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The Halogenation of the *N,N'*-Ethylenebis(5,5,5-trifluoro-4-oxo-2-pentaniminato)nickel(II) Complex and the Reaction Intermediate

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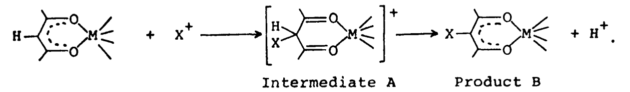
Synopsis. [Ni(tfac$_2$en)] reacted with NXS (*N*-chloro- or *N*-bromosuccinimide) in an alcoholic solvent to give the halogenated complexes at the γ-carbon atoms. The reaction intermediate was successfully isolated and was characterized by the use of the ^{1}H-NMR, IR, and AB spectra.

It is well known that the γ-protons of metal β-diketonates[1)] and their Schiff-base derivatives[2,3)] can be replaced by halogen atoms by the use of NXS. These halogenations have been regarded as examples of the electrophilic substitution reaction of the γ-protons with X$^+$, and the following reaction mechanism has been proposed:[1)]



However, there have been few detailed studies of the reaction mechanism.[4,5)]

In the course of our study[6)] for the halogenation of Ni(II) complexes of *N,N'*-ethylenebis(β-oxo imine) in an alcoholic solvent, we found that the titled complex, abbreviated as [Ni(tfac$_2$en)],[7)] gives a pretty stable reaction intermediate.

Experimental

Chlorination. A methanol solution (100 cm^3) of NCS (1.3 g) was added to a slurry of [Ni(tfac$_2$en)][8)] (1.0 g) in methanol (200 cm^3). The mixture was stirred for 10 min at 35 °C to give a homogenious red solution. It was then concentrated to about 30 cm^3 under reduced pressure below 35 °C. When the solution was allowed to stand for 1 h, red crystals were separated out, and were washed with cold methanol. Yield, about 21%. Found: C, 32.04; H, 3.48; N, 5.48%. Calcd for $NiC_{14}H_{18}N_2O_4F_6Cl_2$: C, 32.21, H, 3.48; N, 5.37%. (Complex I).

On the other hand, the red solution obtained above was heated on a water bath for 30 min and then concentrated to about 100 cm^3. When water was added to the solution, a light-green precipitate was separated out. It was subsequently recrystallized from methanol. Yield, about 40%. Found: C, 31.48; H, 2.39; N, 6.24%. Calcd for $NiC_{12}H_{10}N_2O_2F_6Cl_2$: C, 31.48; H, 2.21; N, 6.12%. (Complex II).

When Complex I was allowed to stand in the atomosphere, it gradually decomposed to [Ni(tfac$_2$en)] in the solid state. When water was added to a methanol or DMSO solution of Complex I, it decomposed rapidly to give [Ni(tfac$_2$en)]. However, when the methanol solution of Complex I was heated at about 90 °C, it decomposed to form Complex II.

Bromination. The brominated complexes were obtained by using NBS by a method similar to that for the chloronation. From the red reaction mixture, reddish crystals were separated out in about a 30% yeild. Found: C, 27.38; H, 2.79; N, 4.66%. Calcd for $NiC_{14}H_{18}N_2O_4F_6Br_2$: C, 27.53; H, 2.98; N, 4.59%. (Complex III). When ethanol was used as the solvent, reddish crystals were obtained in about a 60% yield. Found: C, 29.91; H, 3.27; N, 4.52%. Calcd for $NiC_{16}H_{22}N_2O_4F_6Br_2$: C, 30.08; H, 3.48; N, 4.39%. (Complex IV).

When the red reaction mixture was treated by a method similar to that employed for the red solution with NCS, light-green crystals were obtained in about a 80% yield. Found: C, 26.53; H, 1.95; N, 5.33%. Calcd for $NiC_{12}H_{10}N_2O_2F_6Br_2$: C, 26.36; H, 1.95; N, 5.31%. (Complex V).

Results and Discussion

The characterization data are listed in Table 1. It is well known that *N,N'*-ethylenebis(β-oxo iminato)-nickel(II) complexes are diamagnetic and take a square planar structure. Since Complexes II and V are also diamagnetic and show AB spectra similar to that of [Ni(tfac$_2$en)], it is evident that Complexes II and V take the planar structure. In the ^{1}H-NMR spectra of Complexes II and V, no signal which corresponds to the γ-proton is observed. Accordingly, it is clear that they are the halogen-substituted complexes at the γ-carbon atoms. The two strong IR bands at 1500—1600 cm^{-1} for [Ni(tfac$_2$en)] shift to a somewhat lower energy site in Complexes II and V.

Further, the π-π^* transitions at 26.3—28.0 kcm^{-1} for [Ni(tfac$_2$en)] also shift to a somewhat lower energy site in the halogenated complexes II and V. These lower energy shifts of the IR and AB spectra are characteristic of the halogenated complexes at the γ-carbon atom.[1,3,4,9)]

Complexes I, III, and IV are also diamagnetic and show the d-d transitions at about 20.8 kcm^{-1} which is characteristic of the square planar Ni(II) complexes. In their ^{1}H-NMR spectra, the signal of the γ-proton is observed at about 4.7 ppm; this position is at a somewhat higher field as compared with that of [Ni(tfac$_2$en)]. This higher field shift may be due to the saturation of the γ-carbon atom upon the addition of the halogen atom to it. Further, Complexes I, III, and IV exhibit the signals corresponding to methoxyl or ethoxyl groups. These groups are thought to be attached to the carbon atom, where the CF_3 group is bonded, and they may stabilize the halogenated intermediate like A. This is because it has been shown for the (trifluoroacetylacetonato)antimony(V)-complex that the complex reacts with water to give a complex in which the hydroxyl group is attached at the carbon atom, where the CF_3 group is bonded, and in which two protons are attached at the γ-carbon atom.[10)] The proposed structure for Complexes I, III, and IV is shown in Fig. 1. (Intermediate II). Complexes I, III, and IV exhibit a broad IR band at about 1660 cm^{-1} which can be assigned to the $\nu_{C=N}$ of the C=N group with no conjugation.[11)] The π-π^* transitions of these complexes are observed at a higher energy site than those of complexes II and V. This higher energy shift supports the idea that Complexes I, III, and IV take a structure in which the C=N groups do not conjugate with the other group, as is shown in Fig. 1.

Table 1. The characterization data

Complex	^{1}H-NMR spectra δ[a]			Others	IR[g]		AB spectra[h] $\tilde{\nu}$/kcm^{-1} (log ε)		
	γ-CH	CH$_2$–CH$_2$	CH$_3$		$\nu_{C=N}$/cm^{-1}	$\nu_{C=C}$/cm^{-1}	d-d	CT	π-π^*
[Ni(tfac$_2$en)][b]	5.49[2]	3.15[4]	2.02[6][d]		1619	1534	17.5(1.91)	21.7(2.34)	26.3(3.51)[i] 28.0(3.54)
I[c]	4.67[2]	3.5[e]	2.18[6]	3.84[6] (OCH$_3$)	1665		20.6(2.42)		29.7(3.06)[j]
II[b]		3.37[4]	2.36[6]		1584	1490	17.2(1.98)	22.2(2.83)	25.6(3.49)[i] 26.7(3.45)
III[c]	4.79[2]	3.5[e]	2.22[6]	3.92[6] (OCH$_3$)	1655		20.8(2.41)		28.6(3.38)[i]
IV[c]	4.81[2]	3.5[e]	2.29[6]	$\left.\begin{matrix}1.55\\1.43\\1.31\end{matrix}\right\}$ [6][f] (OCH$_2$C$\underline{H}_3$)	1660		20.8(2.48)		27.8(3.36)[k]
V[b]		3.36[4]	2.41[6]		1573	1488	17.4(2.06)	22.2(2.83)	25.6(3.51)[i] 26.9(3.47)

a) [ ] represents the number of protons. b) Data in CDCl$_3$. c) Data in DMSO-d_6. d) Ref. 12. e) Overlap with the peak of DMSO. f) Triplet; the OC$\underline{H}_2$CH$_3$ signal appears at 3.6—3.7 ppm. g) Ref. 13. h) Ref. 14. i) Data in CH$_3$OH. j) Data in DMSO. k) Data in acetone.

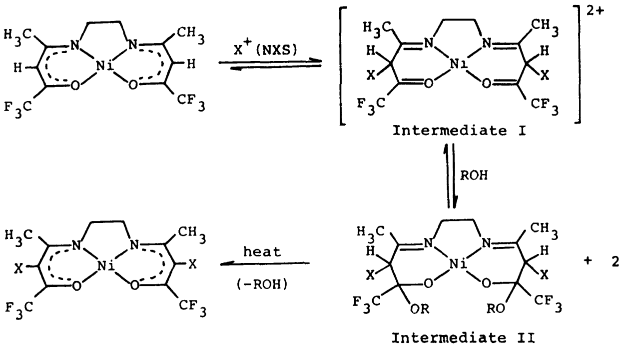


Fig. 1. The reaction scheme and the proposed structure of the reaction intermediate.

The proposed reaction mechanism is also shown in Fig. 1. Since the haloganation of [Ni(tfac$_2$en)] with NXS has also taken place in the presence of 2,6-di-*t*-butylphenol, a kind of radical scavenger, the reaction of NXS can be regarded as the electrophilic attack of the X$^+$ ion, which is formed by the ionic dissociation of NXS, on the γ-carbon atoms of [Ni(tfac$_2$en)]. Thus, in the first step of the reaction, Intermediate I in Fig. 1 should be formed. This Intermediate I has two positive charges. Further, the electron-withdrawing CF$_3$ group is attached. Therefore, the carbon atom, where CF$_3$ group is bonded, should be quite electron-deficient. Therefore, the attack of the alcoholic solvent may occur at the carbon atom to produce Intermediate II. As has been mentioned in the Experimental section, Complexes I, III, and IV decompose to give not only Complexes II or V but also [Ni(tfac$_2$en)]. This fact means that the reverse reaction from Intermediate II to [Ni(tfac$_2$en)] is possible. When water is added to the methanol solutions of Complexes II or IV, [Ni(tfac$_2$en)] is formed quite rapidly. Probably, in the presence of water, the elimination of alcohol from Intermediate II readily occurs upon the attack of the proton which is formed by the dissociation of water to give Intermediate I, and then [Ni(tfac$_2$en)].

The haloganation occurred also in a chloroform solvent. In that case, [Ni(tfac$_2$en)] (reddish brown) turned brown at the initial stage of the reaction, and then it turned to a brownish green with heating. The brown material could not be isolated well. However, when methanol was added to the brown solution, the solution turned to red, and reddish crystals, which correspond to Complex I, could be isolated from the solution. These facts suggest that the brown material may correspond to Intermediate I.

It should be noted that trifluoroacetylacetone, its metal complexes, and its Schiff base ligand itself are not halogenated by NXS.

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