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Chloroacetylation or Bromoacetylation on the Methine Carbon of an Asymmetrical Quadridentate Schiff Base Copper(II) Complex

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Abstract

Chloroacetylation or bromoacetylation on the methine carbon of the title complex was performed, in the absence of a catalyst with chloroacetyl chloride or bromoacetyl bromide respectively. The compounds obtained were confirmed by means of electronic and IR spectra, as well as elemental analyses.

The fact that electrophilic substitutions occurred on the chelate ring of the complex might demonstrate a quasiaromaticity of the ring.

Introduction

The nature of the bonding in β-diketone metal complexes has been the subject of considerable controversy. A π-bonding between ligands and the metal ion in the complexes was once proposed [1–3]. However, an aromaticity of the chelate ring was suspected on the basis of electronic spectral and ^{1}H NMR data [4]. Collman and his coworkers subsequently proposed the aromatic character of the chelate ring on the basis of replacement studies of methine protons of the complexes by electrophiles such as bromine, iodine, *N*-halogenosuccinimide, nitro derivatives and sulfur [5]. Because Friedel and Crafts acetylation is one of the best-known aromatic reactions, Collman *et al.* also attempted to carry out the acetylation of tris(2,4-pentanedionato)chromium(III) with acetic anhydride and boron trifluoride etherate in dichloromethane [6].

In this paper, we report a chloroacetylation or bromoacetylation on the methine carbon of the tetradentate Schiff base copper(II) complex to investigate the aromatic character of the chelate ring containing both nitrogen and oxygen atoms (Fig. 1).

Experimental

Syntheses

[*N*-(1-Methyl-3-oxobutylidene)-*N*′-salicylidene-ethylenediaminato]copper(II), CuLH, was prepared according to the procedure of Kusuka *et al.* [7].

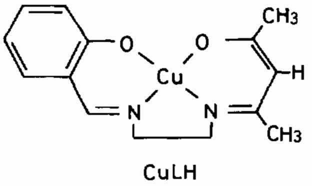

Fig. 1. Abbreviation of the copper(II) Schiff base complex.

Chloroacetylation

The dichloromethane solution (10 ml) of chloroacetyl chloride (0.6 ml, 7.7 mmol) was added dropwise to 300 ml of the dichloromethane solution of CuLH (2.0 g, 6.5 mmol) and pyridine (2.6 ml, 32 mmol), and then the mixture solution was stirred at room temperature for several minutes. After the solution was concentrated to *ca.* 20 ml under a reduced pressure, it was chromatographed on silica gel. Using dichloromethane as an eluent, the non-reacted CuLH complex was first eluted out, followed by unknown greenish compounds. The purple–blue $CuLCOCH_2Cl$ complex was then obtained by further elution with a mixed solvent of ethanol and dichloromethane (1:9). *Anal.* Found: C, 45.38; H, 4.45; N, 6.40. Calc. for $C_{16}H_{17}N_2O_3ClCu\cdot 0.7CH_2Cl_2$: C, 45.20; H, 4.19; N, 6.31%. Electronic spectra (chloroform): λ_{max} 325sh, 390sh and 562 nm. IR spectra: ν(CO) 1734 and 1798 cm^{-1}.

Bromoacetylation

The benzene solution (10 ml) of 0.6 ml (7.7 mmol) bromoacetyl bromide was added to 400 ml of the benzene solution containing 2.0 g (6.5 mmol) CuLH and 7.7 ml (32 mmol) n-tributylamine, and then the mixture was stirred at room temperature for 3 h. The precipitates were then obtained by adding an adequate amount of hexane to the solution. The objective compound was purified by reprecipitation from the mixed solvent of chloroform and hexane. *Anal.* Found: C, 37.28; H, 3.62; N, 4.92. Calc. for $C_{16}H_{17}N_2O_3BrCu\cdot CHCl_3$: C, 37.25; H, 3.32; N, 5.11%. Electronic spectra (chloroform): λ_{max} 325, 370, 390sh and 562 nm. IR spectra: ν(CO) 1755 cm^{-1}.

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Measurements

The electronic spectra in solution and the infrared spectra (KBr pellets) were measured on a Hitachi 200-20 spectrophotometer and a Hitachi 260-50 spectrophotometer, respectively. The elemental analyses were carried out by means of a Yanagimoto MT2 CHN recorder.

Results and Discussion

In electronic spectra, the d–d absorption bands of the copper(II) complexes are subjected to little effects of the chloroacetylation or bromoacetylation reaction: the substituent groups on the methine carbon are known to exercise large effects on the bands in the nickel(II) complexes, but small effects in the copper(II) complexes [8]. On the contrary, the π–π^* absorption bands of the $CuLCOCH_2Cl$ (λ_{max}: 380 nm) and $CuLCOCH_2Br$ (382 nm) derivatives are slightly shifted to the shorter wavelengths compared with that of the CuLH complex (387 nm), probably due to the electron-withdrawing effect of the substituents. In IR spectra, the copper(II) derivatives indicate new bands in the region of 1700–1800 cm^{-1}, arising from C=O stretching vibrations, which confirms the chloroacetyl or bromoacetyl group in the derivatives. The catalyst such as aluminum trichloride or boron trifluoride was employed in the acetylation replacement of the methine protons of the tris(2,4-pentanedionato)-chromium(III) complex [6], whereas the chloroacylation or bromoacylation reaction could be carried out without the catalyst. The electron-withdrawing effect of a halogen in the electrophile might facilitate the generation of its carbon cation promoting the replacement reaction. The fact that the electrophilic substitution occurred on the methine carbon might demonstrate the quasiaromaticity in the chelate ring of the Schiff base copper(II) complex. Further studies using different methods will confirm if the ring in the Schiff base complex has the aromatic character.

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