Copper(II) Complexes with Schiff Base Ligands. Synthesis of some Copper(II) Complexes with Ligands Derived from the Reaction of Pyridine-2-carboxaldehydes and Aromatic Amines

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Abstract

A series of copper(II) complexes with ligands derived from the Schiff base reaction of pyridine-2-carboxaldehyde or 6-methylpyridine-2-carboxaldehyde with aniline, benzylamine or 2-phenylethylamine has been prepared. These complexes have been characterized by spectroscopic methods. The electronic spectrum of bis(*N*-phenyl-(6-methyl-2-pyridyl)methylimine) copper(II) tetrafluoroborate has an absorption band at a much higher energy and molar absorptivity than the other complexes. The appearance of this band indicates a major change in geometry caused by the combined steric demands of the 6-methyl group on the pyridine aromatic ring and the rigid aromatic ring of the phenyl group on the imine nitrogen atom.

Introduction

Copper(II) complexes, primarily because of the presence of one or more copper ions at the active site of numerous enzymes [1], have attracted considerable attention. Structural studies of the proteins azurine [2] and plastocyanine [3] have indicated the presence of two aromatic nitrogen atoms (from the amino acid hystidine) and two sulfur atoms (one from the amino acid cysteine and the second from methionine) in the coordination sphere of the copper center. These four donor atoms plus a possible fifth donor atom are arranged in a distorted tetrahedral arrangement around the copper center.

In order to gain a more complete understanding of the chemistry of these proteins, models of the active site have become necessary. A number of workers have prepared models which have some of the features of the coordination sphere of the copper ion. Copper(II) complexes with distorted coordination spheres of nitrogen donors have been prepared by Karlin and co-workers [4]. Complexes with polythiaether macrocycle ligands, having reduction potentials near those of the proteins, have been prepared by Rorabacher *et al.* [5]. Copper(II) and copper(I) complexes of a ligand which mimicks the coordination sphere of the protein (2 aromatic nitrogen and 2 sulfur donors) have been studied crystallographically by Brubaker and co-workers [6]. All of these model studies have successfully exhibited some of the features and properties found in the protein.

In this study, a series of copper(II) complexes with Schiff base ligands incorporating an aromatic nitrogen donor has been prepared. The ligands are derived from the reaction of pyridine-2-carboxaldehydes with aniline, benzylamine and 2-phenylethylamine. In this series of complexes, the steric requirements vary depending on the substitution of the imine nitrogen atom and the 6 position of the pyridine ring.

Experimental

Physical Methods

Elemental analyses (C, H, N) were determined by Guelph Chemical Laboratories, Guelph, Ontario, Canada. Copper analyses were measured using a Perkin-Elmer Model 363 atomic absorption spectrophotometer. Samples were dissolved in 5 ml nitric acid and 5 ml sulfuric acid and heated to destroy the organic ligands. Nuclear magnetic resonance spectra were measured in deuterochloroform solution using a Varian EM-360L NMR spectrometer. Vibrational spectra were measured as either neat liquids between KBr disks, nujol mulls between KBr disks or nujol mulls between polyethylene sheets using a Perkin-Elmer model 283 infrared spectrophotometer. Electronic spectra were measured using a Perkin-Elmer Lambda 4B spectrophotometer over the wavelength range 900–300 nm. Solutions were typically 1×10^{-3} M complex dissolved in spectrophotometeric grade methanol or acetonitrile.

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Synthesis

Ligands

All ligands were prepared by refluxing 0.050 mol of the aldehyde (either pyridine-2-carboxaldehyde or 6-methyl-pyridine-2-carboxaldehyde) with 0.050 mol of the appropriate amine (either aniline, benzylamine or 2-phenylethylamine) in 100 ml benzene. When the appropriate amount of water had been removed by azeotropic distillation, the solution was cooled and the benzene was removed under reduced pressure. The resulting imine was used without further purification.

Complexes

Bis(2-pyridyl-N-phenylmethylimine)copper(II) tetrafluoroborate [CuPH–PY). A hot solution of 4.73 g (13.5 mmol) copper(II) tetrafluoroborate hydrate in 25 ml methanol was added to a hot solution of 2-pyridyl-*N*-phenylmethylimine (5.00 g, 27 mmol) in 25 ml methanol. The solution was allowed to cool and the solvent allowed to evaporate at atmospheric pressure and room temperature, yielding a viscous oil. The oil was taken up in hot methanol: isopropanol (10:1; *v:v*). Cooling the solution resulted in the formation of a crystalline solid which was filtered, washed with a small amount of cold methanol, followed by isopropanol. The solid was dried at 56 °C under vacuum. Yield: 4.77 g (57%). *Anal.* Calc. for $CuB_2F_8C_{24}H_{20}N_4$: C, 47.92; H, 3.35; N, 9.31; Cu, 10.56. Found: C, 47.94; H, 3.37; N, 9.40; Cu, 10.70%.

Bis(2-pyridyl-N-benzylmethylimine(copper(II) tetrafluroborate (CuBZ–PY). This complex was prepared by the same method as CuPH–PY, substituting 2-pyridyl-*N*-benzylmethylimine for 2-pyridyl-*N*-phenylmethylimine. Yield: 4.98 (56%). *Anal.* Calc. for $CuB_2F_8C_{26}H_{24}N_4$: C, 49.59; H, 3.83; N, 8.90; Cu, 10.09. Found: C, 49.54; H, 3.80; N, 8.93; Cu, 10.18%.

Bis(2-pyridyl-N-(2-phenylethyl)methylimine)-copper(II) tetrafluoroborate (CuPE–PY). This complex was prepared by the same method as CuPH–PY, substituting 2-pyridyl-*N*-(2-phenylethyl)methylimine for 2-pyridyl-*N*-phenylmethylimine. Yield: 5.42 g (59%). *Anal.* Calc. for $CuB_2F_8C_{28}H_{28}N_4$: C, 51.13; H, 4.29; N, 9.31; Cu, 9.66. Found: C, 51.08; H, 4.32; N, 9.26; Cu, 9.70%.

Bis((6-methyl-2-pyridyl)-N-phenylmethylimine)-copper(II) tetrafluoroborate (CuPH–MPY). A hot solution of (6-methyl-2-pyridyl)-*N*-phenylmethylimine (5.26 g, 27 mmol) in 25 ml methanol was added to a hot solution of 4.73 g (13.5 mmol) copper(II) tetrafluoroborate hydrate in 25 ml methanol. Upon cooling, a solid precipitate formed. The solid was filtered, recrystallized from methanol and dried at 56 °C under vacuum. Yield: 5.83 g (68%). *Anal.* Calc. for $CuB_2F_8C_{26}H_{24}N_4$: C, 49.59; H, 3.93; N, 8.90; Cu, 10.09. Found: C, 49.50; H, 3.90; N, 8.98; Cu, 9.94%.

Bis((6-methyl-2-pyridyl)-N-benzylmethylimine)-copper(II) tetrafluoroborate (CuBZ–MPY). This complex was prepared by the method used to prepare CuPH–MPY, substituting (6-methyl-2-pyridyl)-*N*-benzylmethylimine for (6-methyl-2-pyridyl)-*N*-phenylmethylimine. Yield: 5.23 g (59%). *Anal.* Calc. for $CuB_2F_8C_{28}H_{28}N_4$: C, 51.13; H, 4.29; N, 8.52; Cu, 9.66. Found: C, 50.88; H, 4.25; N, 8.64; Cu, 9.74%.

Bis((6-methyl-2-pyridyl)-N-(2-phenylethyl)-methylimine)copper(II) tetrafluoroborate (CuPE–MPY). This complex was prepared by the method used for CuPH–MPY, substituting (6-methyl-2-pyridyl)-*N*-(2-phenylethyl)methylimine for (6-methyl-2-pyridyl)-*N*-phenylmethylimine. Yield: 5.65 g (61%). *Anal.* Calc. for $CuB_2F_8C_{30}H_{32}N_4$: C, 52.54; H, 4.70; N, 8.14; Cu, 9.29. Found: C, 52.40; H, 4.78; N, 8.14; Cu, 9.30%.

The analogous perchlorate salts for all complexes mentioned above were prepared by the same method as the tetrafluoroborate salts, substituting copper(II) perchlorate hydrate for copper(II) tetrafluoroborate.

Caution: Perchlorate salts are potentially explosive. While we have not experienced any explosions, the complexes were regarded as explosion hazards and were prepared only on small scales and handled with caution.

Results and Discussion

The reaction of pyridine-2-carboxaldehydes with the various amines provided a convenient route to the desired imine ligands. The use of benzene as a solvent provides for easy removal of the water formed in the reaction, driving the reaction to completion. The imines prepared in this way are formed in nearly quantitative yields and in high purity. The imines are isolated by simple removal of the solvent at 45 °C under vacuum, followed by final removal of solvent under high vacuum. The imines are clear yellow oils which solidify upon standing. The NMR spectra confirm the identity of the imine. The proton NMR spectra of the product imines show no evidence of unreacted aldehyde or amine [7]. Based upon the proton NMR spectra, the imines were judged to be greater than 98% pure and were used without further purification.

The reaction of copper(II) tetrafluoroborate with the imine ligands in methanolic solution provides

TABLE I. Infrared Absorption Data for some Copper(II) Complexes with Schiff Base Ligands

Complex	ν(C=N)^a (cm^{-1})	Ring deformation bands^a (cm^{-1})
PH–PY	1710, 1630	610, 550, 532, 400
CuPH–PY	1598	610, 550, 530, 486, 420
BZ–PY	1710, 1642	610, 500, 451, 401
CuBZ–PY	1643, 1602	614, 502, 480, 417
PE–PY	1712, 1650	610, 515, 490, 401
CuPE–PY	1630, 1590	605, 505, 490, 421
PH–MPY	1640, 1630	643, 548, 542, 500, 405, 380
CuPH–MPY	1630	690, 610, 578, 560, 480, 415
BZ–MPY	1642, 1630	644, 560, 541, 500, 405, 380
CuBZ–MPY	1651, 1639	661, 610, 560, 500, 450, 435
PE–MPY	1651, 1590	641, 564, 540, 500, 422, 405
CuPE–MPY	1630	564, 500, 460, 420

^{a}From ref. 9.

an adequate yield of the desired complexes. The solubility of these complexes in methanol is a hindrance in the preparation of these complexes in higher yield. The complexes are insoluble in water, but soluble in methnaol, actone, acetonitrile and dimethylsulfoxide. After recrystallization, the complexes are light blue to dark green microcrystalline solids. The perchlorate salts were prepared in a similar manner, however the yields were substantially smaller due presumably to the increased solubility of the perchlorate salt in methanol.

Vibrational Spectroscopy

The infrared absorption spectrum of the isolated imine products was measured in order to assist in the identification of the copper(II) complexes and to confirm the identity of the imine [8]. A partial list of the infrared absorptions for the ligands and complexes, along with assignments are given in Table I.

The vibrational spectra of the complexes were measured as nujol mulls between KBr disks in order to avoid possible reactions between the complex and KBr under the high pressures used to form the pellet. A careful comparison of the vibrational spectra of the copper(II) complexes leads to several conclusions. The absence of bands in the range of 3400–3100 cm^{-1} eliminates the possibility of coordinated methanol or water from the waters of hydration of copper(II) tetrafluoroborate [9].

The infrared spectrum of the complexes isolated as perchlorate salts indicates that the perchlorate groups are ionic and not coordinated to the copper center [10]. A comparison of the pyridine deformation bands (near 400 cm^{-1}, see Table I.) in the infrared spectra of the free imines and the copper(II) complexes indicates that the pyridine nitrogen atom is coordinated to the copper center [11]. The high energy absorption bands are not found to change substantially, except for decrease in the energy of the C=N vibration frequency, indicating coordination of the imine to the copper center [12].

Electronic Spectroscopy

The electronic spectra of the complexes were measured in methanol. The visible absorption maximum is broad without any apparent fine structure. The spectra showed one absorption band which may be assigned to the d–d transition of the copper ion [13]. At higher energy several intense absorption bands were observed, and have been assigned to primarily ligand centered transitions. In some complexes, the possibility of a second band at lower energy (λ_{max} > 900 nm) exists. This low energy absorption band may be caused by a splitting of the electronic states of the copper center by a distorted tetragonal ligand field [14].

The energy of the visible absorption maximum and the molar absorptivity of this absorption band does depend upon the details of the imine ligand. The visible absorption data for this series of complexes is given in Table II. The electronic spectrum of CuPH–MPY along with CuBZ–MPY and CuPE–MPY are shown in Fig. 1. The electronic spectrum

TABLE II. Electronic Spectral Data for some Copper(II) Complexes with Schiff Base Ligands

Complex	d–d transition^a		Change transfer^b		Ligand transitions^c λ_{max} (nm)
	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})	
CuPh–PY	704	58	(–)	(–)	294
CuPh–MPY	590(sh)	470	507	2880	313, 236
CuBz–PY	705	80	(–)	(–)	287 –
CuBz–MPY	808	101	(–)	(–)	290, 237
CuPE–PY	702	50	(–)	(–)	283
CuPE–MPY	826	97	(–)	(–)	288, 232

^{a}Assignment based on data contained in ref. 13. ^{b}Assignment based on data contained in ref. 16. ^{c}Absorptions at approximately these energies are also present in the ligand absorption spectrum measured in methanol.

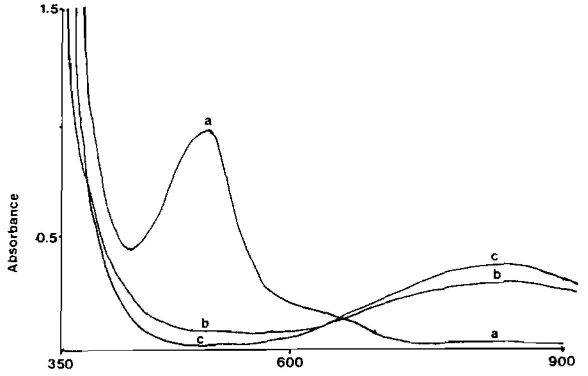

Fig. 1. Electronic spectrum of (a) 3.3×10^{-4} M CuPH–MPY, (b) 3.0×10^{-3} M CuBZ–MPY, (c) 3.2×10^{-3} M PE–MPY, recorded in methanolic solution.

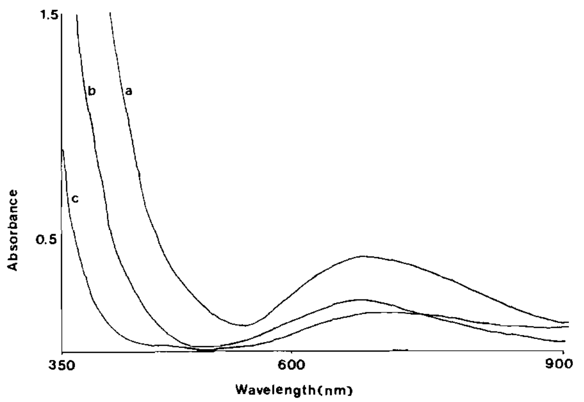

Fig. 2. Electronic spectrum of (a) 7.3×10^{-3} M CuPH–PY, (b) 3.2×10^{-3} M CuBZ–PY, (c) 2.9×10^{-3} M CuPE–PY, recorded in methanolic solution.

of CuPH–MPY shows an absorption maximum at substantially higher energy and higher molar absorptivity (Fig. 1) than the other complexes with ligands derived from 6-methylpyridine-2-carboxaldehyde.

A comparison of the electronic spectra of the complexes CuPH–PY, CuBZ–PY and CuPE–PY is shown in Fig. 2. The electronic spectra of these complexes are remarkably similar, showing d–d adsorption bands at roughly the same energy and intensity in all of the complexes. These spectra of all complexes exhibit absorption maxima in the ultraviolet region of the spectrum. These absorption maxima also appear at similar energies in the uncomplexed ligand and are therefore assigned to primarily ligand centered transitions. The energies of the visible absorption maxima are similar in energy to those found in similar complexes with imines derived from pyridine-2-carboxaldehyde and aliphatic amines [15].

In comparing the electronic spectra of the two series of complexes (Figs. 1 and 2), there appears to be a major change in the electronic spectrum of CuPH–MPY but not CuPH–PY. The visible absorption band in the complex CuPH–MPY is at a higher energy and a higher molar absorptivity. A lower energy shoulder on this absorption band is assigned to the d–d transition in this complex, while the intense band is assigned to a ligand–metal charge transfer transition [16]. This change in the observed electronic spectrum is attributed to the steric bulk of the extended planar ligand system causing a change in the geometry of the copper center. It is apparent that the added size of the 6-methyl group on the pyridine ring is sufficient to cause the change in geometry. In the unsubstituted complex, a similar shift in absorption maximum is not observed, eliminating the possibility of the electronic delocalization of the conjugated ring system giving rise to the observed changes in the electronic spectrum. The electronic spectra of the other complexes of the two series are remarkably similar, indicating these complexes are all similar in geometry.

Conclusions

In this study, we have prepared a series of copper(II) complexes with imine ligands that differ mainly in size. We have seen that the addition of a methyl group on the pyridine ring of a large planar ligand system can be sufficient to cause a substantial change in the electronic spectrum of the copper complex. The observed changes in the electronic spectrum are attributed to a lowering of the energy of a ligand to metal charge transfer absorption by forcing a change in the geometry of the metal center. The lower energy of the ligand–metal charge transfer absorption band observed for the complex CuPh–MPY as a result of the distorted coordination sphere suggests that the distortions present in this complex may be similar to those observed for copper centers in proteins [1–3, 17]. It is hoped that through additional changes in the ligand system, perhaps through substitution on the aromatic ring of the imine substituent, copper complexes with bidentate ligands which are stable in both the copper(II) and copper(I) states and with optical properties similar to those of copper proteins can be prepared.

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