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Synthesis and spectral studies of macrocyclic Cu(II) complexes by reaction of various diamines, copper(II) perchlorate and 1,4-bis(2-carboxyaldehyde phenoxy)butane

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Synthesis and spectral studies of macrocyclic Cu(II) complexes by reaction of various diamines, copper(II) perchlorate and 1,4-bis(2-carboxyaldehyde phenoxy)butane

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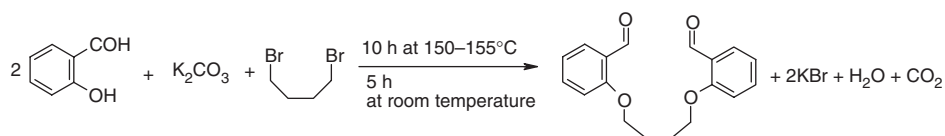
Six macrocyclic complexes, were synthesized by reaction of 1,4-bis(2-carboxyaldehyde phenoxy)butane and various amines and their copper(II) perchlorate complexes were synthesized by template effect reaction of 1,4-bis(2-carboxyaldehyde phenoxy)butane, Cu(ClO₄)₂ · 6H₂O and amines. The metal-to-ligand ratios were found to be 1 : 1. Cu(II) metal complexes are 1 : 2 electrolytes as shown by their molar conductivities (Λ_M) in DMF (dimethyl formamide) at 10⁻³ M. The Cu(II) complexes are proposed to be square planar based on elemental analysis, FT-IR, UV-Vis, magnetic susceptibility measurements, molar conductivity measurements, and mass spectra.

Keywords: Macrocyclic Schiff-base complexes; 1,4-bis(2-carboxyaldehyde phenoxy)butane and Copper(II) complexes

1. Introduction

Cyclic and macrocyclic complexes of transition metals are of interest because of their use as diagnostic agents in magnetic resonance imaging and their resemblance to natural systems [1–3]. Macrocyclic ligands containing a heteroatom are important complexing agents for cations, anions and molecules [4–5]. The stability of macrocyclic metal complexes depends upon a number of factors, including the number and type of donor atoms present in the ligand, their relative positions within the macrocyclic skeleton, and the number and size of the chelate rings formed on complexation. For transition metal ions, features such as the nature and magnitude of crystal-field effects also play an important role [6]. Synthetic macrocycles are a growing class of compounds

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Scheme 1. Synthesis of 1,4-*bis*(2-carboxyaldehyde phenoxy)butane.

with varying chemistry and a wide range of different molecular topologies and sets of donor atoms [7–13]. We are particularly interested in using transition metal complexes of appended macrocycles as models for copper-containing proteins. Copper is a component of a variety of proteins which function as mono-oxygenases, dioxygenases in dioxygen transport, and in electron-transfer systems [14, 15]. Synthesis of Schiff-base complexes is achieved through the template reaction [16–19] or transmetallation reactions [20–23] which are used when the transition metal cations are ineffective as templates. In the present work, we have synthesized six macrocyclic Schiff-base complexes by template effect reaction of 1,4-*bis*(2-carboxyaldehyde phenoxy)butane and various diamines with Cu(ClO₄)₂ · 6H₂O; spectral and magnetic properties of the new compounds were studied in detail.

2. Experimental

2.1. Methods

Elemental analysis was carried out on a LECO CHNS model 932 elemental analyzer. IR spectra were recorded on a PERKIN ELMER SPECTRUM RX1 FTIR spectrophotometer with KBr pellets in the wave number range of 4000–400 cm⁻¹. Electronic spectral studies were conducted on a SHIMADZU model 160 UV Visible spectrophotometer between 200–900 nm. Molar conductivity was measured with a WTW LF model 330 conductivity meter, using solutions of the complexes in DMF. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature (20°C) using Hg[Co(SCN)₄] as calibrant; diamagnetic corrections were calculated from Pascal's constants [24]. Mass spectra were recorded using a AGILENT model 1100 MSD mass spectrometer.

2.2. Chemical and starting materials

The aldehyde used in the synthesis was prepared from salicylaldehyde, 1,4-dibromobutane and K₂CO₃ as shown in scheme 1. All the chemicals and solvents were of analytical grade and used as received.

2.3. Synthesis of 1,4-*bis*(2-carboxyaldehyde phenoxy)butane

To a stirred solution of salicylaldehyde (24.4 g, 0.2 mol) and K₂CO₃ (13.8 g, 0.1 mol) in DMF (100 mL) was added dropwise 1,4-dibromobutane (21.6 g, 0.1 mol) in

DMF (40 mL). The reaction was continued for 10h at 150–155°C and then 5 h at room temperature. After the addition was complete, 200 mL distilled water was added and it was put in a refrigerator; 1 h later the precipitate was filtered and washed with 500 mL water, dried in air, recrystallized from ethanol and filtered in vacuum. Yield: 23.8 g (80%), Melting Point: 105–107°C, Color: Bright brown. (scheme 1). Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.47, H, 6.08, O, 21.45. Found: C, 72.62, H, 6.15, O, 21.58. Selected IR data (KBr, $\nu\text{ cm}^{-1}$): 3107 $\nu(\text{Ar}-\text{CH})$, 2951, 2875 $\nu(\text{Alph.}-\text{CH})$, 1678 $\nu(\text{C}=\text{O})$, 1488, 1460 $\nu(\text{Ar}-\text{C}=\text{C})$, 1287, 1238 $\nu(\text{Ar}-\text{O})$, 1170, 1042 $\nu(\text{R}-\text{O})$, 757 $\nu(\text{Substituted benzene})$.

2.4. Synthesis of complexes

To a stirred solution of 1,4-bis(2-carboxyaldehyde phenoxy)butane (1.5 g, 5 mmol) and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.85 g, 5 mmol) in methanol (60 mL) was added dropwise diamines (5 mmol) in methanol (40 mL). After the addition was completed, the stirring was continued for 2 h. Then precipitate was filtered, washed with methanol and dried in air.

2.5. Spectral characterization of $[\text{CuL}^1](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$

Yield: 0.50 g (16.6%). Anal. Calcd for $\text{CuC}_{20}\text{H}_{22}\text{N}_2\text{O}_{10}\text{Cl}_2 \cdot \text{H}_2\text{O}$: C, 39.74, H, 3.97, N, 4.64. Found: C, 39.72, H, 3.64, N, 4.28. Selected IR data (KBr, $\nu\text{ cm}^{-1}$): 3365 $\nu(\text{H}_2\text{O})$, 3137 $\nu(\text{Ar}-\text{CH})$, 2964, 2884 $\nu(\text{Alph.}-\text{CH})$, 1636 $\nu(\text{C}=\text{N})$, 1453, 1450 $\nu(\text{Ar}-\text{C}=\text{C})$, 1118, 627 $\nu(\text{ClO}_4^-)$, 1277, 1246 $\nu(\text{Ar}-\text{O})$, 1144, 1043 $\nu(\text{R}-\text{O})$, 755 $\nu(\text{Substituted benzene})$, 525 $\nu(\text{Cu}-\text{O})$, 478 $\nu(\text{Cu}-\text{N})$. $\Lambda_M = 158\text{ W}^{-1}\text{ mol}^{-1}\text{ cm}^2$ (in DMF). UV-Vis (λ_{max} , nm) in DMSO: 273, 281, 298, 562; in DMF: 229, 269, 318, 553. Mass spectra: 605 $[[\text{CuL}^1](\text{ClO}_4)_2 \cdot \text{H}_2\text{O} + \text{H}]^+$, $\mu_{\text{eff}} = 1.91\text{ BM}$.

2.6. Spectral characterization of $[\text{CuL}^2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$

Yield: 0.58 g (18.3%). Anal. Calcd for $\text{CuC}_{21}\text{H}_{24}\text{N}_2\text{O}_{10}\text{Cl}_2 \cdot \text{H}_2\text{O}$: C, 39.69, H, 4.09, N, 4.41. Found: C, 39.14, H, 3.57, N, 4.08. Selected IR data (KBr, $\nu\text{ cm}^{-1}$): 3346 $\nu(\text{H}_2\text{O})$, 3078 $\nu(\text{Ar}-\text{CH})$, 2934, 2882 $\nu(\text{Alph.}-\text{CH})$, 1635 $\nu(\text{C}=\text{N})$, 1490, 1457 $\nu(\text{Ar}-\text{C}=\text{C})$, 1121, 624 $\nu(\text{ClO}_4^-)$, 1298, 1246 $\nu(\text{Ar}-\text{O})$, 1159, 1042, $\nu(\text{R}-\text{O})$, 758 $\nu(\text{Substituted benzene})$, 524 $\nu(\text{Cu}-\text{O})$, 472 $\nu(\text{Cu}-\text{N})$. $\Lambda = 166\text{ W}^{-1}\text{ mol}^{-1}\text{ cm}^2$ (in DMF). UV-Vis (λ_{max} , nm) in DMSO: 238, 272, 290, 311, 654; in DMF: 235, 270, 309, 643. Mass spectra: 635 $[[\text{CuL}^2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}]^+$, $\mu_{\text{eff}} = 1.70\text{ BM}$.

2.7. Spectral characterization of $[\text{CuL}^3](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$

Yield: 0.98 g (31.1%). Anal. Calcd for $\text{CuC}_{22}\text{H}_{26}\text{N}_2\text{O}_{10}\text{Cl}_2 \cdot 2\text{H}_2\text{O}$: C, 40.55, H, 4.75, N, 4.61. Found: C, 40.04, H, 4.56, N, 4.79. Selected IR data (KBr, $\nu\text{ cm}^{-1}$): 3321 $\nu(\text{H}_2\text{O})$, 3072 $\nu(\text{Ar}-\text{CH})$, 2935, 2829 $\nu(\text{Alph.}-\text{CH})$, 1635 $\nu(\text{C}=\text{N})$, 1490, 1456 $\nu(\text{Ar}-\text{C}=\text{C})$, 1139, 624 $\nu(\text{ClO}_4^-)$, 1287, 1246 $\nu(\text{Ar}-\text{O})$, 1195, 1089, $\nu(\text{R}-\text{O})$, 758 $\nu(\text{Substituted benzene})$, 515 $\nu(\text{Cu}-\text{O})$, 472 $\nu(\text{Cu}-\text{N})$. $\Lambda = 174\text{ W}^{-1}\text{ mol}^{-1}\text{ cm}^2$ (in DMF). UV-Vis (λ_{max} , nm) in DMSO: 237, 263, 310, 713; in DMF: 234, 267, 313, 697. Mass spectra: 587 $[[\text{CuL}^3](\text{ClO}_4)_2 \cdot (\text{CH}_2\text{CH}_2)]^+$, $\mu_{\text{eff}} = 2.08\text{ BM}$.

2.8. Spectral characterization of $[\text{CuL}^4](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$

Yield: 1.20 g (36.4%). Anal. Calcd for $\text{CuC}_{24}\text{H}_{30}\text{N}_2\text{O}_{10}\text{Cl}_2 \cdot \text{H}_2\text{O}$: C, 43.57, H, 4.84, N, 4.24. Found: C, 43.04, H, 4.48, N, 4.52. Selected IR data (KBr, $\nu \text{ cm}^{-1}$): 3318 $\nu(\text{H}_2\text{O})$, 3061 $\nu(\text{Ar}-\text{CH})$, 2930, 2857 $\nu(\text{Alph.}-\text{CH})$, 1636 $\nu(\text{C}=\text{N})$, 1489, 1457 $\nu(\text{Ar}-\text{C}=\text{C})$, 1139, 624 $\nu(\text{ClO}_4^-)$, 1287, 1245 $\nu(\text{Ar}-\text{O})$, 1174, 1050, $\nu(\text{R}-\text{O})$, 758 $\nu(\text{Substituted benzene})$, 524 $\nu(\text{Cu}-\text{O})$ 472 $\nu(\text{Cu}-\text{N})$. $\Lambda = 146 \text{ W}^{-1} \text{ mol}^{-1} \text{ cm}^2$ (in DMF). UV-Vis (λ_{max} , nm) in DMSO: 236, 281, 359*, 619; in DMF: 238, 272, 367*, 627 (*: shoulder peak). Mass spectra: 543 $[[\text{CuL}^4](\text{ClO}_4) + \text{H}]^+$. $\mu_{\text{eff}} = 1.93 \text{ BM}$.

2.9. Spectral characterization of $[\text{CuL}^5](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$

Yield: 0.75 g (22.8%). Anal. Calcd for $\text{Cu}_2\text{C}_{24}\text{H}_{28}\text{N}_2\text{O}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$: C, 43.84, H, 4.57, N, 4.26. Found: C, 44.04, H, 4.36, N, 4.51. Selected IR data (KBr, $\nu \text{ cm}^{-1}$): 3326 $\nu(\text{H}_2\text{O})$, 3122 $\nu(\text{Ar}-\text{CH})$, 2924, 2857 $\nu(\text{Alph.}-\text{CH})$, 1636 $\nu(\text{C}=\text{N})$, 1489, 1456 $\nu(\text{Ar}-\text{C}=\text{C})$, 1136, 627 $\nu(\text{ClO}_4^-)$, 1307, 1237 $\nu(\text{Ar}-\text{O})$, 1090, 1036, $\nu(\text{R}-\text{O})$, 755 $\nu(\text{Substituted benzene})$, 545 $\nu(\text{Cu}-\text{O})$ 492 $\nu(\text{Cu}-\text{N})$. $\Lambda = 161 \text{ W}^{-1} \text{ mol}^{-1} \text{ cm}^2$ (in DMF). UV-Vis (λ_{max} , nm) in DMSO: 235, 280, 292, 318, 567; in DMF: 238, 274, 315, 574. Mass spectra: 601 $[[\text{CuL}^5](\text{ClO}_4)_2 \cdot (\text{CH}_2\text{CH}_2\text{CH}_2)]^+$. $\mu_{\text{eff}} = 1.78 \text{ BM}$.

2.10. Spectral characterization of $[\text{CuL}^6](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$

Yield: 0.99 g (26.5%). Anal. Calcd for $\text{CuC}_{28}\text{H}_{38}\text{N}_2\text{O}_{12}\text{Cl}_2 \cdot \text{H}_2\text{O}$: C, 44.98, H, 5.35, N, 3.75. Found: C, 44.64, H, 5.66, N, 3.34. Selected IR data (KBr, $\nu \text{ cm}^{-1}$): 3445 $\nu(\text{H}_2\text{O})$, 3066 $\nu(\text{Ar}-\text{CH})$, 2935, 2877 $\nu(\text{Alph.}-\text{CH})$, 1635 $\nu(\text{C}=\text{N})$, 1490, 1456 $\nu(\text{Ar}-\text{C}=\text{C})$, 1139, 626 $\nu(\text{ClO}_4^-)$, 1286, 1245 $\nu(\text{Ar}-\text{O})$, 1192, 1047, $\nu(\text{R}-\text{O})$, 758 $\nu(\text{Substituted benzene})$, 506 $\nu(\text{Cu}-\text{O})$ 474 $\nu(\text{Cu}-\text{N})$. $\Lambda = 176 \text{ W}^{-1} \text{ mol}^{-1} \text{ cm}^2$ (in DMF). UV-Vis (λ_{max} , nm) in DMSO: 233, 276, 302, 660; in DMF: 239, 275, 306, 678. Mass spectra: 727 $[\text{CuL}^6](\text{ClO}_4)_2 \cdot 2\text{H}]^+$. $\mu_{\text{eff}} = 2.20 \text{ BM}$.

3. Results and discussion

3.1. Macrocyclic Schiff-base complexes

Reaction between 1,4-bis(2-carboxyaldehyde phenoxy)butane, copper(II) perchlorate and amines in methanol gives the [1 + 1] macrocycle Schiff-base complexes as the major product. The macrocyclic complexes were characterized by elemental analysis, mass and IR spectrometry. The mass spectrum of complexes plays an important role in confirming the monomeric [1 + 1] (dicarbonyl and diamine) nature of complexes. (table 1). The crystals were unsuitable for single-crystal X-ray structure determination and are insoluble in most common solvents, including water, ethanol, ethyl acetate, and acetonitrile.

The characteristic infrared spectral data are given in the experimental section. Infrared spectra of Cu(II) metal complexes were recorded in KBr pellet from 4000 to 400 cm^{-1} . Broad bands within the range 3365–3318 cm^{-1} for all Cu(II) metal complexes can be attributed to stretching vibrations of water $\nu(\text{H}_2\text{O})$ [25]. A strong band observed

Table 1. Physical characterization, analytical, molar conductance and mass spectral data of the complexes.

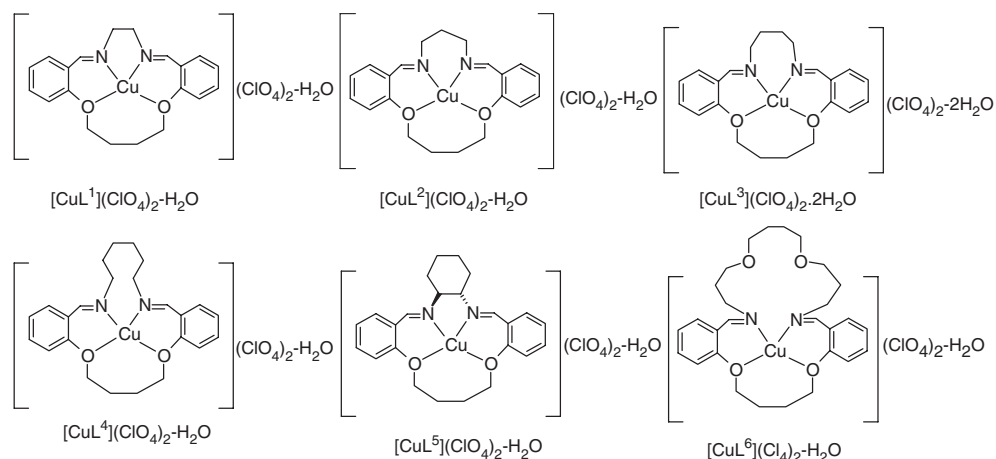
Compound	(Calcd %)		Found %		λ_M (ohm ¹ cm ² mol ⁻¹)	Formula weight	MS/EI	Assignment	μ_{eff} (BM)
	C	H	N						
[CuL ¹](ClO ₄) ₂ · H ₂ O	(39.74) 39.72	(3.97) 3.64	(4.64) 4.28		158	604	605	[[CuL ¹](ClO ₄) ₂ · H ₂ O + H] ⁺	1.91
[CuL ²](ClO ₄) ₂ · H ₂ O	(39.69) 39.14	(4.09) 3.57	(4.41) 4.08		166	635	635	[[CuL ²](ClO ₄) ₂ · H ₂ O] ⁺	1.70
[CuL ³](ClO ₄) ₂ · 2H ₂ O	(40.55) 40.04	(4.75) 4.56	(4.61) 4.79		174	631	587	[[CuL ³](ClO ₄) ₂ · (CH ₂ CH ₂) ⁺	2.08
[CuL ⁴](ClO ₄) ₂ · H ₂ O	(43.57) 43.04	(4.84) 4.48	(4.24) 4.52		146	659	543	[[CuL ⁴](ClO ₄) ₂ + H] ⁺	1.93
[CuL ⁵](ClO ₄) ₂ · H ₂ O	(43.84) 44.04	(4.57) 4.36	(4.26) 4.51		161	657	601	[[CuL ⁵](ClO ₄) ₂ · (CH ₂ CH ₂ CH ₂) ⁺	1.78
[CuL ⁶](ClO ₄) ₂ · H ₂ O	(44.98) 44.64	(5.35) 5.66	(3.75) 3.34		176	747	727	[CuL ⁶](ClO ₄) ₂ · 2H] ⁺	2.20

in the IR spectra of the Cu(II) metal complexes in the $1636\text{--}1635\text{ cm}^{-1}$ region is attributed to the $\nu(\text{C}=\text{N})$ stretch, indicating coordination of the azomethine nitrogen to copper [26]. Spectra of all the Cu(II) complexes are dominated by bands between $2964\text{--}2857\text{ cm}^{-1}$ due to $\nu(\text{Alph.}-\text{CH})$ groups. A new band in the $1195\text{--}1090\text{ cm}^{-1}$ region was assigned to $\nu(\text{R}-\text{O})$ mode [27]. Conclusive evidence of the bonding is also shown by the observation that new bands in the IR spectra of the Cu(II) metal complexes appear at $545\text{--}506\text{ cm}^{-1}$ and $492\text{--}472\text{ cm}^{-1}$ assigned to $\nu(\text{Cu}-\text{O})$ and $\nu(\text{Cu}-\text{N})$ stretching vibrations [28].

Electronic absorption spectral data of Cu(II) complexes in DMSO and DMF at room temperature are presented in the experimental section. The electronic spectra of Cu(II) complexes in DMSO show four or five peaks and four peaks in DMF in the visible-ultraviolet region. The absorption bands below 298 nm are practically identical and can be attributed to $\pi \rightarrow \pi^*$ transitions in the benzene ring and azomethine ($-\text{C}=\text{N}$) groups. The absorption bands observed within the $302\text{--}318\text{ nm}$ range are probably due to $n \rightarrow \pi^*$ transitions of imine groups [29]. The general character of these spectra is very similar to that of the corresponding complexes of unsymmetrically disubstituted phenoxy groups due to the fact that metal-to-ligand charge transfer and ligand-to-metal charge transfer transitions have similar energy differences [30]. The electronic spectra also show an absorption band at range $553\text{--}713\text{ nm}$ attributed to the ${}^2E_g \rightarrow {}^2T_{2g}$ transitions, characteristic for tetragonally elongated octahedral or square planar geometry [29, 31]. The energy of the band assigned to d-d transitions provides a rough estimate of the ligand field strength, since one of the transitions comprised in the band envelope is $d_{x^2-y^2}^2 - d_{xy}$, and the energy associated with this transitions is 10 Dq-C [32].

The metal-ligand mole ratio was 1:1, according to elemental analysis. Since all of the Cu(II) complexes are paramagnetic, their NMR spectra could not be obtained. The magnetic moments of the Cu(II) complexes carried out at room temperature range from $1.70\text{--}2.20\text{ BM}$, typical for mononuclear Cu(II) complexes with a $S = 1/2$ spin-state and do not indicate antiferromagnetic coupling of spins at this temperature.

The Cu(II) metal complexes are 2:1 electrolytes as shown by their molar conductivities (Λ_M) in DMF at 10^{-3} M , which are in the range $146\text{--}176\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$.



Scheme 2. Suggested structure of the complexes.

The molar conductivities of the compounds in DMF are in the range reported for 2 : 1 electrolytes [33–36] (scheme 2).

The mass spectra of the complexes have peaks attributable to the molecular ions. (m/z) 605 $[[\text{CuL}^1](\text{ClO}_4)_2 \cdot \text{H}_2\text{O} + \text{H}]^+$, 635 $[[\text{CuL}^2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}]^+$, 587 $[[\text{CuL}^3](\text{ClO}_4)_2 \cdot (\text{CH}_2\text{CH}_2)]^+$, 543 $[[\text{CuL}^4](\text{ClO}_4) + \text{H}]^+$, 601 $[[\text{CuL}^5](\text{ClO}_4)_2 \cdot (\text{CH}_2\text{CH}_2\text{CH}_2)]^+$, 727 $[\text{CuL}^5](\text{ClO}_4)_2 \cdot 2\text{H}]^+$ [37, 38].

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