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Preparation and Characterization of *cis*-Λ-[Ru(bpy)$_2$(py)(O)]$^{2+}$

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Introduction

High-oxidation-state oxo complexes of ruthenium with polypyridine ligands such as *cis*-[Ru(bpy)$_2$(py)O]$^{2+}$ (bpy = 2,2′-bipyridine, py = pyridine) are efficient stoichiometric and catalytic oxidants in a variety of organic and inorganic oxidation reactions.[1] Recently, it was also reported that *cis*-[Ru(bpy)$_2$(py)O]$^{2+}$ is an efficient DNA cleavage agent.[2] The results of mechanistic studies involving *cis*-[Ru(bpy)$_2$(py)(O)]$^{2+}$ suggest that oxidation of PPh$_3$ to Ph$_3$PO or (CH$_3$)$_2$S to (CH$_3$)$_2$SO occurs by O atom transfer,[3a] oxidation of alcohols to aldehydes may occur by hydride transfer,[3b] and oxidation of hydroquinones occurs by proton-coupled electron transfer.[3c] The complex *cis*-[Ru(bpy)$_2$(py)(O)]$^{2+}$ and its reduced form, *cis*-[Ru(bpy)$_2$(py)(H$_2$O)]$^{2+}$, are chiral at the metal center. Stereoselective oxygen atom transfer from the chiral oxidant to an organic substrate is a possibility. Most well-studied asymmetric oxidation reactions of this sort are dependent on the selectivity of chiral ligands.[4] Stereoselective oxidation directly involving the chiral metal center has not been studied extensively although the topic has been addressed.[3a,5] In this paper, the preparation and characterization of optically active *cis*-[Ru(bpy)$_2$(py)(O)]$^{2+}$ from optically active *cis*-[Ru(bpy)$_2$(py)(H$_2$O)]$^{2+}$ and the asymmetric oxidation of methyl *p*-tolyl sulfide by this chiral oxidant to chiral sulfoxide are reported.

Experimental Section

The complex *cis*-[Ru(bpy)$_2$(py)$_2$]Cl$_2$ was prepared from Ru(bpy)$_2$Cl$_2$·3H$_2$O (Strem) as described previously.[6] Resolution of *cis*-[Ru(bpy)$_2$(py)$_2$]$^{2+}$ was achieved by the addition of 45 mL of 0.5 M aqueous solution of disodium *O,O*′-dibenzoyl-(*R,R*)-tartrate to *cis*-[Ru(bpy)$_2$(py)$_2$]Cl$_2$ (4.5 g) in 90 mL water and stirring for 10 min at 23 °C. Red crystals of *cis*-Λ-[Ru(bpy)$_2$(py)$_2$][*O,O*′-dibenzoyl-(*R,R*)-tartrate]·12H$_2$O were obtained after slow evaporation of the solvent over a period of 8−10 days.[7] After conversion to *cis*-Λ-[Ru(bpy)$_2$(py)$_2$](PF$_6$)$_2$ by the addition of NH$_4$PF$_6$, the chloride salt, *cis*-Λ-[Ru(bpy)$_2$(py)$_2$]Cl$_2$ (ϵ_{454} = 10 600 M^{-1} cm^{-1}, $\Delta\epsilon_{295}$ = +114 M^{-1} cm^{-1}, $\Delta\epsilon_{280}$ = −13.3 M^{-1} cm^{-1}), was isolated by addition of LiCl to a solution of the salt in acetone. The enantiomeric compound is obtained with use of disodium *O,O*′-dibenzoyl-(*S,S*)-tartrate. All manipulations of the optically active compounds were carried out in subdued light.

The complex *cis*-Λ-[Ru(bpy)$_2$(py)(H$_2$O)](ClO$_4$)$_2$ was prepared by a modification of methods used for the racemic species.[6,8] Thus, *cis*-Λ-[Ru(bpy)$_2$(py)$_2$]Cl$_2$ (0.50 g) was refluxed in water for 4 h. The resulting dark brown solution was cooled, lithium chloride (5 g) was added, and the mixture was boiled for a further 15 min. Upon addition of NH$_4$PF$_6$, *cis*-Λ-[Ru(bpy)$_2$(py)Cl]PF$_6$ (0.3 g) precipitated and was purified by recystallization from CH$_2$Cl$_2$/ether and CHCl$_3$/ether, sequentially. The product *cis*-Λ-[Ru(bpy)$_2$(py)(H$_2$O)](ClO$_4$)$_2$ was made from *cis*-Λ-[Ru(bpy)$_2$(py)Cl]PF$_6$ by use of the method described for the racemic complex except that precautions were taken to avoid exposure to light.[8] Optical purity was determined by the reaction with 1(*R*),2(*R*)-diaminocyclohexane (*R,R*-dach, Aldrich) which reacts stereospecifically to give a mixture of the diastereomers Λ-[Ru(bpy)$_2$(*R,R*-dach)]$^{2+}$ and Δ-[Ru(bpy)$_2$(*R,R*-dach)]$^{2+}$.[7] The diastereomers are readily identified by ^{1}H-NMR (H$_6$ of the coordinated bpy at $\delta \approx 9.0$). Typically, the *cis*-[Ru(bpy)$_2$(py)(H$_2$O)]$^{2+}$ formed with 60% ee of the Λ isomer. For *cis*-Λ-[Ru(bpy)$_2$(py)(H$_2$O)](ClO$_4$)$_2$: UV−visible λ, nm (ϵ, M^{-1} cm^{-1}) 468 (8800), 336 (10 800), 289 (57 500), 243 (24 300); circular dichroism λ, nm ($\Delta\epsilon$, M^{-1} cm^{-1}) 520 (+2.1), 445 (−4.8), 420 (−2.5), 365 (−8.8), 325 (+6.8), 294 (+170), 279 (−36); MS/FAB peak is found at 610 corresponding to [Ru(bpy)$_2$(py)(H$_2$O)](ClO$_4$)$^+$.

The oxidized complex *cis*-Λ-[Ru(bpy)$_2$(py)(O)](ClO$_4$)$_2$ was made by reacting *cis*-Λ-[Ru(bpy)$_2$(py)(H$_2$O)](ClO$_4$)$_2$ with cerium(IV) in aqueous 1 M HClO$_4$ as reported for the racemic compound.[9] Optical purity was measured in *cis*-Λ-[Ru(bpy)$_2$(py)(NCCH$_3$)](ClO$_4$)$_2$ formed after reduction of [Ru(bpy)$_2$(py)(O)](ClO$_4$)$_2$ in acetonitrile solution. Typically, the *cis*-Λ-[Ru(bpy)$_2$(py)(NCCH$_3$)]$^{2+}$, formed from *cis*-Λ-[Ru(bpy)$_2$(py)(H$_2$O)]$^{2+}$ of 60% optical purity, was 40% optically pure after one cycle of oxidation and reduction.[10] It is likely that this modest racemization occurs in the reduction step which involves substitution at the ruthenium center. For *cis*-Λ-[Ru(bpy)$_2$(py)(O)](ClO$_4$)$_2$: UV−visible λ, nm (ϵ, M^{-1} cm^{-1}) 300 (23 000), 248 (26 000), circular dichroism λ, nm ($\Delta\epsilon$, M^{-1} cm^{-1}) 370 (−0.8), 310 (+14.0), 298 (+7.7), 278 (−3.8).

For the oxidation of methyl *p*-tolyl sulfide (Aldrich) to (*R,S*)-methyl *p*-tolyl sulfoxide, a solution of 25 mg of *cis*-Δ-[Ru(bpy)$_2$(py)(O)](ClO$_4$)$_2$ of 60% optical purity in 2 mL of acetonitrile was added dropwise to a 10-fold excess of methyl *p*-tolyl sulfide in 2 mL of 1:1 (v/v) acetonitrile/water under argon. After reaction for 4 days in the dark at 23 °C, solvent was removed and the residue was extracted (×2) with 4 mL of ether. Ether and unreacted sulfide were removed under vacuum. The ^{1}H-NMR gives pure methyl *p*-tolyl sulfoxide with 20 ± 2% ee of the *R*-form determined from the CH$_3$ signal at $\delta \approx 2.7$ ppm in the presence of (*R*)-(−)-*N*-(3,5-dinitrobenzoyl) (α-methylbenzyl)amine (Aldrich).[11]

NMR spectra were obtained on a General Electric GN 300-MHz instrument. Circular dichroism measurements were made on an Aviv 62DS spectrophotometer. UV−visible spectra were run on a Varian Instruments Cary 3 spectrometer. MS/FAB analyses were performed on a JEOL JMS-AX505HX instrument.

Results and Discussion

The complex *cis*-[Ru(bpy)$_2$(py)(O)](ClO$_4$)$_2$ is a moderately strong oxidant, and resolution by conventional methods such

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(10) The same optical purity is determined for [Ru(bpy)$_2$(py)(CH$_3$CN)]$^{2+}$ formed in reduction by methyl *p*-tolyl sulfide immediately after the initial reduction, <1 h, and after 4 days. Interestingly, reduction with hydroquinone which does not require an oxo-transfer reaction gives [Ru(bpy)$_2$(py)(CH$_3$CN)]$^{2+}$ which is only 30% optically pure.

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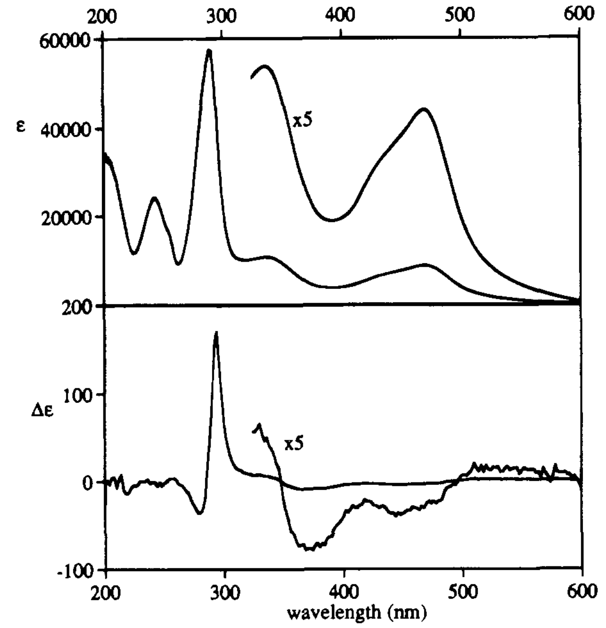

Figure 1. UV–visible and circular dichroism spectra of *cis*-Λ-$[Ru(bpy)_2(py)(H_2O)](ClO_4)_2$ (5×10^{-5} M) in 1 M $HClO_4$.

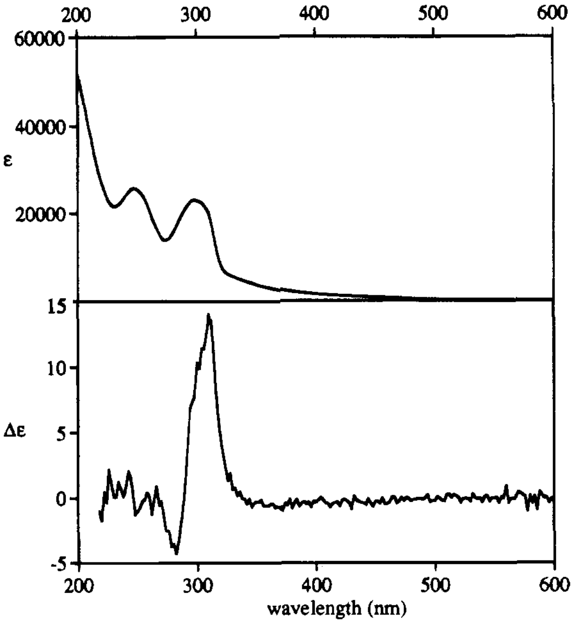

Figure 2. UV–visible and circular dichroism spectra of *cis*-Λ-$[Ru(bpy)_2(py)(O)](ClO_4)_2$ (5×10^{-5} M) in water.

as selective crystallization of diastereoisomeric salts or chiral column chromatography is problematic. However, the recent,[7] efficient resolution of *cis*-$[Ru(bpy)_2(py)_2]Cl_2$ affords a route to the chiral oxidant by hydrolysis to optically active *cis*-$[Ru(bpy)_2(py)(H_2O)](ClO_4)_2$ and subsequent reaction with cerium(IV) in 1 M $HClO_4$.[9] Thermal substitution of optically active *cis*-Λ-$[Ru(bpy)_2(py)_2]Cl_2$ gives optically active *cis*-$[Ru(bpy)_2(py)(H_2O)]^{2+}$. The optical purity of this aqua complex was determined by ^1H-NMR by forming the two diastereoisomers of the $[Ru(bpy)_2(R,R\text{-dach})]^{2+}$ complex,[7] giving 60% ee for the major form after optimizing the reaction for product formation.[12] Longer reaction times (10 h) did not significantly reduce the optical purity of the product, and although mechanistic details have not been investigated, it seems likely that improved optical purities will be difficult to achieve. The *cis*-$[Ru(bpy)_2(py)(H_2O)](ClO_4)_2$ obtained by this method has the circular dichroism spectrum shown in Figure 1. There is a strong couplet associated with the 289 nm band which is assigned to the ligand–ligand transition. Comparisons with the circular dichroism spectra of similar species suggest that the absolute configuration is Λ.[13] Thus, although some racemization does occur, the hydrolysis reaction appears to proceed with substantial retention of configuration. No significant racemization of the aqua complex was observed during the experimental measurements. The half-life for racemization is in excess of 24 h. Optically active *cis*-$[Ru(bpy)_2(py)(H_2O)]^{2+}$ may also be obtained by directly heating optically active *cis*-$[Ru(bpy)_2(py)_2](ClO_4)_2$ in water, but the reaction is complicated by the formation of a number of side products.[6] It was found that refluxing optically active *cis*-$[Ru(bpy)_2(py)_2](PF_6)_2$ in water for 6 h gives a higher yield of the desired product.

The circular dichroism spectrum of *cis*-$[Ru(bpy)_2(py)(O)]^{2+}$ obtained from oxidizing *cis*-Λ-$[Ru(bpy)_2(py)(H_2O)](ClO_4)_2$ is much weaker than that of the parent complex, Figure 2. The couplet associated with the 300 nm absorption band suggests that oxidation proceeds with retention of the absolute configuration although it is possible that some racemization occurs since the product of immediate reduction is 30% less optically pure than the initial *cis*-Λ-$[Ru(bpy)_2(py)(H_2O)](ClO_4)_2$. No change in the circular dichroism spectrum of *cis*-$[Ru(bpy)_2(py)(O)]^{2+}$ was detected over a period of 4 h. The detection of optical activity in this complex strongly supports the *cis* configuration (chiral) of *cis*-$[Ru(bpy)_2(py)(O)]^{2+}$ originally suggested by Meyer et al.[8,9] Oxidation involves only loss of two electrons and two protons; no Ru–N bond breaking or other coordination rearrangement is required.[14]

After 10 mg of *cis*-Δ-$[Ru(bpy)_2(py)(O)](ClO_4)_2$ in acetonitrile-d_3 was added to a 10-fold excess methyl *p*-tolyl sulfide in the same solvent, the reaction mixture was monitored by ^1H-NMR throughout the reaction course. The relatively long-lived ruthenium S-bound intermediate[3a] was identified by comparison with the complex $[Ru(bpy)_2(py)(OS(CH_3)(p\text{-}C_6H_4CH_3))]^{2+}$ isolated independently from the reaction of *cis*-$[Ru(bpy)_2(py)(H_2O)]^{2+}$ with methyl *p*-tolyl sulfide. No discernible diastereoselectivity was observed in the formation of this complex. The methyl *p*-tolyl sulfoxide isolated from the reaction with the chiral oxidant was found to be enriched with 15% ee of the *R* form.[11,15] *R* and *S* enantiomers, respectively, were produced in excess when Δ- and Λ-$[Ru(bpy)_2(py)(O)]^{2+}$ were used. Interestingly, when the oxidation reactions were carried out in the presence of 50% water, a higher, 30% ee was observed. Further variation in the proportion of water in the reaction mixture showed that the enantiomeric excess was independent of the water:acetonitrile ratio in the range 25–75%. Solvent-dependent selectivities have been reported in other systems.[4,16] In addition, the reaction temperature was varied from −20 °C to room temperature with no significant change in the stereoselectivity.

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(12) It has been shown[7] that two pyridine ligands in $[Ru(bpy)_2(py)_2]^{2+}$ can be substituted by a bidentate ligand such as bpy with retention of the absolute configuration, giving ≥96% ee. The lower optically active purity of $[Ru(bpy)_2(py)(H_2O)]^{2+}$ formed from optically pure $[Ru(bpy)_2(py)_2]^{2+}$ might reflect the stereochemical course of the substitution mechanism or to the more labile chromophore. See, for example: Porter, G. R.; Sparks, R. H. *J. Chem. Soc., Chem. Commun.* **1979**, 1094–1095.

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(15) The isolated (*R*,*S*)-methyl *p*-tolyl sulfoxide is 10% optically pure. Correction for the optical purity (60%) of the oxidant gives the stereoselectivity of the reaction of 15 ± 2% ee with *R* formed from Δ.

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The selectivity observed in the reaction is modest, particularly when compared with other results which incorporate chiral ligand systems.[4] However, the importance of the study is that it provides a benchmark for the reactions of an optically active octahedral complex where chirality is due only to the metal center. Interpretation of the result is complicated by the presence of a sulfur-bonded intermediate in the reaction. Although chiral induction is most likely to occur in the initial formation of the sulfoxide, the stereochemical consequences of the subsequent intermediate formation and decay cannot be forgotten. Molecular modeling considerations of the sulfoxide formation reveal that the oxo face of the $[Ru(bpy)_2(py)(O)]^{2+}$ complex provides little in the way of a steric constraint on the incoming prochiral sulfide, consistent with the modest selectivity. If it is assumed that the p-tolyl group will participate in a stacking interaction with the planar bpy ligand on this face, then the methyl group on the sulfur avoids the stereochemically more flexible pyridine ligand. This suggests that there may be considerable utility in modifying the reactivity with bulky chiral ligands. It is noted that comparable selectivities have been obtained in reactions of ruthenium complexes with chiral oxazoline ligands.[17] The fact that the optically active octahedral species $[Ru(bpy)_2(py)(O)]^{2+}$ can be prepared by oxidation of optically active *cis*-$[Ru(bpy)_2(py)(H_2O)]^{2+}$ with substantial retention of the absolute configuration suggests that it should be possible to prepare chiral reagents with the potential for electrochemical and catalytic asymmetric oxidation of organic and inorganic substrates.

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