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Rare-earth metal complexes derived from the acids $Ph_2C(X)CO_2H$ (X= OH, NH_2): Structural and ring opening polymerization (ROP) studies.

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Abstract: Treatment of $Ln(NO_3)_3{\cdot}6H_2O$ (Ln = La, Ce) with an equimolar amount of 2,2'-diphenylglycine (DpgH) in ethanol afforded the corresponding hexacoordinated complexes $(DpgH^{\pm})_3Ln(NO_3)_3{\cdot}H_2O$ ($DpgH^{\pm}$ = zwitterionic 2,2'-diphenylglycine, Ln = La (**1**), Ce (**2**)). The spectroscopic and structural features of these compounds have been investigated. Similar reactions with the related benzilic acid ($BenzH_2$) were unsuccessful. The catalytic behaviour of **1** and **2** in the homo- and copolymerization of ε-caprolactone (ε-CL) and *rac*-lactide (*r*-LA) has been investigated herein. In the case of ε-CL, the two complexes exhibited comparable activity, allowing for complete monomer conversion under aerobic and solvent-free conditions at 150 °C in 24 h. With respect to the ROP of *r*-LA, **1** was found to be completely inactive, while only 8% conversion was achieved in the presence of **2**. Liquid oligomers were isolated during ε-CL/*r*-LA co-polymerization in the presence of both complexes. The catalytic activity of the pre-ligands DpgH and $BenzH_2$ (*i.e.* metal-free) was also examined. Interestingly, only $BenzH_2$ was found to be active, although it required a higher catalyst loading and the presence of benzyl alcohol as co-activator.

Keywords: Lanthanide, Magic Acids, Diphenylglycine, Ring Opening Polymerization, Biodegradable

Introduction

During the past decade, significant efforts have been devoted to the development of polymers that are both biodegradable and derived from renewable sources. These are typically synthesized by the ring opening polymerization (ROP) of lactides and lactones, a process usually requiring a metal catalyst [1]. In this scenario, polymers obtained from the homo- and co-polymerization of ε-caprolactone (ε-CL) and *rac*-lactide (*r*-LA) have been used for several applications, such as packaging and temporary medical implants [2] or as bio-adhesives [3]. Since the nature of the catalyst has a dramatic impact on the polymerization, in terms of both efficiency and polymer microstructure, a plethora of catalytic systems featuring various metal/ligand combinations have been explored [1]. Nevertheless, reports concerning the activity of metal complexes bearing ligands containing the motif $Ph_2(X)(CO_2)$, derived from the *magic acids* benzilic acid or 2,2'-diphenylglycine (X = OH or NH_2, respectively), so called because the Ph_2C motif is known to afford highly crystalline products, [4] are scant. [5] In this context, systems involving Al [6], Zn [7] and Li [8] have been recently screened by our group. Since metal complexes based on rare-earth metals are known to be efficient catalysts for the ROP of cyclic esters [9], we have decided to extend the use of these *magic acids* to metals belonging to the lanthanide series. Herein, we report the synthesis and molecular structures of La and Ce complexes derived from 2,2'-diphenylglycine (DpgH) and their use as catalysts for the homo- and co-polymerization of ε-CL and *r*-LA, as well as ROP investigations using the metal-free *magic acids*.

Experimental

Pro-ligands were purchased from Sigma Aldrich or TCI UK and used as received. IR spectra (neat, KBr windows) were recorded on a Nicolet Avatar 360 FT IR spectrometer ^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Varian VXR 400 S spectrometer at 400 MHz or 100MHz respectively. The NMR spectra were calibrated against the residual signal of the deuterated solvent.

*Synthesis of complex **1***

$La(NO_3)_3{\cdot}6H_2O$ (0.43 g, 1 mmol, 1 equiv.) was dissolved in ethanol (25 mL) and the solution was added to a suspension of 2,2'-diphenylglycine (0.23 g, 1 mmol, 1 equiv.) in ethanol (25 mL). Two drops of an aqueous solution (40% w/w) of $(n\text{-Bu})_4NOH$ were added and the mixture was stirred at room temperature for 3 h. Colourless crystals of **1** were obtained by slow evaporation of the solvent (0.34 g, 92%). ^{1}H NMR (DMSO-d_6, 400 MHz, 25 ºC): δ = 8.47 (bs, 9H, NH_3), 7.37 (m, 15H, Ar*H*), 7.29 (m, 15H, Ar*H*). ^{13}C NMR (DMSO-d_6, 74 MHz, 25 ºC): δ = 140.5 (s, *C*H Ar), 128.8 (s, *C*H Ar), 128. 4 (C^{IV} Ar), 128.3 (s, *C*H Ar), 69.5 (s, C^{IV}). The carboxylate carbon not observed in the spectral range -20-230 ppm. $C_{42}H_{45}LaN_6O_{19}{\cdot}6H_2O$ requires: C 42.58, H 4.85, N 7.09; Found C 42.98, H 4.43, N 7.50%.

*Synthesis of complex **2***

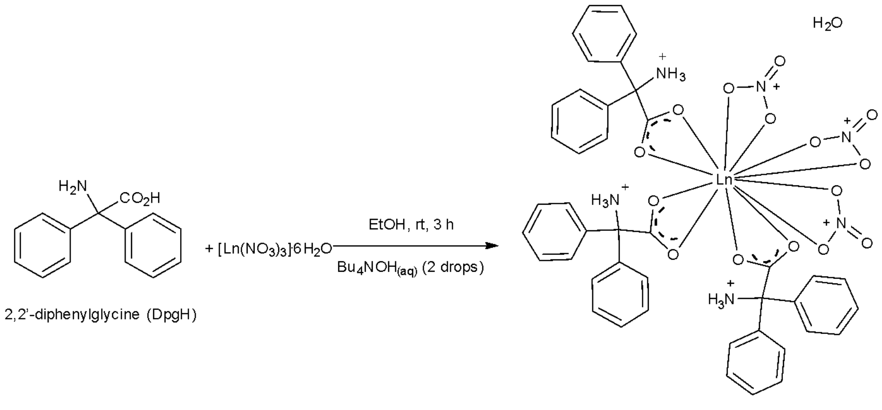
Following the procedure for **1**, complex **2** was obtained by reaction of $Ce(NO_3)_3{\cdot}6\,H_2O$ (0.42 g, 1 mmol, 1 equiv.) and 2,2'-diphenylglycine (0.23 g, 1 mmol, 1 equiv.). Yield 0.33 g (89%). $C_{42}H_{45}CeN_6O_{19}{\cdot}6H_2O$ requires: C 42.53, H 4.84, N 7.09; Found: C 43.21, H 4.49, N 7.79%.

General procedure for the Ring Opening Polymerization (ROP) of cyclic esters

A 20 mL screw-top glass vial equipped with a magnetic stirrer bar was charged in air with the required amount of the catalyst and the monomer (0.5 mL for ε-CL and 0.70 g for *r*-LA, respectively). The vial was sealed and the reaction was stirred at 150 °C for 24 h. The mixture was then quenched with acidified methanol (250 mL), the polymer was recovered by filtration and dried at 60 °C for 16 h.

Results and discussion

By reacting $Ln(NO_3)_3{\cdot}6H_2O$ (Ln = La, Ce) with an equimolar amount of 2,2'-diphenylglycine (DpgH) in ethanol in the presence of a few drop of $(n\text{-Bu})_4NOH$, two complexes of the type $(DpgH^{\pm})_3Ln(NO_3)_3{\cdot}H_2O$ ($DpgH^{\pm}$= zwitterionic 2,2'-diphenylglycine, Ln = La (**1**), Ce (**2**)) were obtained (Scheme 1). The ammonium salt was introduced to adjust the pH of the solution (pH ~ 9), which allowed the DpgH to completely solubilize. Nevertheless, the reactions occurred also in the absence of such additive, albeit with a significantly lower rate (1 day *versus* 3 h).



1 Ln = La
2 Ln = Ce

Scheme 1. Synthesis of complexes **1** and **2**.

For both compounds, crystals suitable for X-ray diffraction were obtained by slow evaporation of solvent from concentrated ethanol solutions. The molecular structure of **1** (CCDC No. 1997947) is shown in figure 1, with selected bond lengths and angles given in the caption. The La center is surrounded by three DpgH moieties in their zwitterionic form (DpgH$^{\pm}$), with the carboxylate groups bound to the metal in a bidentate chelating fashion. The zwitterion nature of the 2,2'-diphenylglycine moieties was confirmed by ^{1}H NMR spectroscopy in DMSO-d_6; in fact, a broad resonance accountable to the NH_3^+ fragment was observed in the spectrum of **1**. In turn, the carboxylic acid proton peak was not detected. For the sake of clarity, the same pattern could be observed in the ^{1}H NMR spectrum of DpgH. This was not surprising, since the α-amino acids are normally present in solutions in their zwitterionic form [10].

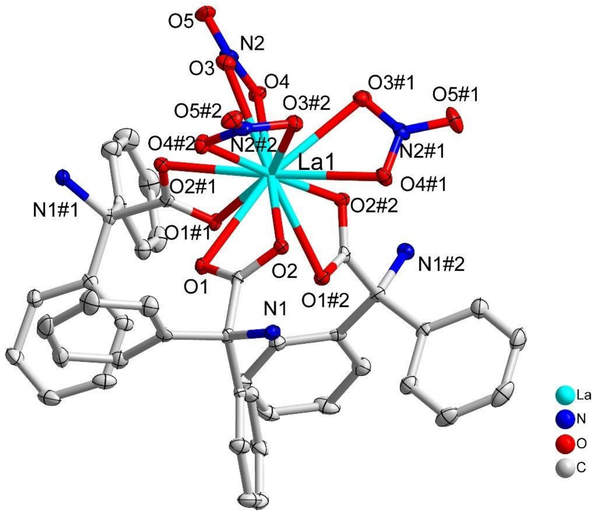


Figure 1. Molecular structure of **1** (hydrogens and water molecule are omitted for clarity; Symmetry codes: #1: 1-x+y, 1-x, z; #2: 1-y, x-y, z-1). Selected bond lengths (Å) and angles (°): La(1)-O(1) 2.701(3), La(1)-O(2) 2.589(3), La(1)-O(3) 2.709(3), La(1)-O(4) 2.679(3), C(1)-O(1) 1.254(4), C(1)-O(2) 1.254(5), N(2)-O(4) 1.264(5), N(2)-O(3) 1.253(4), O(1)-La(1)-O(2) 49.33(8), O(3)-La(1)-O(4) 47.03(9), O(1)-C(1)-O(2) 118.9(3), O(3)-N(2)-O(4) 117.3(3), O(2)-La(1)-O(3) 129.44(9).

In order to obtain further structural information, ^{13}C NMR spectroscopy studies on **1** (in the range between -20 and 230 ppm) were undertaken. Compared to the spectrum of the parental DpgH ligand, the resonance of the aromatic quaternary carbon was shifted downfield by *ca.* 2ppm and overlapped with the peak of the carbons in the *ortho* position. Moreover, while the carbonyl peak for DpgH was identified at 168 ppm, the corresponding resonance for **1** could not be observed in the spectral range considered. This suggested a significant downfield shift (above 230 ppm) due to the binding of the carboxylate unit to the metal center. Finally, a very broad band in the 3600-2600 cm^{-1} range was observed in the FT-IR spectrum of **1**. This is presumably due to the vibrations of the NH_3^+ group, as previously observed in the FT-IR spectra of zwitterionic amino acids. [11] Moreover, signals at 2482 and 1651 cm^{-1} accountable to the symmetric stretching of $-NH_3$ and $-COO^-$, respectively, were detected.

The molecular structure of **2** (CCDC No. 1997948) (Figure 2) was found to be very similar to that of its La-congener. Nevertheless, a few differences can be found; the Ln-O bonds (both for the nitrate and the Dpg- units) in **2** were found to be slightly shorter than in **1** (*i.e.* Ln-O(1) 2.686(2) and 2.701(3) for **2** and **1**, respectively). On the other hand, the O-C-O angle in the carboxylate group is larger in **2** than in **1** (123.8(3) *vs* 118.9(3)º). Given Ce(III) is paramagnetic, only broad resonances that could not provide any useful structural information were observed in its ^{1}H NMR spectrum.

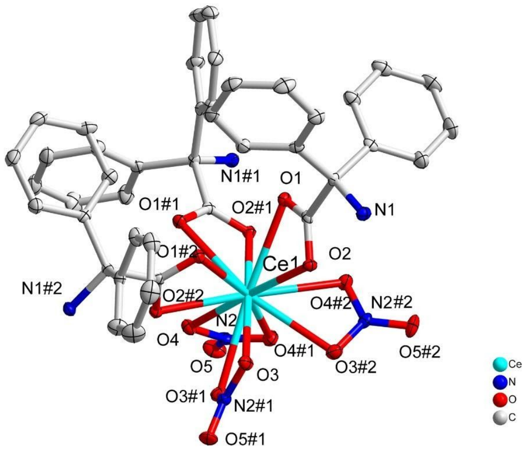
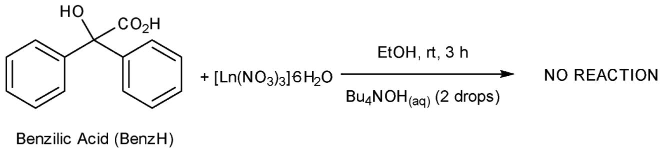


Figure 2. Molecular structure of **2** (hydrogens and water are omitted for clarity; Symmetry codes: #1: 1-x+y, 1-x, z; #2: 1-y, x-y, z-1)**.** Selected bond lengths (Å) and angles (°): Ce(1)-O(1) 2.686(3), Ce(1)-O(2) 2.567(2), Ce(1)-O(3) 2.685(2), Ce(1)-O(4) 2.657(2), C(1)-O(1) 1.253(3), C(1)-O(2) 1.257(4), N(2)-O(4) 1.270(3), N(2)-O(3) 1.252(3), O(1)-Ce(1)-O(2) 49.80(6), O(3)-Ce(1)-O(4) 47.47(7), O(1)-C(1)-O(2) 123.8(3), O(3)-N(2)-O(4) 117.0(2), O(2)-Ce(1)-O(3) 129.31(7).

For comparative studies, we have also investigated the coordination behavior of another *magic acid*, namely benzilic acid ($BenzH_2$), whose structure is closely related to that of DpgH. In fact, they only differ in the nature of one substituent on the α-carbon (NH_2 and OH for DpgH and $BenzH_2$, respectively). Unfortunately, synthetic attempts to prepare La- and Ce complexes bearing $BenzH_2$ under the same reaction conditions used for **1** and **2** were unsuccessful (Scheme 2).



Scheme 2. Synthetic attempts towards Ln complexes of benzylic acid ($BenzH_2$).

Ring Opening Polymerization (ROP) of cyclic esters

Both complexes, along with their metal precursors $Ln(NO_3)_3 \cdot 6H_2O$, were tested as catalysts in the homo- and co-polymerization of ε-caprolactone (ε-CL) and *rac*-lactide (*r*-LA) under aerobic and *solvent-free* and conditions (Table 1). In the case of ε-CL, high conversion (> 90%) was achieved with complexes **1** and **2** (runs 1 and 2), while lower activity (~80% conversion) was observed in the presence of their metal precursors (runs 3 and 4). Polymers with molecular weight of *ca*. 3.0 kDa and polydispersity of 1.6 were isolated by using **1** and **2**; lower M_n and less control were observed when the lanthanide precursors were employed. Hence, the presence of the Dpg-moieties bound to the metal center proved to be beneficial. The rather low M_n and the poor control is attributed to the occurrence of undesired side-reactions occurring at high temperature. However, tests performed at lower temperature (ie. 80 °C) proved unsuccessful, justifying the use of such relatively harsh reaction conditions. It has to be noted that by performing the reaction in the presence of solely DpgH under the same reaction conditions, no conversion was achieved. This highlighted that the ligand itself in not able to initiate the reaction. For all polymers, a triplet resonating at *ca*. 3.6 ppm was observed by ^{1}H NMR spectroscopy. The presence of a such signal is diagnostic for the -CH_2OH terminal group suggested the formation of α-hydroxyl-ω-(carboxylic acid)-terminated polymers. For the sake of clarity, the presence of the ω-carboxylic acid group could not be clearly assessed by ^{1}H NMR spectroscopy. This is probably due to the overlapping of its diagnostic signal to that of the α-CH$_2$ of the main polymer chain (2.35 and 2.33-2.30 ppm, respectively) [12]. On the other hand, signals accountable to Dpg-based end groups were not observed either, indicating H_2O as the actual initiator of the ROP process [13]. In the case of *r*-LA, no conversion was observed in the presence of both La-based species (runs 5 and 7), while only traces (*ca*. 8% conversion) were obtained upon using **2** and its corresponding metal precursor (runs 6 and 8). Concerning the co-polymerization tests, liquid oligomers were obtained in the presence of **1** and **2** (runs 9 and 10). Unfortunately, the M_n of the product was found to be too low to be determined by GPC. In both cases, ^{1}H NMR spectroscopy analysis on the crude reaction mixtures showed higher conversion of *r*-LA over ε -CL. This result seems counterintuitive, since the catalysts proved efficient in the homo-polymerization of ε -CL and rather inactive for that of *r*-LA. However, the inversion of the activity trend in the co-polymerization of these monomer has been previously observed in the case of other catalytic systems and rationalized considering the higher reaction rate of *r*-LA over that of ε -CL. [14] In the present case, it can also be assumed that ε -CL acts as a solvent, favoring the ROP of the co-monomer compared to its bulk polymerization. In order to corroborate this assumption, the ROP of *r*-LA was carried out in toluene. No conversion was observed, suggesting that in the co-polymerization, ε -CL could serve also as an activator. This is reasonable, since cyclic monomers (*i.e.* propylene oxide) are known to play the dual solvent/activator role in the ROP of lactide. [15] In the presence of $\mathrm{La(NO_3)_3{\cdot}6H_2O}$, only moderate ε -CL conversion (30%) was observed, while all *r*-LA remained unreacted (run 11).

Table 1. Homo- and copolymerization of ε -CL and *r*-LA catalyzed by La- and Ce-species.

Run	**Catalyst**	**Monomer(s)**	**Monomer:M**	**Conv.**[a] (%)	M_n[b,c] (kDa)	M_w/M_n[b]
1	**1**	ε -CL	250:1	94	3.2	1.57
2	**2**		250:1	93	2.8	1.56
3	$\mathrm{La(NO_3)_3\,6\,H_2O}$		250:1	84	1.6	1.82
4	$\mathrm{Ce(NO_3)_3\,6\,H_2O}$		250:1	84	1.9	1.89
5	**1**	*r*-LA	250:1	none	-	-
6	**2**		250:1	8	nd	nd
7	$\mathrm{La(NO_3)_3\,6\,H_2O}$		250:1	none	-	-
8	$\mathrm{Ce(NO_3)_3\,6\,H_2O}$		250:1	9	nd	nd
9	**1**	ε -CL *co* *r*-LA	250:250:1	31/72	Liquid Oligomers	
10	**2**		250:250:1	14/91	Liquid Oligomers	
11	$\mathrm{La(NO_3)_3\,6\,H_2O}$		250:250:1	0/31	nd	nd
12	$\mathrm{Ce(NO_3)_3\,6\,H_2O}$		250:250:1	0/0	-	-

Reaction conditions: Solvent-free, T = 150 ºC, 24 h, ambient atmosphere. [a] Determined by ^{1}H NMR spectroscopy on the crude reaction mixture. [b] From GPC. [c] Values corrected considering Mark–Houwink factor (0.56 for ε -CL) from polystyrene standards in THF.

Neither of the co-monomers was converted in the presence of $Ce(NO_3)_3 \cdot 6H_2O$ (run 12). Overall these catalysts proved less efficient than recently reported Ln-based species, both in terms of activity and polymer M_n [16].

Since carboxylic acids have shown to be efficient organo-catalysts for the ROP of cyclic esters [17], the catalytic activity of DpgH in the polymerization of ε-CL was investigated (Table 2). No monomer conversion was achieved under the same conditions as employed for **1** and **2** (run 1). Moreover, only 5% conversion was achieved upon performing the reaction in the presence of a *ca.*10-fold higher catalyst loading (run 2). For the sake of completeness, the catalytic activity of benzilic acid was also tested. Under the optimized reaction conditions, 14% conversion was achieved (run 3). A positive effect was observed upon employing benzyl alcohol (BnOH) as an activator. Indeed, 33 and 50% conversion were obtained in the presence of 1 and 2 equivalents of BnOH, respectively (runs 4 and 5). However, no further improvement was observed in the presence of a higher amounts of alcohol (25 equiv., run 6).

Table 2. Homo- and copolymerization of ε-CL and *r*-LA catalyzed by DpgH and $BenzH_2$.

Run	Catalyst	Monomer(s)	Monomer:M:BnOH	Conversion[a] (%)	M_w[b, c] (KDa)	M_w/M_n[b]
1	DpgH	ε-CL	250:1:0	none	nd	nd
2			20:1:1	5	nd	nd
3	$BenzH_2$	ε-CL	250:1:0	14	nd	nd
4			250:1:1	33	nd	nd
5			250:1:2	50	nd	nd
6			250:1:25	50	nd	nd
7			20:1:1	>99	2,850	1.53
8			20:1:0	>99	5,600	1.58
9		*r*-LA	20:1:0	None	-	-
10			20:1:1	Trace	-	-
11		ε-CL co *r*-LA	20:20:1:0	50 (LA)/28 (CL)	Liquid Oligomers	
12			20:20:1:1	35 (LA)/50 (CL)	Liquid Oligomers	

Reaction conditions: T = 150 ºC, 24 h, neat, air. [a] Determined by ^1H NMR spectroscopy on the crude reaction mixture. [b] From GPC. [c] Values corrected considering Mark–Houwink factor (0.56 for CL and 0.58 for LA) from polystyrene standards in THF.

To our delight, full monomer conversion was achieved by increasing the catalyst loading, both in the presence and in the absence of activator (runs 7 and 8, respectively). The M_n of the PCL obtained without BnOH was found to be *ca*. 2-fold higher than that of the polymer isolated in the presence of the alcohol (5.6 *vs* 2.9 KDa).

This could be ascribed to the occurrence of undesired chain-transfer to the co-activator [18]. The polydispersity values were found to be in a very narrow range (1.5-1.6). The ^1H NMR spectrum of the polymer isolated in the absence of BnOH was found to be similar to that obtained in the presence of **1** and **2**, suggesting the formation α-hydroxyl-ω-(carboxylic acid)-terminated PCL also in this case. Hence, it was not possible to assess the nature of the initiating group, which was thought to be cleaved during the quenching with acidified methanol. However, considering that DpgH was inactive under the same reaction conditions, it was hypothesized that the ROP mechanism involved the α-hydroxy group of $BenzH_2$.

Under the same reaction conditions, the ROP of *r*-LA was unsuccessful, regardless from the presence of BnOH (runs 9 and 10). Low M_n oligomers were isolated in the case of CL/LA copolymerization (runs 11 and 12).

Conclusions

In conclusion, we have synthesized two novel lanthanide complexes supported by 2,2'-diphenylglycine derived ligation. The structure of these species was determined by means of X-ray diffraction on single crystals. No reaction was observed upon using the related pro-ligand benzilic acid. Complexes **1** and **2** proved to be active in the ROP of ε-CL under aerobic and solvent-free conditions, and were shown to be better performing than their corresponding metal precursors, both in terms of monomer conversion and polymer molecular weight. Neither of the catalysts was able to promote the ROP of *r*-LA, while only liquid oligomers were isolated during CL/LA co-polymerizations. Both DpgH and $BenzH_2$ were also tested in the ROP of cyclic esters, and only the latter proved to be active, albeit requiring higher catalyst loadings and the presence of a co-activator.

Acknowledgements

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Table 3. Crystallographic data for complexes **1** and **2**.

Compound	**1**	**2**
Formula	$C_{42}H_{45}LaN_6O_{19}$	$C_{42}H_{45}CeN_6O_{19}$
Formula weight	1076.75	1077.96
Crystal system	Trigonal	Trigonal
Space group	R -3 :H	R -3 :H
a (Å)	15.1745(9)	15.1395(7)
b (Å)	15.1745(9)	15.1395(7)
c (Å)	34.352(3)	34.223(2)
α (º)	90	90
β (º)	90	90
γ (º)	120	120
V (Å^3)	6850.3(10)	6793.3(8)
Z	6	6
Temperature (K)	150(2)	150(2)
Wavelength, λ (Å)	0.71073	0.71073
Calculated density (g.cm^{-3})	1.566	1.581
Absorption coefficient, μ (mm^{-1})	1.020	1.090
Transmission factors (min./max.)	0.975/0.966	0.791/0.773
Crystal size (mm^3)	0.190 x 0.170 x 0.050	0.280 x 0.160 x 0.080
θ(max) (°)	26.372	26.372
Reflections measured	9961	14130
Unique reflections	3104	3090
R_{int}	0.0908	0.0827
Number of parameters	214	214
R_1 [$F^2 > 2\sigma(F^2)$]	0.0415	0.0322
wR_2 (all data)	0.0691	0.0648
GOOF, S	0.821	0.891
Largest difference peak and hole (e Å^{-3})	1.146 and -0.509	1.507 and -0.435

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