



The multinuclear cobaloxime complexes-based catalysts for direct synthesis of cyclic carbonate from of epichlorohydrin using carbon dioxide: Synthesis and characterization



Ahmet Kilic*, Mahmut Ulusoy, Mustafa Durgun, Emine Aytar

Harran University, Science and Art Faculty, Chemistry Department, Osmanbey Campus, Sanliurfa TR-63190, Turkey

ARTICLE INFO

Article history:

Received 4 June 2013

Received in revised form 23 October 2013

Accepted 10 November 2013

Available online 20 November 2013

Keywords:

Dicobaloxime

Organodicobaloxime

Spectroscopy

Carbon dioxide

Cyclic carbonate

ABSTRACT

The novel examples of dicobaloxime $[(\text{dmgH})_2\text{ClCo}-(4,4'\text{-bpy})\text{-CoCl}(\text{dmgH})_2]$ (**1**), organodicobaloxime $[(\text{dmgH})_2\text{PhCH}_2\text{Co}-(4,4'\text{-bpy})\text{-CoCH}_2\text{Ph}(\text{dmgH})_2]$ (**2**), and the intramolecular hydrogen (O–H···O) bridges were replaced Cu(II) containing multinuclear cobaloxime complexes $[(\text{dmgCu}(\text{N}–\text{N}))_2\text{ClCo}-(4,4'\text{-bpy})\text{-CoCl}\{\text{dmgCu}(\text{N}–\text{N})\}_2](\text{ClO}_4)_4$ (**3–9**) were synthesized, characterized and used in direct synthesis cyclic carbonates from carbon dioxide and various epoxides. The dicobaloxime complex (**1**) was used as precursors for building the intramolecular hydrogen (O–H···O) bridges replaced Cu(II) ions containing complexes (**3–9**). All of compounds have been characterized by ^1H and ^{13}C NMR spectra, FT-IR spectra, UV-Vis spectra, elemental analysis, melting point measurements, LC-MS spectra, molar conductivity measurements, and magnetic susceptibility techniques. Among the nine metal complexes, complex (**2**) (bearing cobalt–carbon bond) displayed the higher catalytic efficient than other complexes (**1** and **3–9**) under the same catalytic conditions. The intramolecular hydrogen (O–H···O) bridges were replaced Cu(II) containing complexes (**3–9**) that bear the dimethyl glyoximate ligands and linked ligands exhibited much lower catalytic efficiencies as compared with complexes (**1**) and (**2**).

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Cobaloximes and dicobaloximes have been extensively studied and investigated for more than four decades [1–4]. Cobaloximes or dicobaloximes have the general formula $\text{RCo}(\text{L}_2)\text{B}$, where R is an organic group σ -bonded to cobalt. B is an axial base *trans* to the organic group, and L is a monoanionic dioxime ligand. This ligands: glyoxime (gH), dimethylglyoxime (dmgH), 1,2-cyclohexanedione dioxime (chgH), diphenylglyoxime (dpgH) and other symmetric and unsymmetric dioxime are given as an example [5]. For a long time, cobaloxime and organocobaloximes have been studied as vitamin B₁₂ models [6], but also for their use in various field as polymerization catalysts [7,8], as templates in organic synthesis [7,9,10], as transition metal dioxygen carriers [11], as very efficient and cheap photocatalysts and as electrocatalysts for hydrogen evolution from water splitting [12–16], as catalytic chain transfer polymerization of methacrylates and styrene [17,18] and as functional models for hydrogenase enzymes [16]. The N₄ macrocycle in the cobaloxime or dicobaloxime model complexes is made up of two monodeprotonated dioxime molecules linked at two points by hydrogen bonding. The result is a planar macrocyclic ligand essentially. Cobaloximes and organocobaloximes with one

or both of the intramolecular hydrogen (O–H···O) bridges replaced by organoboryl groups are well known and have recently been commented [19]. Whereas, the intramolecular hydrogen (O–H···O) bridges replaced Cu(II) ions or other metal ions containing cobaloxime or dicobaloxime compounds are not well known in literature. The literature also has lack of information on their general properties like stability in solution, sensitivity towards oxygen, electrochemical behavior, structural and spectroscopic studies and catalytic properties (especially for direct synthesis cyclic carbonates from carbon dioxide and epoxides) for the intramolecular hydrogen (O–H···O) bridges replaced Cu(II) ions or other metal ions containing cobaloxime or dicobaloxime compounds.

So far, to our best knowledge, there is no literature report that the cobaloxime, dicobaloxime, and the intramolecular hydrogen (O–H···O) bridges replaced Cu(II) ions or other metal ions containing complexes have been utilized as catalyst for the coupling reactions of carbon dioxide (CO₂) and epoxides. Thus, the synthesis of dicobaloxime complexes and their different derivatives have been the subject of study for very a long time. However, carbon dioxide fixation has received much attention in last decades since carbon dioxide is the most inexpensive and infinite carbon resource [20,21]. Also, carbon dioxide and its steadily increasing concentration in the atmosphere over the most recent part of human history is a permanent subject in the media, politics, and science [22]. The majority of these studies involve the reaction of CO₂ with epoxides

* Corresponding author. Tel.: +90 414 318 3587; fax: +90 414 318 3541.

E-mail address: kilica63@harran.edu.tr (A. Kilic).

to generate polycarbonates and-or cyclic carbonates and these have recently become commercially important. For example; cyclic carbonates are used industrially as polar aprotic solvents, substrates for small molecule synthesis, additives, antifoam agents for antifreeze, and plasticizers [23,24]. For metal complex catalysts, salen-type metal complexes in conjunction with Lewis base or organic salts as co-catalysts have been of significant interest [25–28]. The most distinct advantages of the metal complexes are easy synthesis and good stability against moisture and air [29–31]. The development of efficient recoverable and reusable catalysts that can be easily prepared, recovered and reused without losing their activities have received much attention from a practical and environmental point of view [32].

In this study, dicobaloxime, organodicobaloxime and the intramolecular hydrogen (O–H...O) bridges replaced Cu(II) ions containing multinuclear cobaloxime complexes were synthesized and characterized by ^1H and ^{13}C NMR spectra, FT-IR, UV-Vis, elemental analysis, melting point measurements, LC-MS spectra, molar conductivity measurements, and magnetic susceptibility techniques. Then, these compounds as catalysts were used in direct synthesis cyclic carbonates from carbon dioxide and various epoxides.

2. Experimental

2.1. Materials and measurements

All reagents and solvents were of reagent-grade quality and obtained from commercial suppliers. Elemental analysis was carried out on a LECO CHNS model 932 elemental analyzer. ^1H and ^{13}C NMR spectra were recorded on a Bruker-Avance 300 MHz spectrometers for spectroscopic characterization. FT-IR spectra were recorded on a Perkin Elmer Spectrum RXI FT-IR Spectrometer as KBr pellets in the wavenumber range of 4000–400 cm^{-1} . Magnetic Susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature (20 °C) using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a calibrant; diamagnetic corrections were calculated from Pascal's constants [33]. Electronic spectral studies were conducted on a Perkin-Elmer model Lambda 25 UV-Vis spectrophotometer in the wavelength range from 200 to 1100 nm. Melting points were measured in open capillary tubes with an Electrothermal 9100 melting point apparatus and are uncorrected. Molar conductivities (Λ_{M}) were recorded on a Inolab Terminal 740 WTW Series. Mass Spectra results were recorded on an Agilent LC/MSD LC-MS/MS spectrometer. Catalytic tests were performed in a PARR 4560 50 mL stainless pressure reactor. Gas chromatography was performed on a Agilent 7820A GC system and hydrogen as the carrier gas. The conditions used were: initial temperature 60 °C, hold at initial temperature for 3 min then ramp rate 18 °C min^{-1} to 222 °C; hold at final temperature for 5 min. 4,5-Diazafluoren-9-one (dafo) [34], 3,3'-dicarboxy-2,2'-bipyridine (dcbpy) [35], 1,10-phenanthroline-5,6-dione (dione) [36] and 4,5-diazafluoren-9-oxime (dafoxi) [37] were prepared according to the literature procedures.

2.2. Synthesis of the $[(\text{dmgH})_2\text{ClCo}-(4,4'\text{-bpy})-\text{CoCl}(\text{dmgH})_2]$ complex (1)

A solution of dimethyl glyoxime (2.32 g, 20 mmol) and 4,4'-bipyridine (0.8 g, 5 mmol) in 100 mL of absolute ethanol was added to a refluxing solution of cobalt(II) chloride hexahydrate (2.38 g, 10 mmol) in 100 mL of absolute ethanol. After the two solution were mixed and stirred for 15–20 min. and it was cooled to room temperature, a very gentle stream of air was allowed to pass through it with occasional swirling. Then 5 mL water was added and the mixture aerated for another 2 h. The volume was re-

duced to ca. 75 mL and a brown powder separated; it was recrystallized from $\text{CH}_2\text{Cl}_2/\text{C}_2\text{H}_5\text{OH}$, and finally dried *in vacuo*. Color: Dark brown, yield (%): 78, m.p: 270 °C, *Anal. Calc.* for $[\text{C}_{26}\text{H}_{36}\text{N}_{10}\text{O}_8\text{Cl}_2\text{Co}_2]$ (F.W: 805.4 g/mol): C, 38.77; H, 4.51; N, 17.39. Found: C, 38.72; H, 4.43; N, 17.35%. $\Lambda_{\text{M}} = 12 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$, $\mu_{\text{eff}} = \text{Dia}$, LC-MS (Scan ES^+): m/z (%) 806.2 (100) $[\text{M}+\text{H}]^+$. FT-IR (KBr pellets, $\nu_{\text{max}}/\text{cm}^{-1}$): 3596–3274 $\nu(\text{O}-\text{H}\cdots\text{O})$, 3105–3048 $\nu(\text{Ar}-\text{CH})$, 2924–2830 $\nu(\text{Aliph}-\text{CH})$, 1615 $\nu(\text{C}=\text{N}$ of oxime), 1595 $\nu(\text{C}=\text{N}$ of 4,4'-bipyridine), 1494–1412 $\nu(\text{C}=\text{C})$, 1242 $\nu(\text{N}-\text{O})$ and 515 $\nu(\text{Co}-\text{N})$. ^1H NMR (DMSO- d_6 , TMS, 300 MHz, δ ppm): 18.52 (s, 4H, O–H...O), 8.13 (d, 4H, $J = 6.6$ Hz, *ortho* H of 4,4'-bipyridine), 7.95 (d, 4H, $J = 6.6$ Hz, *meta* of 4,4'-bipyridine) and 2.34 (s, 24H, $\text{CH}_3-\text{C}=\text{NOH}$), ^{13}C NMR (DMSO- d_6 , TMS, 75 MHz, δ ppm): 153.22 ($\text{CH}_3-\text{C}=\text{NOH}$), 151.22 (*ortho* C of 4,4'-bipyridine), 148.00 (*para* C of 4,4'-bipyridine), 124.18 (*meta* C of 4,4'-bipyridine) and 13.17 ($\text{CH}_3-\text{C}=\text{NOH}$). UV-Vis (λ_{max} , nm, * = shoulder peak): 251 and 375 (in $\text{C}_2\text{H}_5\text{OH}$); 245, 261, 304*, 383 and 506* (in DMSO).

2.3. Synthesis of the $[(\text{dmgH})_2\text{PhCH}_2\text{Co}-(4,4'\text{-bpy})-\text{CoCH}_2\text{Ph}(\text{dmgH})_2]$ complex (2)

A solution of complex (1) (2.0 g, 2.48 mmol) suspended in absolute ethanol (100 mL) and NaOH (0.79 g, 19.84 mmol) dissolved in water (10 mL) was added. Nitrogen was bubbled through the resulting dark brown solution for 25 min. and cooled to 0 °C with stirring. Then, 10-fold excess of sodium borohydride (NaBH_4) (1.88 g, 49.66 mmol) dissolved in water (10 mL) was added by dropping cone; the solution turned dark blue. An excess of benzyl bromide (4.25 g, 24.83 mmol) was added by syringe and the solution turned brown. After stirring approximately 2 h, then the reaction mixture was exposed to air and 15 mL acetone and 10 mL water were added. The volume of the reaction mixture was reduced 10 mL by evaporation and then poured into 30 mL water. The resulting brown precipitate was filtered, washed with hexane and diethyl ether and dried. The produced was recrystallized from $\text{CH}_2\text{Cl}_2/\text{C}_2\text{H}_5\text{OH}$ (1:2) solution instead of silica gel column separation and finally dried *in vacuo*. Color: Pale brown, yield (%): 73, m.p: 283 °C, *Anal. Calc.* for $[\text{C}_{40}\text{H}_{50}\text{N}_{10}\text{O}_8\text{Co}_2]$ (F.W: 916.8 g/mol): C, 52.41; H, 5.50; N, 15.28. Found: C, 52.38; H, 5.46; N, 15.23%. $\Lambda_{\text{M}} = 15 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$, $\mu_{\text{eff}} = \text{Dia}$, LC-MS (Scan ES^+): m/z (%) 916.3 (15) $[\text{M}]^+$. FT-IR (KBr pellets, $\nu_{\text{max}}/\text{cm}^{-1}$): 3558–3173 $\nu(\text{O}-\text{H}\cdots\text{O})$, 3096–3048 $\nu(\text{Ar}-\text{CH})$, 2923–2835 $\nu(\text{Aliph}-\text{CH})$, 1609 $\nu(\text{C}=\text{N}$ of oxime), 1566 $\nu(\text{C}=\text{N}$ of 4,4'-bipyridine), 1492–1420 $\nu(\text{C}=\text{C})$, 1240 $\nu(\text{N}-\text{O})$ and 516 $\nu(\text{Co}-\text{N})$. ^1H NMR (DMSO- d_6 , TMS, 300 MHz, δ ppm): 18.47 (s, 4H, O–H...O), 8.21 (d, 4H, $J = 6.9$ Hz, *ortho* H of 4,4'-bipyridine), 7.92 (d, 4H, $J = 6.9$ Hz, *meta* H of 4,4'-bipyridine), 7.73 (d, 4H, $J = 6.9$ Hz, *ortho* H of Ph- CH_2), 7.62 (t, 2H, $J = 7.5$ Hz, *para* H of Ph- CH_2), 7.32 (t, 4H, $J = 7.5$ Hz, *meta* H of Ph- CH_2) and 2.98 (s, 4H, Ph- CH_2), 1.94 (s, 24H, $\text{CH}_3-\text{C}=\text{NOH}$), ^{13}C NMR (DMSO- d_6 , TMS, 75 MHz, δ ppm): 153.53 ($\text{CH}_3-\text{C}=\text{NOH}$), 150.13 (*ortho* C of 4,4'-bipyridine), 147.53 (*para* C of 4,4'-bipyridine), 129.64 (*meta* C of 4,4'-bipyridine), 135.07 (*ortho* C of phenyl), 129.96 (*para* C of phenyl), 123.76 (*meta* C of phenyl), 77.52 (CH_2-Ph) and 9.80 ($\text{CH}_3-\text{C}=\text{NOH}$). UV-Vis (λ_{max} , nm, * = shoulder peak): 249, 362* and 632* (in $\text{C}_2\text{H}_5\text{OH}$); 250, 262, 365* and 531* (in DMSO).

2.4. Synthesis of the $[(\text{dmgCu}(\text{N}-\text{N}))_2\text{ClCo}-(4,4'\text{-bpy})-\text{CoCl}(\text{dmgCu}(\text{N}-\text{N}))_2](\text{ClO}_4)_4$ complexes (3–9)

The complexes $[(\text{dmgCu}(\text{N}-\text{N}))_2\text{ClCo}-(4,4'\text{-bpy})-\text{CoCl}(\text{dmgCu}(\text{N}-\text{N}))_2](\text{ClO}_4)_4$ (3–9) and as linked ligands, N-N = 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), 3,3'-dicarboxy-2,2'-bipyridine (dcbpy), 4,5-diazafluoren-9-one (dafo), 1,10-phenanthroline-5,6-dione (dione), 4,4'-ditertbutyl-2,2'-bipyridine (dtbpy) and 4,5-diazafluoren-9-oxime (dafoxi) containing these multinuclear

Download English Version:

<https://daneshyari.com/en/article/1306965>

Download Persian Version:

<https://daneshyari.com/article/1306965>

[Daneshyari.com](https://daneshyari.com)