

Synthesis of the Multinuclear Cobaloxime Complexes via Click Chemistry as Catalysts for the Formation of Cyclic Carbonates from Carbon Dioxide and Epoxides

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Abstract. In this study, the structurally similar multinuclear cobaloxime complexes based on dioxime ligands were synthesized and characterized as trinuclear complexes with respect to varied axial groups. The multinuclear cobaloxime complexes were characterized by ^1H , ^{13}C -NMR, FT-IR, UV-Vis, LC-MS spectra, melting point and magnetic susceptibility measurements. These multinuclear cobaloxime complexes have been successfully applied to the synthesis of cyclic carbonates from CO_2 and epoxides under optimized conditions and without using any solvent. All multinuclear cobaloxime complexes obtained by click chemistry are good catalysts for the cycloaddition of CO_2 to different epoxides in the presence of pyridine as a co-catalyst. Additionally, the effects of epoxides, bases, temperature, pressure, and time on the yield of cyclic carbonates were investigated.

Keywords. Click chemistry; multinuclear cobaloxime complexes; carbon dioxide; epoxides; cyclic carbonate.

1. Introduction

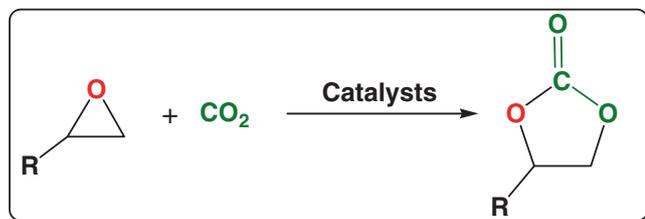
Over the past several decades, the average atmospheric concentration of CO_2 has increased from 280 ppm to 400 ppm (summer of 2013) and as a result, the average temperature has increased between 0.6°C and 1°C in the same period.^{1,2} As a solution to such a serious problem, carbon dioxide conversion to important chemicals and materials is needed. However, carbon dioxide capture and utilization used in conjunction with carbon storage not only can provide an alternative and renewable feedstock for the chemical industry but also can generate revenue to offset the cost of carbon capture and storage.³ In this regard, one of the most common ways in chemical industry has been the synthesis of five-membered cyclic carbonates via coupling of carbon dioxide and epoxides for effective utilization of CO_2 , as shown in scheme 1.

The synthesized five-membered cyclic organic carbonates are used both in industrial chemistry and in academic chemistry studies as monomers, aprotic polar solvents and pharmaceutical/fine chemical intermediates, in many biomedical applications,^{4,5} as electrolytes for secondary batteries,⁶ and as starting materials for polycarbonates,⁷ enantiopure aminoalcohols,⁸ and thermosetting coatings.⁹

For the synthesis of cyclic carbonates from carbon dioxide and epoxides, many efficient and cost effective homogeneous catalytic systems with different yields and turnover frequencies (TOFs) have been developed by the academia and industry. These include metal salts, metallic complexes, ionic liquids, metal-organic frameworks, organocatalysts, and N-heterocyclic carbenes.¹⁰

Although many efficient and cost effective homogeneous catalytic systems have been proposed for the synthesis of cyclic organic carbonates, the search for new homogeneous or heterogeneous catalytic systems still remains an exciting topic. To the best of our knowledge, there are not many reports using multinuclear cobaloxime complexes as homogeneous catalysts for the conversion of carbon dioxide to cyclic carbonates. Thus, in the present paper we report preparation and characterization of a new series multinuclear cobaloxime complexes obtained by click chemistry. Further, these complexes were used as homogeneous catalytic systems for conversion of carbon dioxide to a five-membered cyclic organic carbonate. Additionally, the effects of reaction temperature, pressure, and time on the yield of cyclic carbonate were investigated. The multinuclear cobaloxime complexes were characterized by ^1H and ^{13}C -NMR spectra, FT-IR, UV-Vis, LC-MS spectra, melting point and magnetic susceptibility measurements.

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Scheme 1. The synthesis of cyclic organic carbonate from CO_2 and epoxides.

2. Experimental

2.1 Chemicals and measurements

All chemicals and solvents were purchased from commercial suppliers and were used as received without any further treatment. ^1H and ^{13}C -NMR spectra were recorded in 5-mm tubes at room temperature with a Bruker Avance 300 NMR or an Agilent-VNMRS-400 NMR at 400 MHz. All chemical shifts are reported in δ units with reference to the residual protons of the deuterated solvents for proton chemical shifts. Signals are quoted relative to tetramethylsilane ($\delta = 0.00$ ppm) and coupling constants (J) are in hertz. Elemental analyses (C, H and N) were performed on a LECO CHNS model 932 elemental analyzer. Infrared spectra were obtained from KBr pellets (3 mg sample in 300 mg KBr) on a Perkin Elmer Spectrum Two FT-IR Fourier Transform spectrometer ($4000\text{--}400\text{ cm}^{-1}$). UV-Vis spectra were obtained on a Perkin-Elmer Lambda 25 spectrophotometer in the wavelength range from 200 to 1100 nm in CH_3OH and CH_2Cl_2 solvents. Magnetic Susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature (25°C) using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a calibrant; diamagnetic corrections were calculated from Pascal's constants.¹¹ Melting points were measured in open capillary tubes with an Electrothermal 9100 melting point apparatus and are uncorrected. LC-MS 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 an Agilent 7820A GC system with nitrogen as the carrier gas.

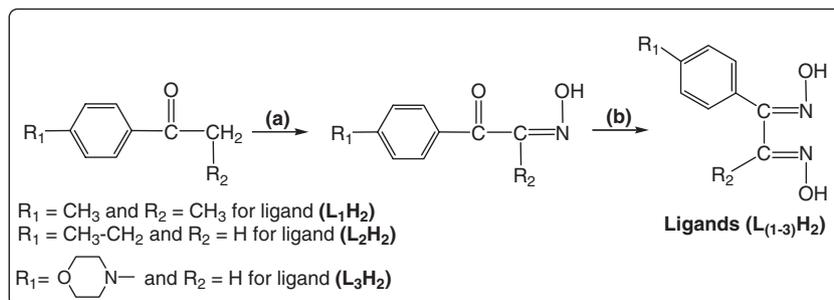
2.2 Synthesis of the ligand (L_3H_2)

The ligands (L_1H_2) and (L_2H_2) were synthesized according to the literature method.^{12,13} However, the ligand (L_3H_2) was synthesized by a similar procedure as new product. The synthesis details are given briefly in scheme 2.

2.2a (L_3H_2) ligand: Color: Pale yellow, yield: 82%, M.p.: 182°C , Anal. Calc. (%) for $[\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_3]$ (F.W: 249.3 g/mol): C, 57.82; H, 6.07; N, 16.86. Found: C, 57.72; H, 6.00; N, 16.75 %. LC-MS (Scan ES^+): m/z (%) 249.2 (35) $[\text{M}]^+$, FT-IR (KBr pellets, $\nu_{\text{max}}/\text{cm}^{-1}$): 3357-3086 $\nu(\text{O-H})$, 3038 $\nu(\text{Ar-CH})$, 2967-2859 $\nu(\text{Aliph-CH})$, 1656 $\nu(\text{C=N})$, 1465-1417 $\nu(\text{C=C})$ and 1270 $\nu(\text{N-O})$. ^1H -NMR (DMSO- d_6 , TMS, 400 MHz, δ ppm): 10.88 (s, 2H, C=N-OH), 8.04 (s, 1H, HC=N), 7.54 (d, 2H, $J = 8.8$ Hz, Ar-CH), 6.95 (d, 2H, $J = 8.8$ Hz, Ar-CH), 3.75 (t, 4H, $J = 4.8$ Hz, O-CH_2), and 3.15 (t, 4H, N-CH_2). ^{13}C -NMR (DMSO- d_6 , TMS, 100 MHz, δ ppm): 155.42 and 148.68 (C=N-OH), 142.01, 133.41, 130.12, 115.36 and 113.93 (Ar-CH), 66.82 (O-CH_2) and 47.65 (N-CH_2). UV-Vis ($\lambda_{\text{max}}/\text{nm}$): 233, 297 and 353 (in CH_3OH); 232, 256, 305, and 356 (in CH_2Cl_2).

2.3 Synthesis of the multinuclear cobaloxime complexes (**I-3**)

In a two-necked, 100 mL round-bottom flask and equipped with a blanket of argon (Ar) was placed 50 mL of 96% EtOH. To this solution, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1.19 g, 5.0 mmol) was added slowly at room temperature under



Scheme 2. Synthesis of the dioxime ligands (L_{1-3}H_2); (a) $n\text{-C}_4\text{H}_9\text{ONO}$, $\text{C}_2\text{H}_5\text{ONa}$, -5°C ; (b) CH_3COONa , $\text{NH}_2\text{OH} \cdot \text{HCl}$, EtOH, reflux temperature.

argon atmosphere and with vigorous mechanical stirring. Then, the solution of dioxime ligand ($\mathbf{L}_1\mathbf{H}_2$) (1.92 g, 10.0 mmol), ($\mathbf{L}_2\mathbf{H}_2$) (1.92 g, 10.0 mmol) and ($\mathbf{L}_3\mathbf{H}_2$) (2.49 g, 10.0 mmol) was quickly injected into the reaction mixture in one portion. The mixtures were vigorously stirred for 40 min with occasional swirling, during which the solution turned green, and the mixtures were again heated for 3 h at reflux temperature. Later the mixtures were allowed to cool to room temperature and then 1.70 mmol tris (2-aminoethyl) amine (**TAEA**) was added to mixture as axial base and a very gentle stream of air was passed through the solution for about 6 h. After completion of the reaction, 5 mL water was added to get the desired product and the crude product obtained was recrystallized from $\text{CH}_2\text{Cl}_2/\text{C}_2\text{H}_5\text{OH}$. The mixtures were set aside for 5 h, after which the product was collected on sintered glass and washed successively with small amounts of water, and diethyl ether and finally air-dried.

2.3a [$(\mathbf{L}_1\mathbf{H})_6\text{Cl}_3\text{Co}_3(\text{TAEA})$] (**1**): Color: Brown, yield: 62%, M.p.: 223°C, Anal. Calc. (%) for $[\text{C}_{66}\text{H}_{84}\text{Cl}_3\text{Co}_3\text{N}_{16}\text{O}_{12}]$ (F.W: 1576.6 g/mol): C, 50.28; H, 5.37; N, 14.21. Found: C, 50.19; H, 5.24; N, 14.14 %. $\mu_{\text{eff}} = \text{Dia}$, LC-MS (Scan ES^+): m/z (%) 1576.7 (18) $[\text{M}]^+$. FT-IR (KBr pellet, $\nu_{\text{max}}/\text{cm}^{-1}$): 3540-3301 $\nu(\text{O}-\text{H}\cdots\text{O})$, 3221 and 3130 $\nu(\text{NH}_2)$, 3030 $\nu(\text{Ar}-\text{CH})$, 2954-2863 $\nu(\text{Aliph}-\text{CH})$, 1616 $\nu(\text{C}=\text{N})$, 1553-1445 $\nu(\text{C}=\text{C})$, 1264 $\nu(\text{N}-\text{O})$ and 502 $\nu(\text{Co}-\text{N})$. ^1H -NMR (DMSO- d_6 , TMS, 300 MHz, δ ppm): 18.74 (d, 3H, $\text{O}-\underline{\text{H}}\cdots\text{O}$), 18.60 (s, 3H, $\text{O}-\underline{\text{H}}\cdots\text{O}$), 7.59-7.06 (m, 24H, Ar- $\underline{\text{C}}\text{H}$), 2.40 (s, 18H, Ar- $\underline{\text{C}}\text{H}_3$), 2.31 (s, 18H, C- $\underline{\text{C}}\text{H}_3$), 2.28 (d, 6H, $\text{J} = 6.0$ Hz, C- $\underline{\text{C}}\text{H}_2$), 2.06 (s, 6H, N- $\underline{\text{C}}\text{H}_2$), and 1.09-1.04 (m, 6H, $\text{CH}_2-\underline{\text{N}}\text{H}_2$). ^{13}C -NMR (DMSO- d_6 , TMS, 75 MHz, δ ppm): 155.58 and 149.78 ($\underline{\text{C}}=\text{NOH}$), 143.25, 140.19, 139.21, 137.33, 130.74, 129.53, 128.57, 128.42 and 128.08 (Ar- $\underline{\text{C}}\text{H}$), 56.52 (N- $\underline{\text{C}}\text{H}_2$), 36.93 (C- $\underline{\text{C}}\text{H}_2$), 21.48 (Ar- $\underline{\text{C}}\text{H}_3$) and 14.94 ($\underline{\text{C}}\text{H}_3\text{C}=\text{NOH}$). UV-Vis ($\lambda_{\text{max}}/\text{nm}$, * = shoulder peak): 251, 314*, and 835* (in CH_3OH); 250, 268*, and 315 (in CH_2Cl_2).

2.3b [$(\mathbf{L}_2\mathbf{H})_6\text{Cl}_3\text{Co}_3(\text{TAEA})$] (**2**): Color: Dark brown, yield: 64%, M.p.: 235°C, Anal. Calc. (%) for $[\text{C}_{66}\text{H}_{84}\text{Cl}_3\text{Co}_3\text{N}_{16}\text{O}_{12}]$ (F.W: 1576.6 g/mol): C, 51.28; H, 5.37; N, 14.21. Found: C, 51.19; H, 5.29; N, 14.13 %. $\mu_{\text{eff}} = \text{Dia}$, LC-MS (Scan ES^+): m/z (%) 1576.5 (20) $[\text{M}]^+$. FT-IR (KBr pellet, $\nu_{\text{max}}/\text{cm}^{-1}$): 3569-3329 $\nu(\text{O}-\text{H}\cdots\text{O})$, 3220 and 3122 $\nu(\text{NH}_2)$, 3027 $\nu(\text{Ar}-\text{CH})$, 2967-2867 $\nu(\text{Aliph}-\text{CH})$, 1608 $\nu(\text{C}=\text{N})$, 1545-1453 $\nu(\text{C}=\text{C})$, 1266 $\nu(\text{N}-\text{O})$ and 505 $\nu(\text{Co}-\text{N})$. ^1H -NMR (DMSO- d_6 , TMS, 300 MHz, δ ppm): 19.03 (s, 3H,

$\text{O}-\underline{\text{H}}\cdots\text{O}$), 18.84 (d, 3H, $\text{J} = 6.0$ Hz, $\text{O}-\underline{\text{H}}\cdots\text{O}$), 8.22 (s, 6H, $\underline{\text{C}}\text{H}=\text{N}$), 7.40-6.90 (m, 24H, Ar- $\underline{\text{C}}\text{H}$), 2.70 (d, 12H, $\text{J} = 7.2$ Hz, $\text{CH}_3-\underline{\text{C}}\text{H}_2$), 2.10-1.85 (m, 12H, C- $\underline{\text{C}}\text{H}_2$ and N- $\underline{\text{C}}\text{H}_2$), and 1.23-0.93 (m, 24H, $\underline{\text{C}}\text{H}_3-\text{CH}_2$, and $\text{CH}_2-\underline{\text{N}}\text{H}_2$). ^{13}C -NMR (DMSO- d_6 , TMS, 75 MHz, δ ppm): 147.70 and 147.01 ($\underline{\text{C}}=\text{NOH}$), 143.41, 142.61, 129.42, 128.92, 128.55, 128.23, 127.57 and 126.28 (Ar- $\underline{\text{C}}\text{H}$), 61.14 (N- $\underline{\text{C}}\text{H}_2$), 45.56 (C- $\underline{\text{C}}\text{H}_2$), 28.50 ($\text{CH}_3-\underline{\text{C}}\text{H}_2$) and 15.99 ($\underline{\text{C}}\text{H}_3-\text{CH}_2$). UV-Vis ($\lambda_{\text{max}}/\text{nm}$, * = shoulder peak): 261, 337* and 836* (in CH_3OH); 253, 270 and 312* (in CH_2Cl_2).

2.3c [$(\mathbf{L}_3\mathbf{H})_6\text{Cl}_3\text{Co}_3(\text{TAEA})$] (**3**): Color: Brown, yield: 68%, M.p.: 217°C, Anal. Calc. (%) for $[\text{C}_{78}\text{H}_{102}\text{Cl}_3\text{Co}_3\text{N}_{22}\text{O}_{18}]$ (F.W: 1918.9 g/mol): C, 48.82; H, 5.36; N, 16.06. Found: C, 48.74; H, 5.28; N, 15.96%. $\mu_{\text{eff}} = \text{Dia}$, LC-MS (Scan ES^+): m/z (%) 1918.8 (15) $[\text{M}]^+$. FT-IR (KBr pellet, $\nu_{\text{max}}/\text{cm}^{-1}$): 3548-3297 $\nu(\text{O}-\text{H}\cdots\text{O})$, 3233 and 3146 $\nu(\text{NH}_2)$, 3070 $\nu(\text{Ar}-\text{CH})$, 2963-2851 $\nu(\text{Aliph}-\text{CH})$, 1605 $\nu(\text{C}=\text{N})$, 1521-1446 $\nu(\text{C}=\text{C})$, 1266 $\nu(\text{N}-\text{O})$ and 513 $\nu(\text{Co}-\text{N})$. ^1H -NMR (DMSO- d_6 , TMS, 300 MHz, δ ppm): 19.92 (s, 6H, $\text{O}-\underline{\text{H}}\cdots\text{O}$), 8.23 (s, 6H, $\underline{\text{C}}\text{H}=\text{N}$), 8.02-6.95 (m, 24H, Ar- $\underline{\text{C}}\text{H}$), 3.73 (s, 24H, Ar- $\text{O}-\underline{\text{C}}\text{H}_2$), 3.46 (s, 24H, Ar-N- $\underline{\text{C}}\text{H}_2$). 3.18-2.95 (m, 6H, Aliph-N- $\underline{\text{C}}\text{H}_2$), 2.10 (s, 6H, Aliph-C- $\underline{\text{C}}\text{H}_2$) and 1.16 (t, 6H, $\text{J} = 7.2$ Hz, $\text{CH}_2-\underline{\text{N}}\text{H}_2$). ^{13}C -NMR (DMSO- d_6 , TMS, 75 MHz, δ ppm): 155.30 and 151.64 ($\underline{\text{C}}=\text{NOH}$), 138.85, 131.88, 131.30, 126.79, 122.34, 114.85 and 113.38 (Ar- $\underline{\text{C}}\text{H}$), 66.20 (Ar- $\text{O}-\underline{\text{C}}\text{H}_2$), 48.40 (Ar-N- $\underline{\text{C}}\text{H}_2$), 46.74 (Aliph-N- $\underline{\text{C}}\text{H}_2$), and 46.27 (Aliph- $\underline{\text{C}}\text{H}_2$). UV-Vis ($\lambda_{\text{max}}/\text{nm}$, * = shoulder peak): 223*, 294 and 456 (in CH_3OH); 231, 280 and 452 (in CH_2Cl_2).

2.4 Synthesis of the azido-functionalized multinuclear cobaloxime complexes (**4-6**)

The azido-functionalized multinuclear cobaloxime complexes (**4-6**) were synthesized according to the literature method.¹⁴ In a two-necked, 100 mL round-bottom flask and equipped with a blanket of argon (Ar) was placed 10 mL of CH_3CN . To this solution was added 0.5 mmol of $[(\mathbf{L}_{1-3}\mathbf{H})_6\text{Cl}_3\text{Co}_3(\text{TAEA})]$ (**1-3**) cobaloxime complexes slowly at room temperature under argon atmosphere and with vigorous mechanical stirring. In another a two-necked round-bottom flask, 1.50 mmol of AgClO_4 was dissolved in an equal volume of CH_3CN . The $[(\mathbf{L}_{1-3}\mathbf{H})_6\text{Cl}_3\text{Co}_3(\text{TAEA})]$ (**1-3**) solution was then cannulated into the silver perchlorate solution. Immediate precipitation of AgCl was observed, and the reaction was stirred overnight. 4.5 mmol of NaN_3 was added, keeping exposure to

air at a minimum. The reaction was stirred for an additional 24 h. The mixture was diluted with distilled diethyl ether and the organic portion washed with water to remove NaClO_4 and excess NaN_3 , then dried with Na_2SO_4 and the solvent removed in vacuo and finally the products was dried *in vacuo*.

2.4a $[(L_1H)_6(N_3)_3Co_3(TAEA)]$ (**4**): Color: Dark brown, yield: 60%, M.p.: $>300^\circ\text{C}$, Anal. Calc. for $[\text{C}_{66}\text{H}_{84}\text{Co}_3\text{N}_{25}\text{O}_{12}]$ (F.W: 1596.3 g/mol): C, 49.66; H, 5.30; N, 21.94. Found: C, 49.56; H, 5.24; N, 21.86%. $\mu_{\text{eff}} = \text{Dia}$, LC-MS (Scan ES^+): m/z (%) 1596.4 (12) $[\text{M}]^+$. FT-IR (KBr pellet, $\nu_{\text{max}}/\text{cm}^{-1}$): 3544-3327 $\nu(\text{O}-\text{H}\cdots\text{O})$, 3253 and 3139 $\nu(\text{NH}_2)$, 3031 $\nu(\text{Ar}-\text{CH})$, 2956-2856 $\nu(\text{Aliph}-\text{CH})$, 2021 $\nu(\text{N}_3)$, 1610 $\nu(\text{C}=\text{N})$, 1554-1447 $\nu(\text{C}=\text{C})$, 1270 $\nu(\text{N}-\text{O})$ and 506 $\nu(\text{Co}-\text{N})$. $^1\text{H-NMR}$ (DMSO- d_6 , TMS, 400 MHz, δ ppm): 18.71 (d, 3H, J = 6.0 Hz, $\text{O}-\text{H}\cdots\text{O}$), 18.45 (s, 3H, $\text{O}-\text{H}\cdots\text{O}$), 7.60-7.04 (m, 24H, $\text{Ar}-\text{CH}$), 2.39 (s, 18H, $\text{Ar}-\text{CH}_3$), 2.34 (d, 6H, J = 6.0 Hz, $\text{C}-\text{CH}_2$), 2.28 (s, 18H, $\text{C}-\text{CH}_3$), 2.06 (s, 6H, $\text{N}-\text{CH}_2$), and 1.28-1.03 (m, 6H, CH_2-NH_2). $^{13}\text{C-NMR}$ (DMSO- d_6 , TMS, 100 MHz, δ ppm): 154.31 and 149.28 ($\text{C}=\text{NOH}$), 139.37, 139.19, 137.27, 130.29, 129.83, 129.52, 128.40 and 127.55 ($\text{Ar}-\text{CH}$), 56.48 ($\text{N}-\text{CH}_2$), 36.95 ($\text{C}-\text{CH}_2$), 21.51 ($\text{Ar}-\text{CH}_3$) and 14.32 ($\text{CH}_3\text{C}=\text{NOH}$). UV-Vis ($\lambda_{\text{max}}/\text{nm}$, * = shoulder peak): 246, and 317* (in CH_3OH); 248 and 324* (in CH_2Cl_2).

2.4b $[(L_2H)_6(N_3)_3Co_3(TAEA)]$ (**5**): Color: Dark brown, yield: 62%, M.p.: $>300^\circ\text{C}$, Anal. Calc. for $[\text{C}_{66}\text{H}_{84}\text{Co}_3\text{N}_{25}\text{O}_{12}]$ (F.W: 1596.3 g/mol): C, 49.66; H, 5.30; N, 21.94%. Found: C, 49.52; H, 5.23; N, 21.86%. $\mu_{\text{eff}} = \text{Dia}$, LC-MS (Scan ES^+): m/z (%) 1596.2 (16) $[\text{M}]^+$. FT-IR (KBr pellet, $\nu_{\text{max}}/\text{cm}^{-1}$): 3577-3341 $\nu(\text{O}-\text{H}\cdots\text{O})$, 3235 and 3129 $\nu(\text{NH}_2)$, 3047 $\nu(\text{Ar}-\text{CH})$, 2966-2870 $\nu(\text{Aliph}-\text{CH})$, 2017 $\nu(\text{N}_3)$, 1607 $\nu(\text{C}=\text{N})$, 1568-1455 $\nu(\text{C}=\text{C})$, 1270 $\nu(\text{N}-\text{O})$ and 513 $\nu(\text{Co}-\text{N})$. $^1\text{H-NMR}$ (DMSO- d_6 , TMS, 400 MHz, δ ppm): 18.53 (s, 3H, $\text{O}-\text{H}\cdots\text{O}$), 18.41 (d, 3H, J = 6.0 Hz, $\text{O}-\text{H}\cdots\text{O}$), 8.57 (s, 6H, $\text{CH}=\text{N}$), 8.19-7.25 (m, 24H, $\text{Ar}-\text{CH}$), 2.68 (d, 12H, J = 7.2 Hz, CH_3-CH_2), 2.63-2.59 (m, 12H, $\text{C}-\text{CH}_2$ and $\text{N}-\text{CH}_2$), and 1.23-1.05 (m, 24H, CH_3-CH_2 , and CH_2-NH_2). $^{13}\text{C-NMR}$ (DMSO- d_6 , TMS, 100 MHz, δ ppm): 147.49 and 146.51 ($\text{C}=\text{NOH}$), 142.39, 142.71, 141.71, 131.93, 128.98, 128.89, 128.28, 127.74, 127.38, 126.61 and 126.30 ($\text{Ar}-\text{CH}$), 61.18 ($\text{N}-\text{CH}_2$), 45.73 ($\text{C}-\text{CH}_2$), 28.53 (CH_3-CH_2) and 15.89 (CH_3-CH_2). UV-Vis ($\lambda_{\text{max}}/\text{nm}$, * = shoulder peak): 260 and 346* (in CH_3OH); 253, 262 and 348* (in CH_2Cl_2).

2.4c $[(L_3H)_6(N_3)_3Co_3(TAEA)]$ (**6**): Color: Dark brown, yield: 64%, M.p.: $>300^\circ\text{C}$, Anal. Calc. for $[\text{C}_{78}\text{H}_{102}\text{Co}_3\text{N}_{31}\text{O}_{18}]$ (F.W: 1938.6 g/mol): C, 48.32; H, 5.30; N, 22.40%. Found: C, 48.23; H, 5.29; N, 22.31%. $\mu_{\text{eff}} = \text{Dia}$, LC-MS (Scan ES^+): m/z (%) 1938.5 (10) $[\text{M}]^+$. FT-IR (KBr pellet, $\nu_{\text{max}}/\text{cm}^{-1}$): 3596-3263 $\nu(\text{O}-\text{H}\cdots\text{O})$, 3210 and 3129 $\nu(\text{NH}_2)$, 3072 $\nu(\text{Ar}-\text{CH})$, 2966-2849 $\nu(\text{Aliph}-\text{CH})$, 2035 $\nu(\text{N}_3)$, 1603 $\nu(\text{C}=\text{N})$, 1548-1444 $\nu(\text{C}=\text{C})$, 1264 $\nu(\text{N}-\text{O})$ and 512 $\nu(\text{Co}-\text{N})$. $^1\text{H-NMR}$ (DMSO- d_6 , TMS, 400 MHz, δ ppm): 19.98 (s, 6H, $\text{O}-\text{H}\cdots\text{O}$), 8.20 (s, 6H, $\text{CH}=\text{N}$), 7.98 (d, 12H, J = 5.2 Hz, $\text{Ar}-\text{CH}$), 7.00 (d, 12H, J = 5.2 Hz, $\text{Ar}-\text{CH}$), 3.70 (s, 24H, $\text{Ar}-\text{O}-\text{CH}_2$), 3.40 (s, 24H, $\text{Ar}-\text{N}-\text{CH}_2$), 3.12-3.00 (m, 6H, $\text{Aliph}-\text{N}-\text{CH}_2$), 2.48 (s, 6H, $\text{Aliph}-\text{C}-\text{CH}_2$), and 1.23 (s, 6H, CH_2-NH_2). $^{13}\text{C-NMR}$ (DMSO- d_6 , TMS, 100 MHz, δ ppm): 154.20 and 151.62 ($\text{C}=\text{NOH}$), 137.78, 130.77, 130.12, 126.71, 121.29, 114.13 and 112.28 ($\text{Ar}-\text{CH}$), 65.12 ($\text{Ar}-\text{O}-\text{CH}_2$), 48.32 ($\text{Ar}-\text{N}-\text{CH}_2$), 47.60 ($\text{Aliph}-\text{N}-\text{CH}_2$), and 45.66 ($\text{Aliph}-\text{CH}_2$). UV-Vis ($\lambda_{\text{max}}/\text{nm}$, * = shoulder peak): 225*, 274 and 464 (in CH_3OH); 276, 397* and 460 (in CH_2Cl_2).

2.5 Procedure for click reaction to form 1,2,3-triazole containing multinuclear cobaloxime complexes (**7-9**)

The 1,2,3-triazole containing multinuclear cobaloxime complexes (**7-9**) were synthesized via click reaction according to the literature method.¹⁵ The azido-functionalized cobaloxime complex (**4**) (0.5 g, 0.31 mmol), complex (**5**) (0.5 g, 0.31 mmol), complex (**6**) (0.5 g, 0.26 mmol) and excess quantity of propargyl alcohol (0.08 g, 1.35 mmol) were dissolved in 1:1 (30:30 mL) mixture of THF and water solvent mixture in a round-bottom flask. To the reaction mixture, CuSO_4 (0.08 g, dissolved in 2 mL water) was added followed by freshly prepared sodium ascorbate solution (0.06 g, dissolved in 2 mL water) dropwise. The reaction mixture was stirred for 18 h at room temperature. After removal of the THF under vacuum, dichloromethane (15 mL) and conc. NH_3 (3 mL) were added to the solution, which was allowed to stir for a further 1 h at room temperature. The dichloromethane solution was dried over magnesium sulfate and crude compounds were collected after evaporating the solvent. Finally the products was recrystallized from dichloromethane and hexane.

2.5a $[(L_1H)_6(\text{triazole})_3Co_3(TAEA)]$ (**7**): Color: Brown, yield: 80%, M.p.: 215°C , Anal. Calc. for $[\text{C}_{75}\text{H}_{96}\text{Co}_3\text{N}_{25}\text{O}_{15}]$ (F.W: 1764.5 g/mol): C, 51.05; H, 5.48; N, 19.85%. Found: C, 50.98; H, 5.41; N, 19.76%. $\mu_{\text{eff}} = \text{Dia}$, LC-MS (Scan ES^+): m/z (%) 1764.6

(12) $[M]^+$. FT-IR (KBr pellet, $\nu_{\max}/\text{cm}^{-1}$): 3539-3312 $\nu(\text{O}-\text{H}\cdots\text{O})$, 3249 and 3150 $\nu(\text{NH}_2)$, 3026 $\nu(\text{Ar}-\text{CH})$, 2959-2856 $\nu(\text{Aliph}-\text{CH})$, 1650 $\nu(\text{triazole})$, 1607 $\nu(\text{C}=\text{N})$, 1522-1446 $\nu(\text{C}=\text{C})$, 1267 $\nu(\text{N}-\text{O})$ and 499 $\nu(\text{Co}-\text{N})$. $^1\text{H-NMR}$ (DMSO- d_6 , TMS, 300 MHz, δ ppm): 18.68 (d, 3H, $J = 6.0$ Hz, $\text{O}-\underline{\text{H}}\cdots\text{O}$), 18.49 (s, 3H, $\text{O}-\underline{\text{H}}\cdots\text{O}$), 8.18 (s, 3H, triazole- $\underline{\text{CH}}$), 7.63-7.01 (m, 24H, $\text{Ar}-\underline{\text{CH}}$), 4.52 (br., s, 3H, $\text{CH}_2-\underline{\text{OH}}$), 3.25 (s, 6H, $\text{CH}_2-\underline{\text{OH}}$), 2.36 (s, 18H, $\text{Ar}-\underline{\text{CH}}_3$), 2.30 (d, 6H, $J = 6.0$ Hz, $\text{C}-\underline{\text{CH}}_2$), 2.16 (s, 18H, $\text{C}-\underline{\text{CH}}_3$), 2.03 (s, 6H, $\text{N}-\underline{\text{CH}}_2$), and 1.21-0.99 (m, 6H, $\text{CH}_2-\underline{\text{NH}}_2$). $^{13}\text{C-NMR}$ (DMSO- d_6 , TMS, 75 MHz, δ ppm): 155.32 and 148.56 ($\underline{\text{C}}=\text{NOH}$), 146.77 (triazole $\underline{\text{CH}}$), 139.33, 139.07, 137.18, 130.30, 129.86, 129.62, 128.49 and 127.71 ($\text{Ar}-\underline{\text{CH}}$), 123.32 (triazole $\underline{\text{C}}-\text{CH}_2\text{OH}$), 56.48 ($\text{N}-\underline{\text{CH}}_2$), 55.16 (triazole- $\underline{\text{CH}}_2-\text{OH}$), 37.08 ($\text{C}-\underline{\text{CH}}_2$), 21.32 ($\text{Ar}-\underline{\text{CH}}_3$) and 14.28 ($\underline{\text{CH}}_3\text{C}=\text{NOH}$). UV-Vis (λ_{\max}/nm , * = shoulder peak): 251, and 319* (in CH_3OH); 256 and 328* (in CH_2Cl_2).

2.5b $[(\text{L}_2\text{H})_6(\text{triazole})_3\text{Co}_3(\text{TAEA})]$ (**8**): Color: Brown, yield: 78%, m.p: 125°C, Anal. Calc. for $[\text{C}_{75}\text{H}_{96}\text{Co}_3\text{N}_{25}\text{O}_{15}]$ (F.W: 1764.5 g/mol): C, 51.05; H, 5.48; N, 19.85%. Found: C, 50.92; H, 5.39; N, 19.77%. $\mu_{\text{eff}} = \text{Dia}$, LC-MS (Scan ES^+): m/z (%) 1764.3 (12) $[M]^+$. FT-IR (KBr pellet, $\nu_{\max}/\text{cm}^{-1}$): 3557-3097 $\nu(\text{O}-\text{H}\cdots\text{O}/\text{NH}_2)$, 3032 $\nu(\text{Ar}-\text{CH})$, 2964-2867 $\nu(\text{Aliph}-\text{CH})$, 1646 $\nu(\text{triazole})$, 1610 $\nu(\text{C}=\text{N})$, 1546-1454 $\nu(\text{C}=\text{C})$, 1273 $\nu(\text{N}-\text{O})$ and 516 $\nu(\text{Co}-\text{N})$. $^1\text{H-NMR}$ (DMSO- d_6 , TMS, 300 MHz, δ ppm): 18.62 (s, 3H, $\text{O}-\underline{\text{H}}\cdots\text{O}$), 18.43 (d, 3H, $J = 6.0$ Hz, $\text{O}-\underline{\text{H}}\cdots\text{O}$), 8.46 (s, 6H, $\underline{\text{CH}}=\text{N}$), 8.19 (s, 3H, triazole- $\underline{\text{CH}}$), 7.65-7.15 (m, 24H, $\text{Ar}-\underline{\text{CH}}$), 4.51 (br., s, 3H, $\text{CH}_2-\underline{\text{OH}}$), 3.36 (s, 6H, $\text{CH}_2-\underline{\text{OH}}$), 2.67 (d, 12H, $J = 3.9$ Hz, $\text{CH}_3-\underline{\text{CH}}_2$), 2.65-2.54 (m, 12H, $\text{C}-\underline{\text{CH}}_2$ and $\text{N}-\underline{\text{CH}}_2$), and 1.23-1.18 (m, 24H, $\underline{\text{CH}}_3-\text{CH}_2$, and $\text{CH}_2-\underline{\text{NH}}_2$). $^{13}\text{C-NMR}$ (DMSO- d_6 , TMS, 75 MHz, δ ppm): 150.16 and 146.98 ($\underline{\text{C}}=\text{NOH}$), 143.93 (triazole $\underline{\text{CH}}$), 142.86, 142.73, 140.17, 130.87, 128.58, 128.12, 127.88, 127.31, 126.66, 126.46 and 126.36 ($\text{Ar}-\underline{\text{CH}}$), 124.94 (triazole $\underline{\text{C}}-\text{CH}_2\text{OH}$), 67.88 ($\text{N}-\underline{\text{CH}}_2$), 58.27 (triazole- $\underline{\text{CH}}_2-\text{OH}$), 45.78 ($\text{C}-\underline{\text{CH}}_2$), 27.59 ($\underline{\text{CH}}_3-\underline{\text{CH}}_2$) and 15.93 ($\underline{\text{CH}}_3-\text{CH}_2$). UV-Vis (λ_{\max}/nm , * = shoulder peak): 262 and 411* (in CH_3OH); 234, 261 and 380* (in CH_2Cl_2).

2.5c $[(\text{L}_3\text{H})_6(\text{triazole})_3\text{Co}_3(\text{TAEA})]$ (**9**): Although much effort was made to clarify the structure of the $[(\text{L}_3\text{H})_6(\text{triazole})_3\text{Co}_3(\text{TAEA})]$ (**9**) complex, we failed to isolate their crystals. Thus, the structure of the $[(\text{L}_3\text{H})_6(\text{triazole})_3\text{Co}_3(\text{TAEA})]$ (**9**) complex has not been evaluated through spectroscopic techniques.

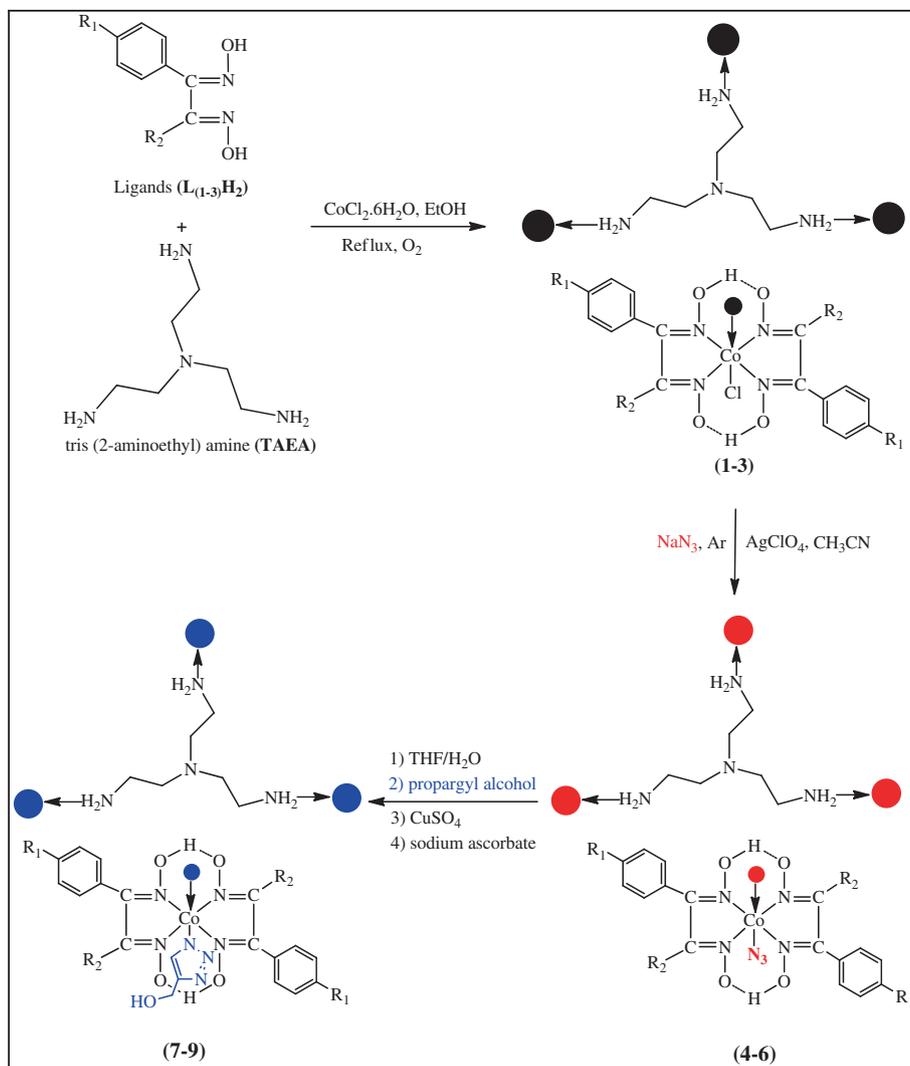
2.6 General procedure of coupling reaction of epoxides and CO_2

All the coupling reactions were performed in a 50 mL stainless steel autoclave equipped with a mechanical stirring. The autoclave reactor was successively charged with multinuclear cobaloxime complexes obtained by click chemistry (4.5×10^{-5} mol), epoxide (4.5×10^{-2} mol) and DMAP (9.0×10^{-5} mol). The reaction vessel was placed under a constant pressure of carbon dioxide for 2 min to allow the system to equilibrate and CO_2 was charged into the autoclave at the desired pressure; then it was heated and stirred at the desired reaction temperature. The pressure was kept constant during the reaction. When the pressure of CO_2 fell to 1–3 atm, the reactor was cooled quickly to 5–10°C in an ice bath after the expiration of the desired reaction time. The pressure was released, and then the excess gases were vented. The crude product in DMSO- d_6 was analyzed by $^1\text{H-NMR}$ spectroscopy and FT-IR to determine if any polycarbonate, epoxides, DMAP or other by-products were present. Also, aliquot of the crude product was taken from the reaction mixture and injected directly without further purification for the by GC (Agilent 7820A) analysis. Ethylene glycol dibutyl ether was used as the internal standard.

3. Results and Discussion

3.1 Synthesis

In this paper, we introduce a simple and rapid two-step method for the synthesis of the three dissymmetrical dioxime ligands ($\text{L}_{(1,2)}\text{H}_2$) from various ketones as described previously by our group.^{12,13} However, the ligand (L_3H_2) was synthesized by a similar procedure as new compounds (scheme 2). Then, using these ligands and tris (2-aminoethyl) amine (TAEA) as axial base, multinuclear cobaloxime complexes (**1-3**) were obtained at reflux temperature and under the basic conditions (scheme 3). The synthesis of the new azido-functionalized multinuclear cobaloxime complexes (**4-6**) were achieved by a one-pot reaction involving azide substitution of chlorine groups in multinuclear cobaloxime complexes (**1-3**) using NaN_3 in CH_3CN through nucleophilic substitution reaction (scheme 3). The azido-functionalized multinuclear cobaloxime complexes (**4-6**) and excess quantity of propargyl alcohol were performed using $\text{CuSO}_4/\text{sodium ascorbate}$ as the catalyst system in $\text{THF}/\text{H}_2\text{O}$ at 30°C, for 18 h to obtain a well-defined 1,2,3-triazole containing multinuclear cobaloxime complexes (**7-9**), as seen in scheme 3. As an exception, although much effort



Scheme 3. The structure of the proposed multinuclear cobaloxime complexes (1-9).

was made to clarify the structure of this complex (9), we failed to isolate their crystals. In continuation of this work, the catalytic efficiency of the multinuclear cobaloxime complexes were obtained by click chemistry have been successfully applied to the synthesis of a five-membered cyclic organic carbonates from CO_2 and epoxides under optimally conditions and without using any solvent. To the best of our knowledge, the multinuclear cobaloxime complexes have not been used as a catalyst system for conversion of carbon dioxide to a five-membered cyclic organic carbonate. Although much effort was made to clarify the structure of the multinuclear cobaloxime complexes, we failed to isolate their single crystals. However, the spectroscopic data 1H and ^{13}C -NMR, FT-IR, UV-Vis spectra, elemental analysis, melting point measurements, LC-MS spectra, and magnetic susceptibility techniques showed high probability that these compounds have the proposed structures.

3.2 Spectroscopic characterization

In the present investigation, FT-IR spectra showed that the formation of three dioxime ligands and their multinuclear cobaloxime complexes (1-3), azido-functionalized multinuclear cobaloxime complexes (4-6) and triazole containing multinuclear cobaloxime complexes (7 and 8) as new compounds (figure S1). The FT-IR of the multinuclear cobaloxime complexes are compared with those of the free dioxime ligands ($L_{(1-3)}H_2$) in order to determine the coordination sites that may be involved in chelation. Formation of the multinuclear cobaloxime complexes (1-8) was established by disappearance of the $\nu(O-H)$ peaks around $3505-3086\text{ cm}^{-1}$ and also the appearance of the intermolecular H-bond $\nu(O-H \cdots O)$ stretching are observed at $3596-3263\text{ cm}^{-1}$.¹⁶ In the FT-IR spectra of the dioxime ligands and their multinuclear cobaloxime complexes, the characteristic absorption

band of the imine $\nu(\text{C}=\text{N})$ groups were observed at $1656\text{--}1603\text{ cm}^{-1}$. The FT-IR spectra of the multinuclear cobaloxime (**1-8**) complexes were compared with those of the free dioxime ($\text{L}_{(1-3)}\text{H}_2$) ligands in order to monitor the change in the vibration frequency of the coordination sites, which a small frequency shift in its position may be because of the formation of $\text{Co(III)}\leftarrow\text{N}$ or $\text{Co(III)}\leftarrow\text{NH}_2$ dative bonds in these complexes, as expected.¹⁷ Next, the powerful evidence for the transformation of chlorine to azido group could be seen in the FT-IR spectra of the azido-functionalized multinuclear cobaloxime complexes (**4-6**) and the characteristic absorption band of the azido groups were observed at 2021 cm^{-1} for complex (**4**), at 2017 cm^{-1} for complex (**5**) (figure S1b) and at 2035 cm^{-1} for complex (**6**) as very strong peaks, consecutively. The click reaction between azidated multinuclear cobaloxime complexes (**4-6**) and propargyl alcohol was proven by the disappearance of the azide peak at $2035\text{--}2017\text{ cm}^{-1}$ (figure S1b) and presence of the aromatic triazole ring stretching peak at about $\sim 1650\text{ cm}^{-1}$ (figure S1c) as new peak in the final FT-IR spectra of triazole containing multinuclear cobaloxime complexes (**7** and **8**), which support the formation of the 1,2,3-triazole containing multinuclear cobaloxime complexes (**7** and **8**) (figure S1c) by the click cyclization reaction. Additionally, the observed absorption bands at range $516\text{--}499\text{ cm}^{-1}$ due to $\text{Co(III)}\leftarrow\text{N}$ or $\text{Co(III)}\leftarrow\text{NH}_2$ stretching vibrations that are not observed in the FT-IR spectra of the dioxime ligands ($\text{L}_{(1-3)}\text{H}_2$) indicates the formation of multinuclear cobaloxime complexes (**1-8**).¹⁸

The ^1H and ^{13}C -NMR spectra for three dioxime ligands ($\text{L}_{(1-3)}\text{H}_2$) and their multinuclear cobaloxime complexes (**1-8**) obtained by click chemistry were in good agreement with the structure of the newly formed compound. Detailed assignments of ^1H and ^{13}C NMR spectra along with coupling constants of the signals for dioxime ligands ($\text{L}_{(1-3)}\text{H}_2$) and their multinuclear cobaloxime complexes (**1-8**) have been presented in experimental section. In the ^1H NMR spectra in $\text{DMSO-}d_6$, the formation of the multinuclear cobaloxime complexes (**1-8**) obtained by click chemistry was confirmed by the disappearance of peaks related to the deuterium-exchangeable protons of the $(\text{C}=\text{N}-\text{OH})$ groups of the dioxime ligands ($\text{L}_{(1-3)}\text{H}_2$) at range $11.69\text{--}10.88\text{ ppm}$ in ^1H NMR spectra. Another result that supports formation of the multinuclear cobaloxime complexes (**1-8**) was new peaks observed, identified as singlet or doublet peaks in range $19.98\text{--}18.41\text{ ppm}$, indicating that the $(\text{C}=\text{N}-\text{OH})$ groups of three dioxime ligands ($\text{L}_{(1-3)}\text{H}_2$) have been transformed to intramolecular D_2O exchangeable H-bridge ($\text{O}-\text{H}\cdots\text{O}$), as expected. However, in the ^{13}C NMR spectra in $\text{DMSO-}d_6$,

the imine ($\text{C}=\text{N}$) carbon signals of dioxime ligands ($\text{L}_{(1-3)}\text{H}_2$) were significantly different field shift compared to the multinuclear cobaloxime complexes (**1-8**), which is powerful evidence to the formation of the multinuclear cobaloxime complexes (**1-8**) and confirm the complex formation via imine nitrogen coordination to Co(III) ion. Analysis of 1,2,3-triazole containing multinuclear cobaloxime complexes (**7** and **8**) by ^1H and ^{13}C NMR spectra revealed that presence of the peaks corresponding to the methine proton in 1,2,3-triazole ring at 8.18 ppm for complex (**7**) and at 8.19 ppm for complex (**8**) in ^1H NMR spectra and methine carbon in 1,2,3-triazole ring at 146.77 ppm for complex (**7**) and at 143.93 ppm for complex (**8**) in ^{13}C NMR spectra. These chemical shift results indicate the occurrence of the click cyclization reaction and formation of 1,2,3-triazole containing multinuclear cobaloxime complexes (**7** and **8**). Another evidence that 1,2,3-triazole containing multinuclear cobaloxime complexes (**7** and **8**) are formed was the new peaks at 4.52 and 3.37 ppm for complex (**7**) and at 4.51 and 3.36 ppm for complex (**8**) belonging to the $\text{CH}_2\text{-OH}$ and the $\text{CH}_2\text{-OH}$ protons of 1,2,3-triazole group, respectively, in the ^1H NMR spectra. Also, other proton and carbon NMR shifts of the dioxime ligands ($\text{L}_{(1-3)}\text{H}_2$) and their multinuclear cobaloxime complexes (**1-8**) indicate the formation of all compounds.

The UV-Vis spectra of the dioxime ligands ($\text{L}_{(1-3)}\text{H}_2$) and their multinuclear cobaloxime complexes (**1-8**) obey well with Lambert-Beer's law in the concentration range studied ($2.10^{-5}\text{--}2.10^{-8}\text{ mol L}^{-1}$) in two solvents (CH_3OH and CH_2Cl_2). The results are summarized in experimental part. As expected for the eight multinuclear cobaloxime complexes (**1-8**) in octahedral environment, the UV-Vis spectrum showed Co(III) d-d transitions at about $\sim 835\text{ nm}$ for complexes (**1**) and (**2**). In the other multinuclear cobaloxime complexes, this characteristic Co(III) d-d transition in the visible region was not observed, most probably owing to their very low molar absorption coefficient. The sharp and strong absorption bands at 353 nm in CH_3OH and at 380 nm in CH_2Cl_2 for both the dioxime ligands ($\text{L}_{(1-3)}\text{H}_2$) and their multinuclear cobaloxime complexes (**1-8**) display similar features for $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions due to the presence of aromatic rings and functional imine ($\text{C}=\text{N}$) groups in the structure of the dioxime ligands. In addition, the absorption spectra of the dioxime ligands ($\text{L}_{(1-3)}\text{H}_2$) and their multinuclear cobaloxime complexes (**1-8**) showed a characteristic strong band corresponding to the intermolecular transition from the dioxime ligand molecules to the vacant orbitals localized on the coordinated Co(III) metal ion in the region

464–411 nm which was clearly separated from the main transition.

The molecular weights of the dioxime ligands ($\mathbf{L}_{(1-3)}\mathbf{H}_2$) and their multinuclear cobaloxime complexes ($\mathbf{1-8}$) were analyzed from LC-MS analysis. The peak positions and the isotopic distributions have been well assigned and the results are summarized in experimental section and figures S2 and S3. From the LC-MS plots, it is seen that the molecular weight corresponding to the highly intense peak in the spectrum has good agreement with theoretical molecular weight which is also verified by elemental analyses and the other spectroscopic analysis. The highest mass peak is detected for the molecular ion peak at $m/z = 249.2$ for ligand ($\mathbf{L}_3\mathbf{H}_2$), corresponding to the $[\mathbf{M}]^+$ peak. The molecular ion peaks at $m/z = 1576.7$ for complex ($\mathbf{1}$), 1576.5 for complex ($\mathbf{2}$), 1918.8 for complex ($\mathbf{3}$), 1596.4 for complex ($\mathbf{4}$), 1576.2 for complex ($\mathbf{5}$), 1938.5 for complex ($\mathbf{6}$), 1764.6 for complex ($\mathbf{7}$), and 1764.4 for complex ($\mathbf{8}$) correspond to the $[\mathbf{M}]^+$ peak, which could be attributed to the trimeric structures of the cobaloxime complexes ($\mathbf{1-8}$).¹⁹

The molar magnetic susceptibility (μ_{eff}) of the multinuclear cobaloxime complexes ($\mathbf{1-8}$) in the solid state was measured at room temperature and found to be diamagnetic in character due to the complete spin pairing as expected, indicating low-spin ($S=0$) octahedral d^6 -systems. Furthermore, the magnetic susceptibility measurement confirms the presence of cobalt centers in the +3 oxidation state, which indicates the formation of the three types multinuclear cobaloxime complexes ($\mathbf{1-8}$). The change in the % C, H, N content of the dioxime ligands ($\mathbf{L}_{(1-3)}\mathbf{H}_2$) and their three types of multinuclear cobaloxime complexes ($\mathbf{1-8}$), as summarized in the experimental section, suggest the formation of all compounds.

3.3 Catalytic properties

In the presence of a series of multinuclear cobaloxime complexes ($\mathbf{1-8}$), the coupling reaction of epichlorohydrin (ECH) and carbon dioxide to form 4-(chloromethyl)-1,3-dioxolan-2-one (ECHC) was carried out under identical reaction conditions (catalyst loading 0.1% ($\mathbf{1-8}$), 0.2% DMAP, CO_2 pressure, 1.6 MPa, 100°C, 2 h) and the corresponding results were summarized in table S1 (see Supplementary Information). In an *in situ* ATR-IR, which can be recorded for continuous monitoring using an attenuated total reflectance probe in FT-IR, the decrease of the stretching carbonyl vibration of carbon dioxide at 2350 cm^{-1} and the increase of the carbonyl vibration of

cyclic organic carbonate at 1795 cm^{-1} were monitored during the reaction of CO_2 and different epoxides for all eight cobaloxime catalysts ($\mathbf{1-8}$).²⁰ However, no peak at 1749 cm^{-1} was detected, which was attributed to the carbonyl group in polycarbonate.²¹ The multinuclear cobaloxime complexes ($\mathbf{1-8}$), using 4-(dimethylamino)pyridine (DMAP) as co-catalyst, showed high catalytic activity and selectivity for the conversion of CO_2 into cyclic carbonates using the epichlorohydrin (ECH) which served as substrate and solvent. Catalytic experiments were carried out at optimized conditions, which were determined in previous studies.^{13,17,22,23} To optimize the reaction conditions for the ECH/ CO_2 cycloaddition reactions, different parameters (epoxide, base, reaction time, and temperature and CO_2 pressure) were investigated, in which DMAP was used as a co-catalyst. The results are summarized in table S1.

The high activity of the cobaloxime complex ($\mathbf{1}$) catalyst relative to the other cobaloxime catalysts can be explained by the electron-withdrawing property of the chloro substituents as axial groups on the Co(III) center. Whereas, in the azido-functionalized multinuclear cobaloxime complexes ($\mathbf{4-6}$) and 1,2,3-triazole containing multinuclear cobaloxime complexes ($\mathbf{7-9}$) the catalytic activity is low, due to the chloro groups transformation to azido or 1,2,3-triazole groups. Due to the Lewis acidity of the Co(III) center in the cobaloxime complex ($\mathbf{1}$) catalysts and its analogue, the epichlorohydrin (ECH) or other epoxides are coordinated more strongly to the Co(III) centers. For the investigation of the efficiency of the catalytic system, different epoxides (propylene oxide (PO), 1, 2-epoxybutane (EB), epichlorohydrin (ECH), styrene oxide (SO) and cyclohexene oxide (CHO)) were used as both solvent and substrate under the optimized reaction conditions. The cobaloxime complex ($\mathbf{1}$) catalyst is also an efficient catalyst for the cycloaddition of CO_2 with epichlorohydrin (ECH). As shown in figure S4, epichlorohydrin (ECH) was found to be the most reactive epoxide, while styrene oxide exhibited the lowest activity among the epoxides surveyed. This result may be due to the higher electron donating substituents linked to C_2 -atom of these epoxides (PO, EB, SO and CHO) which could be coordinately bonded to the metal centre and could be responsible for the catalyst poisoning. Similar effect was observed in our previous studies.^{13,17,22}

In addition to DMAP (4-(dimethylamino)pyridine), CH_3CN (acetonitrile), $\text{C}_5\text{H}_5\text{N}$ (pyridine), NEt_3 (triethylamine) and PPh_3 (triphenylphosphine) were tested to expand the range of the co-catalysts with the cobaloxime complex ($\mathbf{1}$) as catalyst (figure S5). This showed that $\text{C}_5\text{H}_5\text{N}$ (pyridine) was the best co-catalyst for this system with a yield of 90% of 4-(chloromethyl)-1,

3-dioxolan-2-one (EHC) in high selectivity. In contrast to C_5H_5N (pyridine), the use of DMAP (4-(dimethylamino) pyridine), CH_3CN (acetonitrile), NEt_3 (triethylamine) or PPh_3 (triphenylphosphine) as co-catalyst led only to a low yield of EHC (figure S5), probably due to the formation of a stable [Co-co-catalyst] complex as already suggested by the teams of Rieger,²⁴ Lu²⁵ and Zevaco²⁶ for related systems.

It is generally accepted that reaction parameters such as temperature, CO_2 pressure and time have an effect on product yield. We adopted the cobaloxime complex (**1**) catalyst to investigate the effects of reaction parameters because of its good activity. The effect of the reaction temperature on the cycloaddition reaction was studied with the cobaloxime complex (**1**) as catalyst at 1.6 MPa CO_2 pressure, 2 h, epichlorohydrin (ECH) as substrate and C_5H_5N as base, and the results are shown in figure S6(a). It can be seen that temperature has a strong effect on the epichlorohydrin (ECH) conversion. The reaction was carried out at different reaction temperatures ranging from 75, 100, 125 and 150°C. With increase of temperature from 75 to 125°C, yield of 4-(chloromethyl)-1,3-dioxolan-2-one (EHC) increased sharply from 31 to 96%. With increase of temperature from 125 to 150°C, yield of EHC decreased from 96 to 92%. A decrease in the catalytic activity, is possibly due to more side-products formed at the higher temperature, such as, 1-chloroethane-1,2-diol. Thus, 125°C was considered to be the optimum reaction temperature. The effect of CO_2 pressure on the cycloaddition reaction was studied (figure S6(b)). The reaction was conducted at 125°C, 2 h, C_5H_5N as co-catalyst, epichlorohydrin (ECH) as substrate and the cobaloxime complex (**1**) as catalyst. As shown in figure S6(b), there is a rise in yield of EHC (from 94 to 96%) with increase of CO_2 pressure (from 0.5 to 1.6 MPa). Further increase of pressure to 2.5 MPa results in a moderate decrease of EHC yield (94%). In the 0.5-2.5 MPa range, EHC selectivity is over 95%. This can be explained qualitatively by the effect of pressure on the concentration of CO_2 and epoxide in the two phases in the reaction system.²⁷ The upper phase is the vapor phase, and bottom phase is the liquid phase. The reaction took place mainly in the liquid phase because the catalyst was dispersed only in the liquid phase. When the pressure was higher than 2.5 MPa, the CO_2 concentration was too high and inhibited the contact of epichlorohydrin (ECH) with the catalyst by a dilution effect.^{28,29}

As shown in figure S6(c), the effect of the reaction time on the EHC yield was investigated. The reaction was conducted at 125°C, 1.6 MPa CO_2 pressure, C_5H_5N as co-catalyst, epichlorohydrin (ECH) as substrate and the cobaloxime complex (**1**) as catalyst. With

increase of time from 0.5 to 4 h, EHC yield increased from 89 to 96%. This result suggested that the CO_2 fixation on epichlorohydrin (ECH) was completed within 4 h. Similar effects of temperature, CO_2 pressure and time on catalytic activity were observed in previous studies.^{10,12,16,21}

4. Conclusions

In conclusion, three dioxime ligands ($L_{(1-3)}H_2$) and their three types of multinuclear cobaloxime complexes (**1-8**) were synthesized and fully characterized by different spectroscopic techniques. Experimental results indicated trimeric nature for these three types multinuclear cobaloxime complexes (**1-8**). The multinuclear cobaloxime complexes (**1-8**) have been successfully used for the synthesis of five-membered cyclic organic carbonates from CO_2 and epoxides under optimized conditions and without using any solvent. The synthesized homogeneous catalysts are inexpensive, easily synthesized and stable or robust catalytic systems for synthesizing a five-membered cyclic organic carbonates from CO_2 and different epoxides. The cobaloxime complex (**1**) catalyst and DMAP as the co-catalyst showed good catalytic activity and selectivity for the coupling of CO_2 and epichlorohydrin (ECH). The high activity of the cobaloxime complex (**1**) catalyst relative to the other cobaloxime catalysts can be explained by the electron-withdrawing property of the chloro substituents as axial groups on the Co(III) center. Investigation of a range of molecules as co-catalysts showed that pyridine is the best co-catalyst for this system.

Supplementary Information

The catalytic results and spectral data are given as table S1 and figures S1–S6 which are available at www.ias.ac.in/chemsci.

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