

Synthesis of Copper(I) Complexes with Novel N₃S-type Ligands

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Background. It is known that some copper(I) complexes with N₃S-type ligands react with CO₂ in solution to form reduction products of CO₂.^{1,2} However, the structure and dynamic behavior of these copper(I) complexes in solutions are not well understood yet. In this study, we synthesized novel N₃S-type ligands and copper(I) complexes as shown in Fig. 1, and analyzed their structures using ¹H and ¹³C NMR spectroscopy.

Synthesis. Ligands were synthesized by the reaction of 2-(4-*tert*-butylphenylthio) ethylamine with pyridine derivatives and potassium carbonate in acetonitrile for 5 days at 40°C under argon gas flow. Copper(I) complexes were synthesized by stirring the ligands and tetrakis(acetonitrile)copper(I) tetrafluoroborate in acetonitrile for 12 hours under nitrogen atmosphere.

NMR Analysis. The ¹H NMR and ¹³C NMR spectra of the synthesized ligands and complexes were measured. In both ¹H NMR and ¹³C NMR spectra, some signals were broadened in the copper(I) complex. In the ¹H NMR spectra of the synthesized copper(I) complexes, the signals originating from the protons of the pyridine ring of the ligands were only observed as a triplet at around 7.8 ppm for L, and as a doublet at around 7.7 ppm for L". The corresponding signal was broadened for L'. From these results, we concluded that only the proton at position 4 of the pyridine ring was observed in Cu(I)L and Cu(I)L", while the others were broadened. Similar broadening was observed in the ¹³C NMR spectra. It was suggested that the synthesized copper(I) complexes exhibit a dynamic behavior in which the pyridine ring moves around an axis containing Cu, N(pyridine), and C4(pyridine).

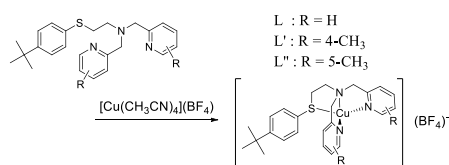


Fig. 2 Synthesis of Cu(I) complexes.

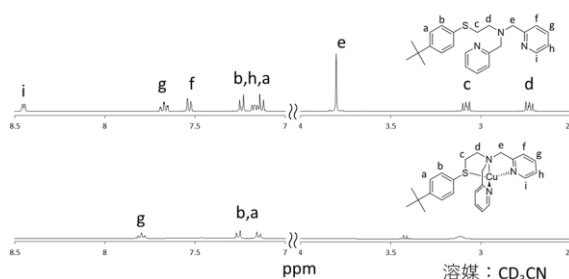


Fig. 1 Comparison of the spectra of L and Cu(I)L.

1) Angamuthu, et al., *Science*, **2010**, 327, 313-315. 2) Dharmalingam S. et al., *J. Ind. Eng. Chem.*, **2020**, 83, 271-278.