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Cis–trans isomerism among the octahedral diaquabis(*N*-substituted ethylenediamine) nickel(II) complexes and their thermal reaction products: the mechanism of the thermal *trans*-diaqua-to-*cis*-dihalogeno configurational change

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Abstract

The thermochemical changes in the coordination structure of diaquabis(*N*-substituted ethylenediamine) nickel(II) complexes ($[Ni(H_2O)_2(diamine)_2]X_2$) were investigated by means of TG and DTA, and electronic spectroscopy, where diamine is *N*-methyl-(*N*-men), *N*-ethyl-(*N*-een), *N*-isopropyl-(*N*-ipen), *N*-phenyl-(*N*-phen), or *N*,*N*-di-*n*-butylethylenediamine(*NN*-dben), and X is Cl^- or Br^-. The diaqua complexes prepared were all trans. The trans complexes with *N*-mono-substituted ethylenediamines brought about a deaquation–anation on heating, retaining the original trans configurations. Only the complex chloride with *NN*-dben transformed into the *cis*-dichloro complex upon thermal dehydration. The mechanism of the trans-to-cis configurational change of the complex chloride with *NN*-dben was proposed, and the effects of *N*-substituent group(s) upon their thermal structural changes were discussed.

Keywords: Co-ordination; Isomer; Nickel compound; Stereochemistry

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1. Introduction

In the stereochemistry of octahedral diaqua- and dianionobis(diamine) nickel(II) complexes, the trans configuration is preferred, the cis configuration only being found in a few limited cases [1–4]. We have recently studied the coordination structures of many diaquabis(*N*- or *C*-substituted ethylenediamine) nickel(II) complexes and the products of their solid-phase thermal reactions, and the effects of *N*- or *C*-substituent group(s) upon their structural changes during the thermal treatment [5,6]. Our previous report [7] clarified the cis–trans isomerism among complexes containing *N,N*- or *N,N'*-dimethylethylenediamine (*NN*- or *NN'*-dmen) and *N,N*- or *N,N'*-diethylethylenediamine (*NN*- or *NN'*-deen) during thermal deaquation–anation, as shown below:

$$[\mathrm{Ni(H_2O)_2(diamine)_2}]\mathrm{X_2} \xrightarrow{-2\mathrm{H_2O}} [\mathrm{NiX_2(diamine)_2}] \qquad (\mathrm{X} = \mathrm{Cl^-}\ \text{or}\ \mathrm{Br^-})$$

The *trans*-diaqua complexes with symmetric (*N,N'*-dialkylated) diamines still retained the original trans configuration upon dehydration, while those with asymmetric (*N,N*-dialkylated) diamines peculiarly transformed into the *cis*-dihalogeno complexes.

In a continuation of these studies, the thermal reactions of the nickel(II) complexes containing five *N*-substituted ethylenediamines were investigated to clarify the details of cis–trans isomerism and the effects of *N*-substituents on the coordination structures of the diaqua and dihalogeno complexes.

2. Experimental

N-methyl-, *N*-ethyl-, *N*-isopropyl-, *N*-phenyl-, and *N,N*-di-*n*-butylethylenediamine (*N*-men, *N*-een, *N*-ipen, *N*-phen, and *NN*-dben, respectively) of commercial reagent grade were used without further purification. The standard procedure for preparing the diaqua complexes, $[\mathrm{Ni(H_2O)_2(diamine)_2}]\mathrm{X_2}$ (where X is $\mathrm{Cl^-}$ or $\mathrm{Br^-}$), is as follows. To an aqueous solution of $\mathrm{NiCl_2 \cdot 6H_2O}$ or $\mathrm{NiBr_2 \cdot 3H_2O}$, an ethanolic solution of the diamine was added dropwise in the molar ratio 1 : 1.5–2. The resulting solution was left to stand for several days to precipitate the desired complex. The violet or blue crystals deposited were collected by filtration, and washed with ethanol and diethyl ether [8]. A small amount of $\mathrm{NH_4Cl}$ or $\mathrm{NH_4Br}$ was added to the solution as necessary in order to increase the yield. In the reactions of *N*-men and *N*-ipen with $\mathrm{NiCl_2 \cdot 6H_2O}$, no diaqua complexes could be isolated and the anhydrous dichloro complexes, [NiCl$_2$(*N*-men)$_2$] [9] and [NiCl$_2$(*N*-ipen)$_2$] [10], were prepared instead. The other anhydrous complexes were obtained on isothermal heating of the corresponding diaqua complexes, by use of the thermal deaquation-anation reaction, at their formation temperatures (which were inferred from the results of the thermal analyses) in an electric furnace under static air [11].

The electronic spectra in the solid phase were measured by the diffuse reflectance method with a Hitachi 340 or U-3400 spectrophotometer equipped with a reflection

Table 1
Electronic spectral data and configurational assignments

Complex	Band maxima, $\tilde{\nu}$ in 10^3 cm^{-1}					Configuration
Diaqua complexes						
$[Ni(H_2O)_2(N\text{-men})_2]Br_2 \cdot 2H_2O$	9.2	12.5		17.9	28.4	Trans
$[Ni(H_2O)_2(N\text{-een})_2]Cl_2$	8.9	12.5	13.5	18.0	28.4	Trans
$[Ni(H_2O)_2(N\text{-een})_2]Br_2$	8.9	12.5	13.5	17.9	28.4	Trans
$[Ni(H_2O)_2(N\text{-ipen})_2]Br_2$	8.7	11.9		17.3	27.8	Trans
$[Ni(H_2O)_2(N\text{-phen})_2]Cl_2$ [a]	8.8	11.9		17.9		Trans
$[Ni(H_2O)_2(N\text{-phen})_2]Br_2$ [a]	8.8	12.0		17.9		Trans
$[Ni(H_2O)_2(NN\text{-dben})_2]Cl_2$	7.3	10.0		16.4	26.9	Trans
$[Ni(H_2O)_2(NN\text{-dben})_2]Br_2$	7.3	10.1		16.4	26.9	Trans
Anhydrous complexes						
$[NiCl_2(N\text{-men})_2]$	8.1	12.2sh	13.5	17.4	27.2	Trans
$[NiBr_2(N\text{-men})_2]$	7.3	11.9sh	13.5	17.3	27.2	Trans
$[NiCl_2(N\text{-een})_2]$	8.3	12.9	14.3	17.3	27.2	Trans
$[NiBr_2(N\text{-een})_2]$	7.4	11.6	13.5	16.7	26.6	Trans
$[NiCl_2(N\text{-ipen})_2]$	8.2	11.2		16.3	26.3	Trans
$[NiBr_2(N\text{-ipen})_2]$	7.7	11.1		16.3	26.1	Trans
$[NiCl_2(N\text{-phen})_2]$ [a]	8.8	11.2		16.9		Trans
$[NiBr_2(N\text{-phen})_2]$ [a]	7.6	11.1		16.7		Trans
$[NiCl_2(NN\text{-dben})_2]$	7.3		14.7		24.9	Cis
$[Ni(NN\text{-dben})_2]Br_2$					21.3	Square planar
cis-$[NiCl_2(NN\text{-deen})_2]$ [7]	8.5		14.9		25.5	
cis-$[NiCl_2(NN\text{-dmen})_2]$ [7]	9.4		15.9		26.3	

[a] The highest energy band is obscured by a charge transfer band.

attachment. Simultaneous TG/DTA measurements were carried out using Seiko SSC/580 TG/DTA-30 apparatus.

3. Results

3.1. Structures of $[Ni(H_2O)_2(diamine)_2]X_2$

Analyses of the configurations of the cis and trans isomers of the titled complexes by electronic spectroscopy have already been published [3,12]. In a tetragonal system (D_{4h}), six spin-allowed transitions are anticipated, of which four or sometimes five bands are observed in practice. In a C_{2v} system more transitions than for a D_{4h} system are possible, owing to a decrease in symmetry. However, the splittings of the respective terms are small; hence for the cis complex, three rather broad bands are observed as in the case of the regular O_h system.

Table 1 summarizes the electronic spectral data and the configurational assignments of the diaqua complexes. According to the above diagnosis, all the complexes are found to have trans configurations. In addition, the fact that the peak maxima

Table 2
Results of thermal analyses

Complex	Dehydration		Color	
	Temperature in °C	Mass loss in % (calc.)	Room temperature	After dehydration
trans-[Ni$(H_2O)_2$(*N*-men)$_2$]$Br_2 \cdot 2H_2O$	67–110	15.7 (16.4)	Violet	Violet
trans-[Ni$(H_2O)_2$(*N*-een)$_2$]Cl_2	70–95	10.3 (10.5)	Violet	Blue
trans-[Ni$(H_2O)_2$(*N*-een)$_2$]Br_2	38–66	8.1 (8.4)	Violet	Blue
trans-[Ni$(H_2O)_2$(*N*-ipen)$_2$]Br_2	42–82	7.2 (7.8)	Blue–violet	Blue
trans-[Ni$(H_2O)_2$(*N*-phen)$_2$]Cl_2	60–90	7.8 (8.2)	Violet	Blue
trans-[Ni$(H_2O)_2$(*N*-phen)$_2$]Br_2	RT–80	7.2 (6.8)	Violet	Green–blue
trans-[Ni$(H_2O)_2$(*NN*-dben)$_2$]Cl_2	67–93	6.9 (7.1)	Blue	Green
trans-[Ni$(H_2O)_2$(*NN*-dben)$_2$]Br_2	79–102	5.7 (6.0)	Blue	Yellow

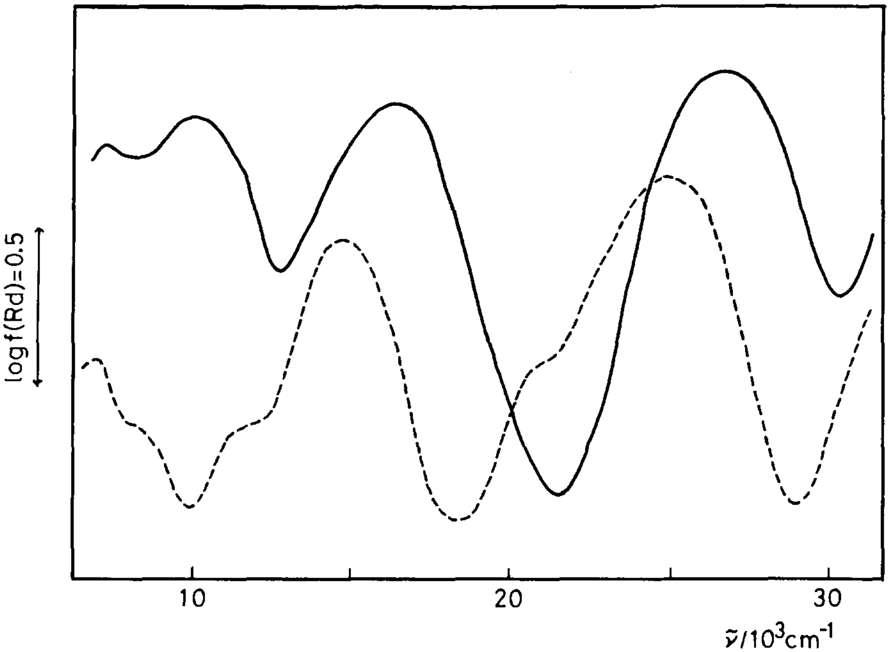


Fig. 1. Electronic spectra of *trans*-[Ni$(H_2O)_2$(*NN*-dben)$_2$]Cl_2 (——), and the anhydrous products obtained on heating the diaqua complex (– – –).

of the complexes with the same diamine are almost unchanged irrespective of the X^- ion yields the formulae *trans*-[Ni$(H_2O)_2$(diamine)$_2$]X_2 (where X is Cl^- or Br^-). Both *NN*-dben complexes, however, give rise to a red shift of all the bands in their spectra. This feature was also observed in the spectra of the corresponding

N,N-dimethylethylenediamine (*NN*-dmen) and *N,N*-diethylethylenediamine (*NN*-deen) complexes [7], showing that, because of the steric effect of the *N*-substituents [13,14], the overall ligand field strength becomes weak in the *NN*-dben complexes compared to the other *N*-mono-substituted diamine complexes.

3.2. Thermal reactions of the diaqua complexes

Table 2 summarizes the results of TG and DTA and the color changes upon dehydration of the diaqua complexes. All the diaqua complexes liberated their water molecules below 110°C with a color change, giving the stable anhydrous products. As indicated in Table 1, all the products, except for those of both the *NN*-dben complexes, show four or five bands in their electronic spectra, suggesting that the trans configurations are retained upon dehydration. In addition, a slight shift of the peak maxima takes place because of the replacement of axial ligands ($H_2O \rightarrow Cl^-$ or Br^-). It can thus be concluded that a simple deaquation–anation (*trans*-diaqua → *trans*-dihalogeno) occurs in the complexes.

Fig. 1 shows the electronic spectra of *trans*-$[Ni(H_2O)_2(NN\text{-dben})_2]Cl_2$ and the anhydrous product obtained on heating the diaqua complex. The spectral pattern of the product is significantly different from that of the mother complex, being characteristic of the cis octahedral configuration. Thus, this thermal reaction must proceed with a trans-to-cis configurational change during deaquation–anation. In a C_{2v} system, each broad band theoretically consists of three components, some of which are actually observed in the spectrum of *cis*-$[NiCl_2(NN\text{-dben})_2]$. The corresponding *NN*-deen complex, *cis*-$[NiCl_2(NN\text{-deen})_2]$, also showed such an appreciable separation of the components [7]. As shown in Table 1, in addition, all the bands gradually shift to the red region as the substituent groups become larger among the asymmetric diamine complexes ($CH_3 \rightarrow C_2H_5 \rightarrow C_4H_9$). This suggests that the overall ligand field strength becomes weaker in the above order. It is thus clear that the dominant factor affecting the coordination structures of the asymmetric diamine complexes is the steric hindrance of *NN*-di-substituents rather than their inductive effects. However, in the case of the complex bromide with *NN*-dben, the yellow anhydrous product displays a broad band at 21 300 cm^{-1} assignable to the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transition of a square planar structure [15]. A pronounced steric effect due to *n*-butyl groups on the diamine is observed in the thermal reactions of *NN*-dben complexes.

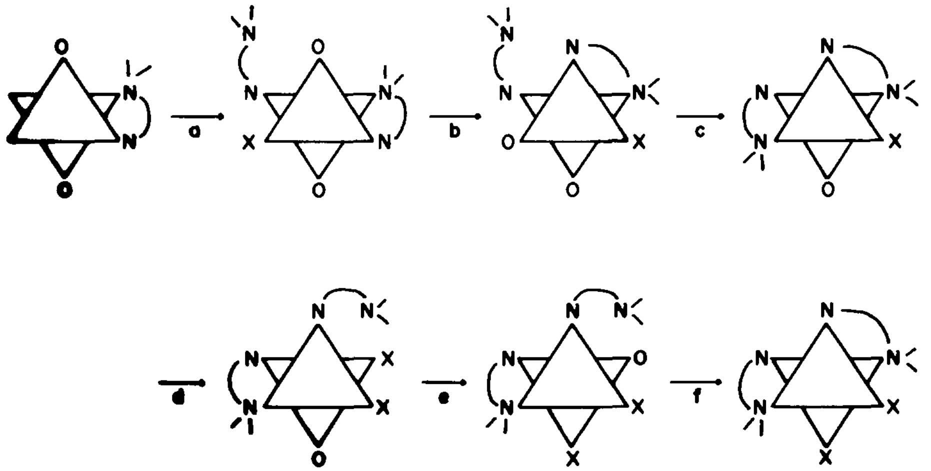
4. Discussion

Table 3 summarizes the thermal reaction pathways of the diaqua complexes along with those of the corresponding *NN*-dmen, *NN'*-dmen, *NN*-deen, and *NN'*-deen complexes. The complexes with *N*-mono-substituted and *N,N'*-di-substituted (symmetric) diamines undergo thermal dehydration–anation, during which their trans configurations are retained; the anation takes place at the axial positions that were occupied by water molecules before heating. In the asymmetric diamine

Table 3
Configurational changes of $[Ni(H_2O)_2(diamine)_2]X_2$ upon thermal dehydration

Diamine	*N*-substituent	X is Cl	X is Br
N-men	$-CH_3$	Trans [a]	Trans → trans
N-een	$-C_2H_5$	Trans → trans	Trans → trans
N-ipen	$-CH(CH_3)_2$	Trans [a]	Trans → trans
N-phen	$-C_6H_5$	Trans → trans	Trans → trans
NN'-dmen [7]	$-CH_3$, $-CH_3$	Trans → trans	Trans → trans
NN'-deen [7]	$-C_2H_5$, $-C_2H_5$	Trans → trans	Trans → trans
NN-dmen [7]	$\langle^{CH_3}_{CH_3}$	Trans → cis	Trans → cis
NN-deen [7]	$\langle^{C_2H_5}_{C_2H_5}$	Trans → cis	Trans → (SP)
NN-dben	$\langle^{C_4H_9}_{C_4H_9}$	Trans → cis	Trans → (SP)

The left- and right-hand-sides of the arrows correspond to the configurations of the diaqua and anhydrous complexes, respectively. SP indicates the formation of a square planar complex. [a] This was directly obtained from solution, since preparation of the corresponding diaqua complexes was difficult.



Scheme 1. a, d, bond rupture; b, e, twist; c, f, dehydration.

complexes, however, the *trans*-diaqua complexes are transformed into the *cis*-dihalogeno ones when the octahedral structures remain unchanged.

It has recently been found from the results of X-ray studies that, in *trans*-$[Ni(H_2O)_2(NN\text{-dmen})_2]Cl_2 \cdot 2H_2O$ and *trans*-$[Ni(H_2O)_2(NN\text{-deen})_2]Cl_2$, (i) the bonds between nickel(II) and alkylated nitrogen are much longer than the other bonds, (ii) the two alkylated nitrogen atoms occupy axial sites distant from each other to minimize their mutual steric hindrance and (iii) the two coordinated water molecules at the trans positions are crystallographically equivalent [16]. These facts seem to be important clues to the explanation of the mechanism of trans-to-cis configurational changes during dehydration–anation of the asymmetric diamine complexes. Moreover, it can be anticipated that the two alkylated nitrogen atoms will also occupy the axial sites in their thermal reaction products. To satisfy this steric requirement, the cleavage of at least one coordinated bond of the diamine chelate ring and a subsequent twist motion must take place, in addition to liberation of one coordinated water molecule, when a cis product is generated. The bond cleavage will naturally occur at the weakest Ni–N bond in the complex. Thus, it appears reasonable to assume that, in the case of the asymmetric diamine complexes, the rupture of a $Ni-N(alkyl)_2$ bond precedes liberation of a coordinated water molecule, providing a driving force for these reactions.

Under this assumption, a probable mechanism for the trans-to-cis configurational change of the asymmetric diamine complexes is illustrated in Scheme 1. The first step is the cleavage of a $Ni-N(alkyl)_2$ bond and anation which occurs at the evacuated coordination site to retain the octahedron (or, possibly, the formation of a seven-coordinated species). The pendant N atom now has a tendency to replace one of the coordinated water molecules; to do so without approaching another diamine ligand too closely, however, requires a rotation of 120° of the octahedron about its threefold axis. One water molecule is lost in this way, and a *cis*-halogenoaqua complex results. Repeating the process, with a rotation about another threefold axis, the remaining water is lost and a *cis*-dihalogeno complex is finally obtained [17]. In fact, *cis*-halogenoaqua species could be isolated as intermediates in the thermal reactions of both *NN*-dmen complexes [7]. However, the *NN*-dben and *NN*-deen complexes showed no formation of the halogenoaqua species in the course of the thermal reactions. This may be due to the effects of steric hindrance; the $Ni-N(C_4H_9)_2$ and $Ni-N(C_2H_5)_2$ bonds are expected to be cleaved with greater ease than the $Ni-N(CH_3)_2$ bonds because of the longer bond distances [16], making completion of the overall changes in Scheme 1 very quick for the former.

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[8] Analysis of the diaqua complexes gives the following data. Found: C, 16.16; H, 6.56; N, 12.67%. (Calculated for $[Ni(H_2O)_2(N\text{-men})_2]Br_2 \cdot 2H_2O$: C, 16.42; H, 6.43; N, 12.77%). Found: C, 27.99; H, 8.44; N, 16.30%. (Calculated for $[Ni(H_2O)_2(N\text{-een})_2]Cl_2$: C, 28.10; H, 8.25; N, 16.38%). Found: C, 22.26; H, 6.44; N, 13.16%. (Calculated for $[Ni(H_2O)_2(N\text{-een})_2]Br_2$: C, 22.30; H, 6.55; N, 13.00%). Found: C, 26.32; H, 7.11; N, 12.24%. (Calculated for $[Ni(H_2O)_2(N\text{-ipen})_2]Br_2$: C, 26.17; H, 7.03; N, 12.21%). Found: C, 43.96; H, 6.41; N, 12.83%. (Calculated for $[Ni(H_2O)_2(N\text{-phen})_2]Cl_2$: C, 43.87; H, 6.44; N, 12.79%). Found: C, 36.75; H, 5.38; N, 10.45%. (Calculated for $[Ni(H_2O)_2(N\text{-phen})_2]Br_2$: C, 36.47; H, 5.36; N, 10.63%). Found: C, 46.77; H, 10.60; N, 10.82%. (Calculated for $[Ni(H_2O)_2(NN\text{-dben})_2]Cl_2$: C, 47.08; H, 10.27; N, 10.98%). Found: C, 39.67; H, 8.95; N, 9.12%. (Calculated for $[Ni(H_2O)_2(NN\text{-dben})_2]Br_2$: C, 40.09; H, 8.75; N, 9.35%).

[9] In the reaction of *N*-men with $NiCl_2 \cdot 6H_2O$, the tris(diamine) complex was produced preferentially. Accordingly, to a solution containing the tris complex prepared in an appropriate solvent beforehand, a solution of a Ni salt was added so that the molar ratio (ligand/Ni) in the resulting solution became 1.5–2. The anhydrous bis(diamine) complex was obtained in this way. However, an attempt to prepare the diaqua complex always failed.

[10] It appears that $[Ni(H_2O)_2(N\text{-ipen})_2]Cl_2$ crystallizes in solution. However, the blue–violet crystals deposited immediately become blue at the time of filtration. The resulting blue crystals correspond to $[NiCl_2(N\text{-ipen})_2]$. This color change is the same as that of $[Ni(H_2O)_2(N\text{-ipen})_2]Br_2$ (blue–violet) → $[NiBr_2(N\text{-ipen})_2]$ (blue) due to thermal deaquation–anation. It is thus found that dehydration readily takes place for the complex chloride even at room temperature. The blue–violet complex could not be characterized because of the instability as stated above.

[11] Analysis of the anhydrous complexes gives the following data. Found: C, 25.59; H, 7.43; N, 19.91%. (Calculated for $[NiCl_2(N\text{-men})_2]$: C, 25.94; H, 7.25; N, 20.16%). Found: C, 19.30; H, 5.73; N, 15.16%. (Calculated for $[NiBr_2(N\text{-men})_2]$: C, 19.65; H, 5.50; N, 15.28%). Found: C, 30.94; H, 8.26; N, 17.88%. (Calculated for $[NiCl_2(N\text{-een})_2]$: C, 31.41; H, 7.91; N, 18.31%). Found: C, 24.11; H, 6.35; N, 13.90%. (Calculated for $[NiBr_2(N\text{-een})_2]$: C, 24.34; H, 6.13; N, 14.19%). Found: C, 35.44; H, 8.68; N, 16.52%. (Calculated for $[NiCl_2(N\text{-ipen})_2]$: C, 35.97; H, 8.45; N, 16.78%). Found: C, 28.18; H, 6.85; N, 13.19%. (Calculated for $[NiBr_2(N\text{-ipen})_2]$: C, 28.40; H, 6.67; N, 13.25%). Found: C, 47.10; H, 6.11; N, 13.80%. (Calculated for $[NiCl_2(N\text{-phen})_2]$: C, 47.81; H, 6.02; N, 13.94%). Found: C, 39.50; H, 4.90; N, 11.39%. (Calculated for $[NiBr_2(N\text{-phen})_2]$: C, 39.15; H, 4.93; N, 11.41%). Found: C, 50.41; H, 10.56; N, 11.66%. (Calculated for $[NiCl_2(NN\text{-dben})_2]$: C, 50.65; H, 10.20; N, 11.81%). Found: C, 42.05; H, 8.77; N, 9.80%. (Calculated for $[Ni(NN\text{-dben})_2]Br_2$: C, 42.66; H, 8.59; N, 9.95%).

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[17] The order of (b) and (c) (or (e) and (f)) is not important; the same product is obtained in either case.