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Zinc complexes with 1,2-disubstituted benzimidazole ligands: Experimental and theoretical studies in the catalytic cycloaddition of CO₂ with epoxides



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ABSTRACT

The synthesis and characterization of four zinc(II) complexes with monodentate 1,2-disubstituted benzimidazole ligands and their catalytic activity in the cycloaddition of CO_2 and epoxides are reported. The complexes were characterized by ¹H and ¹³C NMR, thermal analysis, infrared absorption and FT-Raman spectroscopy and ESI-HRMS. Complex **Zn3** had its structure determined by single-crystal X-ray diffraction and a description of intra- and intermolecular interactions has been done. All complexes were able to catalyze the production of cyclic carbonates selectively, and complex **Zn1** was used in the transformation of various epoxides to carbonates, using tetrabutylammonium bromide as cocatalyst. Quantum chemistry approaches were used to comprehend the initial step of catalytic cycle: the epoxide coordination to the metallic center. The calculations show that one benzimidazole ligand should be dislocated from the metal center before the catalyst interacts with the epoxide to activate it.

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1. Introduction

The future exhaustion of oil resources and the high levels of carbon dioxide in the atmosphere due to anthropogenic emissions have impelled the scientific community to seek ways to utilize CO_2 as a feedstock. Moreover, CO_2 is an inexhaustible, cheap, nontoxic and non-flammable green source of carbon. The cycloaddition reaction of carbon dioxide and epoxides to produce cyclic carbonates is one of the most studied and attractive transformations [1–10]. Cyclic carbonates provide a wide range of applications as polar aprotic solvents, electrolytes in Li-ion batteries, synthetic intermediates, and monomers for the production of polycarbonates [11,12].

Since CO_2 is inert by nature, a catalyst is necessary to achieve satisfactory results in its transformation [13]. Diverse heteroge-

neous and homogeneous catalytic systems have been described to perform the coupling of CO_2 and epoxides. Among homogeneous molecular catalysts, a number of zinc complexes have been reported in the last years [14–27]. Complexes with monodentate ligands have not been much studied and reports are sparse [28,29]. The utilization of zinc is advantageous due to its low price, low toxicity and high stability, associated with good catalytic activities.

Considering the complexity in the mechanism involved in the cycloaddition reaction of carbon dioxide and epoxides to produce cyclic carbonates, application of molecular electronic structure methods to give some insight into the reaction mechanism becomes extremely important. There are several theoretical works involving the process of cycloaddition reaction of carbon dioxide and epoxides using different catalysts. Wang et al. [30], using B3PW91 functional with the 6-311++G(d,p) basis set studied the system of 1,2-benzenediol/tetrabutylammonium bromide (TBAB) and heterogeneous poly-ionic liquids, for the fixation of CO₂ to cyclic carbonates. They observed that the hydrogen bond can significantly decrease the barrier height of the reaction, since it activates the epoxide and stabilizes the stationary points of the

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Scheme 1. Synthesis of Zn1-Zn4.

reaction more effectively. Using BP86 DFT functional, Castro-Gómez et al. provided an useful information on the limitations of catalysts Zn(salphen)/TBAB and revealed conditions to better design the catalysis of these reactions [31]. Several other DFT calculations have been used to evaluate the role of catalysts in the cycloaddition reactions of CO_2 and epoxides, presenting excellent agreement with experimental results, which suggest opening ring as a limiting-rate step [32–34].

Recently, we have described a zinc complex with 2-(2-thienyl)-1-(2-thienylmethyl)-1*H*-benzimidazole as the first example of the utilization of 1,2-disubstituted benzimidazole complex in the chemical fixation of CO₂ [35]. The facility of synthesizing and altering steric and electronic characteristics by changing the substituents of 1,2-disubstituted benzimidazole suggests that they may be a very versatile type of ligands. Now we turn to describe the synthesis and characterization of four zinc complexes with 1,2-disubstituted benzimidazole ligands (Scheme 1) and the catalytic studies in the cycloaddition of CO₂ with epoxides. We also provide theoretical calculations to give some insight into the reaction mechanism, specifically in the epoxide coordination step. The four zinc(II) complexes of formula [ZnCl₂(L)₂] were characterized by ¹H and ¹³C NMR, thermal analysis infrared absorption and FT-Raman spectroscopy and ESI-HRMS. Complex Zn3 had its structure determined by single-crystal X-ray diffraction and a description of intra- and intermolecular interactions has been done.

2. Experimental

2.1. Materials and methods

Zinc chloride, 2-methoxybenzaldehyde, 4-chlorobenzaldehyde and sodium carbonate were purchased from Sigma-Aldrich and used as received. *o*-Phenylenediamine was purchased from TCI Chemicals and it was recrystallized in hot toluene before use. Benzaldehyde and furfural were purchased form Sigma–Aldrich and they were distillated before use. For the catalytic tests, CO₂ gas (99.99%) was purchased from Air Liquide; TBAB, TBAI, TBAC, PPNCI and epoxides were purchased from TCI Chemicals and used without further purification.

FT-IR spectra were recorded on a PerkinElmer Spectrum 400 FT-IR instrument (KBr discs) in the 4000–400 cm⁻¹ region. FT-Raman spectra were recorded on a Bruker MultiRAM Raman spectrometer with a laser line of 1064 nm at the power of 50 mW, with 64 scans taken in the 3500–50 cm⁻¹ range. Solution ¹H and ¹³C NMR spectra were measured with a Bruker Avance III 11.75 Tesla spectrometer at ambient temperature using TMS as internal reference. TG analysis was performed with a DTG 60/60H Shimadzu instrument in dry nitrogen at a heat ingrate of 10 °C/min. DSC analysis was performed with a Shimadzu DSC – 60 plus instrument in dry nitrogen. Mass spectra were recorded in a Bruker micrOTOF-Q III mass spectrometer in positive mode using methanol as solvent. 2.2. Synthesis of 1,2-disubstituted benzimidazoles (L1-L4)

Aldehyde (6.0 mmol) and 1,2-phenylenediamine (3.0 mmol) were added to a solution of HCl (5.0 equiv., 1.5 mL of concentrated hydrochloric acid) in H₂O (15 mL), and the mixture stirred at 50 °C. The progress of the reaction was monitored by TLC. After completion of the reaction, saturated solution of NaHCO₃ was added to the reaction mixture until neutral pH, and the resulting precipitate filtered off. The filtrate was purified by column chromatography in silica-gel as stationary phase and *n*-hexane:ethyl acetate (9:1) as eluent to give analytically pure product.

2.2.1. 1-Benzyl-2-phenyl-1H-benzoimidazole (L1)

White powder, 90% yield, ¹H NMR (298 K, CDCl₃): δ (ppm) = 5.46 (s, 2H), 7.11 (d, *J* = 6.95, 2H), 7.22 (t, *J* = 8.51, 2H), 7.31 (m, 4H), 7.46 (m, 3H), 7.69 (dd, J = 1.51 and 7.77, 2H) and 7.87 (d, J = 8.04, 1H). ¹³C NMR (298 K, CDCl₃): δ (ppm) = 48.40, 110.50, 120.03, 122.66, 123.02, 125.99, 127.77, 128.74, 129.05, 129.29, 129.89, 130.15, 136.09, 136.43, 143.24, 154.19. IR (KBr disc, cm⁻¹): 574 (w), 588 (w), 634 (w), 701 (w), 731 (s), 742 (s), 763 (m), 778 (m), 824 (w), 850 (w), 891 (w), 908 (w), 928 (w), 969 (w), 989 (w), 1003 (w), 1030 (w), 1078 (w), 1108 (w), 1163 (w), 1180 (w), 1251 (w), 1278 (sh), 1285 (w), 1312 (w), 1333 (m), 1360 (m), 1394 (m), 1441 (s), 1448 (s), 1472 (m), 1482 (w), 1492 (w), 1602 (w), 1615 (w), 2957 (w), 3029 (m), 3060 (m), 3082 (w), 3437 (br). FT-Raman (cm⁻¹): 71 (m), 90 (m), 191 (w), 207 (w), 773 (w), 1003 (m), 1031 (w), 1071 (w), 1084 (w), 1113 (w), 1150 (w), 1181 (w), 1252 (m), 1289 (w), 1316 (w), 1366 (w), 1392 (w), 1441 (s), 1473 (s), 1492 (w), 1516 (s), 1549 (w), 1603 (s), 2950 (w), 3059 (w). DSC peaks (°C): 134 (endo), 138 (endo), 243 (endo), 364 (exo).

2.2.2. 2-(Furan-2-yl)-1-(furan-2-ylmethyl)-1H-benzoimidazole (L2)

Brownish powder, 88% yield. ¹H NMR (298 K, CD₃OD): δ (ppm) = 5.57 (s, 2H), 6.35 (m, 2H), 6.72 (dd, J = 1.79 and 3.47, 1H), 7.32 (m, 4H), 7.66 (d, J = 7.98, 2H) and 7.86 (s, 1H). ¹³C NMR (298 K, CD₃OD): δ (ppm) = 41.06, 108.20, 110.10, 110.46, 111.72, 113.15, 118.24, 122.96, 123.96, 135.15, 141.86, 142.74, 143.84, 144.45, 144.76 and 159.63. IR (KBr disc, cm⁻¹): 564 (w), 594 (w), 738 (s), 752 (s), 761 (s), 800 (w), 823 (w), 848 (w), 885 (w), 907 (w), 928 (w), 1008 (m), 1019 (m), 1073 (w), 1142 (w), 1148 (w), 1168 (w), 1237 (w), 1258 (w), 1287 (w), 1327 (w), 1342 (m), 1367 (w), 1358 (w), 1403 (w), 1428 (m), 1447 (m), 1461 (m), 1498 (w), 1516 (m), 1607 (w), 1710 (w), 2849 (w), 2925 (w), 3064 (w), 3090 (m), 3132 (w), 3149 (w), 3430 (br). FT-Raman (cm⁻¹): 86 (w), 109 (w), 224 (w), 772 (w), 907 (w), 1013 (w), 1078 (w), 1149 (w), 1228 (w), 1254 (w), 1273 (w), 1289 (w), 1369 (w), 1409 (w), 1428 (w), 1460 (w), 1515 (s), 1585 (w), 1606 (s), 1621 (s), 1784 (w), 2060 (w), 2076 (w), 2092 (w), 2126 (w), 2157 (w), 2183 (w), 2206 (w), 2219 (w), 2242 (w), 2265 (w), 2282 (w), 2293 (w), 2386 (w), 2976 (w), 3063 (w), 3093 (w), 3137 (w),

3154 (w). DSC peaks (°C): 96 (endo), 210 (endo), 221 (endo), 409 (exo).

2.2.3. 1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-1H-benzoimidazole (L3) White powder, 84% yield. ¹H NMR (298 K, CDCl₃): δ (ppm) = 5.40 (s, 2H), 7.03 (t, J = 9.64, 2H), 7.20 (d, J = 7.98, 1H), 7.31 (m, 4H), 7.43 (dd, J = 3.92 and 10.60, 2H), 7.59 (m, 2H) and 7.86 (t, J = 10.17, 1H). ¹³C NMR (298 K, CDCl₃): δ (ppm) = 47.81, 110.30, 120.19, 123.08, 123.50, 127.26, 129.16, 129.39, 130.46, 134.63 and 152.87. IR (KBr disc, cm⁻¹): 485 (w), 505 (w), 584 (w), 726 (m), 742 (s), 763 (m), 801 (m), 826 (m), 842 (m), 925 (w), 934 (w), 988 (w), 1009 (m), 1092 (s), 1113 (w), 1163 (w), 1179 (w), 1187 (w), 1250 (w), 1275 (w), 1287 (w), 1296 (w), 1325 (w), 1354 (w), 1383 (w), 1404 (s), 1441 (m), 1454 (s), 1470 (s), 1495 (m), 1595 (w), 1612 (w), 2849 (w), 2928 (w), 3033 (w), 3059 (w), 3076 (w), 3432 (br). FT-Raman (cm⁻¹): 78 (m), 90 (m), 110 (sh), 154 (w), 166 (w), 240 (w), 729 (w), 771 (w), 1010 (w), 1079 (w), 1181 (w), 1251 (m), 1292 (w), 1369 (w), 1410 (w), 1443 (w), 1458 (m), 1474 (w), 1522 (m), 1603 (s), 2928 (w), 2954 (w), 3048 (w), 3060 (w). DSC peaks (°C): 143 (endo), 282 (endo), 402 (exo).

2.2.4. 1-(2-Methoxybenzyl)-2-(2-methoxyphenyl)-1H-benzoimidazole (L4)

White powder, 75% yield. ¹H NMR (298 K, CDCl₃): δ (ppm) = 3.61 (s, 3H), 3.80 (s, 3H), 5.26 (s, 2H), 6.72 (m, 1H), 6.79 (td, *J* = 0.74 and 7.50, 1H), 6.84 (t, *J* = 11.71, 1H), 6.98 (d, *J* = 8.25, 1H), 7.07 (td, J = 0.86 and 7.49, 1H), 7.23 (m, 3H), 7.29 (ddd, J = 1.81, 5.73 and 6.50, 2H), 7.47 (ddd, J = 1.75, 7.59 and 8.39, 1H), 7.56 (dd, J = 1.72 and 7.50, 1H). ¹³C NMR (298 K, CDCl₃): δ (ppm) = 43.51, 55.14, 55.21, 109.95, 110.74, 110.85, 119.81, 120.40, 120.79, 121.92, 122.44, 124.60, 127.78, 128.37, 131.38, 132.40, 135.55, 143.36, 152.45, 156.53 and 157.63. IR (KBr disc, cm⁻¹): 537 (w), 559 (w), 591 (w), 623 (w), 752 (s), 766 (s), 784 (w), 859 (w), 891 (w), 952 (w), 973 (w), 1009 (sh, m), 1020 (m), 1041 (w), 1109 (w), 1127 (w), 1166 (m), 1180 (w), 1191 (w), 1255 (s), 1263 (sh, F), 1273 (m), 1291 (m), 1330 (w), 1348 (w), 1370 (w), 1388 (w), 1427 (w), 1438 (w), 1459 (s), 1491 (m), 1498 (s), 1556 (w), 1584 (m), 1607 (s), 2639 (w), 2722 (w), 2839 (w), 2938 (w), 3021 (w), 3189 (sh), 3277 (sh), 3386 (br). FT-Raman (cm⁻¹): 76 (s), 169 (w), 772 (w), 789 (w), 1006 (w), 1045 (w), 1054 (w), 1077 (w), 1162 (w), 1239 (w), 1252 (m), 1285 (w), 1376 (w), 1393 (w), 1437 (w), 1455 (m), 1474 (w), 1520 (m), 1587 (w), 1605 (s), 2842 (w), 2931 (w), 2961 (w), 3012 (w), 3066 (m). DSC peaks (°C): 155 (endo), 262 (endo), 380 (exo).

2.3. Synthesis of complexes Zn1–Zn4

An ethanolic solution of the pro-ligand **L1–L4** (2 mmol) was added in an ethanolic solution of zinc chloride (1 mmol), a precipitated was formed with time. After refluxing for 16 h a white (brownish for **Zn2**) solid was filtered off and it was washed with cold ethanol (3×10 mL) and ethyl ether (2×10 mL) to furnish the pure product after drying in vacuum.

2.3.1. ZnCl₂-1-benzyl-2-phenyl-1H-benzoimidazole (**Zn1**)

Yield, 83%. ¹H NMR (298 K, DMSO-*d*⁶): δ (ppm) = 5.59 (s, 2H), 7.00 (d, *J* = 7.51, 2H), 7.26 (m, 5H), 7.47 (dd, *J* = 1.90, 6.22), 7.54 (dd, *J* = 1.77, 4.95, 3H), 7.73 (dd, *J* = 2.87, 60.70, 3H). ¹³C NMR (298 K, DMSO-*d*⁶): δ (ppm) = 47.43, 111.07, 119.24, 122.18, 122.66, 126.07, 127.44, 128.84, 129.01, 129.79, 130.12, 135.85, 136.89, 142.64 and 153.24. IR (KBr disc, cm⁻¹): 458 (w), 487 (w), 554 (w), 598 (w), 697 (s), 718 (m), 736 (s), 754 (s), 764 (m), 824 (w), 922 (w), 937 (w), 984 (w), 999 (w), 1028 (w), 1076 (w), 1175 (w), 1237 (w), 1255 (w), 1292 (w), 1335 (w), 1354 (w), 1411 (s), 1456 (s), 1467 (s), 1495 (m), 1607 (w), 2928 (w), 3031 (w), 3061 (w), 3436 (br). FT-Raman (cm⁻¹): 74 (m), 94 (m), 133 (w), 164 (w), 192 (w), 213 (w), 287 (w), 789 (w), 1003 (m), 1016 (w), 1032 (w), 1088 (w), 1161 (w), 1176 (w), 1239 (w), 1258 (w), 1296 (w), 1368 (w), 1455 (m), 1470 (m), 1519 (m), 1605 (s), 2945 (w), 2969 (w), 3059 (w). ESI-HRMS: [M-Cl⁺] Calc. 667.1607; observed 667.1421; [M+H]⁺ calcd. 703.1374; observed 703.1157. DSC peaks (°C): 248 (endo), 318 (endo), 395 (endo).

2.3.2. ZnCl₂-2-(furan-2-yl)-1-(furan-2-ylmethyl)-1H-benzoimidazole (**Zn2**)

Yield, 89%. ¹H NMR (298 K, DMSO- d^6): δ (ppm) = 5.77 (s, 2H), 6.38 (dd, J = 1.84, 3.22, 1H), 6.47 (d, J = 3.23, 1H), 6.76 (dd, *J* = 1.77, 3.46, 1 h), 7.27 (m, 3H), 7.54 (dd, *J* = 0.79, 1.77, 1H), 7.65 (d, J = 7.54, 1H), 7.73 (d, J = 7.53, 1H), 8.01 (dd, J = 0,71, 1.71, 1H). ¹³C NMR (298 K, DMSO- d^6): δ (ppm) = 40.93, 108.66, 110.56, 110.87, 112.11, 112.86, 119.00, 122.49, 122.84, 135.29, 142.47, 143.14, 143.40, 144.73, 145.02, 149.75, IR (KBr disc, cm⁻¹); 564 (w), 593 (w), 601 (w), 750 (s), 778 (m), 800 (w), 830 (w), 887 (w), 914 (w), 930 (w), 971 (w), 1016 (m), 1074 (w), 1094 (w), 1146 (w), 1175 (w), 1221 (w), 1234 (w), 1249 (w), 1295 (w), 1347 (m), 1409 (m), 1455 (m), 1467 (s), 1501 (w), 1512 (w), 1592 (w), 1611 (w), 2946 (w), 3031 (w), 3114 (m), 3130 (sh, w), 3145 (w), 3462 (br., w). FT-Raman (cm⁻¹): 75 (m), 161 (w), 331 (w), 780 (w), 1017 (w), 1075 (w), 1094 (w), 1124 (w), 1153 (w), 1221 (w), 1249 (w), 1276 (w), 1296 (w), 1334 (w), 1347 (w), 1366 (w), 1393 (m), 1426 (w), 1467 (w), 1512 (s), 1612 (s), 2945 (w), 3074 (w). ESI-HRMS: [M-Cl⁺] Calc. 627.0778; observed 627.0459. DSC peaks (°C): 297 (endo), 302 (exo).

2.3.3. ZnCl₂-1-(4-chlorobenzyl)-2-(4-chlorophenyl)-1Hbenzoimidazole (**Zn3**)

Yield, 71%. ¹H NMR (298 K, DMSO- d^6): δ (ppm) = 5.59 (s, 2H), 7.01 (d, J = 8.50, 2H), 7.27 (m, 2H), 7.35, (d, J = 8.49, 2H), 7.49 (m, 1H), 7.60 (m, 2H) and 7.74 (m, 3H). 13 C NMR (298 K, DMSO- d^6): δ (ppm) = 46.82, 111.07, 119.36, 122.42, 122.98, 128.00, 128.77, 128.90, 130.77, 132.07, 134.75, 135.81, 142.55 and 152.04. IR (KBr disc, cm⁻¹): 750 (s), 786 (w), 1026 (m), 1046 (w), 1077 (m), 1111 (sh), 1117 (w), 1161 (w), 1178 (w), 1232 (sh), 1254 (s), 1291 (m), 1332 (sh), 1345 (w), 1414 (s), 1448 (sh), 1461 (s), 1477 (m), 1494 (m), 1523 (w), 1587 (w), 1607 (w), 2836 (w), 2938 (m), 2958 (m), 3008 (w), 3068 (w), 3458 (m, br). FT-Raman (cm⁻¹): 75 (s), 105 (m), 167 (w), 241 (w), 308 (w), 318 (w), 731 (w), 763 (w), 1016 (w), 1079 (w), 1095 (w), 1176 (w), 1247 (w), 1292 (w), 1429 (w), 1459 (w), 1519 (m), 1527 (m), 1604 (s), 2952 (w), 2982 (w), 3028 (w), 3051 (w), 3067 (m). ESI-HRMS: [M +H]⁺ Calc. 838.9815; observed 838.9716. DSC peaks (°C): 259 (endo), 394 (exo)

2.3.4. ZnCl₂-1-(2-methoxybenzyl)-2-(2-methoxyphenyl)-1Hbenzoimidazole (**Zn4**)

Yield, 86%. ¹H NMR (298 K, DMSO- d^6): δ (ppm) = 3.67 (d, 6H), 5.21 (s, 2H), 6.59 (d, J = 7.48, 1H), 6.76 (t, J = 7.45, 1H), 6.93 (d, J = 8.23, 1H), 7.08 (t, J = 7.46, 1H), 7.20 (m, 4H), 7.38 (d, J = 7.14, 1H), 7.42 (d, *J* = 7.45, 1H), 7.53 (t, *J* = 7.90, 1H) and 7.70 (m, 1H). ¹³C NMR (298 K, DMSO- d^6): δ (ppm) = 42.77, 55.24, 55.27, 111.80, 111.98, 111.48, 118.98, 120.08, 120.47, 121.71, 122.24, 124.08, 127.48, 128.80, 131.58, 131.88, 135.10, 151.82, 156.35 and 157.07. IR (KBr disc, cm⁻¹): 751 (s), 783 (w), 1020 (m), 1045 (w), 1076 (w), 1110 (w), 1119 (w), 1162 (w), 1181 (w), 1232 (w), 1253 (s), 1290 (m), 1333 (w), 1345 (w), 1413 (s), 1451 (s, sh), 1462 (s), 1478 (m), 1493 (m), 1523 (s), 1585 (s), 1609 (m), 2835 (s), 2936 (s), 2959 (s), 3007 (s), 3068 (s), 3450 (m, br). FT-Raman (cm⁻¹): 75 (s), 154 (w), 250 (w), 306 (w), 674 (w), 720 (w), 755 (w), 787 (w), 1015 (w), 1045 (w), 1076 (w), 1130 (w), 1166 (w), 1248 (w), 1293 (m), 1335 (w), 1377 (w), 1415 (w), 1460 (m), 1523 (m), 1609 (s), 2842 (w), 2947 (m), 3010 (w), 3072 (s).

ESI-HRMS: [M–Cl]⁺ calcd. 787.2030; observed 787.1882. DSC peaks (°C): 216 (endo), 270 (endo), 406 (exo).

2.4. X-ray crystallography

Single-crystal with appropriate dimensions for X-ray diffraction data collection of Zn3 was selected out from the crystallization batch in acetonitrile and mounted on a Bruker-AXS Kappa Duo diffractometer to measure the intensity data. The diffraction frames were recorded by ϕ and ω scans using APEX2 [36], under $CuK\alpha$ radiation at room temperature. The raw dataset treatment was performed using the program SAINT and SADABS [36]. Multi-scan absorption correction has been employed to all dataset [37]. The structure was solved by direct methods with shelxs-2014/7 [38], wherein C, N, Cl and Zn were readily assigned from the Fourier map. Hydrogen atoms were stereochemically positioned and refined with fixed individual isotropic displacement parameters $[U_{iso}(H) = 1.2U_{eq}(C_{sp}^2)$ or $1.5U_{eq}(C_{sp}^3)]$ using a riding model with fixed C–H bond lengths of either 0.93 or 0.97 Å, respectively. All full-matrix refinements were performed on F^2 using SHELXL-2014/7 [38]. The MERCURY [39], ORTEP3 [40] programs were used within the WINGX [41] software package to prepare artwork representations. Crystallographic details are available in the Supporting Information in CIF format, the CCDC number is 1881938.

2.5. Catalysis experiments

Catalytic tests were conducted in a Parr reactor system (model 4560 with controller model 4848) equipped with a 300 mL stainless steel vessel. In a general procedure, the vessel was charged with one of the catalysts **Zn1–Zn4**, a cocatalyst, and the epoxide. Carbon dioxide was pressurized into the mixture and the reaction was performed under predetermined conditions. When the reaction was complete, the vessel was cooled to 0 °C and the pressure was slowly released. The conversion was calculated based on the ¹H NMR spectrum of the crude reaction mixture.

2.6. Computational details

The molecular systems were optimized with Density functional theory (DFT) at B3LYP functional combined with the Pople splitvalence basis set 6-311G(d) for the representative atoms C, H, N, O, Cl and S; and LANL2DZ pseudo-potential for the heavy metal Zn(II) (a mixed basis set 6-311G(d)/LANL2DZ). The stationary points were characterized by analytic harmonic frequency calculations. The absence of imaginary frequencies ensures that the optimized structures are local minimum energy. The global charge in the complexes were considered zero. DFT energies were corrected employing a Petersson–Frisch empirical dispersion term. The interaction energies have been corrected by including basis set superposition error (BSSE) through counterpoise method proposed by Boys and Bernardi [42]. All the quantum chemistry calculations were carried out with GAUSSIAN 09 [43].

The complexation energies, ΔE , were estimated considering the interaction between the complexes (**Zn1** and **Zn3**) with styrene oxide (**SO**) and 1,2-epoxybutane (**EB**) as follow (where Ep designates the epoxide).

$$\Delta E = E_{Zn} - E_{Ep} \tag{1}$$

Bond order parameters [44,45] were performed in terms of Mayer, Fuzzy and Wiberg indexes for metal and specific atoms involved in the interaction at WB97XD/6-311++G(d,p)/Def2-TZVP//B3LYP/6-311G(d)/LANL2DZ level of calculations. A MULTIWFN

package program was used to study the above indexes [46]. Recent theoretical studies in complexation processes support the quantum chemistry apparatus used here [47–49].

3. Results and discussion

3.1. Synthesis and characterization

Production of complexes Zn1-Zn4 was evidenced by the precipitation of a white or brownish powder in the reaction medium. The solids were isolated by simple filtration and subsequently characterized. Infrared absorption spectra indicated coordination through the imidazole nitrogen. By comparing the spectra of the ligands with the respective zinc complexes, most of the peaks are shifted to lower wavenumber. The characteristic imidazole v (C=N) and v(C=C) vibrations are very close to each other and occur between 1411 and 1609 cm⁻¹ [50]. It was observed, in the region of antisymmetric and symmetric C=N-C=C stretching vibrations, other peaks that can be, most probably, attributed as overtones or combination bands [51,52]. Benzene and imidazole ring vibrations, C-H in plane (benzene ring) and CH₂ wagging and twisting (imidazole ring), were observed above 1300 cm⁻¹. The CH stretching of CH₂ was observed around 2800 cm⁻¹, and aromatic Csp²—H in $2900-3100 \text{ cm}^{-1}$.

FT-Raman spectra of the ligands **L1-L4** showed the same profile, with peaks distributed in four characteristic ranges: the aromatic C—H stretching area (2840–3154 cm⁻¹), the ring skeletal area (1000–1620 cm⁻¹), aromatic C—H out-of-plane bending (729–786 cm⁻¹) and the lattice and fundamental peaks area (50–240 cm⁻¹). The FT-Raman spectra of complexes **Zn1–Zn4** presented the same features of the ligands plus the rise of peaks in the range of 287–331 cm⁻¹ that can be attributed to the Zn–N stretching. For both **L2** and **Zn2**, the spectra are broadened owing thermal interference caused by the heating of the sample [52,53].

The NMR analyses were performed for the four zinc tetrahedral complexes using DMSO- d_6 as solvent. The CH_2 link was observed, for all complexes, between 5.21 and 5.77 ppm in ¹H NMR. The chemical shifts in the ¹³C NMR spectrum for the CH_2 were observed in 47.43 (**Zn1**), 40.93 (**Zn2**), 46.82 (**Zn3**) and 42.77 ppm (**Zn4**). For **Zn4**, the methoxyl groups CH_3 O were observed as two peaks (55.24 and 55.27 ppm), which proves the different chemical environment of these two carbon atoms in the complex.

Thermal analyzes showed the expected increase in the decomposition temperature of the complexes compared to the free ligands (see ESI). A weight loss of 1–2% was observed in all analyzes in the initial curves, which is associated with absorbed or lattice water [54–56]. All TG curves presented a decomposition at 213 °C (**Zn1**), 213 °C (**Zn2**), 254 °C (**Zn3**) and 215 °C (**Zn4**), indicating the loss of one ligand moiety. This reveals that the **Zn3** is more thermally stable than the other complexes, probably because chlorine atoms at *para* position of the ligand substituent give a more ionic characteristic to Zn–N_{benzimidazole} bond in **Zn3**. For all complexes, after the first ligand decomposition, the residual [ZnCl₂L] species loses mass without any clear stage. Increasing the temperature, the three-coordinate [ZnCl₂L] species decomposes very rapidly, which demonstrates its thermal instability.

3.2. Description of structure of Zn3

Well-shaped single crystals of **Zn3** were obtained from the recrystallization of the complex in acetonitrile. Crystallographic data and refinement parameters of the structure are summarized in Table 1. The crystal structure contains one unit of **Zn3** ([ZnL₂-Cl₂]) in its asymmetric unit (Fig. 1) and was solved in the *Pbca* space group (see Table 1 for crystallographic details). The Zn²⁺ is

Table 1	
Crystal data and refinement statistics of crystal structure of	Zn3.

Chemical formula Fw (g/mol) Crystal system Space group		C ₄₀ H ₂₈ Cl ₆ N ₄ Zn 842.75 orthorhombic <i>Pbca</i>	O range for data collection (°) Index ranges	h k l	2.088-66.614 -22 to 9 -11 to 11 -49 to 50
Z		8	Observed reflections [$I > 2\sigma(I)$]		34 514
T (K)		296(2)	Unique reflections		6562
Unit cell dimensions	a (Å)	18.7914(7)	Symmetry factor (R_{int})		0.0795
	b (Å)	9.5522(3)	Completeness to θ_{max} (%)		97.8
	c (Å)	42.3087(17)	F(000)		3424
	α (°)	90	Refined parameters		460
	β(°)	90	Goodness-of-fit on $F^2(S)^a$		1.012
	γ(°)	90	Final $R_1^{\rm b}$ factor $[I > 2\sigma(I)]$		0.0467
V (Å ³)		7594.4(5)	wR_2^c factor (all data)		0.1232
D_{calc} (Mg/m ³)		1.474	Largest difference peak/hole ($e \text{ Å}^{-3}$)		0.325/-0.298
Absorption coefficient μ (mm ⁻¹)		5.060	CCDC deposit no.		1881938





Fig. 1. Atom labeling scheme of **Zn3** for C8A and C8B (described in the text) and all non-carbon atoms, which constitutes the asymmetric unit of the crystal structure. Thermal ellipsoids are drawn at the 50% probability level, hydrogen atoms were omitted for clarity.

coordinated to two nitrogen atoms from distinct benzimidazole ligands (A and B) and two chloride ligands, assuming a tetrahedral geometry. The coordination bond lengths ranged from 2.040(3) Å to 2.2555(11) Å and angles from 105.14(9)° to 113.7(9)°. Coordination bond lengths and angles are summarized in Table 2. The deviation parameter value from the idealized T_d geometry for Zn²⁺ was calculated with continuous shape measurement [57] and resulted in a low value of 0.268.

The coordination compound assumed a so-called locked-geometry due to its non-classical hydrogen bonding intramolecular (C–H···Cl) and intermolecular (C–H··· π) interactions, as seen in Fig. 2. In the same figure is verified the intermolecular Cl··· π contacts. In addition, this conformation assumed by the ligand can be expressed as the angle between the least-square (l.s.) planes fitted through the benzimidazole ring atoms and those four l.s. planes fitted through each *p*-chlorobenzyl atoms for ligands A and B. The *p*chlorophenyl groups bonded to N1A (or N1B) and C8A (or C8B) form angles with benzimidazole of 62.01(10)° and 84.63(9)° in ligand A, and 69.77(12)° and 89.86(9)° in ligand B. Whilst, in the whole coordination compound, the l.s. plane fitted through

Table 2					
Coordination bond	lengths ((Å) and	angles (°) in	Zn3.

T-1-1- 0

Length (Å)		Angle (°)	
Zn1—N1A Zn1—N1B Zn1—Cl1 Zn1—Cl2	2.040(3) 2.054(3) 2.2555(11) 2.2283(11)	N1A—Zn1—N1B N1A—Zn1—Cl1 N1A—Zn1—Cl2 N1B—Zn1—Cl1 N1B—Zn1—Cl2 Cl1—Zn1—Cl2	112.59(12) 105.14(9) 110.87(9) 113.77(9) 105.28(9) 109.25(5)

benzimidazole ring atoms from both ligands is almost perpendicular, with an angle of 86.11(7)°.

This type of metal complex with benzimidazole ligands substituted with *p*-Cl-phenyl is being reported here for the first time. On the other hand, complexes containing benzimidazole ligands substituted only with phenyl rings are well known, as those coordinated to Zn^{2+} or Cd^{2+} [58,59], as well as analogous Zn^{2+} complexes with p-methoxyphenyl rings (without crystal structure) [60]. The main difference between the previous ones and the **Zn3** is the loss of $\pi \cdots \pi$ intramolecular interactions in the latter due to halogen substitution enabling other interactions, such as $Cl \cdots \pi$ contacts.

3.3. Catalytic studies

All complexes were able to catalyze the cycloaddition of CO₂ with propylene oxide (PO) producing the respective cyclic carbonate with good conversions and high selectivity. Table 3 summarizes the initial screening reactions conducted under 30 bar of CO₂, at 100 °C and using tetrabutylammonium bromide (TBAB) as cocatalyst. The conversion values varied from 44% to 65%. Although complex **Zn3** possesses an electron-withdrawing substituent in phenyl ring, it presented similar conversion values to **Zn4** and lower conversions than **Zn1** and **Zn2**. It could be expected that electron-withdrawing groups in the ligands would increase the Lewis acidity of zinc metal center facilitating the activation of the epoxide, and the electron donating groups would lead to the contrary. However, this correlation was not observed. It is possible to assume that the steric factors and/or lability of the ligands have a significant influence on the system.

In the spirit of the molecular configuration accessed by X-ray structure of **Zn3** and as it will be demonstrated below, theoretical calculations suggest that the reaction intermediate is a four-coordinate complex produced from the exchange of a benzimidazole ligand by the epoxide. Thus, the initiation of the reaction depends on the ligand exchange by the epoxide. A ligand containing an electron withdrawing group, as in **Zn3**, would weaken the metal-ligand bond and the ligand exchange between L3 and the epoxide should be faster than the displacement of **L4** in **Zn4**. On the other hand, the last step (ring closure, after epoxide opening and CO₂ insertion; for mechanistic details see references [61-63]) should be more difficult because the alkoxide-zinc bond strength of the intermediate is enhanced by the electron withdrawing effect in the benzimidazole ligand. In contrast, Zn4 should suffer slower ligand exchange, since the methoxyl group attached to the ligand can contribute to increase the donating ability of the ligand and



Fig. 2. (a) Intra and (b and c) intermolecular interactions found in crystal structure. Dashed cyan lines denote C–H···Cl interactions and dashed black lines draw C–H··· π and Cl··· π contacts. The centroids Cg1 and Cg2 were calculated through the atoms of benzene ring and *p*-chlorophenyl (bonded to C8A), respectively, of ligand A.

Table 3 Cycloaddition of propylene oxide and CO₂ catalyzed by **Zn1–Zn4**.

		Zn1-4 TBAB CO ₂ (30 bar) 100 °C, 6h		
Entry	Catalyst	Conv. (%) ^a	TON ^b	TOF ^c
1	Zn1	65	1623	271
2	Zn2	60	1506	251
3	Zn3	44	1106	184
4	Zn4	45	1136	189
5	Ref. [35] ^d	60	1488	248
6	e	19	-	-

Reactions conditions: 0.01 mmol Zn catalyst (0.04 mol%), 0.01 mmol TBAB (0.04 mol%), PO (25.00 mmol), T = 100 °C, $P_{[CO2]} = 30$ bar, t = 6 h.

^a Conversions determined on basis of ¹H NMR analysis. The selectivity was >99% in all experiments.

^b Turnover number (mol of carbonate produced/mol catalyst).

^c Turnover frequency (TON.h⁻¹).

^d Previously reported zinc complex with 2-(2-thienyl)-1-(2-thienylmethyl)-1*H*-benzimidazole.

^e Blank experiment with TBAB only.

consequently Zn– N_{L4} bond is stronger than Zn– N_{L3} bond. In the ring closure step, the nucleophilic alkoxide attack is faster for **Zn4** compared to **Zn3**. Thus, the similar conversions for **Zn3** and **Zn4** may be explained by the fact that **Zn3** had more effective epoxide activation while **Zn4** promotes more effective nucleophilic attack to ring closure, being both rate determining steps [64,65]. Complex **Zn2** with the ligand containing a furan substituent presented a catalytic behavior similar to the already reported analogous complex [35] with the more aromatic thiophene substituent in the ligand [66]. The best activity, under screening conditions, was obtained with complex **Zn1** (Table 3, entry 1) and it was selected to perform the optimization.

The temperature has a considerable impact on the system. As observed in several reports with distinct metallic ions [67–70], lower temperatures results in much lower activities and in our case at 70 °C only 6% of conversion was obtained (Table 4, entry 3). Under screening conditions (100 °C, Table 4, entry 1) 65% of propylene cyclic carbonate was produced and raising the temperature to 120 °C and 150 °C led to an increase in conversion to 71% and 82%, respectively (Table 4, entries 4 and 5). However, at 150 °C (Table 4, entry 5), the production of side products was found in ¹H NMR spectra; except for this condition, all other experiments furnished the product with high selectivity (>99%).

Decreasing pressure to 5 bar, much less CO_2 is soluble in the reaction medium and kinetics of the reaction is modified [71], thereby the CO_2 insertion is slow under this condition (conversion of 23%, Table 4, entry 6). In contrast, the decrease in conversion of the experiment under 20 bar compared to 30 bar is slighter (Table 4, entries 1 and 8), indicating that in high pressure the CO_2 insertions are fast.

Binary catalytic systems for the coupling of epoxides and CO₂ involve the Lewis acid catalyst to activate the epoxide and a cocatalyst as a nucleophile source to open the epoxide ring. Different cocatalysts were tested in this work and the studies revealed an interesting result; regardless of the nature of the cation, both cocatalysts providing chloride as nucleophile, tetrabutylammonium chloride (TBAC) and bis(triphenylphosphine)iminium chloride (PPNC), showed nearly the same conversions (Table 4, entries 9 and 11). This is a strong evidence that, in our system, the cation of the nucleophile source cocatalyst does not influence the reaction outcome, as already observed by our group in systems involving Mn^{III}-porphyrin/TBAC and Mn^{III}-porphyrin/PPNC [72]. When tetrabutylammonium iodide (TBAI) was employed as cocatalyst, it resulted in 53% of conversion (Table 4, entry 10), higher than in the experiment with TBAC (23%, Table 4, entry 9), showing that the stronger C-Cl bond hinders the ring closure. Chloride anion is much more nucleophilic than iodide in polar aprotic media, so, the ring opening by TBAC should be faster compared to TBAI. However, the reaction outcome depends on the epoxide

Table 4
Effect of reaction parameters on the cycloaddition of propylene oxide and CO ₂ catalyzed by Zn1 .

Entry	Т (°С)	P _[CO2] (bar)	Conv. (%) ^a	TON ^b	TOF ^c
1	100	30	65	1623	271
2	40	30	2	62	10
3	70	30	6	156	26
4	120	30	71	1786	298
5	150*	30	82	2049	342
6	100	5	23	563	94
7	100	10	56	1404	234
8	100	20	52	1295	216
9 ^d	100	30	23	579	96
10 ^e	100	30	51	1269	212
11 ^f	100	30	22	540	90

Reactions conditions: 0.01 mmol Zn catalyst (0.04 mol%), 0.01 mmol TBAB (0.04 mol%), PO (25.00 mmol), t = 6 h. ^a Conversions determined on basis of ¹H NMR analysis. The selectivity was >99% in all experiments.

^b Turnover number (mol of carbonate produced/mol catalyst).

^c Turnover frequency (TON.h⁻¹).

d TBAC.

^e TBAI.

^f PPNC.

Side products.

opening and ring closure, which is affected by both the nucleophilicity and leaving ability of the anion [73]. The balance of both properties leads to the observed conversion order for the cocatalysts: TBAB > TBAI > TBAC ~ PPNC.

The versatility of the system was evaluated in the cycloaddition reaction of CO₂ with a series of different epoxides, using Zn1 as catalyst. The results are shown in Table 5. Except for cyclohexene oxide (entry 8), all epoxides presented high conversion values to

Table 5

-

Zn1/TBAB-catalyzed cycloaddition reactions with various epoxides.

Entry	Epoxide	Conversion (%) ^a	TON ^b	TOF ^c
1	2	90	2252	750
2	Å	96	2403	801
3	Å.	99	2475	825
4	Å	70	1748	583
5		75	1879	626
6	Д он	>99	2500	833
7	Å	97	2427	809
8	$\overset{\sim}{\wedge}$	27	677	225
9		96	2408	802
10	Å_~	>99	2500	833
11	$\tilde{2}$	>99	2500	833

(continued on next page)

Table 5 (continued)



Reaction conditions: Catalyst Zn1 (0.01 mmol, 0.04 mol%), cocatalyst TBAB (0.1 mmol, 0.4 mol%), epoxide (25 mmol), 30 bar CO₂, 100 °C, 3 h.

^a Conversions was determined on basis of ¹H NMR analysis. The selectivity was >99% for the cyclic carbonate in all experiments, with the exception of glycidol, for which it was 77% (entry 6).

^b Turnover number (TON = mole of carbonate produced per mole of catalyst).

^c Turnover frequency (TOF = TON. h^{-1}).

their respective cyclic carbonates. Cyclohexene oxide is sterically hindered and in general results in much lower conversion. In all cases, the reaction was selective to produce the cyclic carbonate (>99%), with the exception of glycidol, for which the selectivity was 77% (entry 6).

Other zinc metal complexes have been described to catalyze the same transformation, in similar conditions [15,16,19,21,23]. In the present article, we could obtain high conversions values using very lower catalyst/cocatalyst loads compared to other works.

3.4. Theoretical studies

Theoretical calculations were performed in order to understand some aspects of the mechanism for the activation of the epoxide in our system. As mentioned above in Table 3, the electronic effects of ligands with opposed electronic characteristics did not lead to significant modifications in the catalytic activities when comparing complexes **Zn3** and **Zn4** (*p*-chlorophenyl and *p*-methoxyphenyl substituents, respectively). An important role of steric effects in



 $\Delta E_{BSSE} = -22.21 \text{ kcal mol}^{-1}$

 $\Delta E_{BSSE} = -26.91 \text{ kcal mol}^{-1}$

Fig. 3. Calculated structures of possible catalytic active species obtained at B3LYP/6-311G(d) level of calculation with dispersion and BSSE correction. Geometric coordinates of the optimized complexes can be found in ESI. PO and SO stand for propylene oxide and styrene oxide, respectively.

the coordination of epoxide at the metal center was then expected. For the reaction to proceed, an interaction between the epoxide and the catalyst is required. Zinc complexes have a tetrahedral geometry and the coordination of an epoxide molecule at the metal center would lead to breakdown of the geometry with a significant energetic cost, as can be seen in Fig. 3, where Zn1 and Zn3 are coordinated to PO (propylene oxide) and SO (styrene oxide), respectively. From these calculated molecular structures, it can be suggested that the energetic profile for a penta-coordinate trigonal bipyramidal geometry is much higher than for the four-coordinate tetrahedral species, and from these data, it may be supposed that to achieve an active catalytic species, firstly, a ligand exchange between L (L1, L2, L3 or L4) and the epoxide should occur to initiate the catalytic cycle. In the case of Zn1/PO, the optimized molecular structure for bipyramidal intermediate results in $\Delta E = -10.32$ kcal mol⁻¹, whereas, for the tetrahedral analogue, $\Delta E = -22.21$ kcal mol⁻¹. These values support that the active species is tetrahedral derived from the exchange of one benzimidazole ligand by the epoxide. The thermal analyzes support this mechanistic proposition, since all the complexes have lost a benzimidazole ligand (L1-L4) instead of a chloride ligand. The steric effects plays a key role in the displacement of the ligands, besides that, the tetrahedral [ZnCl₂L(Ep)] should be much more stable than the hypothetical $[ZnClL_2(Ep)]^+$ (where Ep is the epoxide).

The same behavior was observed for **Zn3**/SO system, as can be seen by comparing the values obtained for optimized molecular structures: $\Delta E = -6.79$ kcal mol⁻¹ for bipyramidal and $\Delta E = -26.91$ kcal mol⁻¹ for tetrahedral. In the system **Zn3**/SO the difference between the bipyramidal and tetrahedral analogues ($\Delta \Delta E = 20.12$ kcal mol⁻¹) are much higher than in the system **Zn1**/PO ($\Delta \Delta E = 11.89$ kcal mol⁻¹) and it is connected to the steric effects, i.e., the higher steric hindrance of SO compared to PO.

The electronic effect of the ligand was evaluated by NBO indexes, the parameters of the complexes presented in Fig. 3 are listed in Table S1. Assuming the complexation process as an important step in the catalytic cycle, negligible NBO indexes modifications in three-atoms ring of the epoxide were observed (\sim 4%): corroborating that the change in electron-withdrawing character of the ligands did not lead to significant modifications in covalent bonds of the three-atoms ring of the epoxide and consequently on the epoxide opening, which it is considered the limiting-rate step in catalytic cycle.

These data provide strong evidence that the steric effects around the metal center direct the reaction initiation. The production of a bipyramidal active complex is not favored to initiate the catalytic cycle and, the first step should be the exchange of the benzimidazole ligand by the epoxide to form a more energetically favorable tetrahedral complex.

4. Conclusion

In conclusion, four Zn(II) complexes with 1,2-dissubstituted benzimidazole ligands were synthesized and characterized by standard techniques, including the crystal structure of **Zn3**, with a detailed description of intramolecular and intermolecular interactions. The catalytic performance in the cycloaddition reaction of CO_2 and epoxides was evaluated and all complexes were able to produce selectively cyclic carbonates with good conversions, using very low catalyst load. The parameters of the system were studied and it was revealed a high dependence on the temperature. Complex **Zn1** efficiently catalyzed the transformation of various epoxides to carbonates, using TBAB as cocatalyst. Theoretical studies were conducted for a better comprehension of the activation mechanism of the epoxide. The results showed that the tetrahedral intermediates should be much more stable than bipyramidal analogues, suggesting that in the first step the substitution of the benzimidazole ligand by the epoxide in the coordination sphere of the metal center should occur to initiate the catalytic cycle. The results reported here shed light on some aspects of the mechanism of the cycloaddition of CO_2 and epoxides catalyzed by homogeneous metal complexes, and reinforce that zinc based catalysts are promising candidates to promote the chemical fixation of CO_2 .

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Appendix A. Supplementary data

CCDC 1881938 contains the supplementary crystallographic data for **Zn3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data (experimental details) to this article can be found online at https://doi.org/10. 1016/j.poly.2019.114134.

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