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Study of the Reaction Mechanism of Asymmetrical Quadridentate Schiff-base Complexes of Nickel(II) with N-bromosuccinimide

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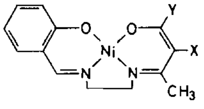
Abstract

In the ring-substitution reaction of [N-(1-methyl-3-oxo-3-phenylpropylidene)-N′-salicylideneethylenediaminato] nickel(II) with N-bromosuccinimide, it was spectrophotometrically confirmed that the bromination occurred first, followed by the succinimido substitution, where N-bromosuccinimide acted as both an electrophile and a nucleophile.

Introduction

The synthetic aspects of electrophilic ring-substitution reactions of metal complexes with β-diketone or quadridentate Schiff-base have been widely investigated [1–3]. Recently, kinetic studies have also been reported to elucidate the reaction mechanism [4]. Further nucleophilic conversions of the halogen-substituted derivatives were carried out with nucleophiles such as benzenethiol, its derivatives and thioglicollic ethyl ester [5–7]. Previously, we reported that both bromo and succinimido substitutions on methine carbons of N,N′-bis(1-methyl-3-oxo-3-phenylpropylideneethylenediaminato)nickel(II) or -copper(II) were carried out by the addition of N-bromosuccinimide (NBS) to the complex [8]. Three products were simultaneously obtained: dibromo-; bromo- and succinimido-; and disuccinimido-derivatives. A few reaction pathways might be possible for this ambiguous reaction. To elucidate the mechanism, we kinetically studied the substitution reaction using asymmetrical quadridentate Schiff-base complexes of nickel(II) which have only one methine carbon in the chelate ring (Fig. 1).



Ni(L-X,Y)

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

Experimental

Syntheses

[N-(1-methyl-3-oxobutylidene)-N′-salicylideneethylenediaminato] nickel(II); Ni(L-H, CH_3), [N-(1-methyl-3-oxo-3-phenylpropyridene)-N′-salicylideneethylenediaminato] nickel(II); Ni(L-H, C_6H_5), and [N-(2-chloro-1-methyl-3-oxo-3-phenylpropylidene)-N′-salicylideneethylenediaminato] nickel(II); Ni(L-Cl, C_6H_5) were prepared by the method reported before [4]. [N-(2-bromo-1-methyl-3-oxo-3-phenylpropylidene)-N′-salicylideneethylenediaminato] nickel(II); Ni(L-Br, C_6H_5) and [N-(1-methyl-3-oxo-3-phenyl-2-succinimidopropylidene)-N′-salicylideneethylenediaminato] nickel(II); Ni(L-$NC_4H_4O_2$,C_6H_5) were prepared as follows. 0.80 g (4.5 mmol) NBS was added to 40 cm^3 of the dichloromethane solution of 1.1 g (3.0 mmol) Ni(L-H, C_6H_5), which was subsequently left standing with stirring below -0.5 °C for 20 min. After the solution was concentrated to *ca.* 10 cm^3 under a reduced pressure, it was chromatographed on alumina. The bromo derivative was eluted with dichloromethane, followed by the succinimido derivative with a small amount of acetone in dichloromethane. The eluent containing the bromo derivative was concentrated under reduced pressure, and then the precipitates were obtained by an adequate amount of methanol (yield, 49%). *Anal.* Found: C, 51.48; H, 4.10; N, 6.52. Calcd. for $C_{19}H_{17}N_2O_2BrNi$: C, 51.39, H, 3.87; N, 6.31%. ^1H NMR ($CDCl_3$ solution): $\delta = 2.48$ (s, 3H, methyl), 3.50–3.83 (m, 4H, ethylene), 7.49–8.33 (m, 10H, aromatic and azomethine) ppm. Absorption spectra (dichloromethane solution): λ max (log ϵ) 303(4.05), 399 (3.75), 452^{sh}(3.37) and 563(2.86) nm. The succinimido derivative was obtained in a similar manner (yield, 16%). *Anal.* Found: C, 59.93; H, 4.21; N, 9.21. Calc. for $C_{23}H_2N_3O_4Ni$: C, 59.77; H, 4.59; N, 9.09%. ^1H NMR ($CDCl_3$ solution): 1.96 (s, 3H, methyl), 2.33–3.00 (m, 4H, ethylene), 3.50–3.83 (m, 4H, ethylene) and 7.16–8.33 (m, 10H, aromatic and azomethine) ppm. Absorption spectra (dichloromethane solution): 320(3.88), 388(3.62), 410^{sh}

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(3.57), 450^{sh}(3.28) and 558(2.77) nm. IR (KBr pellet): ν(CO) = 1695 cm^{-1}.

Measurements

Guaranteed grade dichloromethane was used for absorption spectral measurements without further purification. NBS and N-chlorosuccinimide (NCS) were recrystallized from ethanol and were dried under reduced pressure. The ^{1}H NMR spectra were recorded with a JEOL-MH 100 spectrophotometer at a frequency of 100 MHz. The chemical shifts were determined in ppm, using TMS as the internal standard. The electronic spectra in solution and the infrared spectra (KBr pellets) were measured on a Hitachi 124 spectrophotometer and a Hitachi 215 spectrophotometer, respectively.

Results and Discussion

By the addition of NBS to the dichloromethane solution of Ni(L-H,C_6H_5), both the bromo and succinimido derivatives, Ni(L-Br, C_6H_5) and Ni(L-$NC_4H_4O_2$,C_6H_5), were obtained. Each derivative shows no ^{1}H NMR signal for the methine proton in the parent complex, Ni(L-H,C_6H_5), indicating the replacement of the methine proton with the substituents. In the succinimido derivative, new signals for ethylene protons in the succinimido group appear at 2.33–3.00 ppm. The methyl signal of the bromo derivative (2.48 ppm) is shifted to a lower magnetic field than that of the parent complex (2.05 ppm) due to a large electronegativity of a bromine atom. On the other hand, the methyl signal of the succinimido derivative (1.96 ppm) is almost the same as that of the parent complex, in spite of the strong electron attraction of the carbonyl groups of the substituent. This may be responsible for the magnetic anisotropy effect; the plane of the imido group is perpendicular to the chelate ring so that the effect shifts the signal to a higher magnetic field [9]. An infrared spectrum of the succinimido derivative shows the strong band arising from the carbonyl groups at 1695 cm^{-1}. The complexes show d–d absorption bands characteristic of a square planner nickel(II) complex at 550–570 nm, and also π–π* and charge transfer bands at 300–460 nm.

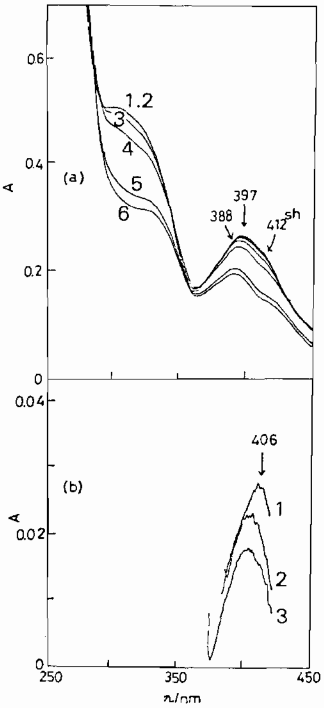
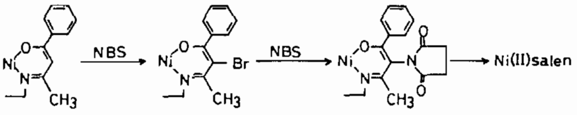


Fig. 2. Spectral changes during the reaction of Ni(L-H,C_6H_5) with NBS in the dichloromethane solution at 20 ℃; (a) [Ni-(L-H,C_6H_5)] = 3.00×10^{-5} mol dm^{-3}, [NBS] = 1.20×10^{-4} mol dm^{-3}: (1) 15 s, (2) 1 min 15 s, (3) 4 min 15 s, (4) 11 min, (5) 60 min, and (6) 90 min, after the reaction. (b) [Ni(L-H,C_6H_5)] = 2.70×10^{-6} mol dm^{-3}, [NBS] = 2.70×10^{-6} mol dm^{-3}: (1) 10 s, (2) 15 s and (3) 60 s, after the reaction.



Scheme 1.

The spectral change of the dichloromethane solution of Ni(L-H,C_6H_5) by the addition of NBS is shown in Fig. 2. The peak of Ni(L-H,C_6H_5), at 406 nm was rapidly shifted to 399 nm, which was subsequently shifted to 388 nm with the appearance of a shoulder at 410 nm; isosbestic points were found at 342 and 358 nm. Then, the intensity of the spectrum was gradually decreased as a whole, and the isosbestic points disappeared. Namely, by the addition of NBS, the Ni(L-H,C_6H_5) complex (λ max = 306 and 406 nm) was converted to the bromo derivative (303 and 399 nm), followed by the conversion to the succinimido derivative (320, 388 and 410^{sh} nm). Finally, the succinimido derivative might be slowly decomposed to N,N′-disalicylideneethylenediaminatonickel(II), Ni(II)salen (329 and 413 nm). While the peak of Ni(L-Br,C_6H_5) at 399 nm was shifted to 388 nm with NBS, the spectrum was not changed with succinimide. Therefore, the reaction might proceed as in Scheme 1. Furthermore, by the addition of NBS to the Ni(L-H,CH_3) solution, the spectrum changed to that of the bromo derivative, but the succinimido derivative could not be detected due to its slow formation. This may be due to the fact that the methyl group increases in electron density on the chelate ring, resulting in the depression of the nucleophilic substitution. By the addition of NCS to the dichoromethane solution of Ni(L-H,

C_6H_5), only chlorination occurred. Polarizability of the halogen atom on the methine carbon takes an important role in the nucleophilic substitution; e.g., the reaction of Ni(L-Cl,CH_3) with *p*-nitrophenylthiol was so slow that the rate constant could not be obtained [4]. Consequently, in the ring-substitution reaction of the Ni(L-H,C_6H_5) complex with NBS, the bromination occurred first; then the bromo derivative was attacked by NBS, not by succinimide, resulting in the succinimide derivative. This leads to the conclusion that NBS acts as the nucleophile as well as the electrophile, a result which has been considered previously [3, 10]. The preparation of the succinimido derivative was attempted by the addition of NBS to the dichloromethane solution of the Ni(L-Br,C_6H_5) complex, but it could not be isolated due to its decomposition to the salen complex.

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