Optical Resolution of Di-2-pyridylamine Complexes of Ruthenium(II)

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Synopsis. Through SP-Sephadex ion exchange chromatography $[Ru(Hdpa)_3]^{2+}$ and $[Ru(bpy)_2(Hdpa)]^{2+}$ (Hdpa= di-2-pyridylamine) were resolved by the use of an aqueous sodium *d*-tartrate solution as the eluting agent. *Λ*-$[Ru(Hdpa)_3]^{2+}$ and *Δ*-$[Ru(bpy)_2(Hdpa)]^{2+}$ were eluted in the early fractions. The precipitation of diastereomers with dibenzoyl-*d*-tartrate was also successful in the resolution of $[Ru(Hdpa)_3]^{2+}$ and $[Ru(bpy)(Hdpa)_2]^{2+}$. The absolute configurations of the complexes were assigned by referring to the signs of CD spectra at around 3.2—3.8 μm^{-1}.

Synthetic and spectrochemical studies on a series of complexes $[Ru(bpy)_n(Hdpa)_{3-n}]^{2+}$ (bpy=2,2′-bipyridine, Hdpa=di-2-pyridylamine, n=0—2) have been reported by DeArmond et al.[1,2] The present work describes the resolution of the complexes through SP-Sephadex cation-exchange chromatography and the precipitation of diastereomers with sodium (*R,R*)-dibenzoyltartrate (Na_2dbt). Although $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ can be resolved through the precipitation of diastereomers with sodium bis(*d*-tartrato)diantimonate ($Na_2Sb_2(tart)_2$),[3,4] this resolving agent failed to give precipitate with the above Hdpa-containing complexes.

Experimental

Preparation of $[Ru(bpy)(Hdpa)_2](ClO_4)_2$. A dilute hydrochloric acid solution (100 cm^3) of $RuCl_3 \cdot 3H_2O$ (Koso Chemicals, 1 g) and Hdpa (Aldrich, 200 mg) was refluxed for 8 h, and filtered. The filtrate was concentrated to about 20 cm^3 while precipitating a green product. This contained *cis*-$[RuCl_2(Hdpa)_2]Cl \cdot H_2O$, the X-ray structural study of which will be reported in a separate paper. The green product was suspended in 200 cm^3 of water with bpy (90 mg) and Hdpa (50 mg), and refluxed for 3 h in the presence of sodium phosphinate (2 g). Upon the addition of $NaClO_4$ to the reaction mixture a brown precipitate was formed. For purification it was charged on the top of an SP-Sephadex column (Na^+ form) and eluted with a 0.3 mol dm^{-3} NaCl solution. Fractions of a brown eluate were collected from which $[Ru(bpy)(Hdpa)_2](ClO_4)_2$ was precipitated. The product was washed with an aqueous solution of 0.1 mol dm^{-3} $NaClO_4$, ethanol/2-methyl-2-propanol (1 : 1 v/v), and ether, successively, and dried at 60 °C. Yield 20% (Found: C, 44.98; H, 3.23; N, 13.98%). Other members of the series $[Ru(bpy)_n(Hdpa)_{3-n}]^{2+}$ which were formed as by-products were separated off by chromatography; complexes with higher n values were eluted faster.

$[Ru(Hdpa)_3](ClO_4)_2$[1] and $[Ru(bpy)_2(Hdpa)](ClO_4)_2$[2] were prepared by methods similar to those reported by DeArmond et al., except that both complexes were purified through the chromatography described above.

Optical Resolution. a) Cation-Exchange Chromatography. $[Ru(Hdpa)_3]^{2+}$ was charged on the top of an SP-Sephadex column (ϕ 6 cm×60 cm), and eluted with 0.15 mol dm^{-3} sodium *d*-tartrate (Na_2*d*-tart) solution. Since one elution gave only partial resolution, the earlier and later fractions were collected separately, and again charged on the column. This procedure was repeated three times. From the early fractions $(+)_{\Delta\varepsilon}$-$[Ru(Hdpa)_3](ClO_4)_2$[5] was isolated. Peaks of CD: $\Delta\varepsilon_{410}$=−36.6, $\Delta\varepsilon_{314}$=207, and $\Delta\varepsilon_{283}$=−177 (cm mol $dm^{-3})^{-1}$.

$[Ru(bpy)_2(Hdpa)]^{2+}$ was also resolved almost in the same way as the above. After elutions were repeated three times $(-)_{\Delta\varepsilon}$-$[Ru(bpy)_2(Hdpa)](ClO_4)_2$ was isolated from the early fractions. Peaks of CD: $\Delta\varepsilon_{355}$=6.83, $\Delta\varepsilon_{292}$=−185, and $\Delta\varepsilon_{275}$=119 (cm mol $dm^{-3})^{-1}$. For $[Ru(bpy)(Hdpa)_2]^{2+}$ the chromatography gave only poor resolution.

b) Precipitation of the Diastereomers with Na_2dbt. Four hundred milligrams of $[Ru(Hdpa)_3](ClO_4)_2$ was converted to the chloride through anion exchange. To a 100 cm^3 chloride solution was added 100 mg of Na_2dbt. The solution was allowed to stand at room temperature for 3—4 days during which $(-)_{\Delta\varepsilon}$-$[Ru(Hdpa)_3](dbt)$ was precipitated. The diastereomer was recrystallized from water. Yield: 130 mg. This was converted to the perchlorate, $(-)_{\Delta\varepsilon}$-$[Ru(Hdpa)_3](ClO_4)_2$. CD: $\Delta\varepsilon_{410}$=36.6 (cm mol $dm^{-3})^{-1}$.

A similar procedure was applied to the resolution of $[Ru(bpy)(Hdpa)_2]^{2+}$. From 400 mg of racemic perchlorate 70 mg of the diastereomer, $(+)_{\Delta\varepsilon}$-$[Ru(bpy)(Hdpa)_2](dbt)$ was obtained. CD peaks of $(+)_{\Delta\varepsilon}$-$[Ru(bpy)(Hdpa)_2](ClO_4)_2$: $\Delta\varepsilon_{408}$=−13.7, $\Delta\varepsilon_{296}$=158, and $\Delta\varepsilon_{279}$=−133 (cm mol $dm^{-3})^{-1}$.

$[Ru(bpy)_2(Hdpa)]^{2+}$ gave no precipitate on addition of Na_2dbt.

Measurements. Electronic spectra were recorded on a Hitachi 340 Spectrophotometer, and CD spectra were on a JASCO J-500A Spectropolarimeter. The solvent was water throughout the measurements.

Results and Discussion

The electronic and CD spectra are shown in Figs. 1 and 2, respectively. The two strong bands at around 3.2—3.8 μm^{-1}, which are common to the four complexes, correspond to the intraligand π-π^* transitions in coordinated pyridine groups. The CD bands

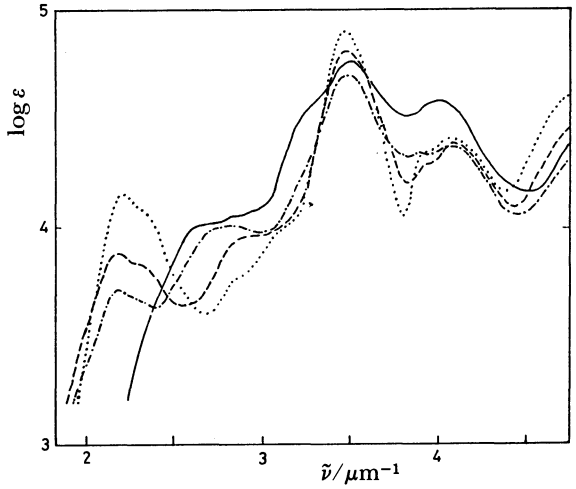

Fig. 1. Electronic spectra of $[Ru(bpy)_n(Hdpa)_{3-n}]^{2+}$. —— $[Ru(Hdpa)_3]^{2+}$;-·-· $[Ru(bpy)(Hdpa)_2]^{2+}$;--- $[Ru(bpy)_2(Hdpa)]^{2+}$; ····· $[Ru(bpy)_3]^{2+}$.

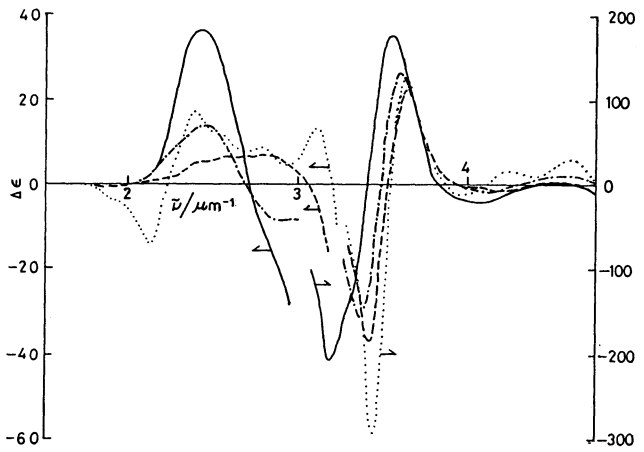

Fig. 2. CD spectra of $(-)_{\Delta\varepsilon}$-$[Ru(bpy)_n(Hdpa)_{3-n}]^{2+}$. The symbols are the same as in Fig. 1.

which are usually observed for tris- and bis(diimine) complexes such as $[M(bpy)_3]^{n+}$, $[M(phen)_3]^{n+}$, and $[M(bpy)_2(py)_2]^{n+}$ are used to assign the absolute configurations of these complexes based on exciton theory;[6-8] that is, an enantiomer whose CD bands corresponding to π-π^* transition show a minus (at lower wavenumbers)-plus (at higher wavenumbers) pattern has a *Δ* configuration. If this rule can be applied to the present system, the CD spectra shown in Fig. 2 are of *Δ* isomers.

The agreement of the absolute values of $\Delta\varepsilon$ of *act*-$[Ru(Hdpa)_3]^{2+}$ resolved by two different methods was sufficiently good to assure complete resolution.

In the precipitation procedure for $[Ru(Hdpa)_3]^{2+}$, when the filtrate after the filtration of $(-)_{\Delta\varepsilon}$-$[Ru(Hdpa)_3](dbt)$ was treated with more Na_2dbt and kept at room temperature for an additional week, often $(+)_{\Delta\varepsilon}$-$[Ru(Hdpa)_3](dbt)$ precipitated, whose optical purity was very good. The perchlorate which was derived from the diastereomer had $\Delta\varepsilon_{410}$ of -36.0 $(cm\ mol\ dm^{-3})^{-1}$. Such "post precipitation" of the other diastereomer was not observed in the resolution of $[Ru(bpy)(Hdpa)_2]^{2+}$.

The enantiomers which form less soluble diastereomers with dbt^{2-} are *Δ*-$[Ru(Hdpa)_3]^{2+}$ and *Λ*-$[Ru(bpy)(Hdpa)_2]^{2+}$. Although the mechanisms of the precipitation and the resolution were not clear, Na_2dbt was found to be a good resolving agent for these two complexes. As described in "Experimental", a single precipitation followed by a recrystallization yielded very pure diastereomers.

Table 1. Enantiomer Which was Eluted in the Early Fractions on the SP-Sephadex Column Chromatography

Complex	Eluting agent		
	Na_2d-tart	$Na_2Sb_2(d\text{-tart})_2$	NaCl
$[Ru(bpy)_3]^{2+}$	*Δ*	*Δ*	*Δ*
$[Ru(bpy)_2(Hdpa)]^{2+}$	*Δ*	*Δ*	*Δ*
$[Ru(bpy)(Hdpa)_2]^{2+}$	*Δ*	*Λ*	*Δ*
$[Ru(Hdpa)_3]^{2+}$	*Λ*	*Δ*	*Λ*

For chromatographic resolution various reagents were tried. Table 1 shows the enantiomers of each complex which were eluted in the early fractions by three kinds of eluting agents. Among them sodium *d*-tartrate was the most efficient agent in the resolution of $[Ru(Hdpa)_3]^{2+}$ and $[Ru(bpy)(Hdpa)_2]^{2+}$. No definite conclusion could be deduced regarding the mechanism of the resolution from the data.

The optical isomers were inert in aqueous solutions against racemization in the dark. Under irradiation with a xenon lamp, however, they racemized with a very slight decomposition. Preliminary experiments showed that the quantum yield of racemization was in the order $[Ru(Hdpa)_3]^{2+} < [Ru(bpy)_3]^{2+} \approx [Ru(bpy)_2(Hdpa)]^{2+}$.

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5) In the present paper the signs, $(+)_{\Delta\varepsilon}$ and $(-)_{\Delta\varepsilon}$, before chemical formula mean that the CD bands corresponding to the intraligand π-π^* transitions have plus-minus patterns and minus-plus patterns of $\Delta\varepsilon$ values, respectively (See "Results and Discussion").
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