Conversion of CO_2 into cyclic carbonates in the presence of metal complexes as catalysts

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The sterically hindered salicylaldimine ligands *N,N′*-(1,5-diaminonaphthalene)-3,5-bu^t_2-salicylaldimine (**L_1**), *N,N′*-(2,7-diaminofluaren)-3,5-bu^t_2-salicylaldimine (**L_2**) and *N,N′*-(1,8-diaminonaphthaline)-3,5-bu^t_2-salicylaldimine (**L_3**) have been synthesised by the condensation of 1,5-diaminonaphthalene, 2,7-diaminofluarene, and 1,8-diaminonaphthaline with 3,5-di-tert-butylsalicylaldehyde, respectively. Dinuclear M(II) complexes of **L_1** and **L_2** and mononuclear M(II) complexes of **L_3** have been prepared using Cu(II), Ni(II), Co(II), and Mn(II) salts and characterised. The synthesised sterically-hindered, salen-type complexes were tested as catalysts for the formation of cyclic carbonates from CO_2 and liquid epoxides (propylene oxide, epichlorohydrine, 1,2-epoxybutane and styrene oxide), which served as both reactant and solvent. Ligand structure and the type of metal centre have a marked influence on the catalytic activity. Mn(II) complexes showed the highest catalytic activity.

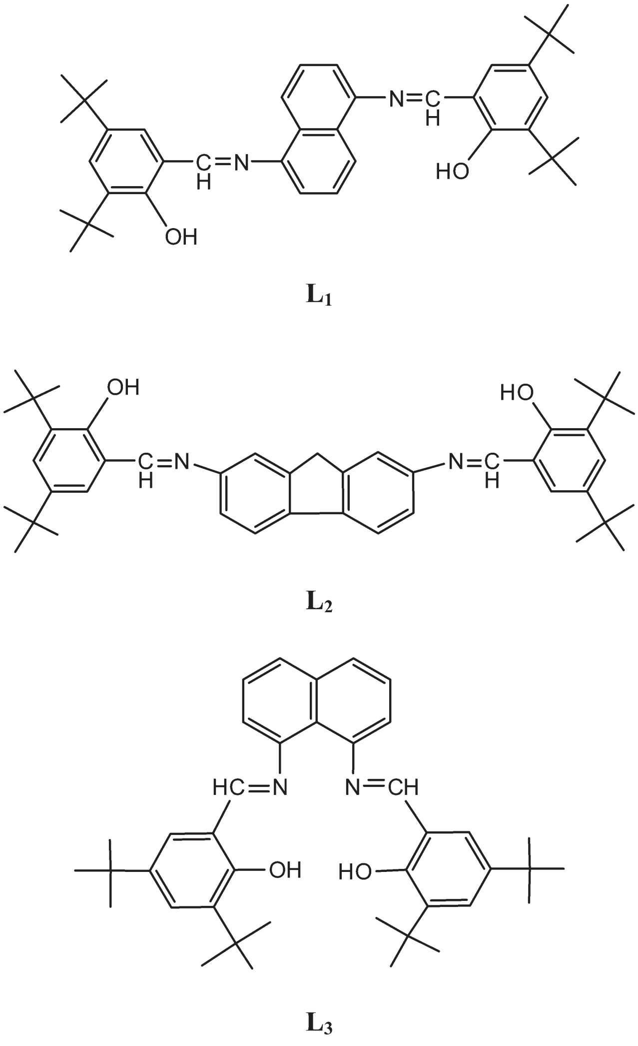
Keywords: catalysis, Schiff bases, spectroscopy, transition metals compounds, CO_2, cyclic carbonate

In recent years, Schiff bases[1,2] and transition metal complexes with bulky, sterically hindered di-*tert*-butylate salen-class ligands have played an important role in the development of coordination chemistry. 2-Hydroxy Schiff bases and their metal complexes have been extensively studied for their various crystallographic, structural and magnetic features.[3,4] Salen-type complexes have been recently used as catalytically active materials for hydrogenations, oxidations, and as anti-cancer, biological, clinical, analytical and antimicrobial agents. Furthermore, Schiff base metal complexes have been used as models for the metal sites in metallo-proteins and –enzymes.[5–7] Also, sterically-hindered ligands bearing salicylaldimines are known to be effective antioxidants. It is well known that some drugs have greater activity when administered as metal complexes than as free organic compounds.[8] Several similar sterically-hindered Schiff base ligands that have different substituents and some of their transition metal complexes have been prepared.[9–11]

Recently, the chemical fixation of carbon dioxide has received a great deal of attention from the viewpoint of preserving carbon resources and controlling environmental problems.[12–14] One of the most common processes is the transformation of carbon dioxide to cyclic carbonates, which are widely used as organic synthetic intermediates, aprotic polar solvents, precursors for biomedical applications, and as raw materials for engineering plastics.[15,16] Various catalysts have been developed for the synthesis of cyclic organic carbonates from CO_2 and epoxides, including homogeneous and heterogenised salen–metal complexes,[17–19] alkali metal halides,[20] organic bases,[21,22] metal oxides,[23,24] zeolites, [25] ionic liquids[26] and metal complexes.[27–29] We now report the synthesis, characterisation and thermal properties of some new salen-type metal complexes and their use as catalysts for the formation of cyclic carbonates from CO_2.

Results and discussion

The reaction steps for the syntheses of the ligands[10] and their di- or mononuclear Ni(II), Cu(II), Co(II) and Mn(II) metal complexes are given in Schemes 1 and 2. First the ligands, (**L_1**, **L_2** and **L_3**), were synthesised by the condensation of 3,5-di-*tert*-butylsalicylaldehyde with different diamines (1,5-diaminonaphthalene, 2,7-diaminofluarene and 1,8-diaminonaphthaline). Secondly, the di- and mononuclear metal complexes were synthesised by the reaction of **L_1**, **L_2** and **L_3** with corresponding metal salts. The metal complexes were obtained in good yields and high purity by slow evaporation of the solvent mixture at atmospheric pressure. Ni(II) complexes of **L_2** and **L_3** could not be obtained, whereas the complex [Ni_2(**L_1**)$_2$] complex was obtained in good yield. The metal-to-ligand ratios in the dinuclear metal complexes were found to



Scheme 1 Supposed structures of the ligands.

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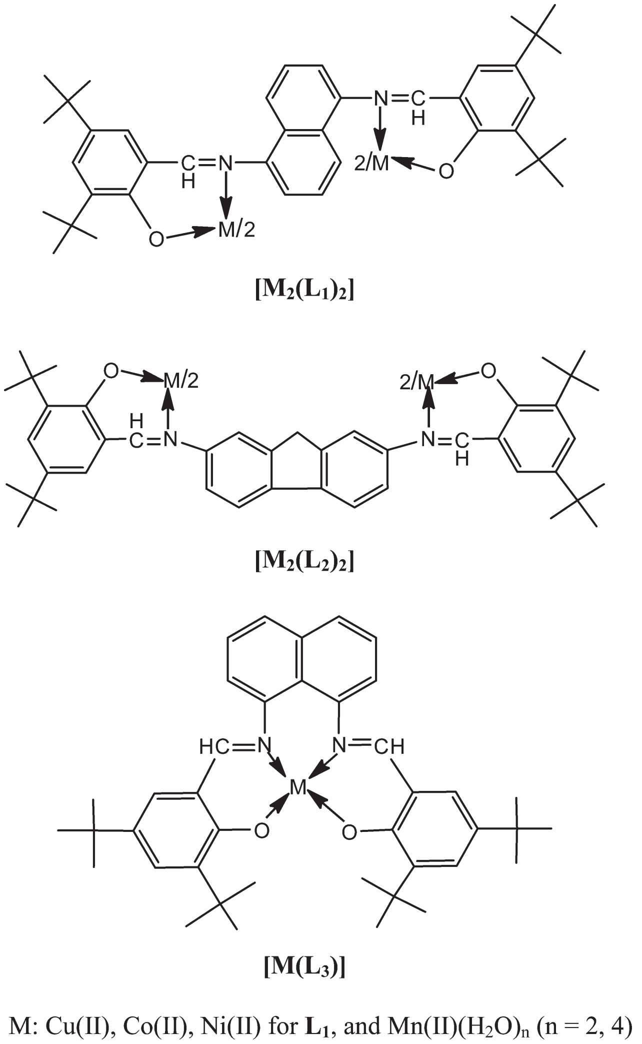


Scheme 2 Supposed structures of the dinuclear $[M_2(L_{1,2})_2]$ and mononuclear $[M(L_3)_2]$ complexes.

be 2:2 for $[M_2(\mathbf{L_1})_2]$ and $[M_2(\mathbf{L_2})_2]$ and in the mononuclear metal complexes were found to be 1:1 for $[M(\mathbf{L_3})]$ (Scheme 2). The ligands and their metal complexes were characterised by FT-IR, UV-Vis, ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, magnetic susceptibility, molar conductance (Λ_M), thermogravimetric analyses (TGA) and differential thermal analyses (DTA) techniques. The analytical and spectral data for the ligands and their metal complexes are presented in the experimental section.

Assignments of the ^{1}H and ^{13}C NMR spectra of the individual $\mathbf{L_n}$ ligands in $CDCl_3$ are given in the experimental section. The proton resonance appearing as a broad singlet at $\delta = 13.84$–13.32 ppm in the spectra is due to the OH/NH protons involved in intramolecular H-bonding.[10] The singlets observed at $\delta = 8.73$ for ($\mathbf{L_1}$), at $\delta = 8.74$ for ($\mathbf{L_2}$) ppm and at $\delta = 8.69$ for ($\mathbf{L_3}$) are assigned to the proton of azomethine (CH=N). The peaks in the ranges 8.22–7.21 ppm ($\mathbf{L_1}$), 7.81–7.25 ppm ($\mathbf{L_2}$) and 7.39–6.58 ppm ($\mathbf{L_3}$) are assignable to the protons of Ar–CH as singlet, doublet or multiplet peaks. Also, the protons of the *t*-butyl groups exhibit singlet peaks at $\delta = 1.51$ and 1.34 ppm ($\mathbf{L_1}$), $\delta = 1.49$ and 1.34 ppm ($\mathbf{L_2}$), and $\delta = 1.45$ and 1.31 ppm ($\mathbf{L_3}$), indicating that the *tert*-butyl protons of these compounds are magnetically nonequivalent.[9] In the ^{13}C NMR spectra, the azomethine carbon resonances were found at 164.97 ppm ($\mathbf{L_1}$), 162.90 and 158.31 ppm for ($\mathbf{L_2}$), and 153.94 ppm ($\mathbf{L_3}$). The other ^{1}H and ^{13}C NMR data of the ligands are given in the experimental section. **IR** group stretching frequencies data of the ligands and their di- and mononuclear metal complexes are given in the experimental section. The FT-IR spectra of ligands and corresponding metal complexes are found to be very similar to each other except for some slight shifts and intensity changes of a few vibration peaks caused by different metal(II) ions, which indicates that the metal complexes have similar structure. However, there are some significant differences between the metal(II) complexes and the free ligands upon chelation, as expected. The IR spectra of ligands show a broad band at 2219–3680 cm^{-1} due to the υ(OH….N) stretching vibration. The broadness is due to intramoleculer hydrogen bonding between the phenolic groups and the azomethine groups.[30] The free salicylaldimine ligands showed strong peaks at 1602–1619 cm^{-1}, which are characteristic of the azomethine υ(C=N) group.[10] These bands, υ(C=N) and υ(O–H), are shifted due to complexation between the oxygen and nitrogen atoms with metal ions.[30–32] The υ(C=N) band (1602–1619 cm^{-1}) is shifted to lower wavenumbers, indicating that the nitrogen atom of the azomethine group is coordinated to the metal (II) ions. A strong peak observed at range 1173–1163 cm^{-1} in the free ligands has been assigned to phenolic C–O stretching. On complexation this band is shifted to a different frequency range (1177–1162 cm^{-1}), indicating coordination through the phenolic oxygen. The bonding of the metal ions to the ligands through the nitrogen and oxygen atom is further supported by the presence of new bands in the 548–525 and 509–485 cm^{-1} range due to υ(M–N) and υ(M–O), respectively. Thus, it is clear that $\mathbf{L_1}$, $\mathbf{L_2}$ and $\mathbf{L_3}$ are bonded to the metal ion in an ONNO fashion through the deprotonated phenolate oxygen and salicylaldimine nitrogen.

The electronic spectra of ligands and their mononuclear Cu(II), Co(II), Ni(II) and Mn(II) metal complexes have been recorded in the 200–1100 nm range in CH_2Cl_2 and DMSO solutions and their corresponding data are given in the experimental section. Each ligand and corresponding metal complexes show several intense absorptions in the visible and UV region. In the electronic spectra of the ligands and their M(II) complexes, the wide ranging bands seem to be due to both the $\pi\rightarrow\pi^*$and $n\rightarrow\pi^*$ transitions of the benzene ring or azomethine (–C=N) groups or charge-transfer transitions arising from π-electron interactions between the metal and ligand, which involves either a metal-to-ligand or ligand-to-metal electron transfer and d–d transitions.[33,34] The bands in the 220–295 nm region are assigned to intraligand $\pi\rightarrow\pi^*$ transitions and the bands at 300–365 nm are attributed to $n\rightarrow\pi^*$ transitions of the benzene ring or the azomethine (–C=N) groups. All the complexes show an intense band in the 225–298 nm range which is assigned to a $\pi\rightarrow\pi^*$ transition associated with the azomethine linkage and the benzene ring. In the spectra of the complexes, the bands of the azomethine chromophore (n–π^* transition) are shifted to lower frequencies, indicating that the imine nitrogen atom is involved in coordination to the metal ion. The spectra of the complexes show intense bands in the high-energy region in the 485–345 nm range which can be assigned to charge transfer (L→M) bands. The bands observed in the 615–540 nm region can be attributed to d–d transitions of the metal ions.[35,36]

The magnetic moments (as B.M.) of the complexes were measured at room temperature and data are given in the experimental section. Analytical and spectroscopic evidences show that the metal ions M(II) have four or six coordination. The magnetic moments of the Cu(II) complexes are found between 1.35 and 1.42 B.M. for dinuclear complexes and 1.74 B.M. for the mononuclear complex, which are typical values for dinuclear complexes with an S = 1 spin state or for a mononuclear Cu(II) complex with a S = 1/2 spin state and indicate (except for $[Cu(\mathbf{L_3})]$) antiferromagnetic coupling of the spins at this temperature. The coordination geometry of the $[Cu(L_3)]$ metal complex is most likely distorted tetrahedral. The magnetic moments of the Co(II) complexes are in the range 3.79–3.68 B.M. which are typical for dinuclear Co(II) complexes with an S = 3 spin state or, for the mononuclear Co(II) complex, an S = 3/2 spin state with no antiferromagnetic coupling of the spins at this temperature. The magnetic moments of $[Mn_2(L_1)_2(H_2O)_4]$ and $[Mn_2(L_2)_2(H_2O)_4]$ complexes are 1.96 and 1.98 B.M respectively, which may be due to the presence of antiferromagnetic coupling, since these values are typical for dinuclear Mn(II) metal complexes with an S = 1 spin state. The magnetic moment of the $[Mn(L_3)]$ complex is 2.15 B.M., which could be attributed to low spin, square planar geometry with an S = 1/2 spin state.[37,38] The coordination geometry of the $[Ni_2(L_1)_2]$ metal complex is most likely square-planar since it is diamagnetic.

The ligands $(\mathbf{L_1})$, $(\mathbf{L_2})$ and $(\mathbf{L_3})$ and their di- and mononuclear Cu(II), Co(II), Ni(II), Mn(II) metal complexes are soluble in C_2H_5OH, CH_3OH, $CHCl_3$, DMSO and DMF solvents. Their molar conductivities (10^{-3} M in dimethyl formamide, DMF) are in the range of 39.1–14.3 $\Omega^{-1}cm^2\ mol^{-1}$ at room temperature, indicating their almost non-electrolytic nature.[39]

The thermal properties of the ligand $(\mathbf{L_1})$ and some metal complexes were investigated by thermal gravimetric analyses (TGA) and thermal differential analyses (DTA). The TGA and DTA curves of ligand and metal complexes were recorded under a nitrogen atmosphere. The samples were heated up at 1 atm pressure with a heating rate of 10 °C min^{-1} and a temperature range of 20–900 °C. As the temperature is increased, the thermal decomposition of $\mathbf{L_1}$ and some metal complexes is irreversible and occurs in three steps. The first degradation step, in the range of 310–430 °C, is at a weight loss of 67% and is associated with endothermic peaks at 276 and 389 °C. The second degradation step, in the range 433–522 °C, is at a weight loss of 73% and is associated with an endothermic peak at 514 °C. The third degradation step in the range 535–900 °C is at a weight loss of 86.5% and is associated with endothermic peaks at 556 and 775 °C. The TGA curves of the metal complexes give two or three-stage decomposition patterns within the ranges 20–900 °C. For Cu(II) metal complexes, the first degradation step takes place in the ranges 147–225 °C for $[Cu_2(L_1)_2]$, 108–160 °C for $[Cu_2(L_2)_2]$, and 135–252 °C for $[Cu(L_3)]$, corresponding to a weight losses of 4%, 1,3%, and 4% and associated with endothermic peaks at 171 and 152 °C, respectively. The second degradation step takes place in the range of 271–396 °C for $[Cu_2(L_1)_2]$, 320–533 °C for $[Cu_2(L_2)_2]$, and 340–522 °C for $[Cu(L_3)]$, corresponding to weight losses of 27%, 40%, and 26.5% and associated with endothermic peaks at 293, 349, 413 °C, respectively. The third degradation step takes place in the range of 400–900 °C for $[Cu_2(L_1)_2]$, 536–900 °C for $[Cu_2(L_2)_2]$, and 543–900 °C for $[Cu(L_3)]$ corresponding to a weight loss 64%, 64%, and 4% and associated with endothermic peaks at 430, 616, 697, 529, 652, and 533 °C, respectively. For $[Co_2(L_1)_2]$ metal complexes, the first degradation step takes place in the range of 316–428 °C, corresponds to a weight loss 35% and is associated with an exothermic peak at 348 °C. The second degradation step takes place in the range of 433–900 °C, is at a weight loss of 80% and associated with an endothermic peak at 707 °C. For $[Co_2(L_2)_2]$ metal complexes, the first degradation step takes place in the range of 57–222 °C at a weight loss of 3%, the second degradation step takes place in the range of 230–355 °C at a weight loss of 19%, the third degradation step takes place in the range of 368–484 °C at a weight loss of 42.5% and the fourth degradation step takes place in the range of 549–900 °C at a weight loss of 79%. The endothermic peaks were at 271, 422, 503, 521, 591 and 687 °C and the exothermic peak at 142 °C. From the TGA and DTA results, mononuclear metal complexes have different thermal stabilities, which may be attributed to the fact that the M–N and M–O bonds are differently highly polarised.[40]

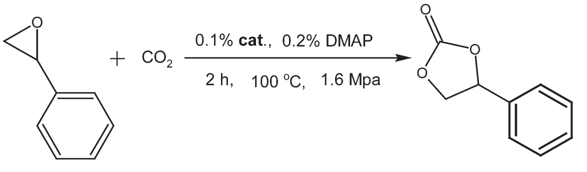
The cycloaddition reaction of carbon dioxide with epoxides in the presence of 0.1% catalyst was conducted as a model reaction for testing and the results are compiled in Table 1. It is clear that the structure of the salen and the nature of the metal centre influence the yield of the cyclic carbonate (Table 1, entries 1–9) under the same catalytic conditions. Ligand structure and the amount of metal centre have a marked influence on the catalytic activity. The conjugated system of the ligand enhances the activity. Bimetallic systems with conjugation of the ligand also enhance the cyclic carbonate formation.

From the results in Table 1, it is evident that the Mn(II) complexes showed more catalytic activity than the other metal complexes. Other epoxides (1,2-epoxybutane, propylene oxide, cyclohexene oxide and epichlorohydrin) were tested as substrates and epichlorohydrin was found to be the most reactive epoxide, while propylene epoxide exhibited the lowest activity of the epoxides surveyed, in accordance with previous studies.[17] DMAP is much more active than NEt_3 which was previously reported by us, so that this co-catalyst was used in every catalytic run.[41]

The reaction conditions such as reaction time, temperature and CO_2 pressure were showed to have an influence on the catalytic activity of transformation of substrate to its related cyclic carbonate using $[Mn_2(L_1)_2(H_2O)_4]$ as the best of the catalysts used. Increasing the reaction temperature and time had a pronounced positive effect on the TOF, whilst increasing CO_2 pressure above 1.6 MPa decreased the yield and the TOF value. A similar effect was reported by Ulusoy[41] and Darensbourg.[42]

The aim of the catalytic study is the comparison of the same metal centres with differing ligands under the same coupling-reaction conditions. Although $[Ni_2(\mathbf{L_1})_2]$ was obtained in good yield, Ni(II) complexes of $\mathbf{L_2}$ and $\mathbf{L_3}$ could not be obtained, so that we could not study the comparative catalytic activities of Ni(II) complexes.

Table 1 Coupling of CO_2 and styrene oxide[a]



Entries	Catalysts	Yield[b]	TON[c]	TOF[d] /h
1.	$[Cu_2(\mathbf{L_1})_2]$	24	240	120
2.	$[Co_2(\mathbf{L_1})_2]$	17	170	85
3.	$[Mn_2(\mathbf{L_1})_2(H_2O)_4]$	75	750	375
4.	$[Cu_2(\mathbf{L_2})_2]$	37	370	185
5.	$[Co_2(\mathbf{L_2})_2]$	22	220	110
6.	$[Mn_2(\mathbf{L_2})_2(H_2O)_4]$	50	500	250
7.	$[Cu(\mathbf{L_3})]$	34	340	170
8.	$[Co(\mathbf{L_3})]$	22	220	110
9.	$[Mn(\mathbf{L_3})(H_2O)_2]$	45	450	225

[a] Catalyst (4.5x 10^{-5} mol), DMAP (9x 10^{-5} mol), epoxide (4.5x 10^{-2} mol), CO_2 (1.6 Mpa), 2h.

[b] Yield of epoxides to corresponding cyclic carbonates was determined by comparing the ratio of product to substrate in the ^1H NMR spectrum of an aliquot of the reaction mixture.

[c] Moles of cyclic carbonate produced per mole of catalyst.

[d] The rate is expressed in terms of the turnover frequency, TOF [(mol of product /mol of catalyst)h^{-1} = turnovers/h].

Experimental

All chemicals and solvents were reagent grade and used as received. The metal salts $Ni(AcO)_2.4H_2O$, $Cu(AcO)_2.H_2O$, $Co(AcO)_2.4H_2O$ and $Mn(AcO)_2.4H_2O$ were used for the preparation of salen complexes. The diamines (1,5-diaminonaphthalene, 2,7-diaminofluorene and 1,8-diaminonaphthaline) and the aldehyde (3,5-di-*tert*-butylsalicylaldehyde) were used for the preparation of salen ligands. All metal salts and diamines were obtained from commercial suppliers (Fluka, Merck and Aldrich). Pure 3,5-di-*tert*-butylsalicylaldehyde was prepared from commercially available 2,4-di-*tert*-butylphenol by the literature method.[43,44]

C, H and N elemental analyses were carried out in the Laboratory of the Scientific and Technical Research Centre of Inonu University (Malatya, Turkey) using a LECO CHNS-932 model analyzer. FT-IR spectra were recorded on a Perkin Elmer RXI FT-IR Spectrometer using KBr discs. ^1H and ^{13}C NMR spectra were recorded on a Bruker-Avance 300 MHz Ultrashield TM spectrometer in the Laboratory of the Scientific and Technical Research Center of Inonu University. The electronic spectral studies were conducted on a Perkin Elmer model Lambda 25 UV–Vis spectrophotometer in the wavelength range 200–1100 nm. The magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature (20 °C) using $Hg[Co(SCN)_4]$ as a calibrant; the diamagnetic corrections were calculated from Pascal's constants.[45] The thermal analyses studies of the compounds were performed on a Seteram Labsys TG-16 DTA/TG thermal system under dinitrogen at a heating rate of 10 °C / min. The molar conductivities (Λ_M) were recorded on a Inolab Terminal 740 WTW Series. Catalytic tests were performed in a PARR 4843 50 mL stainless steel pressure reactor. Previously, we have reported the synthesis, properties and spectroscopic characterisation of $\mathbf{L_1}$, $\mathbf{L_2}$ and $\mathbf{L_3}$ and their Pd(II) complexes.[10]

Syntheses of the metal complexes

These complexes were prepared by following general procedure. A solution of a metal salt (10 mmol) in anhydrous MeOH (30 mL) was added to a solution of an appropriate ligand (10 mmol) in anhydrous MeOH (30 mL) under an argon atmosphere and the mixture was refluxed for 6–8 h. After the completion of the reaction, the precipitates were filtered, washed with EtOH and Et_2O, then recrystallised from EtOH and dried in vacuum at 80 °C.

$[Cu_2(L_1)_2]$: Dark green; m.p. >300 °C; yield (%) 65; Anal. Calcd for $[C_{80}H_{98}N_4O_4Cu_2]$ (F.W: 1305 g mol^{-1}): C, 73.63; H, 7.42; N, 4.29. Found: C, 73.54; H, 6.98; N, 4.49%. IR (KBr pellets, υ_{max}/cm^{-1}): 3066 υ(Ar-CH), 2867–2955 υ(Aliph.C–H), 1612 υ(C=N), 1167 υ(C–O), 531 υ(Cu–N) and 494 υ(Cu–O). μ_{eff} = 1.35 [B.M]. Λ_M = 38.7 $\Omega^{-1}cm^2$ mol^{-1}. UV-Vis (λ_{max}, nm) in CH_2Cl_2: 470, 368, 269, 239; in DMSO: 479, 351*, 364 (*shoulder).

$[Co_2(L_1)_2]$: Dark brown; m.p. >300 °C; yield (%): 65; Anal. Calcd for $[C_{80}H_{98}N_4O_4Co_2]$ (F.W: 1297 g mol^{-1}): C, 74.17; H, 7.47; N, 4.32. Found: C, 74.35; H, 7.73; N, 3.92%. IR KBr pellets, υ_{max}/cm^{-1}): 3043, 525 υ(Co–N) and 485 υ(Co–O)υ(Ar-CH), 2869–2957 υ(Aliph-CH), 1613 υ(C=N), 1162 υ(C–O), 528 υ(Co–N) and 506 υ(Co–O). μ_{eff} = 3.68 [B.M]. Λ_M = 37.5 $\Omega^{-1}cm^2$ mol^{-1}. UV-Vis (λ_{max}, nm) in CH_2Cl_2: 401*, 374, 275, 238; in DMSO: 402*, 352, 276, 260 (*shoulder).

$[Ni_2(L_1)_2]$: Dark green; m.p. >300 °C; yield (%): 50; Anal. Calcd for $[C_{80}H_{98}N_4O_4Ni_2]$ (F.W: 1295 g mol^{-1}): C, 74.10; H, 7.56; N, 4.32. Found: C, 74.23; H, 7.45; N, 4.18%. IR KBr pellets, υ_{max}/cm^{-1}): 3037 υ(Ar-CH), 2867–2953 υ(Aliph-CH), 1614 υ(C=N), 1172 υ(C–O), 548 υ(Ni–N) and 509 υ(Ni–O). μ_{eff} = Dia. [B.M]. Λ_M = 32.6 $\Omega^{-1}cm^2$ mol^{-1}. UV-Vis (λ_{max}, nm) in CH_2Cl_2: 515*, 372, 342, 272, 235; in DMSO: 410*, 347, 274*, 261 (*shoulder).

$[Mn_2(L_1)_2(H_2O)_4]$: Pale brown; m.p. >283 °C; yield (%): 70; Anal. Calcd for $[C_{80}H_{106}N_4O_8Mn_2]$ (F.W: 1360 g mol^{-1}): C, 70.57; H, 7.85; N, 4.11. Found: C, 70.65; H, 7.79; N, 4.07%. IR (KBr pellets, υ_{max}/cm^{-1}): 3615–3152 υ(O–H), 3059 υ(Ar-CH), 2865–2984 υ(Aliph-CH), 1612 υ(C=N), 1177 υ(C–O), 543 υ(Mn–N) and 494 υ(Mn–O). μ_{eff} = 1.96 [B.M]. Λ_M = 33.4 $\Omega^{-1}cm^2$ mol^{-1}. UV-Vis (λ_{max}, nm) in CH_2Cl_2: 553*, 375, 232, 274; in DMSO: 746, 543, 352*, 271.

$[Cu_2(L_2)_2]$: Brown; m.p. >300 °C; yield (%): 65; Anal. Calcd for $[C_{86}H_{102}N_4O_4Cu_2]$ (F.W: 1380 g mol^{-1}): C, 74.70; H, 7.43; N, 4.05. Found: C, 74.64; H, 7.39; N, 4.11%. IR (KBr pellets, υ_{max}/cm^{-1}): 3031 υ(Ar-CH), 2865–2984 υ(Aliph-CH), 1612 υ(C=N), 1169 υ(C–O), 530 υ(Cu–N) and 491 υ(Cu–O). μ_{eff} = 1.42 [B.M]. Λ_M = 36.3 $\Omega^{-1}cm^2$ mol^{-1}. UV-Vis (λ_{max}, nm) in CH_2Cl_2: 423, 338, 278, 239; in DMSO: 705, 400, 349*, 288, 256 (*shoulder).

$[Co_2(L_2)_2]$: Brown; m.p. 250 °C; yield (%): 60; Anal. Calcd for $[C_{86}H_{102}N_4O_4Co_2]$ (F.W: 1371 g mol^{-1}): C, 75.27; H, 7.35; N, 4.08. Found: C, 74.97; H, 7.60; N, 3.90%. IR KBr pellets, υ_{max}/cm^{-1}): 3042 υ(Ar-CH), 2870-2958 υ(Aliph.C–H), 1613 υ(C=N), 1171 υ(C–O), 532 υ(Co–N) and 488 υ(Co–O). μ_{eff} = 3.75 [B.M]. Λ_M = 39.1 $\Omega^{-1}cm^2$ mol^{-1}. UV-Vis (λ_{max}, nm) in CH_2Cl_2: 390, 282, 243; in DMSO: 396, 285, 258.

$[Mn_2(L_2)_2(H_2O)_4]$: Yellow; m.p. 260 °C; yield (%): 60; Anal. Calcd for $[C_{86}H_{110}N_4O_8Mn_2]$ (F.W: 1437 g mol^{-1}): C, 71.85; H, 7.71; N, 3.90. Found: C, 71.57; H, 7.64; N, 3.86%. IR KBr pellets, υ_{max}/cm^{-1}): 3682–3291 υ(O–H), 3048 υ(Ar-CH), 2868–2958 υ(Aliph-CH), 1618 υ(C=N), 1172 υ(C–O), 534 υ(Mn–N) and 494 υ(Mn–O). μ_{eff} = 1.98 [B.M]. Λ_M = 15.8 $\Omega^{-1}cm^2$ mol^{-1}. UV-Vis (λ_{max}, nm) in CH_2Cl_2: 391, 281, 240; in DMSO: 395, 381, 282.

$[Cu(L_3)]$: Dark green; m.p. >300 °C; yield (%): 65; Anal. Calcd for $[C_{40}H_{48}N_2O_2Cu]$ (F.W: 651 g mol^{-1}): C, 73.64; H, 7.42; N, 4.29. Found: C, 73.52; H, 7.48; N, 4.16%. IR (KBr pellets, υ_{max}/cm^{-1}): 3057 υ(Ar-CH), 2868–2960 υ(Aliph-CH), 1615 υ(C=N), 1170 υ(C–O), 538 υ(Cu–N) and 488 υ(Cu–O). μ_{eff} = 1.74 [B.M]. Λ_M = 14.3 $\Omega^{-1}cm^2$ mol^{-1}. UV-Vis (λ_{max}, nm) in CH_2Cl_2: 572*, 446, 328, 270, 232; in DMSO: 710, 683, 560, 429, 418, 366, 355, 312, 299 (*shoulder).

$[Co(L_3)]$: Dark brown; m.p. >300 °C; yield (%): 45; Anal. Calcd for $[C_{40}H_{48}N_2O_2Co]$ (F.W: 647 g mol^{-1}): C, 74.17; H, 7.47; N, 4.32. Found: C, 74.08; H, 7.54; N, 4.22%. IR (KBr pellets, υ_{max}/cm^{-1}): 3048 υ(Ar-CH), 2862–2952 υ(Aliph-CH), 1609 υ(C=N), 1170 υ(C–O), 525 υ(Co–N) and 485 υ(Co–O). μ_{eff} = 3.79 [B.M]. Λ_M = 15.1 $\Omega^{-1}cm^2$ mol^{-1}. UV-Vis (λ_{max}, nm) in CH_2Cl_2: 458*, 343, 328, 270, 232; in DMSO: 800, 650, 585, 454, 388, 347, 333 (*shoulder).

$[Mn(L_3)(H_2O)_2]$: Dark green; m.p. >300 °C; yield (%): 65; Anal. Calcd for $[C_{40}H_{52}N_2O_4Mn]$ (F.W: 679 g mol^{-1}): C, 70.67; H, 7.71; N, 4.12. Found: C, 70.55; H, 7.80; N, 4.19%. IR (KBr pellets, υ_{max}/cm^{-1}): 3564–3321 υ(O–H), 3060 υ(Ar-CH), 2858–2968 υ(Aliph-CH), 1609 υ(C=N), 1173 υ(C–O), 527 υ(Mn–N) and 489 υ(Mn–O). μ_{eff} = 2.15 [B.M]. Λ_M = 16.9 $\Omega^{-1}cm^2$ mol^{-1}. UV-Vis (λ_{max}, nm) in CH_2Cl_2: 947*, 579, 447, 353*, 302, 232; in DMSO: 525, 417, 335, 261 (*shoulder).

Ccycloaddition of epoxides to CO_2; general procedure

A 50 mL stainless steel pressure reactor was charged with complex (4.5×10^{-5} mol), epoxide (4.5×10^{-2} mol) and DMAP (11 mg, 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 to the desired pressure then heated to the desired temperature. The pressure was kept constant during the reaction. The vessel was then cooled to 5–10 ºC in an ice bath after completion of the desired time of reaction, then the pressure was released and the excess gases were vented. The yields of epoxides to corresponding cyclic carbonates were determined by comparing the ratio of product to substrate in the ^1H NMR spectrum of an aliquot of the reaction mixture.

Conclusions

In this study, the sterically-hindered salicylaldimine ligands and their di- or mononuclear metal(II) complexes were synthesised and characterised by a range of physical techniques. In these metal complexes, the ligands are coordinated through imine nitrogen and the phenolic OH groups. The synthesised sterically-hindered salen- type complexes were tested as catalysts for the formation of cyclic carbonates from CO_2 and liquid epoxides (propylene oxide, epichlorohydrine, 1,2-epoxybutane and styrene oxide), which served as both reactant and solvent. From the results shown in Table 1, it is evident that the Mn(II) metal complexes are more efficient than the other M(II) metal complexes for the formation of cyclic carbonates from CO_2. Increasing the reaction temperature and time had a pronounced positive effect on the TOF.

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