$e)($CH_3COO)_2$]	($\mathbf{2}^{gua}$)	48	66	17,900	1.6	

[a] Reaction conditions: catalyst (0.2 mol%), 150 °C.
[b] PD = M_w/M_n where M_n is the number-average molar mass.
[c] From analysis of the ^{1}H homonuclear decoupled NMR spectrum using the equation $P_r^2 = 2[sis]$ [30].

tive. Concomitantly, the positive charge on the zinc atom is slightly increased (~0.01 Mulliken charge, less than 0.01 NBO charge). In addition, the positive charge on the imine C atoms is slightly higher in the guanidine systems. This effect is due to a better delocalisation of the positive charge within imidazole ring systems. Interestingly, the differences between the Mulliken charge distribution in tetramethylguanidine and dimethylethyleneguanidine groups are more pronounced than the differences between imidazolin-2-imines and guanidines discussed herein [19]. In summary, the imidazolin-2-imine complexes should show a slightly enhanced Lewis acidity of the zinc atoms compared to their guanidine counterparts and therefore act as good initiators for the lactide polymerisation.

3.4. Polymerisation activity

We reported recently [18,19] that guanidine zinc complexes possess catalytic activity in the ring-opening polymerisation of D,L-lactide and offer the advantage of acceptable or even high stability towards air and moisture. We observed that in most cases active catalysts feature high Mulliken charges at the N-donor atoms which lead to an improved Lewis acidity of the zinc centre [19]. The zinc complexes stabilised by imidazolin-2-imine ligands are expected to be more active catalysts in comparison to the corresponding zinc bisguanidine complexes due to the higher basicity of the imidazolin-2-imines. Following DFT analysis, in these ligands the positive charge is strongly delocalised in the imidazoline rings and thus the zinc centre in these complexes should exhibit a stronger Lewis acidity leading to good catalytic properties. Thus, the imidazolin-2-imine zinc complexes were investigated concerning their activity in the bulk polymerisation of D,L-lactide.

For the polymerisation procedure the monomer D,L-lactide and the initiator (I/M ratio 1:500) were heated at 150 °C. It has to be noted that the monomer was used as purchased without further purification. After the reaction time of 24 or 48 h, the melt was dissolved in dichloromethane, and then the PLA was precipitated in cold ethanol, isolated and dried under vacuum at 50 °C. In order to rate the catalytic activity of the complexes, the polymer yield was defined and the molecular weights as well as the polydispersity of the obtained PLA were determined by gel permeation chromatography (see Table 7). The tacticity and the probability of heterotactic enchainment (P_r) were analyzed by homonuclear decoupled ^{1}H NMR spectroscopy [30].

We found that the complexes **1** and **2** initiate the ring-opening polymerisation of D,L-lactide and show in general similar results to the corresponding bisguanidine zinc complexes $\mathbf{1}^{gua}$ and $\mathbf{2}^{gua}$. In the case of **1** and **2**, the yields are slightly higher than for $\mathbf{1}^{gua}$ and $\mathbf{2}^{gua}$. The dichloro complex **1** affords higher molecular weights than its guanidine counterpart $\mathbf{1}^{gua}$, and they both generate higher M_w values than the diacetato complexes, whose values are in the same range. Whereas the extension of reaction time from 24 to 48 h leads in the case of **1** to a slight increase of molecular weight, in polymerisations initiated with **2**, $\mathbf{1}^{gua}$ and $\mathbf{2}^{gua}$ a decrease of molecular weight can be observed which may be caused by side reactions such as interchain or intrachain transesterification resulting in a chain-transfer reaction [40]. The P_r values of 0.50 or 0.53 imply that the complex structure shows no ability to affect the tacticity of the formed polymer.

The catalytic study supports the findings of the DFT calculations: the imidazolin-2-imines feature a slightly higher positive charge at the zinc atom and more negative charges at the imine N atoms, such that a slightly higher catalytic activity had to be expected. A continuation of this thought implies that systems with exceedingly high Lewis acidity on the zinc atom and great basicity on the N-donor function are excellent initiators for the ROP of lactide. By using bis-chelated zinc guanidine complexes, we have already shown that in these systems very high positive charge at the zinc atom correlates with high catalytic activity [19]. All these findings are in good accordance with the coordination-insertion-mechanism proposed for the lactide polymerisation with transition metal alkoxide complexes [1,3,4]. In this mechanism, the pre-coordination of the substrate lactide to the metal centre is crucial for the subsequent ring-opening step. The co-ligands which are usually alkoxides act then as nucleophiles and open the lactide ring [1,3]. It has to be remarked that the complexes **1**, **2**, $\mathbf{1}^{gua}$ and $\mathbf{2}^{gua}$ initiate the ROP of lactide without any addition of alkoxide or other co-catalysts. We propose that the highly nucleophilic imidazolin-2-imine and guanidine N-donor systems act as ring-opening agents.

In summary, these findings lead to two mechanistic evidences: (a) enhanced Lewis acidity of the zinc centre directly correlates with the enhanced polymerisation activity and (b) by using exclusively neutral N-donor ligands for the stabilisation of the catalysts, we could prove that anionic (co-)ligands are not necessary prerequisites for the nucleophilic lactide-opening step.

4. Conclusions

In this contribution we reported on the synthesis and complete characterisation of the first examples of imidazolin-2-imine zinc complexes. The structural and theoretical analysis revealed that the dichloro and diacetato complexes of the ligand 8MeBL are very similar to those of the corresponding guanidine $DMEG_2$e. DFT calculations with B3LYP and M05-2X functionals in combination with the 6-31g(d) basis set were in good agreement with the solid-state structures. A charge distribution analysis using Mulliken and NBO charges exhibited that the imidazolin-2-imine complexes possess more negative charge on the imine N atoms and slightly more positive charge on the zinc atom than their guanidine counterparts. Notably, **1** and **2** were active in the solvent-free polymerisation of lactide. The resulting poly-D,L-lactide could be

obtained with yields of app. 85% and molecular weights (M_w) of up to 54,800 g mol^{-1} with a polydispersity of 2. This is consistent with the slightly higher activity of **1** and **2** in the ROP of lactide compared to the activity of $\mathbf{1}^{gua}$ and $\mathbf{2}^{gua}$. Hence, the strategy of using neutral, strongly nucleophilic ligand systems for the stabilisation of catalytically active and environmentally benign zinc complexes has again been positively evaluated. Further experimental and theoretical studies on the ring-opening polymerisation mechanism without the presence of alkoxides are conducted at the moment.

Acknowledgements

Financial support by the Fonds der Chemischen Industrie and by the Universität Paderborn (fellowships for S.H.-P.) is gratefully acknowledged. J.B. thanks the Stiftung der Deutschen Wirtschaft sdw for granting a doctoral fellowship. Furthermore, S.H.-P. thanks Prof. Dr. G. Henkel and Prof. Dr. K. Jurkschat for their valuable support.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2009.10.012.

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