# Synthesis of some Copper(II) Complexes with Ligands Derived from the Schiff Base Reaction between 2-Pyridinecarboxaldehyde and Aliphatic Amines

DAVID W. JOHNSON* and HELEN K. MAYER

*Department of Chemistry, University of Dayton, 300 College Park, Dayton, Ohio 45469, U.S.A.*

(Received August 14, 1986)

As part of our continuing investigations of the influence of stereochemical demands of ligands on the spectroscopy of transition metal complexes [1], we have prepared a series of copper(II) complexes with ligands derived from the Schiff base reaction of 2-pyridinecarboxaldehyde or 6-methyl-2-pyridinecarboxaldehyde and various aliphatic amines [2]. These imine complexes are structurally similar to some dicopper(II) complexes which have interesting optical and magnetic properties [3]. The complexes, differing only in steric bulk, are a systematic method of studying the effects of the steric bulk of the ligand on the spectroscopy of the copper(II) complex.

The required ligands are prepared by refluxing the appropriate amine and aldehyde in benzene until the calculated amount of water is removed by azeotropic distillation. The remaining benzene is removed at 30 °C under reduced pressure. The resulting imines appeared as oils which solidified upon storage in the freezer. The imines were converted to the copper(II) complexes without further purification or isolation. The identity of the imines was, however, verified by infrared spectroscopy and proton NMR.

The complexes bis(2-pyridyl-*N*-isopropylmethylimine)copper(II) perchlorate (ipro-PY), bis(6-methyl-2-pyridyl-*N*-isopropylmethylimine)copper(II) perchlorate (ipro-MPY), bis(2-pyridyl-*N*-sec-butylmethylimine)copper(II) perchlorate (sbu-PY), bis(6-methyl-2-pyridyl-*N*-sec-butylmethylimine)copper(II) perchlorate (sbu-MPY), bis(2-pyridyl-*N*-tert-butylmethylimine)copper(II) perchlorate (tbu-PY), bis(6-methyl-2-pyridyl-*N*-tert-butylmethylimine(copper(II) perchlorate (tbu-MPY), bis(2-pyridyl-*N*-cyclohexylmethylimine)copper(II) perchlorate (cyhx-PY) and bis(6-methyl-2-pyridyl-*N*-cyclohexylmethylimine)copper(II) perchlorate (cyhx-MPY) have been prepared. All complexes were prepared by slow addition of the imine (35 mmol) to a warm methanolic solution of copper(II) perchlorate hexahydrate (6.25 g, 17 mmol) and 15 g lithium perchlorate. Slow evaporation of the methanol at room temperature yielded the complex either as a solid or as a viscous oil. Redissolving the complex in hot methanol, followed by slow cooling yielded the solid product. The complexes were filtered, washed with a small amount of cold methanol and ethylether and dried under vacuum at 56 °C.

Vibrational spectra were measured as nujol mulls between KBr plates (4000–400 cm$^{-1}$) or between polyethylene sheets (600–200 cm$^{-1}$). KBr pellets were not used since KBr has the potential for reacting with the complex under high pressure, displacing the imine resulting in formation of the tetrabromocuprate ion as indicated by the vibrational spectrum [4]. The absence of OH stretching vibrations between 3500 and 3200 cm$^{-1}$ precludes the presence of coordinated methanol or water. The vibrational spectra of these complexes contained a large number of bands similar in energy to those in the free ligand. Vibrational bands which appear in the complex but not in the free ligand included those at 1675 and 500 cm$^{-1}$ which must be due to the presence of copper. A strong band at 1100 cm$^{-1}$ is indicative of the ionic nature of the perchlorate in these complexes. Vibrational bands at 900 cm$^{-1}$, indicative of coordinated perchlorate ions, were not present further supporting our assertion that the perchlorates are present as the free ions [5]. An unambiguous assignment of the remaining vibrational bands is beyond the scope of this work.

The electronic spectra of all complexes were measured in acetonitrile solution and the data are shown in Table I. The electronic spectrum of each complex had broad absorption bands in both the ultraviolet and visible regions of the spectrum. Complexes with ligands derived from 2-pyridinecarboxaldehyde all showed an absorption between 660 and 680 nm due to the d–d transitions at the copper(II) center [5]. Complexes with ligands derived from 6-methyl-2-pyridinecarboxaldehyde all showed similar absorption maxima between 700 and 720 nm. Several of these complexes indicated the possibility

TABLE I. Electronic Spectral Data for Copper(II) Complexes with Schiff Base Ligands in Acetonitrile Solution

| Complex | Absorption maximum (nm) | $\epsilon$ (l mol$^{-1}$ cm$^{-1}$) |
|---|---|---|
| ipro-PY | 668 | 84 |
| ipro-MPY | 714 | 80 |
| sbu-PY | 678 | 81 |
| sbu-MPY | 717 | 86 |
| tbu-PY | 666 | 73 |
| tbu-MPY | 715 | 78 |
| cyhx-PY | 665 | 140 |
| cyhx-MPY | 736 | 92 |

---

*Author to whom correspondence should be addressed.

0020-1693/87/$3.50

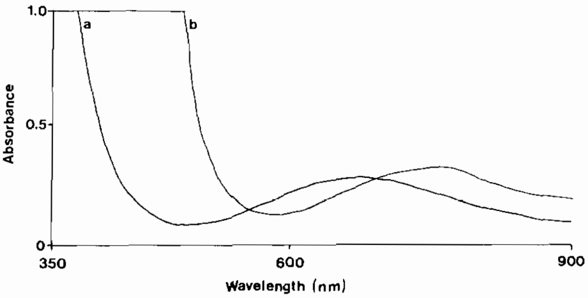

Fig. 1. Electronic spectrum of (a) bis(2-pyridyl-*N*-tert-butylmethylimine)copper(II) perchlorate, (b) bis(6-methyl-2-pyridyl-*N*-tert-butylmethylimine)copper(II) perchlorate.

of a second absorption at lower energy, possiblity due to a second allowed transition or vibronic coupling [6]. A comparison of the electronic spectrum of the complexes tbu-PY and tbu-MPY is shown in Fig. 1. The shift of the d–d absorption band to lower energy is indicative of increased distortion at the metal center caused by the steric demands of the ligand [7]. Other absorption bands which appear near 480 nm in the electronic spectra of these complexes are probably charge transfer in nature [5]. Several other bands were observed in the ultraviolet region of the spectrum. These bands are probably due to a combination of charge transfer and ligand transitions [5]. The energy and molar absorptivity of visible and ultraviolet absorption bands are observed to be solvent dependent. The detailed study of the solvent dependence will be conducted.

The complexes prepared in this study illustrate the importance of steric bulk on the spectroscopy of metal complexes. It was found that a methyl group attached on the [α] position of the pyridine ring has a substantial effect on the electronic spectrum. Substitution on the imine nitrogen appears to be much less important. The above observations may be due to the rigidity of the pyridine ring acting as an additional constraint, or may arise from the narrow range of groups which were substituted on the imine nitrogen atom.

## References

1 G. R. Brubaker and D. W. Johnson, *Inorg. Chem., 23,* 1591 (1984); D. W. Johnson and G. R. Brubaker, *Inorg. Chim. Acta, 119,* 131 (1986).

2 J. March, 'Advanced Organic Chemistry: Reactions, Mechanisms and Structure', 2nd edn., McGraw-Hill, New York, 1977, pp. 816–819.

3 L. K. Thompson, A. W. Hanson and B. S. Ramaswamy, *Inorg. Chem., 23,* 2459 (1984); L. K. Thompson, T. C. Woon, D. B. Murphy, E. J. Gabe, F. L. Lee and Y. LePage, *Inorg. Chem., 24,* 4719 (1985).

4 K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds', 3rd edn., Wiley, New York, 1978.

5 P. Sharma and G. S. Vigie, *Inorg. Chim. Acta, 88,* 29 (1984); D. E. Billing and A. E. Underhill, *J. Inorg. Nucl. Chem., 30,* 2147 (1968).

6 L. Griffiths, B. Straughan and D. J. Gardiner, *J. Chem. Soc., Dalton Trans.,* 305 (1983).

7 G. R. Brubaker, J. N. Brown, M. K. Yoo, R. A. Kinsey, T. M. Kutchan and E. A. Mottel, *Inorg. Chem., 18,* 299 (1979); T. E. Jones, L. L. Zimmer, L. L. Diaddario, D. B. Rorabacher and L. A. Ochrymowycz, *J. Am. Chem. Soc., 97,* 7163 (1975).