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THERMAL SYNTHESES AND THE ELECTRONIC SPECTRA OF *cis*-DIHALOGENO-(2,2′,2″-TRIAMINOTRIETHYLAMINE)NICKEL(II) COMPLEXES

Y. IHARA and M. SAKURA

Laboratory of Chemistry, Faculty of Education, Kanazawa University, Kanazawa 920 (Japan)

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ABSTRACT

The thermal reactions of the complexes, *cis*-$[Ni(H_2O)(py)(tren)]X_2$ and $[Ni(en)(tren)]X_2$ (py, pyridine; tren, 2,2′,2″-triaminotriethylamine; en, ethylenediamine; X = Cl, Br or I) were investigated in the solid phase. The pyridine-containing complexes lost their coordinated H_2O and py molecules on heating, resulting in the six-coordinated *cis*-$[NiX'_2(tren)]$ (X′ = Cl or Br) or the five-coordinated trigonal-bipyramidal [NiI(tren)]I. The electronic spectra of *cis*-$[NiX'_2(tren)]$ can be widely used as reference for *cis* octahedral complexes with the general formula, *cis*-$[NiX_2N_4]$, where N is a nitrogen-donating ligand. The ethylenediamine-containing complexes hardly showed any changes on thermal treatment until they decomposed.

INTRODUCTION

There is little information in the literature on the *cis–trans* isomerism of octahedral nickel(II) complexes. The main reason for this is that the isomers are indistinguishable in terms of their visible spectra. The properties of the isomers cannot be compared directly as the isolation of two isomers with identical formulas has not yet been reported. The methods for their identification using visible [1–4] and IR spectra [5] are not so well established as those of Co(III) and Cr(III) complexes; diagnosis has often been carried out by making use of the IR data of other metal complexes with the same ligands as the Ni(II) complexes [6–9].

Lever [10] has recently clarified a diagnosis for the *cis* and *trans* isomers of $[NiA_2N_4]$ (A; univalent anion; N, nitrogen-donating ligand) in terms of the normalized spherical harmonic Hamiltonian method, showing that a feature of the solid-phase electronic spectrum in the near-IR region is especially useful. The application of this method to a series of dianionobis(diamine)nickel(II) complexes showed that almost all of these types of complexes were in the *trans* form and only in a few limited cases was *cis* geometry found [11]. Accordingly, the standard spectral data of the *cis* complexes, whose structures are determined by X-ray diffraction, or which should be forced to take the geometry due to the steric properties of the ligand(s), are now required for the establishment of this method.

2,2′,2″-Triaminotriethylamine (tren) is a good ligand to use for this purpose, because it acts as a tripod-like quadridentate ligand on a metal ion due to steric effects; thus the other ligand(s) should be forced to occupy a *cis* position when an octahedral complex is formed [12,13]. If the complexes of the general formula *cis*-$[NiX_2(tren)]$ (X = Cl, Br or I) can be prepared, their spectra can become the standard for *cis*-$[NiA_2N_4]$. However, no preparative methods have been reported on the above tren complexes.

In this study, we report the synthesis of *cis*-$[NiX_2(tren)]$. We make use of the thermal reactions of $[Ni(H_2O)(py)(tren)]X_2$ and $[Ni(en)(tren)]X_2$ which can easily be produced; *cis*-$[NiX_2(tren)]$ can be obtained by the liberation of the neutral ligands (H_2O and py, or en) and the successive anation of the X ions on heating the starting materials.

EXPERIMENTAL

Preparation

2,2′,2″-Triaminotriethylamine was synthesized by the known method [14]. The starting complexes of the thermal reactions, $[Ni(H_2O)(py)(tren)]X_2$ and $[Ni(en)(tren)]X_2$ (X = Cl, Br or I), were prepared by the following method. Solutions of tren in methanol and then pyridine in methanol (in the case of the former complexes) or ethylenediamine in methanol (in the case of the latter complexes) were slowly added to a solution of the appropriate nickel(II) salt in methanol. The molar ratios of the Ni(II) salt, tren and either py or en added were the same. When no complex precipitated immediately, the solution was allowed to stand for several days in a refrigerator. The violet crystals formed were collected by filtration, and washed with ethanol and/or diethyl ether. Their chemical formulae were determined by means of elemental analyses and spectral and magnetic measurements (see later).

The thermal reaction products were obtained on isothermal heating of the starting complexes at their formation temperatures (which were inferred from the results of the thermal analyses) in an electric furnace under static air.

Measurements

Simultaneous TG–DTA was carried out with a Seiko SSC/580 TG/DTA-30 apparatus. The conditions of the runs are given in the appropriate figures. 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. The effective magnetic moments were evaluated from the susceptibilities measured by the Gouy method at room temperature.

RESULTS AND DISCUSSION

Structures of the starting complexes

The analytical data and the magnetic moments in Table 1 show that the complexes prepared have the compositions, $Ni(H_2O)(py)(tren)X_2$ and $Ni(en)(tren)X_2$ ($X = Cl$, Br or I), and are high spin complexes. All the complexes are violet, and give the same spectral patterns, which are characteristic of those of octahedral Ni(II) complexes. The spectrum of $Ni(H_2O)(py)(tren)Cl_2$ is illustrated in Fig. 1 (together with the spectra of its thermal reaction products; see later). The configuration of this complex is *cis* owing to the steric effect of the coordinated tren; tren cannot be oriented so that the four donor nitrogen atoms lie at the corners of a square, but can function as a tetrahedral quadridentate. This also applies to the other py-containing complexes and to all the en-containing complexes; moreover, it is impossible to coordinate an en molecule at a *trans* position of an octahedral complex. The spectral data of all the complexes and the formulas deduced from them are also indicated in Table 1.

TABLE 1

Data on the elemental analyses, electronic spectra and magnetic moments of the starting complexes

Complex	Analytical data [a]			Abs max, $\tilde{\nu}$ (10^3 cm^{-1})			μ_{eff}/μ_B
	H (%)	C (%)	N (%)				
cis-$[Ni(H_2O)(py)(tren)]Cl_2$	7.06(6.77)	35.50(35.42)	18.56(18.78)	10.8	18.5	$\geqslant 29.5$	3.13
cis-$[Ni(H_2O)(py)(tren)]Br_2$	5.63(5.46)	28.61(28.61)	14.99(15.16)	11.3	18.5	$\geqslant 28.0$	3.19
cis-$[Ni(H_2O)(py)(tren)]I_2$	4.40(4.54)	23.83(23.76)	12.56(12.60)	10.9	18.2	$\geqslant 29.0$	3.04
$[Ni(en)(tren)]Cl_2$	8.00(7.26)	25.85(26.56)	23.57(23.24)	11.3	19.0	28.7	2.95
$[Ni(en)(tren)]Br_2$	6.54(6.17)	22.08(22.62)	19.42(19.78)	11.3	19.0	28.5	3.08
$[Ni(en)(tren)]I_2$	5.16(5.05)	18.22(18.52)	15.52(16.20)	11.2	19.0	28.7	3.01

[a] Calculated values are in parentheses.

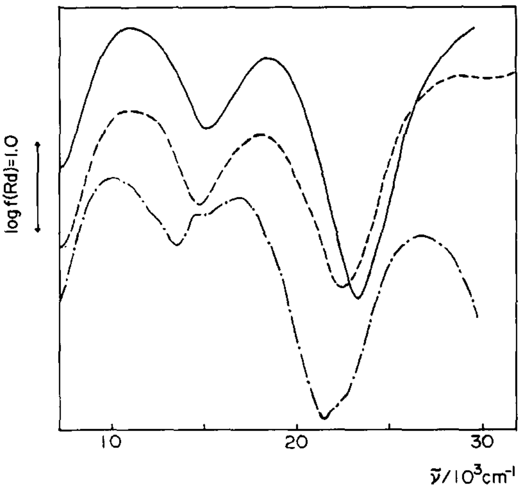

Fig. 1. Electronic spectrum of *cis*-[Ni(H_2O)(py)(tren)]Cl_2 (———) and those of the violet blue and the blue products obtained after heating at 100 °C (— — —) and at 160 °C (·—·—·), respectively.

Thermal analyses

Figure 2 shows the results of simultaneous TG–DTA for the three complexes containing pyridine. The TG and DTA patterns of the chloride suggest that the reaction accompanying weight loss proceeds endothermically in two steps: a dehydration step followed by the liberation of pyridine. The weight losses observed for the first step (4.8%) and for the second step (21.2%) are in good agreement with the calculated values for water (4.8%) and for pyridine (20.0%). A smell of pyridine was detected as soon as the liberation in the second step began. This means that the weight loss for the second step can be undoubtedly ascribed to the liberation of pyridine. Therefore, the final product of this thermal reaction has the composition Ni(tren)Cl_2.

The endothermic DTA peaks for the bromide and iodide also indicate that the liberation of water and pyridine takes place stepwise. The total weight losses observed are 21.4% for the bromide and 17.2% for the iodide; these are consistent with the calculated values of 21.0% and 17.5%, respectively. It would be expected from the TG and/or DTG results for the above two complexes that the complexes with the formula Ni(py)(tren)X''_2 (X'' = Br or I) are formed temporarily during the course of these endothermic reactions. However, they could not be isolated in pure form, in contrast with the case of the chloride.

Thermal analyses of the three en-containing complexes were also carried out, but these complexes showed scarcely any change in the TG, DTA and DTG patterns until they decomposed above 250 °C.

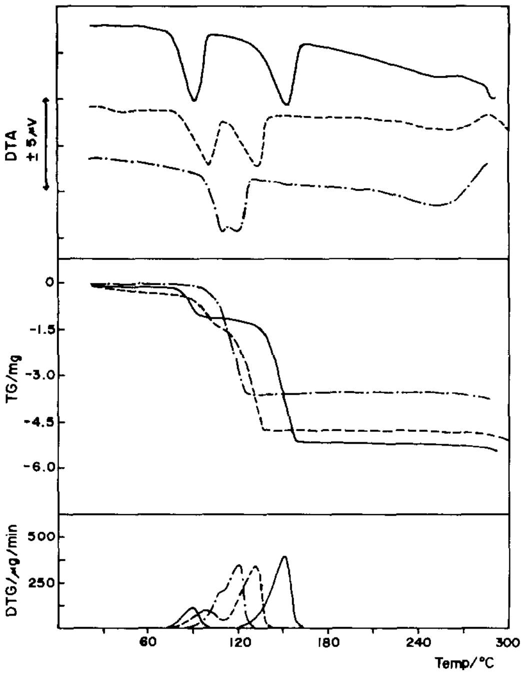

Fig. 2. TG–DTA patterns of *cis*-$[Ni(H_2O)(py)(tren)]X_2$, where X = Cl (———), Br(— — —) and I (·–·–·), under a constant flow of N_2 at 200 ml min^{-1} (heating rate, 2° C min^{-1} for all runs; sample weights, 20.7 mg, 21.8 mg and 21.0 mg for the chloride, bromide and iodide, respectively).

Electronic spectra

The thermal reactions of the py-containing complexes were accompanied by thermochromism. The chloride turned violet blue on thermal dehydration and then turned blue when the pyridine had been eliminated after continuous heating. The reaction product of the bromide (after loss of water and pyridine) was blue and that of the iodide was green.

These products were obtained by means of isothermal heating of the original complexes, and were stable enough to permit the usual measurements. However, the intermediate $Ni(py)(tren)Cl_2$ was studied immediately after preparation, or under a carefully dried atmosphere, to avoid the occurrence of the backward reaction toward *cis*-$[Ni(H_2O)(py)(tren)]Cl_2$.

The powder reflectance spectra of both the violet blue and the blue products of the chloride are compared with that of the mother complex in Fig. 1. The spectral patterns remain nearly unchanged, showing that a *cis* octahedral configuration is retained throughout the thermal reaction. A slight shift of the bands indicates a partial exchange of the ligands.

The blue product of the bromide can be identified as *cis*-$[NiBr_2(tren)]$ in a similar manner on the basis of its spectrum shown in Fig. 3. The product of

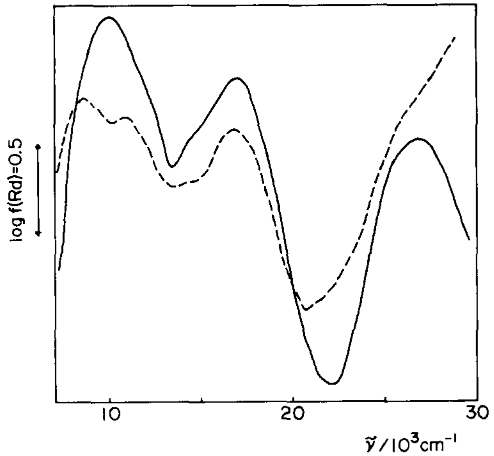

Fig. 3. Electronic spectra of *cis*-$[NiBr_2(tren)]$ (———) and [NiI(tren)]I (— — —).

the iodide is different from the two dihalogeno complexes above and shows a spectral pattern similar to that of $[NiX(Me_6tren)]X$ (Me_6tren, tris(2-dimethylaminoethyl)amine; X = Cl, Br or I) which was determined to be a high-spin trigonal-bipyramidal five-coordinated complex [15]. The finding that only the iodide converts to the five-coordinated complex on heating is reasonable because the ionic radius of I^- is larger than that of Cl^- or Br^- and thus only one of the counter iodide ions can coordinate to Ni^{2+} when H_2O and py are eliminated.

Magnetic moments

Table 2 summarizes the magnetic moments of all the complexes obtained on heating. Their values and the analytical data shown in the table support the above view of the structural identification. Both a five-coordinated

TABLE 2

Data on the elemental analyses, electronic spectra and magnetic moments of the complexes obtained on heating

Complex	Analytical data			Abs max, $\tilde{\nu}$ (10^3 cm^{-1})				μ_{eff}/
	H (%)	C (%)	N (%)					μ_B
cis-[NiCl(py)(tren)]Cl [a]				10.9		17.9	28.7	3.26
cis-$[NiCl_2(tren)]$ [b]	6.53(6.59)	24.15(26.12)	18.56(20.31)	9.9		16.7	26.3	3.11
cis-$[NiBr_2(tren)]$	5.31(4.98)	19.39(19.75)	15.31(15.36)	9.8		16.8	26.7	3.07
[NiI(tren)]I	4.03(3.96)	15.79(15.71)	12.31(12.22)	8.5	10.9	16.7	25.5sh	3.07

[a] This complex readily absorbs water molecules in air, forming the mother complex again and giving nearly the same analytical data as that for *cis*-$[Ni(H_2O)(py)(tren)]Cl_2$.

[b] Very hygroscopic.

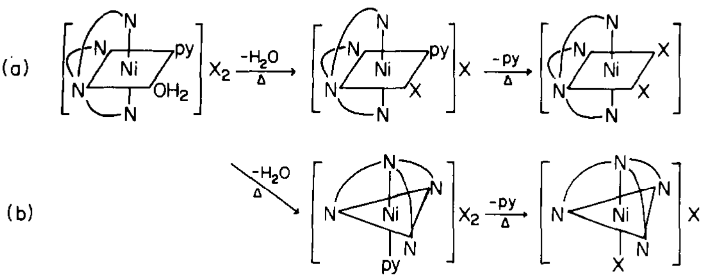

Fig. 4. Thermal reaction schemes of *cis*-[Ni(H_2O)(py)(tren)]X_2: (a) the reaction of X = Cl or Br; (b) the reaction of X = I.

(trigonal bipyramidal) nickel(II) complex and a six-coordinated (octahedral) complex of high spin are known to give nearly the same values of magnetic moment. The identification of [NiI(tren)]I is dependent on the spectral data.

Thermal reaction

The thermal reactions of the py-containing complexes can be represented by the following equations, and are also shown in Fig. 4 with the structural formulas.

$$\textit{cis}\text{-}[\mathrm{Ni(H_2O)(py)(tren)}]\mathrm{Cl_2} \xrightarrow[\Delta]{-\mathrm{H_2O}} \textit{cis}\text{-}[\mathrm{NiCl(py)(tren)}]\mathrm{Cl}$$

$$\xrightarrow[\Delta]{-\mathrm{py}} \textit{cis}\text{-}[\mathrm{NiCl_2(tren)}]$$

$$\textit{cis}\text{-}[\mathrm{Ni(H_2O)(py)(tren)}]\mathrm{Br_2} \xrightarrow[\Delta]{-\mathrm{H_2O}} (\textit{cis}\text{-}[\mathrm{NiBr(py)(tren)}]\mathrm{Br})$$

$$\xrightarrow[\Delta]{-\mathrm{py}} \textit{cis}\text{-}[\mathrm{NiBr_2(tren)}]$$

$$\textit{cis}\text{-}[\mathrm{Ni(H_2O)(py)(tren)}]\mathrm{I_2} \xrightarrow[\Delta]{-\mathrm{H_2O}} ([\mathrm{Ni(py)(tren)}]\mathrm{I_2}) \xrightarrow[\Delta]{-\mathrm{py}} [\mathrm{NiI(tren)}]\mathrm{I}$$

The view that the reactions of the bromide and iodide also consist of two steps has already been described on the basis of the results of their thermal analyses. The formulas in parentheses in the above equations are indicative of intermediates which were not actually isolated, but are anticipated to be produced. No formation of the octahedral tren complex containing py and I^- in a *cis* position at the same time would be expected because of the bulkiness of the ligands.

CONCLUSION

Some *cis* octahedral nickel(II) complexes containing tren were obtained. The *cis*-dihalogeno complexes (*cis*-[NiX'_2(tren)], X′ = Cl or Br) were synthesized using the thermal reaction. The spectra of these complexes showed the same features as pointed out by Lever theoretically and experimentally for the *cis* octahedral complexes, *cis*-[NiX_2(diamine)$_2$] [16]. Three rather broad bands (one in the near-IR region and the other two in the visible region) were observed as in the case of a regular octahedral system. However, in the corresponding *trans* isomer (*trans*-[NiX_2(diamine)$_2$]) an absorption peak in the near-IR region was split into two bands (one in the near-IR region and the other in the red region) [16].

For *trans* complexes possessing a donor set of A_2B_4, it is expected that the splitting would become much larger with an increase in the difference in the ligand field strengths of A and B; Lever's method is particularly useful for such a case [11]. Of all the complexes treated in this paper, *cis*-[NiX'_2(tren)] is of particular importance because it has an ideal donor set, consisting of two halogens and four nitrogens, and can therefore be used as a standard for *cis* complexes in electronic spectrometry.

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