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Tracking the Structure-Reactivity Relationship of Zinc Guanidine-Pyridine Hybrid Complexes Initiating Lactide Polymerisation

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Summary: Three zinc guanidine-pyridine hybrid complexes [Zn(TMGqu)$_2$(CH$_3$SO$_3$)][CH$_3$SO$_3$] (**1**), [Zn(DMEGqu)(CH$_3$SO$_3$)$_2$] (**2**) and [Zn(DMEGqu)$_2$(CH$_3$SO$_3$)][CH$_3$SO$_3$] (**3**) were synthesised, completely characterised and investigated on their activity in the solvent-free ring-opening polymerisation of D,L-lactide. It was proven that the bis-chelate trigonal-bipyramidally coordinated compounds **1** and **3** are able to act as initiators for lactide polymerisation, and polylactides with molecular weights (M_w) of around 28000 g/mol could be obtained with relatively narrow polydispersities. The tetrahedral complex **2** does not initiate lactide polymerisation. In an integrated approach of structural studies and DFT calculations, the active complexes **1** and **3** were analysed towards their structural and electronical pre-requisites in comparison to their more active triflate analogues **1**$^{\mathbf{OTf}}$ and **3**$^{\mathbf{OTf}}$. The influence of coordination strength of the anionic component on the charge distribution within the complex and on the substrate accessibility to the zinc centre is highlighted as crucial factor for the polymerisation initiation. As result, it is shown that the mesylate complexes **1** and **3** have less positive charge on the zinc centre and the mesylate is stronger bound than the corresponding triflate in the triflate complexes **1**$^{\mathbf{OTf}}$ and **3**$^{\mathbf{OTf}}$. Consequently, the reactivity of the complexes is directly correlated to the coordinational behaviour of the anionic component.

Keywords: biodegradable biopolymers; density functional calculations; guanidine ligands; lactide; ring-opening polymerisation; structure-property relations; zinc

Introduction

The advanced production of biodegradable and biocompatible polymers in order to substitute petrochemical-based plastic plays a significant role in context of green and sustainable chemistry. The aliphatic polyester polylactide (PLA) possesses good mechanical properties and can be easily converted into films, fibres, spun bond and melt blown products on existing processing equipment, resulting in a wide range of applications.[1] This biodegradable polymer is commercially produced by metal-initiated ring-opening polymerisation (ROP) of the corresponding cyclic ester lactide (Scheme 1).[2] The monomer lactide can be received in large scale from glucose syrup which originates from annually renewing sources like corn, sugar beets or agricultural by-products.[3] These qualities make PLA to one of the most auspicious environmentally friendly and potentially carbon neutral alternatives to conventional polymers.[2]

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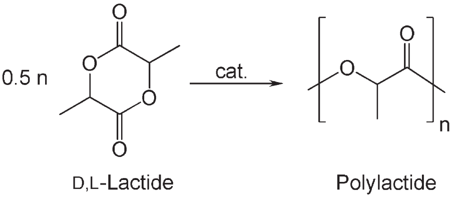


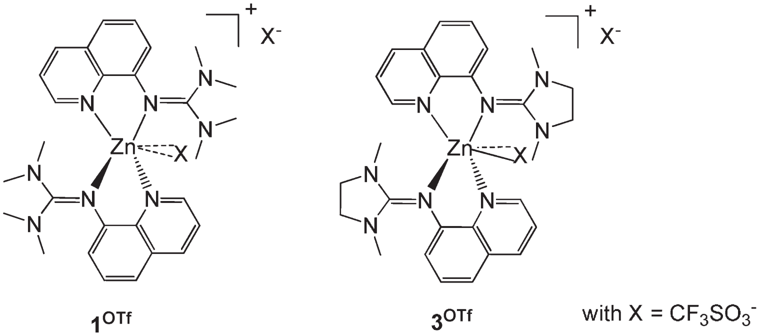
Scheme 1.
ROP of D,L-lactide.

Consequently the development of improved single-site metal catalysts for the ROP of lactide is an area of active research. A vast multiplicity of metal centres of group 2, 3 and 4 metals and lanthanides stabilized by several important ligand classes shows activity through a coordination-insertion mechanism.[2,4–13] But the biotoxicity of some metals remaining in the polymer limits their application and drives the focus towards the investigation of active zinc initiators. In this context, a great variety of highly active zinc complexes has been prepared.[13a],[14–17] But the drawback that restricts the qualification for industrial purposes is their sensitivity to air, moisture and impurities in the monomer. So there is still an exigent need for initiators which possess high polymerisation activity and at the same time a great robustness.

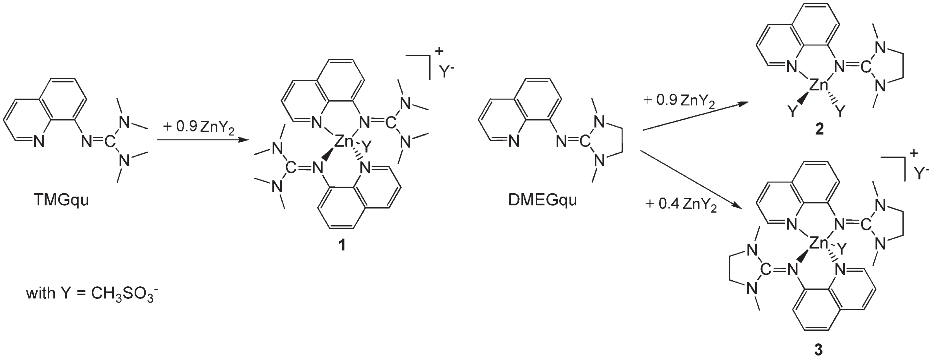
We found that zinc guanidine-pyridine hybrid complexes are excellent and environmentally benign initiators in the solvent-free ROP of D,L-lactide. They possess high stability towards air and moisture and the monomer can be used without further purification. The most auspicious candidates were the bis-chelate complexes $[Zn(TMGqu)_2(CF_3SO_3)][CF_3SO_3]$ (**1**^{OTF}) and $[Zn(DMEGqu)_2(CF_3SO_3)][CF_3SO_3]$ (**3**^{OTf}) (see Scheme 2 and 3).[18]

Their outstanding catalytic activity compared to those of other guanidine-pyridine hybrid zinc complexes results from their structural properties and enhanced Lewis acidity. Seemingly, the weak coordination of the triflate anion allows a good accessibility to the zinc centre which favours coordination of lactide and therefore accelerates the reaction. We also found the correlation that complexes with greater positive charge on the zinc atom exhibit a greater catalytic activity.[18]

To elucidate the structural and electronical influences on the structure-reactivity relationship of zinc guanidine-pyridine complexes in the solvent-free polymerisation of D,L-lactide we synthesised three different complexes with the slightly stronger coordinating anion mesylate. They were investigated concerning the structural and electronical influence of the anionic component on the polymerisation activity. These studies are situated in the mechanistic context of neutral N-donor stabilised zinc complexes and serve the understanding of the functional principle of this special catalyst class.



Scheme 2.
$[Zn(TMGqu)_2(CF_3SO_3)][CF_3SO_3]$ (**1**^{OTf}) and $[Zn(DMEGqu)_2(CF_3SO_3)][CF_3SO_3]$ (**3**^{OTf}).[18]



Scheme 3.
Complex synthesis of **1**, **2** and **3** in dependence of molar ratio.

Results

Synthesis of the Zinc Complexes

Guanidine-pyridine hybrid ligands TMGqu and DMEGqu were synthesised by condensation of N,N,N',N'-tetramethylchloroformamidinium chloride (TMG) and N,N'-dimethylethylenechloroformamidinium chloride (DMEG) (analogues of Vilsmeier salts) with 8-aminoquinoline in high yields of up to 98%.[19]

Their reaction with zinc mesylate (molar ratio ligand to zinc salt 1.1: 1) in a dry, aprotic solvent (MeCN, THF) resulted in straightforward formation of zinc complexes $[Zn(TMGqu)_2(CH_3SO_3)][CH_3SO_3]$ (**1**) and $[Zn(DMEGqu)(CH_3SO_3)_2]$ (**2**). Complex $[Zn(DMEGqu)_2(CH_3SO_3)][CH_3SO_3]$ (**3**) can be obtained if an excess of DMEGqu (molar ratio ligand to zinc salt 2.5: 1) is used (see Scheme 3). They could be isolated as yellow crystals in yields of 96–99%. Single crystals of the complexes were obtained either by cooling a saturated solution slowly to room temperature or by slow diffusion of diethyl ether into the solution. The resulting crystals have high stability towards moisture and air. They can be handled and stored in air, whereas the corresponding guanidine-pyridine hybrid ligands and the zinc salt are sensitive towards hydrolysis or rather hygroscopic.

Structure of the Zinc Complexes

The molecular structures of **1**–**3** (Figures 1–3) were determined by X-ray crystallography. In the complexes **1** and **3** the zinc atom is fourfold coordinated by the nitrogen atoms of two chelate ligands and possesses an additional contact to one oxygen atom of one mesylate ion, while the other mesylate ion is far away from the complex centre and acts as counterion. Contrastingly, in complex **2** the zinc atom is twofold coordinated by the two N-donor atoms of the DMEGqu ligand and the remaining coordination sites are occupied by two oxygen atoms of two mesylate ions (Scheme 3). Selected bond lengths and angles of the compounds are collected in Table 1.

In the bis-chelate complexes **1** and **3** the coordination geometry of the zinc centre can be best described as trigonal-bipyramidal. The axial positions are occupied by the pyridine nitrogen atoms and in the equatorial plane the guanidine nitrogen atoms as well as one oxygen atom of the mesylate ion are located around the zinc atom. The angle between the guanidine nitrogen atoms and the zinc atom is with 121.5 ° (av.) in accordance with the value expected for an ideal trigonal-bipyramid which is 120 °. The bite angles of the chelate ligands with an averaged value of 80.1 ° (90 °) and the angle between the pyridine nitrogen atoms and the zinc centre with 171.3 ° (av.) (180 °) are each to small and therefore leading to a distortion of the structure. In complex **2** the coordination geometry of the zinc centre is dictated by the bite angles of the chelate ligand which possesses a value of 83.6 ° and therefore

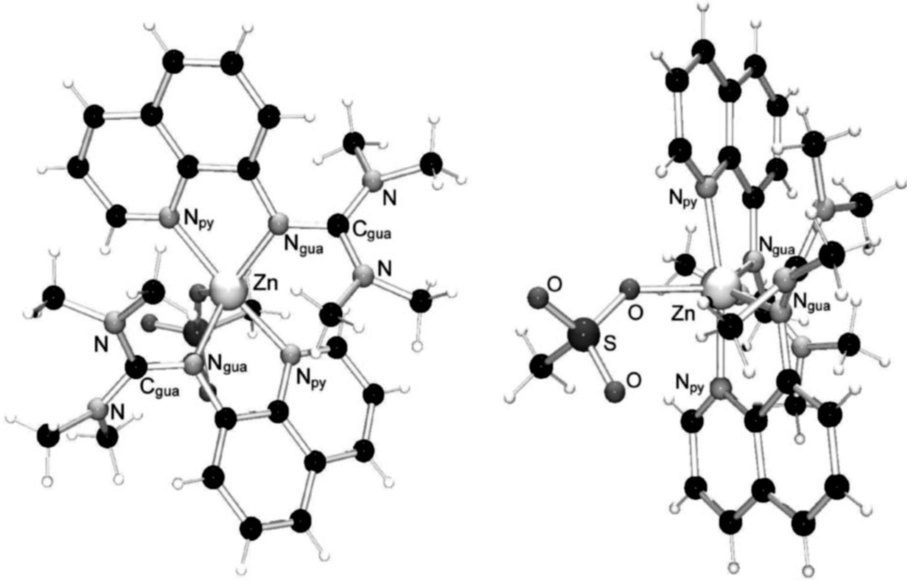


Figure 1.
Molecular structure of $[Zn(TMGqu)_2(CH_3SO_3)]^+$ in crystals of $[Zn(TMGqu)_2(CH_3SO_3)][CH_3SO_3]$ (**1**) as determined at 120 K (depicted in two different orientations).

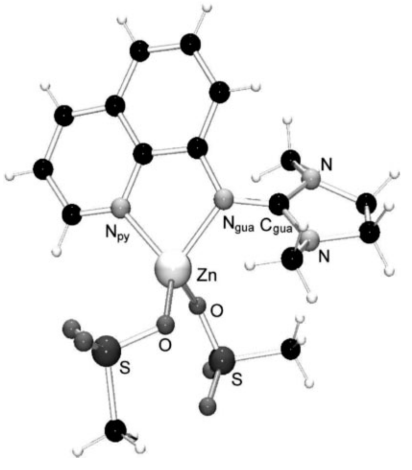


Figure 2.
Molecular structure of $[Zn(DMEGqu)(CH_3SO_3)_2]$ (**2**) as determined at 120 K.

differs considerably from the angle expected for an ideal tetrahedron (109.47 °). This leads to distorted tetrahedral coordination geometry.

The distances between the zinc atom and the pyridine donor atom are in the same range in each complex (**1**: av 2.096; **2**: 2.031; **3**: av 2.088 Å) and significantly longer than the corresponding Zn-N_{gua} bond lengths (**1**: av 2.061; **2**: 2.017; **3**: av 2.063 Å). It is noticeable that the Zn-N bonds in the tetrahedral complex **2** are in general shorter than the corresponding bonds in the bipyramidal complexes due to the smaller coordination number. This effect is also reflected in the distances between the zinc centre and the oxygen atom(s). In **2** it is significantly shorter (av. 1.947 Å) than in the complexes **1** and **3** (**1**: 2.103; **3**: 2.072 Å).

The distances between the nitrogen and the carbon atoms of the guanidine function are in all three complexes very alike and lie in the range of 1.330 to 1.354 Å which is indicative for good delocalisation in this moiety.

The dihedral angles between the $C_{gua}N_3$ and the NC_3 plane show the characteristic twisting within the guanidine moiety which can be found for all peralkylated guanidine units.[18–20] This twisting is a result of the interplay between the electronic effect of the intraguanidine conjugation (driving towards planarity) and the evasion of the alkyl substituents. The angles average a

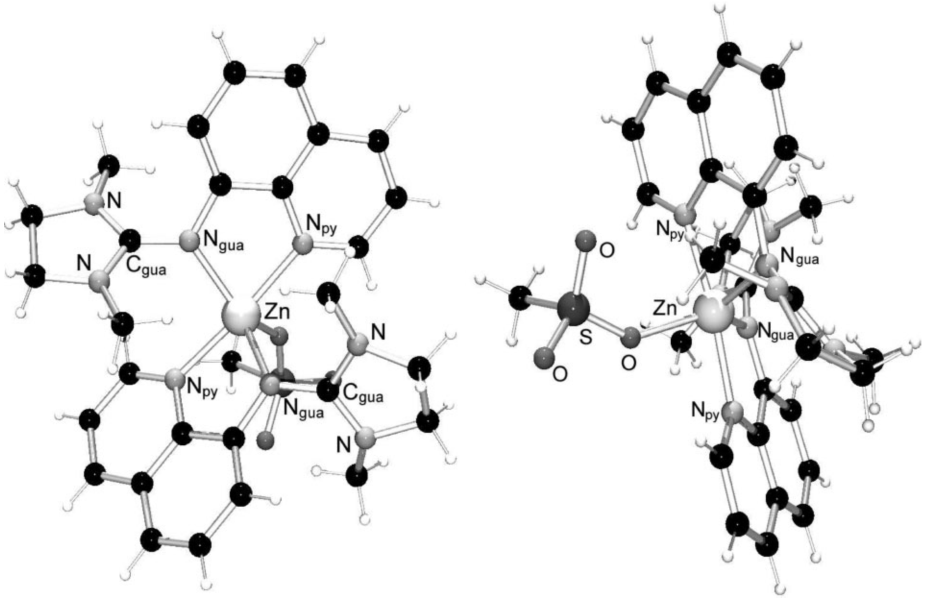


Figure 3.
Molecular structure of $[Zn(DMEGqu)_2(CH_3SO_3)]^+$ in crystals of $[Zn(DMEGqu)_2(CH_3SO_3)][CH_3SO_3]$ (**3**) as determined at 120 K (depicted in two different orientations).

Table 1.
Selected bond lengths (Å) and bond angles (°) of **1**, **2** and **3**.

	1	2	3
Zn-N_{gua}	2.043(1), 2.079(1)	2.017(1)	2.053(3), 2.072(3)
Zn-N_{py}	2.088(1), 2.103(1)	2.031(1)	2.087(3), 2.089(3)
Zn-O	2.103(1)	1.937(1), 1.956(1)	2.072(3)
C_{gua}-N_{gua}	1.354(2), 1.342(2)	1.337(2)	1.341(5), 1.330(5)
C_{gua}-N_{amine}	1.344(2), 1.346(2), 1.348(2), 1.350(2)	1.354(2), 1.343(2)	1.327(5), 1.335(5), 1.352(5), 1.338(5)
N_{gua}-Zn-N_{gua}	121.1(1)	-	121.8(1)
N_{gua}-Zn-N_{py} (bite)	80.8(1), 79.2(1)	83.6(1)	80.9(1), 79.3(1)
N_{py}-Zn-N_{py}	170.7(1)	-	171.8(1)
$<$ ($C_{gua}N_3$, NC_3) (av.)	29.6	11.8	9.6

higher value for TMGqu (29.6) than in DMEGqu (11.8 and 9.6) because twisting within TMG is more distinct due to the free rotation of the methyl groups connected to the amine function, whereas in DMEG twisting is hindered by the rigid ethylene bridge between the amine groups of the guanidine moiety.

DFT Calculations

The structural trends described above are discussed under consideration of gas phase DFT calculations. The electronic structures of the zinc complexes **1**–**3** have been examined using the B3LYP hybrid DFT functional[21] in combination with the 6–31g(d) basis set, implemented by the Gaussian 03 suite of programs.[22] Geometry optimisations were performed using the coordinates from X-ray data as starting points. The results of the optimisations are presented in Table 2.

The computed complex structures are in good agreement with their solid state structures. By trend, the Zn-N distances are predicted 0.01 to 0.05 Å too long. This

Table 2.
Summary of key geometric parameters of the calculated structures of **1–3** (RB3LYP/6-31G(d), bond lengths in Å and angles in °).

	1	2	3
Zn- N_{gua}	2.140, 2.077	2.111	2.136, 2.089
Zn-N_{py}	2.127, 2.147	2.057	2.120, 2.142
Zn-O	2.054	1.929, 2.056, 2.271	2.029
C_{gua}-N_{gua}	1.344, 1.345	1.329	1.338, 1.338
C_{gua}-N_{amine}	1.367, 1.356	1.375, 1.348	1.359, 1.351
	1.363, 1.356		1.353, 1.365
N_{gua}-Zn-N_{gua}	116.8	-	116.4
N_{gua}-Zn-N_{py} (bite)	78.4, 79. 7	80.5	78.4, 79.6
N_{py}-Zn-N_{py}	165.9	-	169.7
$<$ ($C_{gua}N_3$, NC_3)	30. 9	11.5	8.7

tendency has been observed quite frequently for such systems.[18,23,24] In contrast, the Zn-O distances in **1** and **3** are predicted around 0.5 Å too short, thus overestimating the donor strength of the mesylate. For this reason, the donor strength of the N donor might be underestimated. The trigonal-bipyramidal coordination in **1** and **3** is correctly described with regard to the critical angles like the bite angles and the N_{gua}-Zn-N_{gua} and N_{py}-Zn-N_{py} angles.

Complex **2** seems to represent a more complicated case: the Zn-N distances are predicted clearly too long whereas one of the Zn-O distances is predicted slightly too short. Concomitantly, the coordination of the mesylate anions is not correctly described: in the solid-state, both anions act a monodentate ligands with short Zn-O bonds (1.937(1) and 1.956(1) Å) whereas the DFT predicts one monodentate mesylate donor and the other mesylate as bidentate donor. In fact, the donor strength of the mesylate is stronger in reality.

For a more detailed analysis of the electronic structure the Mulliken charges have been determined. The resulting charges are summarized in Table 3. These charges do not represent absolute charges but the trends among the complexes give an impression of electronic effects.

The comparison between the bis-chelate complex cations **1** and **3** and the tetrahedral complex **2** reveals that the zinc centre is significantly more positively charged in the bis-chelates. This effect goes along with the great positive charge found for the bis-chelate triflate systems $\mathbf{1^{OTf}}$ and $\mathbf{3^{OTf}}$.[18] The guanidine N atoms are more negatively charged in the DMEG-containing ligands in **2** and **3** which is in accordance with the results for similar TMG and DMEG complexes.[18] The greater negative charge on the guanidine N atoms in **2** and **3** is consequentially accompanied by greater positive charges on the guanidine C atoms in **2** and **3**.

Polymerisation Activity

The guanidine-pyridine zinc complexes **1**, **2** and **3** were investigated towards their activity in the bulk polymerisation of D,L-lactide. For the polymerisation procedure

Table 3.
Mulliken charges in electron units (charge of electron is equal to -1) of **1–3** (RB3LYP/6-31g(d)).

	1	2	3
Zn	+0.968	+0.899	+0.974
N_{gua}	−0.741, −0.756	−0.788	−0.791, −0.798
N_{py}	−0.633, −0.607	−0.663	−0.619, −0.636
O	−0.686	−0.678, −0.698	−0.682
C_{gua}	+0.668, +0.653	+0.792	+0.773, +0.773
N_{amine}	−0.399, −0.394	−0.435, −0.457	−0.445, −0.444
	−0.394, −0.407		−0.448, −0.440

Table 4.
Polymerisation[a] of D,L-lactide in the presence of the guanidine zinc complexes **1**, **2** and **3**, as well with $\mathbf{1^{OTf}}$ and $\mathbf{3^{OTf}}$.[18]

Initiator		Time [h]	Yield [%]	M_w [g/mol]	PD[b]
$[Zn(TMGqu)_2(CH_3SO_3)][CH_3SO_3]$	(**1**)	48	33	28000	1.6
$[Zn(DMEGqu)(CH_3SO_3)_2]$	(**2**)	48	0	-	-
$[Zn(DMEGqu)_2(CH_3SO_3)][CH_3SO_3]$	(**3**)	48	29	28000	1.5
$[Zn(TMGqu)_2(CF_3SO_3)][CF_3SO_3]$	($\mathbf{1^{OTf}}$)	24	93	155000	2.2
$[Zn(DMEGqu)_2(CF_3SO_3)][CF_3SO_3]$	($\mathbf{3^{OTf}}$)	24	92	162000	2.1

[a] Reaction conditions: Catalyst (0.2 mol%), 150 °C.
[b] $PD = M_w/M_n$ where M_n is the number-average molar mass.

the monomer D,L-lactide and the initiator (I/M ratio 1:500) were heated at 150 °C. The monomer was used as purchased without further purification. After the reaction time of 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 4). In contrast to earlier studies[18], the reaction time was extended because after 24 h the yield was too small for the determination of the molecular weight distribution.

We found that the complexes **1** and **3** initiate the ring-opening polymerisation of D,L-lactide and produce very similar results whereas the tetrahedral complex **2** shows even after 48 h no polymerisation activity. But the comparison of the results of the bis-chelate mesylate complexes to those of the corresponding triflate complexes demonstrates clearly that the polymerisation activity decreases dramatically if the complexes contain the mesylate anion instead of the triflate ion. Application of $\mathbf{1^{OTf}}$ and $\mathbf{3^{OTf}}$ leads in half reaction time to polymers with a three times higher yield and more than five times higher molecular weights. The smaller PD values in the case of **1** and **3** may be due to the smaller yield.

Discussion

In our investigations we found a high dependence of the polymerisation activity of the zinc complexes on their structural and electronical properties. The comparison of the mesylate complexes **1** and **3** to their more active triflate analogues[18] $\mathbf{1^{OTf}}$ and $\mathbf{3^{OTf}}$ allows to elucidate the influence of coordination strength of the anionic component on the charge distribution within the complex and on the substrate accessibility to the zinc centre as crucial factors for the polymerisation initiation. An overview of the compared complex features is given in Table 5. For reasons of clarity, only the features of the DMEGqu containing complexes **2**, **3** and $\mathbf{3^{OTf}}$ are listed. The bis-chelate complexes **1** and **3** are structurally and electronically very similar to each other and consequently show almost the same polymerisation activity, indicating that the properties of the guanidine function have no effect in this case.

The tetrahedral zinc mesylate complex **2** was found to be inactive under the given conditions. It is remarkable that the initiator activity increases from **2** over **3** to $\mathbf{3^{OTf}}$ with increasing Zn-O distance and decreasing bond strength. This effect reinforces our hypothesis that the anion acts as placeholder for the monomer. Hence, the weak coordination of the triflate anion allows a good accessibility to the zinc centre which favours coordination of lactide and therefore accelerates the reaction. The slightly stronger donating property of the mesylate anion prevents fast coordination of the lactide.

In addition, the electronic properties of the complexes influence their activity as well. The positive charge at the zinc atom increases in the same direction as the polymerisation activity: from **2** over **3** to

Table 5.
Correlation of structural and electronical properties of **2**, **3** and $\mathbf{3}^{\mathbf{OTf}}$ with their ROP activity.

Complex		Bond length	Mulliken Charge		ROP activity	
with **L** = DMEGqu		Zn-O	Zn^{2+}	av. N_{gua}	Yield	M_w
$[Zn(\mathbf{L})(CH_3SO_3)_2]$	**2**	1.937, 1.956 Å	+0.899	−0.788	0	-
$[Zn(\mathbf{L})_2(CH_3SO_3)][CH_3SO_3]$	**3**	2.072 Å	+0.974	−0.795	29%	28000 g/mol
$[Zn(\mathbf{L})_2(CF_3SO_3)][CF_3SO_3]$	$\mathbf{3}^{\mathbf{OTf}}$	2.700, 2.452 Å	+1.004	−0.837	92%	162000 g/mol

$\mathbf{3}^{\mathbf{OTf}}$. So we could demonstrate that a great positive charge at the zinc atom promotes the ability to initiate the lactide polymerisation. In addition, we propose that the highly nucleophilic guanidine donor system act as ring-opening agent. With regard to these influences, it is comprehensible that the polymerisation presented here proceeds without the presence of alkoxides or alcohols which are traditionally necessary.[1–4]

In summary, in the case of guanidine-pyridine hybrid zinc complexes an auspicious initiator for the polymerisation of lactide should be a bis-chelate complex with very long or weak Zn-O bonds which possesses a high positive charge at the zinc atom.

Conclusion

In this contribution we reported on the synthesis and complete characterisation of three zinc guanidine-pyridine hybrid complexes $[Zn(TMGqu)_2(CH_3SO_3)][CH_3SO_3]$ (**1**), $[Zn(DMEGqu)(CH_3SO_3)_2]$ (**2**) and $[Zn(DMEGqu)_2(CH_3SO_3)][CH_3SO_3]$ (**3**). They were investigated towards their activity in the solvent-free ring-opening polymerisation of D,L-lactide and it was proven that the bis-chelate trigonal-bipyramidally coordinated compounds **1** and **3** are able to act as initiators for lactide polymerisation. Polylactides with molecular weights (M_w) of around 28000 g/mol could be obtained with relatively narrow polydispersities. The tetrahedral complex **2** does not initiate lactide polymerisation under the given conditions. In an integrated approach of structural studies and DFT calculations, the activity of the complexes **1** and **3** was correlated with their structural and electronical prerequisites in comparison to their more active triflate analogues $\mathbf{1}^{\mathbf{OTf}}$ and $\mathbf{3}^{\mathbf{OTf}}$. We found that the coordination strength of the anionic component has a significant impact on two issues of the polymerisation initiation: the charge distribution within the complex (especially the positive charge on the zinc atom) influences the attraction towards the substrate lactide and the accessibility to the zinc centre regulates the substrate coordination. DFT analysis shows that the mesylate complexes **1** and **3** have less positive charge on the zinc centre and the mesylate is stronger bound than the corresponding triflate in the triflate complexes $\mathbf{1}^{\mathbf{OTf}}$ and $\mathbf{3}^{\mathbf{OTf}}$. Consequently, the reactivity of the complexes is directly correlated to the coordinational behaviour of the anionic component. Further studies on the ring-opening polymerisation mechanism without the presence of alkoxides are conducted at the moment.

Experimental Part

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. D,L-Lactide (3,6-Dimethyl-1,4-dioxane-2,5-dione, Purac) was used as purchased. Zinc mesylate was prepared according to a procedure described by Wang et al.[25] and dehydrated by drying at 150 °C. The ligands DMEGqu and TMGqu were prepared according to literature procedures.[19]

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 $\delta_H = 1.94$ ppm). – IR: Nicolet P510. – MS (EI, 70eV): Finnigan MAT 95. –Elemental analyses: elementar vario MICRO cube.

Crystal Structure Analyses

Crystal data for compounds **1**, **2** and **3** are presented in Table 6. Data were collected with a Bruker-AXS SMART[26] APEX CCD, using MoKα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. Data reduction and absorption correction were done with SAINT and SADABS.[26] 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[26]). Hydrogen atoms were derived from difference Fourier maps and placed at idealized positions, riding on their parent C atoms, with isotropic displacement parameters $U_{iso}(H) = 1.2U_{eq}(C)$ and $1.5U_{eq}$(C methyl). All methyl groups were allowed to rotate but not to tip. Full crystallographic data (excluding structure factors) for **1**, **2** and **3** have been deposited with the Cambridge Crystallographic Data Centre as supplementary no. CCDC-743877 (**1**), -743878 (**2**) and -743879 (**3**). 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).

Computational Details

Density functional theory (DFT) calculations were performed with the program suite Gaussian 03.[22] The geometries of the complexes and ligands species were optimised (Table 2) using the B3LYP hybrid DFT functional[21] 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** and **3** 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.

Gel Permeation Chromatography

The molecular weight and molecular weight distribution of obtained polylactide samples were determined by gel permeation chromatography (GPC) in THF as

Table 6.
Crystallographic data for the compounds **1**, **2** and **3**.

	1	2	3
Empirical formula	$C_{30}H_{42}N_8O_6S_2Zn$	$C_{16}H_{22}N_4O_6S_2Zn$	$C_{30}H_{38}N_8O_6S_2Zn$
Molecular mass	740.21	495.87	736.17
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	16.961(2)	14.6607(18)	16.599(4)
b/Å	9.1946(12)	15.4456(18)	9.020(3)
c/Å	22.674(3)	8.7244(10)	22.821(6)
β/°	107.600(3)	93.843(2)	106.919(6)
$V/Å^3$	3370.4(8)	1971.1(4)	3268.9(16)
Z	4	4	4
$D_{calc}/g\ cm^{-3}$	1.459	1.671	1.496
μ/mm^{-1}	0.908	1.501	0.935
Temperature/K	120(2)	120(2)	120(2)
$\Theta_{max}/°$	1.88 to 27.87	1.39 to 27.88	1.87 to 27.88
Reflections collected	28944	17140	27345
Independent reflections	8024	4684	7786
R1 $[I \geq 2\sigma(I)]$	0.0323	0.0275	0.0620
wR2 (all data)	0.0851	0.0726	0.1690
Largest diff. peak, hole/e $Å^{-3}$	0.502, −0.270	0.465, −0.292	0.915, −0.765

mobile phase at a flow rate of 1 mL/min. A combination of PSS SDV columns with porosities of 10^5 Å 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[27]. Previous GPC measurements utilizing online viscosimetry detection revealed the KMH parameters for polylactide ($K_{PLa} = 0.053$ ml/g, $a_{PLa} = 0.610$).[28]

Preparation of Compounds

[Zn(TMGqu)$_2$(CH$_3$SO$_3$)][CH$_3$SO$_3$] (1)

To a suspension of 1.0 mmol of zinc(II) mesylate in dry THF, a solution of the ligand TMGqu (1.1 mmol) in THF was added under stirring. The resulting solution was stirred for 2 h while a green precipitate formed. The reaction mixture was slowly heated under reflux. Dry MeCN was added to give a clear light green solution. Yellow crystals suitable for X-ray diffraction could be obtained by diffusion of diethyl ether (m.p. 264 °C); yield: 96% (0.36 g). ^{1}H-NMR (500 MHz, CD$_3$CN, 25 °C): δ [ppm] = 2.32 (s, 6H, CH$_3$), 2.37 (m, 12H, CH$_3$), 2.79 (s, 6H, CH$_3$), 3.03 (s, 6H, CH$_3$), 6.85 (dd, 2H, CH, $^3J = 7.6$ Hz, $^4J = 1.2$ Hz), 7.61 (dd, 2H, CH, $^3J = 8.2$ Hz, $^4J = 1.2$ Hz), 7.68 (dd, 2H, CH, $^3J = 8.2$ Hz, $^3J = 7.6$ Hz), 7.82 (dd, 2H, CH, $^3J = 8.4$ Hz, $^3J = 4.6$ Hz), 8.62 (dd, 2H, CH, $^3J = 8.4$ Hz, $^4J = 1.6$ Hz), 8.92 (dd, 2H, CH, $^3J = 4.6$ Hz, $^4J = 1.6$ Hz). ^{13}C-NMR (125 MHz, CD$_3$CN, 25 °C): δ [ppm] = 38.9 (CH$_3$), 39.4 (CH$_3$), 41.0 (CH$_3$), 115.7 (CH), 118.6 (CH), 122.3 (CH), 129.0 (CH), 129.5 (C), 137.9 (C), 139.9 (CH), 143.6 (C), 148.5 (CH), 165.9 (C$_{\text{gua}}$). IR (KBr, $\tilde{\nu}$[cm^{-1}]): 3103 *w* (ν(C-H$_{\text{arom.}}$)), 3037 *w* (ν(C-H$_{\text{arom.}}$)), 3001 *w* (ν(C-H$_{\text{arom.}}$)), 2929 *w* (ν(C-H$_{\text{aliph.}}$)), 2877 *w* (ν(C-H$_{\text{aliph.}}$)), 2806 *w* (ν(C-H$_{\text{aliph.}}$)), 1576 *m* (ν(C=N)), 1525 *s* (ν(C=N)), 1502 *m*, 1468 *s*, 1421 *m*, 1400 *s*, 1388 *m*, 1379 *m*, 1331 *m*, 1277 *w*, 1248 *m*, 1205 *s*, 1194 *vs*, 1165 *m*, 1159 *s*, 1103 *m*, 1059 *w*, 1038 *m*, 1032 *m*, 962 *vw*, 924 *vw*, 903 *vw*, 881 *vw*, 849 *m*, 833 *m*, 823 *w*, 806 *m*, 796 *w*, 783 *w*, 775 *w*, 764 *m*, 750 *m*, 702 *w*, 669 *vw*, 652 *vw*, 633 *w*, 586 *w*, 550 *m*, 538 *m*, 526 *m*. EI-MS (m/z, (%)): 643 (4) [M$^+$- CH$_3$SO$_3$], 242 (100) [M$^+$ - Zn(CH$_3$SO$_3$)$_2$], 199 (18) [M$^+$ - Zn(CH$_3$SO$_3$)$_2$ - N(CH$_3$)$_2$ +H], 198 (74) [M$^+$ - Zn(CH$_3$SO$_3$)$_2$ - N(CH$_3$)$_2$], 184 (74) [M$^+$ - Zn(CH$_3$SO$_3$)$_2$ - N(CH$_3$)$_2$ - CH$_3$ +H], 183 (18) [M$^+$ - Zn(CH$_3$SO$_3$)$_2$ - N(CH$_3$)$_2$ - CH$_3$], 182 (17) [M$^+$ - Zn(CH$_3$SO$_3$)$_2$ - N(CH$_3$)$_2$ - CH$_3$ -H], 171 (44), 157 (35) [C$_{10}$H$_6$N$_2^+$ +H], 156 (25) [C$_{10}$H$_6$N$_2^+$], 155 (69), 143 (17) [M$^+$ - Zn(CH$_3$SO$_3$)$_2$ - C(N(CH$_3$)$_2$)$_2$ +H], 142 (18) [M$^+$ - Zn(CH$_3$SO$_3$)$_2$ - C(N(CH$_3$)$_2$)$_2$], 129 (24) [M$^+$ - Zn(CH$_3$SO$_3$)$_2$ - C(N)(N(CH$_3$)$_2$)$_2$ +H], 128 (13) [M$^+$ - Zn(CH$_3$SO$_3$)$_2$ - C(N)(N(CH$_3$)$_2$)$_2$], 100 (36) [C(N(CH$_3$)$_2$)$_2^+$]. Anal. Calcd. for C$_{30}$H$_{42}$N$_8$O$_6$S$_2$Zn (M = 741.41 g/mol): C, 48.56; H, 5.66; N, 15.11, Found: C, 48.60; H, 5.76; N, 15.14.

[Zn(DMEGqu)(CH$_3$SO$_3$)$_2$] (2)

A solution of the ligand DMEGqu (1.1 mmol) in abs. THF was added to a suspension of zinc mesylate (1.0 mmol) in abs. THF whilst stirring. A green precipitate formed and this reaction mixture was slowly heated under reflux. To obtain a clear solution abs. MeCN was added. Yellow crystals suitable for X-ray diffraction could be obtained by diffusion of diethyl ether (m.p. 185 °C); yield: 99% (0.50 g). ^{1}H-NMR (500 MHz, CD$_3$CN, 25 °C): δ [ppm] = 2.76 (s, 6H, CH$_3$), 2.88 (s, 6H, CH$_3$), 3.75 (m, 4H, CH$_2$), 7.14 (d, 1H, CH, $^3J = 7.6$ Hz), 7.52 (d, 1H, CH, $^3J = 8.1$ Hz), 7.61 (dd, 1H, CH, $^3J = 8.1$ Hz, $^3J = 7.6$ Hz), 7.78 (dd, 1H, CH, $^3J = 8.3$ Hz, $^3J = 4.7$ Hz), 8.59 (dd, 1H, CH, $^3J = 8.3$ Hz, $^4J = 1.3$ Hz), 9.00 (dd, 1H, CH, $^3J = 4.7$ Hz, $^4J = 1.3$ Hz). ^{13}C-NMR (125 MHz, CD$_3$CN, 25 °C): δ [ppm] = 34.4 (CH$_3$), 38.7 (CH$_3$), 48.1 (CH$_2$), 116.7 (CH), 118.2 (CH), 122.4 (CH), 128.6 (CH), 129.4 (C), 137.9 (C), 140.9 (CH), 142.2 (C), 148.9 (CH), 164.5 (C$_{\text{gua}}$). IR (KBr, $\tilde{\nu}$[cm^{-1}]): 3016 *vw* (ν(C-H$_{\text{arom.}}$)), 2933 *vw* (ν(C-H$_{\text{aliph.}}$)), 2889 *vw* (ν(C-H$_{\text{aliph.}}$)), 1595 *m* (ν(C=N)), 1560 *m*

(ν(C = N)), 1502 *m*, 1468 *m*, 1417 *m*, 1392 *m*, 1327 *m*, 1298 *w*, 1273 *w*, 1240 *m*, 1207*s*, 1194 *vs*, 1157 *m*, 1103 *w*, 1059 *m*, 1026 *m*, 978 *vw*, 912 *vw*, 827 *w*, 806 *w*, 785 *m*, 773 *m*, 696 *vw*, 669 *vw*, 638 *w*, 611 *vw*, 582 *w*, 563 *m*, 536 *m*, 526 *m*. EI-MS (m/z, (%)): 494 (2) [M^+], 399 (8) [M^+ - CH_3SO_3], 241 (27), 240 (100) [M^+ - $Zn(CH_3SO_3)_2$], 239 (70), 183 (11) [$C_{11}H_9N_3^+$], 155 (27) [$C_{10}H_6N_2^+$ +H], 142 (10) [$C_9H_6N_2^+$], 129 (14) [$C_9H_6N^+$ +H], 98 (42) [$C_5H_{10}N_2^+$]. Anal. Calcd. for $C_{16}H_{22}N_4O_6S_2Zn$ (M = 496.70 g/mol): C, 38.67; H, 4.43; N, 11.27, Found: C, 38.84; H, 4.56; N, 11.33.

[Zn(DMEGqu)$_2$(CH$_3$SO$_3$)][CH$_3$SO$_3$] (3)

To a suspension of 1.0 mmol of zinc(II) mesylate in dry THF, a solution of the ligand DMEGqu (2.5 mmol) in THF was added under stirring. The resulting reaction mixture was stirred for 20 minutes. Due to the precipitation of the corresponding complex, the reaction mixture was slowly heated under reflux. Dry MeCN was added to give a clear yellow solution. Yellow crystals suitable for X-ray diffraction could be obtained by slowly cooling to room temperature (m.p. 268 °C); yield: 98% (0.72 g). ^{1}H-NMR (500 MHz, CD_3CN, 25 °C): δ [ppm] = 2.32 (s, 6H, CH_3), 2.47 (b, 12H, CH_3), 3.56 (b, 8H, CH_2), 7.00 (dd, 2H, CH, $^3J = 7.6$ Hz, $^4J = 1.0$ Hz), 7.49 (dd, 2H, CH, $^3J = 8.2$ Hz, $^4J = 1.0$ Hz), 7.60 (dd, 2H, CH, $^3J = 8.2$ Hz, $^3J = 7.6$ Hz), 7.82 (dd, 2H, CH, $^3J = 8.3$ Hz, $^3J = 4.6$ Hz), 8.60 (dd, 2H, CH, $^3J = 8.3$ Hz, $^4J = 1.5$ Hz), 8.89 (dd, 2H, CH, $^3J = 4.6$ Hz, $^4J = 1.5$ Hz). ^{13}C-NMR (125 MHz, CD_3CN, 25 °C): δ [ppm] = 38.9 (CH_3), 47.3 (CH_2), 114.8 (CH), 117.0 (CH), 122.0 (CH), 128.7 (CH), 129.6 (C), 137.8 (C), 139.9 (CH), 143.2 (C), 147.7 (CH), 165.1 (C_{gua}). IR (KBr, $\tilde{\nu}$[cm^{-1}]): 3109 *w* (ν(C-H$_{arom.}$)), 3070 *w* (ν(C-H$_{arom.}$)), 3045 *w* (ν(C-H$_{arom.}$)), 3008 *w* (ν(C-H$_{arom.}$)), 2997 *w* (ν(C-H$_{aliph.}$)), 2962 *w* (ν(C-H$_{aliph.}$)), 2927 *w* (ν(C-H$_{aliph.}$)), 2877 *w* (ν(C-H$_{aliph.}$)), 1558*s* (ν(C = N)), 1502*s*, 1483 *m*, 1468*s*, 1423 *m*, 1392*s*, 1327 *m*, 1300 *m*, 1248*s*, 1207*s*, 1196*s*, 1161*s*, 1107 *m*, 1059 *w*, 1039*s*, 1026 *m*, 974 *w*, 910 *vw*, 829 *m*, 806 *w*, 793 *m*, 773 *m*,762 *m*, 748 *m*, 694 *w*, 662 *vw*, 640 *w*, 609 *vw*, 582 *w*, 550 *m*, 536 *w*, 521 *m*. EI-MS (m/z, (%)): 448 (13) [M^+- 2 CH_3SO_3 – $C_5H_{10}N_2$ +2H], 422 (12), 240 (10) [M^+ - $Zn(CH_3SO_3)_2$], 204 (15), 189 (44) [$C_{11}H_{13}N_3^+$ +2H], 174 (13), 146 (98), 145 (59), 131 (42), 123 (100) [$C_6H_{11}N_3^+$ -H], 119 (45), 117 (62) [$C_8H_6N^+$ +H], 115 (31), 105 (18) [$C_7H_4N^+$ +3H], 103 (22) [$C_7H_4N^+$ +H], 91 (35) [$C_6H_3N^+$ +2H], 77 (23) [$C_5H_3N^+$], 57 (16) [$C_3H_7N^+$]. Anal. Calcd. for $C_{30}H_{38}N_8O_6S_2Zn$ (M = 737.37 g/mol): C, 48.82; H, 5.15; N, 15.19, Found: C, 48.87; H, 5.08; N, 15.16.

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 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.

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