Synthesis and Characterization of a New Family of Binuclear Chelate Ligands and Their Copper(II) Complexes

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Abstract

A new family of binuclear copper(II) complexes with a flexible bridging group has been prepared by the electrophilic substitution reaction of N-salicylaldehyde-N′-acetylacetoneethylenediiminocopper(II) with *m*-xylene disocyanate or hexamethylene diisocyanate. The de-metallation reaction of the copper(II) complexes with hydrogen sulfide gave the corresponding binuclear chelate ligands.

Introduction

Binuclear metal complexes in which the ligand framework is positioned to promote the substrate bindings are of current interest with respect to model systems of the oxygen carrier or metal enzymes such as hemocyanin, hemerythrin, laccase, cytochrome oxidase and phenolase, and a number of binuchelating ligands have been designed and synthesized [1]. We wish here to report a new family of binuclear chelate ligands with a flexible bridging group. The binuclear copper(II) complexes and the ligands were prepared by electrophilic substitution reactions according to the reaction scheme shown in Fig. 1.

Experimental

Physical Measurements

Melting points were measured on a Yanagimoto micromelting point apparatus and were uncorrected. Elemental analyses were performed at the Technical Service Center of Kumamoto University. Visible and ultraviolet spectra were recorded with a Hitachi recording spectrophotometer 323; infrared spectra were recorded as KBr discs with a Shimadzu recording spectrophotometer IR-410. The 100 MHz ^{1}H NMR spectra were recorded on a JEOL MH 100 spectrometer, where the solvent used was chloroform-d_1 and shift measurements were made relative to tetramethylsilane. ESR spectra were recorded by using a JEOL JES-FEAX (X-band) spectrometer, where MnO doped in MgO was used as the standard marker. Molecular weights were estimated in chloroform solutions on a Corona 114 vapor pressure osmometer.

Syntheses

The parent copper(II) complex ([CuL–H]) was prepared by the method of Kuska *et al.* [2]. The

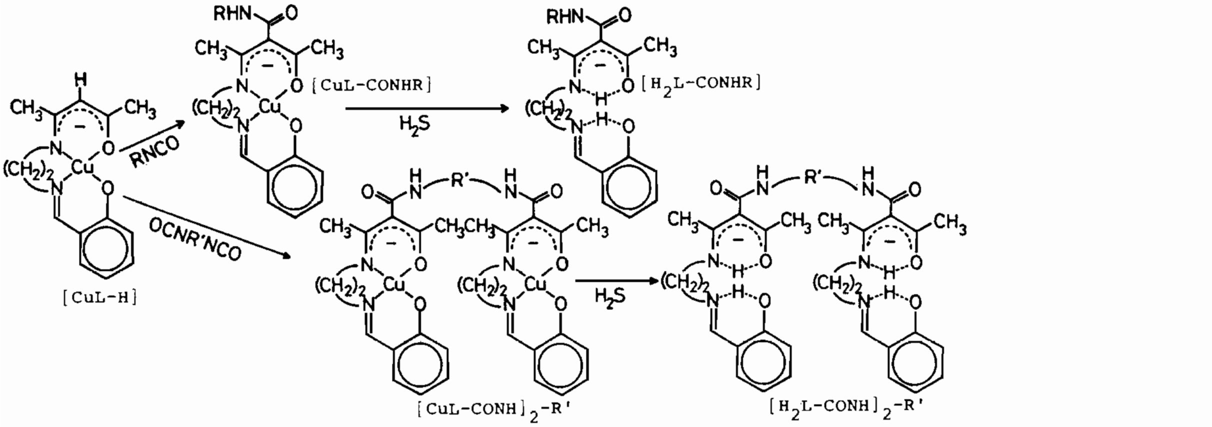

Fig. 1. Reaction scheme from parent copper(II) complex [CuL–H] to substituted mononuclear complexes ([CuL–CONHC$_2$H$_5$], [CuL–CONHPh]), binuclear complexes ([CuL–CONH]$_2$*m*-Xyl, [CuL–CONH]$_2$(CH$_2$)$_6$), and ligands ([H$_2$L–CONHC$_2$H$_5$], [H$_2$L–CONHPh], [H$_2$L–CONH]$_2$*m*-Xyl, [H$_2$L–CONH]$_2$–(CH$_2$)$_6$).

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TABLE I. Elemental Analytical Data, Melting Points, and Molecular Weights.

Complex	C(%)	H(%)	N(%)	M.p. (°C)	Mol. weight
[CuL–CONHC$_2$H$_5$]	53.89(53.65)	5.59(5.72)	11.09(11.09)	208–210	–
[CuL–CONHPh]	59.04(59.08)	4.91(4.96)	9.85 (9.84)	239–241	–
[CuL–CONH]$_2$–*m*-Xyl	56.75(56.78)	4.96(5.02)	10.41(10.45)	290	–
[CuL–CONH]$_2$–(CH$_2$)$_6$[a]	53.62(53.92)	5.93(5.78)	10.50(10.48)	217–219	–
[H$_2$L–H]	68.25(68.27)	7.50(7.37)	11.19(11.37)	59–61	–
[H$_2$L–CONHC$_2$H$_5$]	63.90(64.33)	7.38(7.30)	13.09(13.24)	152–153	311(317.4)
[H$_2$L–CONHPh]	67.78(67.36)	6.45(6.44)	11.18(11.18)	127–129	375(365.4)
[H$_2$L–CONH]$_2$–*m*-Xyl	67.10(67.04)	6.57(6.51)	11.89(12.34)	128 dec	662(680.8)
[H$_2$L–CONH]$_2$–(CH$_2$)$_6$	62.87(63.70)	7.33(7.42)	12.49(12.38)	137–140	686(660.8)
[NiL–H]	56.42(55.50)	5.44(5.32)	9.08 (9.25)	242–244	–
[NiL–CONHC$_2$H$_5$]	54.51(54.58)	5.63(5.66)	11.23(11.23)	290	–
[NiL–CONHPh]	60.07(59.75)	5.19(5.01)	10.01 (9.95)	290	–
[NiL–CONH]$_2$–*m*-Xyl	57.06(57.47)	5.09(5.08)	10.45(10.58)	290	–

[a] H_2O Calculated values are in parentheses.

substituted mononuclear complexes ([CuL–CONHC$_2$H$_5$], [CuL–CONHPh]) were prepared by mixing [CuL–H] and ethyl isocyanate or phenyl isocyanate in a mole ratio of 1:1 in dichloromethane at room temperature for 6 h. The binuclear copper(II) complexes ([CuL–CONH]$_2$– *m*-Xyl, [CuL–CONH]$_2$–(CH$_2$)$_6$) were prepared according to a method similar to that for the mononuclear copper(II) complex, unless [CuL–H] and *m*-xylene diisocyanate or hexamethylene diisocyanate were reacted in a mole ratio of 2:1.

The demetallation reaction of the copper(II) complexes by passing gaseous hydrogen sulfide gave the corresponding metal free ligands. The reintroduction of the metal ion (Ni^{2+}) was performed by mixing the ligands and nickel(II) acetate tetrahydrate in methanol.

Results and Discussion

The elemental analytical data, melting points, and molecular weights obtained by vapor pressure osmometry are given in Table I. According to the reaction procedure shown in Fig. 1, the binuclear copper(II) complexes were obtained selectively and almost quantitatively without the formation of monomeric and polymeric species, because the starting copper(II) complex ([CuL–H]) and diisocynate possess a nucleophilic and two electrophilic centers respectively. The other advantages of the present synthetic route for the binuclear metal complexes are as follows: the structural parameters associated with the coordination sphere such as the distortion of the coordination geometry and those of the bridging moiety such as the length of metal to metal and the orientation between two coordination planes can be varied easily and independently; the binuclear chelate ligands can be obtained by the de-metallation reaction of the corresponding copper(II) complexes with gaseous hydrogen sulfide and the re-introduction of the metal ion (Ni^{2+}) can be easily performed.

Infrared spectra of the reaction products of the copper(II) complex [CuL–H] with isocyanates differ from those of the starting compounds, most notably in the absence of the intense band at *ca.* 2250 cm^{-1} assignable to ν(C=N) stretching mode of isocyanates. The reaction products exhibit new infrared absorptions at *ca.* 1650 and 3250 (broad) cm^{-1}, assignable to ν(C=O) and ν(NH) of the substituted –CONH– group based on the analogy of the reaction products of N,N′-diacetylacetoneethylenediiminocopper(II) with isocyanates [3].

The 100 MHz proton NMR spectra for [H$_2$L–H], [H$_2$L–CONH]$_2$*m*-Xyl, and [H$_2$L–CONH]$_2$(CH$_2$)$_6$ are shown in Fig. 2. The spectra consist in general of five distinct regions: methyl(doublet), methylene(multiplet), methine(singlet), aromatic(multiplet), and imine(singlet) proton resonances. The methine proton resonance of the acetylacetonato residue at 5.0 ppm appeared in the spectrum of the unsubstituted ligand [H$_2$L–H] disappeared in those of the substituted mononuclear and binuclear chelate ligands, being indicative of substitution. The methylene proton resonances of the ethylenediamine residue and *m*-xylene dicarbamoyl as a bridging group appear respectively at 3.4–3.8 and 4.4–4.5 ppm as multiplets, and the ratio of the integrated intensities between them is 2:1, consistent with the formation of the binuclear species. For the ligand bridged by hexamethylene dicarbamoyl the terminal methylene (N-bonded) resonance appears at *ca.* 3.6–3.9

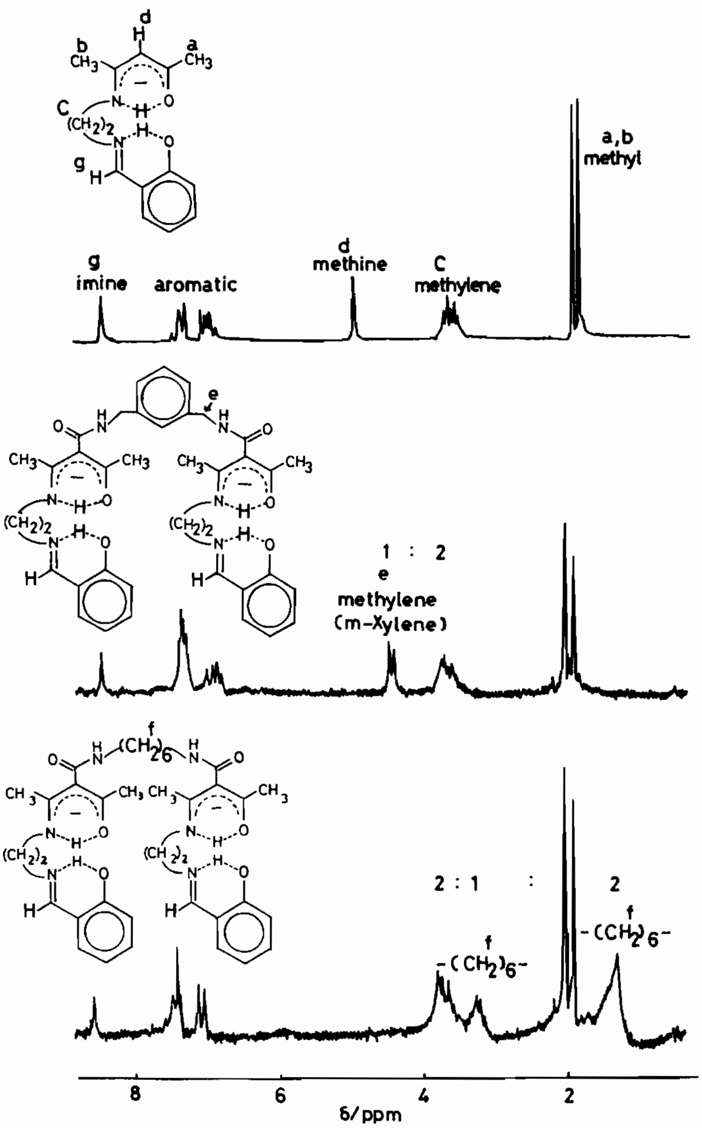

Fig. 2. The 100 MHz proton NMR spectra for $[H_2L-H]$, $[H_2L-CONH]_2m$-Xyl, and $[H_2L-CONH]_2(CH_2)_6$.

ppm and the central methylene $(-(CH_2)_4-)$ resonance appears at 1.3–1.6 ppm, and the integrated ratio of the methylene resonances between the ethylenediamine residue and the bridging moiety is 2:3, consistent with the formation of the binuclear species. The molecular weights measurements give further evidence for the formation of the binuclear chelate ligands.

The electronic absorption spectra of the copper(II) complexes were measured in dimethylformamide and the data are given in Table II, along with the ESR spectral data. The spectra of the binuclear copper(II) complexes exhibit a broad band at 17.9×10^3 cm^{-1} with an extinction coefficient of the order of 300 mol^{-1} dm^3 cm^{-1}, assignable to the d–d transition, and several bands in the ultraviolet region, assignable to the charge-transfer bands. The spectra of the binuclear copper(II) complexes resemble those of the mononuclear substituted and parent copper(II) complexes, so that the effects due to the substitution and the formation of the binuclear species were not observed in the electronic spectra.*

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*A striking difference between the binuclear and mononuclear copper(II) complexes was observed in their molecular complexes with 1,3,5-trinitrobenzene(TNB). The analogous binuclear copper(II) complex derived from N-2-hydroxy-1-naphthaldehyde-N'-acetyl-acetonetrimethylenediiminocopper(II) (abbreviated as [CuL'–H] and hexamethylene diisocyanate formed a 1:1 molecular complex with TNB, and the molecular complex showed a new band characteristic for charge-transfer transition both in solid and dimethylformamide solution, while the 1:1 molecular complex between [CuL'–H] and TNB showed the charge-transfer band in solid (but not in solution).

TABLE II. Electronic and ESR Spectral Data obtained in Dimethylformamide.

Complex	Maxima nm (log ϵ)			g_o	$g_\parallel$	$g_\perp$	A_o (Gauss)	$A_\parallel$ (Gauss)	$A_\perp$ (Gauss)
[CuL–H]	560(2.45)	383(3.66)	326(4.13)	2.115	2.179	2.083	91	218	27
[CuL–CONHPh]	560(2.53)	381(3.69)	328(4.10)	2.114	2.196	2.073	92	217	30
[CuL–CONH]$_2$(CH$_2$)$_6$	558(2.74)	382(3.92)	330(4.36)	2.113	2.188	2.076	93	210	35
[CuL–CONH]$_2$*m*-Xyl	558(2.76)	382(3.91)	329(4.34)	2.115	2.188	2.079	90	210	31

ESR spectra were measured in dimethylformamide at room temperature and at liquid nitrogen temperature. The spectra of the binuclear copper(II) complexes showed an axial pattern and resemble those of the mononuclear copper(II) complexes both in the g and A values. This implies that metal–metal interaction is very weak in the present binuclear copper(II) complexes [4].

Acknowledgements

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