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An attempt to prepare *cis*-dianionobis(diamine)nickel(II) complexes. Cis–trans isomerism among the dianionobis(diamine)nickel(II) complexes obtained by thermal reactions of the corresponding tris(diamine) complexes

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Abstract

Twenty-seven tris(diamine)nickel(II) complexes ([Ni(diamine)$_3$]X$_2$) were prepared and their thermal reactions were investigated in the solid phase, where the diamine is ethylenediamine(en), *N*-methylethylenediamine (*N*-men), *N*-ethylethylenediamine (*N*-een), 1,2-propanediamine (1,2-pn), 1,3-propanediamine (1,3-pn), 1,2-butanediamine (1,2-bn), D,L-2,3-butanediamine (D,L-bn), iso-butanediamine (i-bn), or D,L-1,2-cyclohexanediamine (D,L-chxn); and X is Cl^-, Br^-, or NO_3^-. Of these, twelve tris(diamine) complexes lost their one mole of coordinated diamine upon heating, resulting in the stable, uniform bis(diamine) complexes, [NiX$_2$(diamine)$_2$]. The configurations of the bis complexes were determined by means of electronic spectroscopy. Almost all the bis complexes have trans configurations; the formation of a *cis*-dianiono complex was observed only in the thermal reactions of [Ni(en)$_3$]Cl$_2$, [Ni(en)$_3$]Br$_2$, and [Ni(i-bn)$_3$]Cl$_2$.

INTRODUCTION

Many synthetic studies of diaqua- and dianionobis(diamine)nickel(II) complexes have indicated that the complexes commonly prefer a trans configuration; a cis configuration is found in only a few limited cases [1–4]. In addition, because either a trans or cis configuration is strongly stabilized for a particular combination of ligands, the isolation of both (trans and cis) isomers has not yet been reported. Among the alkyl-substituted diamine complexes, in particular, two effects due to the substituent groups on the diamines seem to influence the coordination structure of the complexes. One is their inductive effect, and the other is their steric hindrance.

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In a combination of ligands which is liable to form a *trans*-[NiX_2(diamine)$_2$] (where X is a univalent anion), a thermochemical reaction may be available for preparing the corresponding cis complex. The methods are (i) thermal deaquation-anation, (ii) thermal trans-to-cis isomerization, and (iii) thermal elimination of one mole of coordinated diamine from the tris(diamine) complex and a subsequent anation, respectively, i.e.

(i) *trans*- or *cis*-$[Ni(H_2O)_2(\text{diamine})_2]X_2 \xrightarrow{-2H_2O}$ *cis*-$[NiX_2(\text{diamine})_2]$
(ii) *trans*-$[NiX_2(\text{diamine})_2] \rightarrow$ *cis*-$[NiX_2(\text{diamine})_2]$
(iii) $[Ni(\text{diamine})_3]X_2 \xrightarrow{-\text{diamine}}$ *cis*-$[NiX_2(\text{diamine})_2]$

In this study, method (iii) applies to an attempt to prepare *cis*-[NiX_2(diamine)$_2$], where the diamine is ethylenediamine, *N*-methylethylenediamine, *N*-ethylethylenediamine, 1,2-propanediamine, 1,3-propanediamine, 1,2-butanediamine, D,L-2,3-butanediamine, iso-butanediamine, or D,L-1,2-cyclohexanediamine; and X is Cl^-, Br^-, or NO_3^-.

EXPERIMENTAL

Ethylenediamine (en), *N*-methylethylenediamine (*N*-men), *N*-ethylethylenediamine (*N*-een), 1,2-propanediamine (1,2-pn), 1,3-propanediamine (1,3-pn), and iso-butanediamine (i-bn) of commercial reagent grade were used without further purification. 1,2-Butanediamine (1,2-bn) [5, 6], D,L-2,3-butanediamine (D,L-bn) [7] and D,L-1,2-cyclohexanediamine (D,L-chxn) [8, 9] were prepared by the known methods. The tris(diamine)nickel(II) complexes, [Ni(diamine)$_3$]X_2 (X is Cl^-, Br^-, or NO_3^-), were obtained using the methods described in refs. 10 (en), 11 (*N*-men), 12 (*N*-een), 13 (1,2-pn), 14 (1,3-pn), 15 (1,2-bn), 16 (D,L-bn), 17 (i-bn), and 18 (D,L-chxn). The bis(diamine) complexes were obtained on isothermal heating of the corresponding tris complexes, by the elimination of one mole of diamine, at their formation temperatures (which were inferred from the results of the thermal analyses) in an electric furnace under static air.

Simultaneous TG–DTA measurements were carried out with a Seiko SSC/580 TG/DTA-30 apparatus. Each run was under a constant flow of nitrogen (200 ml min^{-1}) at a heating rate of 2.0°C min^{-1}; about 20–30 mg of sample was used. The electronic spectra in the solid phase were measured by the diffuse reflectance method with a Jasco UVIDEC-410 spectrophotometer equipped with a reflection attachment. For the spectra in the near-IR region, a Hitachi 340 spectrophotometer was used.

RESULTS AND DISCUSSION

Thermal analyses

Figure 1 shows the TG curves of [Ni(1,3-pn)$_3$]$(NO_3)_2$, [Ni(D,L-bn)$_3$]$Cl_2 \cdot H_2O$, and [Ni(en)$_3$]$(NO_3)_2$. The 1,3-pn complex loses one mole of

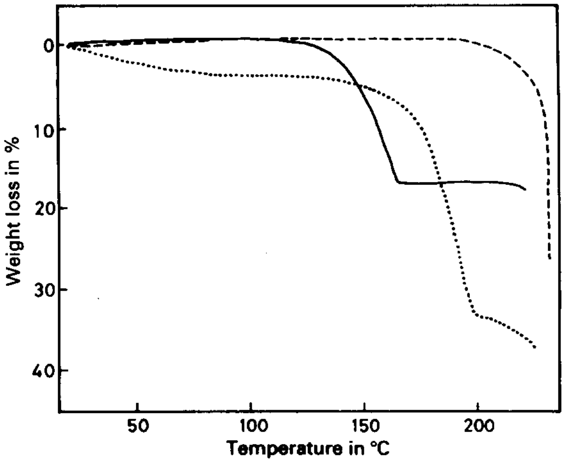

Fig. 1. TG curves of $[Ni(1,3\text{-pn})_3](NO_3)_2$ (——), $[Ni(\text{D,L-bn})_3]Cl_2 \cdot H_2O$ (···), and $[Ni(en)_3](NO_3)_2$ (– – –).

the coordinated diamine at 119–172°C, giving the stable bis(1,3-pn) complex (type A). The D,L-bn complex similarly loses one mole of the diamine at 131–205°C after dehydration below 100°C; however, it may be difficult to obtain a pure bis(D,L-bn) complex because a distinct plateau is not observed on the TG curve following liberation of the diamine (type B). The en complex decomposes at the same time as the liberation of diamine; no formation of the bis(en) complex could be observed (type C).

The TG curves of the 27 complexes studied could be classified into the above three types, the results of which are summarized in Table 1. Ten complexes belonging to type A yielded stable, uniform products of formulae $NiX_2(\text{diamine})_2$ (X is Cl^-, Br^-, or NO_3^-) on isothermal heating of the corresponding tris complexes, as expected from the nature of their TG curves. Among the six complexes of type B, $[Ni(1,3\text{-pn})_3]Cl_2$, $[Ni(\text{D,L-bn})_3]Cl_2$, and $[Ni(\text{D,L-chxn})_3]Cl_2$ also gave satisfactory bis(diamine) species. For the other 3 complexes of type B, however, the bis(diamine) complexes

TABLE 1

Classification of TG patterns of $[Ni(\text{diamine})_3]X_2$ [a]

Diamine	X is Cl^-	X is Br^-	X is NO_3^-	Diamine	X is Cl^-	X is Br^-	X is NO_3^-
en	A	A	C	1,2-bn	C	C	C
N-men	A	A	C	D,L-bn	B	B	C
N-een	A	A	B	i-bn	A	A	C
1,2-pn	C	C	C	D,L-chxn	B	B	C
1,3-pn	B	A	A				

[a] See text for definitions of A, B and C.

TABLE 2

Results of thermal analyses

Complex	Liberation of diamine		Color	
	Temp./°C	% Mass loss (calcd.)	Room temp.	Product
$[Ni(en)_3]Cl_2$	64–104	19.4 (19.4)	Red–violet	Blue
$[Ni(en)_3]Br_2$	52–73	14.9 (15.1)	Red–violet	Blue
$[Ni(N\text{-men})_3]Cl_2$	46–81	20.8 (21.1)	Violet	Blue
$[Ni(N\text{-men})_3]Br_2$	52–82	16.5 (16.8)	Violet	Blue
$[Ni(N\text{-een})_3]Cl_2$	80–143	22.0 (22.4)	Violet	Blue
$[Ni(N\text{-een})_3]Br_2$	125–177	18.5 (18.3)	Violet	Blue
$[Ni(1,3\text{-pn})_3]Cl_2$	129–185	21.2 (21.1)	Violet	Blue–violet
$[Ni(1,3\text{-pn})_3]Br_2$	140–196	17.0 (16.8)	Violet	Blue–violet
$[Ni(1,3\text{-pn})_3](NO_3)_2$	119–172	17.9 (18.3)	Vilet	Blue–violet
$[Ni(\text{D,L-bn})_3]Cl_2$	131–205	30.6 (22.4)	Violet	Gray
$[Ni(\text{i-bn})_3]Cl_2$	90–165	26.1 (22.4)	Violet	Blue
$[Ni(\text{i-bn})_3]Br_2$	125–194	18.8 (18.3)	Violet	Yellow
$[Ni(\text{D,L-chxn})_3]Cl_2$	223–260	24.0 (24.2)	Violet	Gray–blue

could not be produced, either on isothermal heating at various temperatures or on heating at various rates.

Table 2 lists the 13 bis(diamine) complexes obtained by thermal reaction of the tris complexes, along with the reaction temperatures, mass losses observed, and the color changes accompanying the liberation of one mole of diamine. Almost all the complexes turn blue; $[Ni(\text{i-bn})_3]Br_2$ turns yellow. The complexes with *N*-substituted diamines liberate their diamines at relatively lower temperatures than those of the complexes with *C*-substituted ones.

Configurations of bis(diamine) complexes

Analyses of the configurations of cis and trans isomers of $[NiX_2(\text{diamine})_2]$ by electronic spectroscopy have already been published [3, 19]. In a tetragonal system (D_{4h}), six spin-allowed transitions are anticipated, among which four or sometimes five bands are observed in practice. However, 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; so, when the complex is cis, three rather broad bands are observed as in the case of the regular Oh system.

Figure 2 shows the electronic spectra of $[NiCl_2(en)_2]$ and $[NiBr_2(1,3\text{-pn})_2]$ which are the representative instances of cis and trans configurations, respectively. Table 3 summarizes the electronic spectral data and the configurational assignments of the bis(diamine) complexes. According to

TABLE 3

Analytical and spectral data of $[NiX_2(diamine)_2]$

Complex	Analytical data in % [a]			Abs. max.	Configuration
	C	H	N	$\nu/10^3\ cm^{-1}$	
$[NiCl_2(en)_2]$	19.34 (19.23)	6.93 (6.46)	22.26 (22.43)	10.2 17.0 27.2	cis
$[NiBr_2(en)_2]$	14.27 (14.18)	5.15 (4.76)	16.38 (16.54)	10.0 17.2 26.9	cis
$[NiCl_2(N\text{-men})_2]$	25.05 (25.94)	7.63 (7.25)	19.57 (20.16)	8.1 13.5 17.6 27.5	trans
$[NiBr_2(N\text{-men})_2]$	20.26 (19.65)	5.93 (5.50)	14.81 (15.28)	7.4 13.5 17.4 27.2	trans
$[NiCl_2(N\text{-een})_2]$	30.94 (31.41)	8.26 (7.91)	17.88 (18.31)	8.1 11.9 13.9 17.4 27.2	trans
$[NiBr_2(N\text{-een})_2]$	24.11 (24.34)	6.35 (6.13)	13.90 (14.19)	7.6 11.6 13.5 16.7 26.6	trans
$[NiCl_2(1,3\text{-pn})_2]$	25.59 (25.94)	7.48 (7.25)	19.99 (20.16)	8.1 14.3 17.2 27.5	trans
$[NiBr_2(1,3\text{-pn})_2]$	19.19 (19.65)	5.91 (5.50)	15.12 (15.28)	7.6 13.3 17.2 27.0	trans
$[Ni(NO_3)_2(1,3\text{-pn})_2]$	21.43 (21.77)	6.43 (6.09)	25.54 (25.39)	8.3 13.9 18.2 28.7sh	trans
$[NiCl_2(\text{D,L-bn})_2]H_2O$ [b]	29.30 (29.66)	7.96 (8.09)	16.90 (17.29)	8.3 14.3 18.5 28.3	trans
$[NiCl_2(\text{i-bn})_2]$	31.11 (31.41)	8.43 (7.91)	18.26 (18.31)	10.2 17.0 27.2	cis
$[Ni(\text{i-bn})_2]Br_2$	24.22 (24.34)	6.21 (6.13)	14.00 (14.19)	22.9	SP [c]
$[NiCl_2(\text{D,L-chxn})_2]H_2O$ [b]	38.19 (38.33)	7.83 (8.04)	14.81 (14.90)	8.3 14.3 18.2 28.1	trans

[a] Calculated values are in parentheses. [b] Very hygroscopic. [c] Square-planar structure.

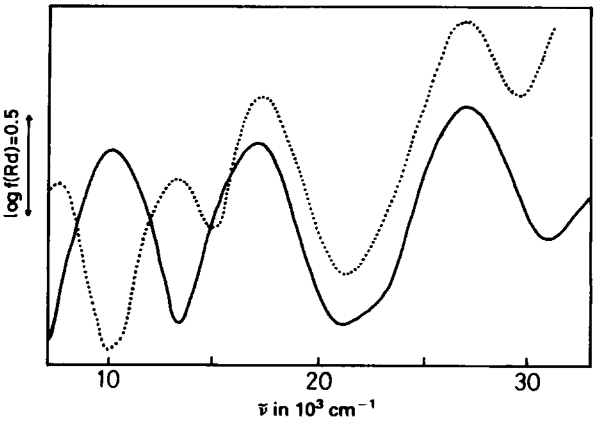

Fig. 2. Electronic spectra of bis(diamine) complexes obtained by thermal reactions of $[Ni(en)_3]Cl_2$ (——) and $[Ni(1,3\text{-}pn)_3]Br_2$ (· · ·).

the above diagnosis, both en complexes and $[NiCl_2(i\text{-}bn)_2]$ are cis, while the other complexes, except for $[Ni(i\text{-}bn)_2]Br_2$, are trans. $[Ni(i\text{-}bn)_2]Br_2$ shows a single band at 22,900 cm^{-1} assignable to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition of a square-planar structure [20].

In Table 4, summarizing the configurations of $[NiX_2(diamine)_2]$, the descriptions in parentheses correspond to those of bis(diamine) complexes obtained by another method, i.e. thermal deaquation-anation [21–23]

$$[Ni(H_2O)_2(diamine)_2]X_2 \xrightarrow{-2H_2O} [NiX_2(diamine)_2]$$

When the octahedral diaqua complexes containing the diamines in Table 4 could be produced as the starting materials of thermal deaquation-anation,

TABLE 4

Configurations of $[NiX_2(diamine)_2]$ [a]

Diamine	X is Cl^-		X is Br^-		X is NO_3^-	
en	cis	(cis)	cis	(cis)	–	
N-men	trans	(trans)	trans	(trans)	–	(trans)
N-een	trans	(trans)	trans	(trans)	–	(trans)
1,2-pn	–	(trans)	–	(trans)	–	(trans)
1,3-pn	trans	(trans)	trans	(trans)	trans	(trans)
1,2-bn	–	(trans)	–	(trans)	–	(trans)
D,L-bn	trans	(trans)	–	(trans)	–	(SP)
i-bn	cis	(cis)	SP	(SP)	–	(SP)
D,L-chxn	trans	(trans)	–	(trans)	–	(trans)

[a] Configurations of the complexes obtained by thermal deaquation-anation of *trans*-$[Ni(H_2O)_2(diamine)_2]X_2$ are in parentheses; – indicates no formation of the bis(diamine) complexes; SP, square-planar complex.

the configurations were all trans, and the corresponding *cis*-diaqua complexes could not be isolated. Almost all the *trans*-diaqua complexes brought about a deaquation-anation upon heating, retaining the original trans configuration. Only *trans*-$[Ni(H_2O)_2(en)_2]Cl_2$, *trans*-$[Ni(H_2O)_2(en)_2]Br_2$, and *trans*-$[Ni(H_2O)_2(i\text{-}bn)_2]Cl_2$ were transformed into *cis*-dihalogeno complexes upon thermal dehydration. The configurations of dianionobis(diamine) complexes obtained from thermal reactions of the tris(diamine) complexes are identical with the results of thermal deaquation-anation of the diaquabis(diamine) complexes, i.e. the same products are obtained with either thermal procedure. This implies that either a trans or cis configuration is strongly stabilized for a particular combination of ligands in $[Ni(H_2O)_2(diamine)_2]X_2$ and $[NiX_2(diamine)_2]$ (where X is Cl^-, Br^-, or NO_3^-).

It has recently been shown that in the thermal deaquation-anation of *trans*-$[Ni(H_2O)_2(diamine)_2]Cl_2$ (diamine is *N*,*N*- or *N*,*N'*-dialkyl-substituted ethylenediamines), the complexes with asymmetric diamines such as *N*,*N*-dimethylethylenediamine, *N*,*N*-diethylethylenediamine, and *N*,*N*-di-*n*-butylethylenediamine underwent trans-to-cis configurational changes, giving the *cis*-dichloro complexes [24]. However, among the (*N*- or *C*-substituted diamine)nickel(II) complexes treated in this study, only $[Ni(i\text{-}bn)_3]Cl_2$ yielded the cis product by its thermal reaction. Rearranging these results, it may be concluded that only asymmetric diamines possessing two substituent groups on the same N or C atom stabilize *cis*-dianiono complexes in the stereochemistry of $[NiX_2(diamine)_2]$ complexes.

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