An Anionic $\{[MnCo(ox)_3]^-\}_n$ Network with Appropriate Cavities for the Enantioselective Recognition and Resolution of the Hexacoordinated Monocation $[Ru(bpy)_2(ppy)]^+$ (bpy = bipyridine, ppy = phenylpyridine)

Muriel Brissard,[a][‡] Michel Gruselle,*[a] Bernard Malézieux,[a] René Thouvenot,[a]
Carine Guyard-Duhayon,[a] and Odile Convert[b]

Keywords: Circular dichroism / Chiral resolution / Ruthenium / NMR spectroscopy / Polymers

Partial resolution of the *rac*-$[Ru(bpy)_2(ppy)]^+$ monocation into $[\Delta\text{-}Ru(bpy)_2(ppy)]PF_6$ (**1Δ**) (*ee* = 44%) and $[\Lambda\text{-}Ru(bpy)_2(ppy)]PF_6$ (**1Λ**) (*ee* = 50%) enantiomers was achieved by an unprecedented resolving process which involves the diastereoselective preparation of optically active networks of the type $\{[\Lambda\text{-}Ru(bpy)_2(ppy)][Mn\text{-}\Lambda\text{-}Co(ox)_3]\}_n$ (**2Λ**) and $\{[\Delta\text{-}Ru(bpy)_2(ppy)][Mn\text{-}\Delta\text{-}Co(ox)_3]\}_n$ (**2Δ**). In these optically active inorganic polymers, the counter-monocation $[Ru(bpy)_2(ppy)]^+$ of appropriate configuration occupies the cavities while the excess $[Ru(bpy)_2(ppy)]^+$, of opposite configuration, remains in solution and is thus recovered. Anion metathesis of the optically active $[Ru(bpy)_2(ppy)]PF_6$ (**1Δ**) (*ee* = 44%) and (**1Λ**) (*ee* = 50%) with [l-cinchonidinium]-[Δ-trisphat] [trisphat = tris(tetrachlorobenzenediolato)-phosphate(V)] provides the related diastereomers $[\Delta\text{-}Ru(bpy)_2(ppy)][\Delta\text{-trisphat}]$ (**3Δ**) (*de* = 44%) and $[\Lambda\text{-}Ru(bpy)_2(ppy)][\Delta\text{-trisphat}]$ (**3Λ**) (*de* = 50%) in 60% yield. Their diastereomeric excesses were assessed by ^1H NMR analysis. All products were fully characterized and the absolute configuration was determined by circular dichroism techniques in solution or in the solid state. Additionally the X-ray structure of $[Ru(bpy)_2(ppy)]PF_6$ (**1**) was determined.

Introduction

The design and synthesis of networks possessing chiral cavities aimed to resolve optically active molecules represents a big challenge in the area of supramolecular material chemistry.[1] Ruthenium bis-bipyridine complexes $[Ru(bpy)_2L]^{n+}$ (L = bpy, phen...) (bpy = bipyridine; phen = phenanthroline) have been extensively studied for many years for their properties in biology,[2,3] and photo- and electrochemistry.[4−7] Most of these species have already been reported in the literature by several groups, with emphasis on the preparation of pure enantiomers of such propeller-like coordination complexes (Δ and Λ). Various resolution methods have commonly been used such as diastereomeric salt formation[8,9] or chromatographic separation techniques.[8,10] Another route to obtain optically active $[Ru(bpy)_2L]^{n+}$ complexes is based on the use of chiral precursors such as *cis*-$[Ru(bpy)_2(py)_2]^{2+}$ [11,12] (py = pyridine), *cis*-$[Ru(bpy)_2(CO)_2]^{2+}$ [8,13] or *cis*-$[Ru(bpy)_2(DMSO)Cl]^+$;[14−16] subsequent treatment with nucleophiles (phen, bpy...) provides the target complexes with retention of the configuration at the metal center. More recently a stereoselective synthesis has been proposed by Hesek[17] using the chiral ligand *R*-(+)- or *S*-(−)-methyl *p*-tolylsulfoxide that leads to the corresponding ruthenium bis-bipyridine complex with a diastereomeric excess of 50%.

In a pioneering work, Decurtins[18−21] described the synthesis of racemic bimetallic oxalate-bridged networks $\{[M^1(bpy)_3][M^2M^3(ox)_3]\}_n$ ($M^1 = Ni^{II}, Fe^{II}$; $M^2 = Li^I$ and $M^3 = Cr^{III}$ or $M^2 = M^3 = Mn^{II}$) starting from racemic materials. We recently reported the synthesis[22,23] of optically active homochiral polymers $\{[M^1(bpy)_3][M^2M^3(ox)_3]\}_n$ ($M^1 = Ni^{II}, Ru^{II}$; $M^2 = Li^I$ and $M^3 = Cr^{III}$ or $M^2 = M^3 = Mn^{II}$) and $\{[Ru^{II}(bpy)_2(ppy)][MCr^{III}(ox)_3]\}_n$ ($M = Ni^{II}, Mn^{II}$, ppy = phenylpyridine) using the tris-chelate complexes $[Cr(ox)_3]^{3-}$, $[M^1(bpy)_3]^{2+}$ and $[Ru^{II}(bpy)_2(ppy)]PF_6$ described by Constable.[24] We have shown that the formation of these polymers is highly diastereoselective and that the chirality control of only one type of building block leads to the selective precipitation of the corresponding homochiral enantiomeric polymer. Furthermore, the $\{[M^{II}M^{III}(ox)_3]^-\}_n$ network presented magnetic properties which can be tuned by modifying the nature of the M^{II}-M^{III} couple. As some of the $[M^{III}(ox)_3]^{3-}$ cannot always be resolved, we have to ensure the control of the chirality of the polymer via an optically active $[Ru(bpy)_2(ppy)]^+$ complex acting as a template. The separation of the latter into its two enantiomeric forms has not been reported so far. All attempts to resolve this $[Ru(bpy)_2(ppy)]^+$ complex by conventional procedures have been unsuccessful. Therefore we explored the possibility of employing the same resolution method that we have applied for $[Ni(bpy)_3]^{2+}$. Previously,[22] we have shown that using resolved $[\Delta\text{-}Cr(ox)_3]^{3-}$, a twofold excess of racemic $[Ni(bpy)_3]^{2+}$ and Li^+, afforded

---

[a] Laboratoire de Chimie Inorganique et Matériaux Moléculaires, ESA 7071, case courrier 42, Université Pierre et Marie Curie
4 Place Jussieu, 75252 Paris Cedex 05, France
Fax: (internat.) +33-1/4427-3841
E-mail: gruselle@ccr.jussieu.fr

[b] Laboratoire de Chimie Structurale Organique et Biologique, UMR 7613, case courrier 45, Université Pierre et Marie Curie
4 Place Jussieu, 75252 Paris Cedex 05, France
Fax: (internat.) +33-1/4427-3843

[‡] This work is a part of the Ph. D. thesis of M. Brissard.

1434−1948/01/0707−1745 $ 17.50+.50/0

an optically active insoluble polymer in which all the metal centers possessed the Δ configuration, leaving in solution the unreacted enriched $[\Lambda\text{-Ni(bpy)}_3]^{2+}$. Therefore the diastereomeric formation of these polymers could be of general use for the separation of the two enantiomers of tris-chelate complexes.

In this paper, we describe the partial resolution of the racemic $[\text{Ru(bpy)}_2\text{(ppy)}]\text{PF}_6$ (**1**) complex into $[\Delta\text{-Ru(bpy)}_2\text{(ppy)}]\text{PF}_6$ (**1Δ**) (*ee* = 44%) and $[\Lambda\text{-Ru(bpy)}_2\text{(ppy)}]\text{PF}_6$ (**1Λ**) (*ee* = 50%) enantiomers via the formation of the polymers $\{[\Lambda\text{-Ru(bpy)}_2\text{(ppy)}][\text{Mn-}\Lambda\text{-Co(ox)}_3]\}_n$ (**2Λ**) and $\{[\Delta\text{-Ru(bpy)}_2\text{(ppy)}][\text{Mn-}\Delta\text{-Co(ox)}_3]\}_n$ (**2Δ**), respectively. Their absolute configuration was determined by circular dichroism. In addition we describe the preparation of the diastereomeric salts $[\Delta\text{-Ru(bpy)}_2\text{(ppy)}]$[Δ-trisphat] (**3Δ**) (*de* = 44%) and $[\Lambda\text{-Ru(bpy)}_2\text{(ppy)}]$[Δ-trisphat] (**3Λ**) (*de* = 50%) from [l-cinchonidinium][Δ-trisphat] and the enriched $[\text{Ru(bpy)}_2\text{(ppy)}]\text{PF}_6$ complexes **1Δ** and **1Λ**, respectively. Finally the optical purity of these species was determined by ^{1}H NMR spectroscopy.

Results and Discussion

X-ray Structure of $[\text{Ru(bpy)}_2\text{(ppy)}]\text{PF}_6$

Single crystals of $[\text{Ru(bpy)}_2\text{(ppy)}]\text{PF}_6$ (**1**) were obtained by diffusion of diethyl ether into a solution of **1** in acetone. The crystallographic data and structure determination parameters obtained by X-ray diffraction studies for $[\text{Ru(bpy)}_2\text{(ppy)}]\text{PF}_6$ (**1**) are given in Table 1. $[\text{Ru(bpy)}_2\text{(ppy)}]\text{PF}_6$ crystallizes in the space group *C*2/*c* with *Z* = 8. As depicted in Figure 1, we notice that the $[\text{Ru(bpy)}_2\text{(ppy)}]^+$ cation is hexacoordinated and presents a structure similar to that of the dication $[\text{Ru(bpy)}_3]^{2+}$ [a C atom (C31) replaces an N atom]. The C atom (C31) was arbitrarily placed on the Figure 1 (in fact its distribution is equal on the six atomic sites bonded to the Ru atom). The bond lengths and angles for $[\text{Ru(bpy)}_2\text{(ppy)}]\text{PF}_6$ (**1**) and in $[\text{Ru(bpy)}_3]\text{Cl}_2$ [22,25] are quite similar (Table 2). The symmetry of the monocation $[\text{Ru(bpy)}_2\text{ppy}]^+$ is formally C_1. However, as the external shell geometry is very close to that of $[\text{Ru(bpy)}_3]^{2+}$, one can assume that $[\text{Ru(bpy)}_2\text{ppy}]^+$ has a quasi D_3 symmetry.

Ideally, to differentiate a chiral cationic complex of D_3 symmetry such as $[\text{Ru(bpy)}_2\text{ppy}]^+$, it is essential to choose a chiral shift anionic reagent that also possesses a D_3 symmetry. Therefore we choose the [Δ-trisphat] anion (previously described by Lacour[26−28]) to prepare the related diastereomers of $[\text{Ru(bpy)}_2\text{ppy}]^+$; the results are shown in the next section.

Resolution of the $[\text{Ru(bpy)}_2\text{(ppy)}]^+$ Cation 1Δ and 1Λ by the Synthesis of the Optically Active Polymers 2Λ and 2Δ

Treatment of [l-cinchonidinium][Δ-trisphat] with a stoichiometric amount of *rac*-$[\text{Ru(bpy)}_2\text{(ppy)}]\text{PF}_6$ (in acetone, MeOH or acetone/MeOH in ratios 1:1 and 2:3) followed by crystallization provided deep purple powders. Circular

Table 1. Crystal data for $[\text{Ru(bpy)}_2\text{(ppy)}]\text{PF}_6$ (**1**)

	$[\text{Ru(bpy)}_2\text{(ppy)}]\text{PF}_6$ **1**
Formula	$C_{31}H_{24}N_5Ru{\cdot}PF_6$
Fw (g.mol^{-1})	712.60
Temperature (K)	295
Crystal system	Monoclinic
Space group	*C*2/*c*
a (Å)	23.749 (16)
b (Å)	13.715 (3)
c (Å)	19.334 (6)
α (°)	90
β (°)	114.16 (3)
γ (°)	90
V (Å^3)	5745 (5)
Z	8
Linear abs coef μ (mm^{-1})	0.672
Density ρ (g.cm^{-3})	1.65
Crystal size (mm)	0.4 × 0.4 × 0.3
Color	brown
Shape	parallelepiped
Diffractometer	Enraf−Nonius Cad 4
Radiation	Mo-K_α (λ = 0.71069 Å)
Scan type	2θ/ω
θ limits (°)	1−26
Index range, *h*, *k*, *l*	0, 29; 0, 16; −23, 21
Secondary extinction coeff	505
Percent decay	0.063
Reflections measured	6034
Independent reflections	5626
Reflections used	2486
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\|F_o\|$	0.0668
$Rw^* = [\Sigma w(\|\|F_o\| - \|F_c\|\|)^2/\Sigma wF_o^2]^{1/2}$	0.0738
Weight coefficients[a]	3.11, 0.901, 2.45
Δρmin (e/ Å^3)	−1.06
Δρmax (e/ Å^3)	1.77
σ(I) limit	3.00
Number of parameters	364
Goodness of fit	0.965

[a] $w = w'\{1\text{-}[(||F_o| - |F_c||)/6.\sigma(F_o)]^2\}^2$ with $w' = 1/\Sigma_r T_r(X)$ with three coefficients for a Chebyshev series for which $X = F_c/F_c(\text{max})$.

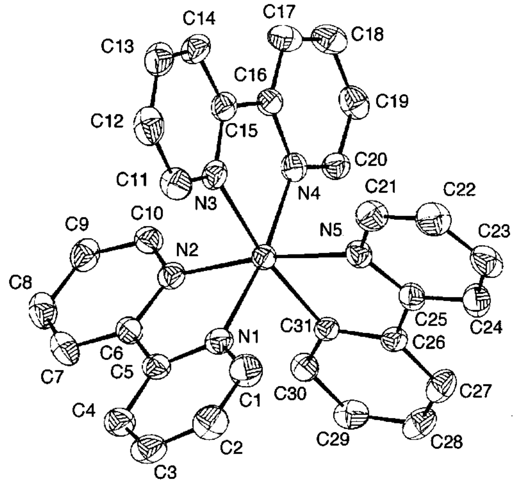


Figure 1. X-ray molecular structure of $[\text{Ru(bpy)}_2\text{(ppy)}]\text{PF}_6$ (**1**) with atomic number system

Table 2. Selected bond lengths [Å] and angles [°] for $[Ru(bpy)_2(ppy)]PF_6$ (**1**) and $[Ru(bpy)_3]Cl_2$

	$[Ru(bpy)_2(ppy)]^+$ (**1**)	$[Ru(bpy)_3]^{2+}$ [22]
N1[a]−Ru−N1	95.4 (6)	95.3 (2)
N1−Ru−N2	78.0 (6)	78.9 (2)
N2[a] (C31)−Ru−N2	96.5 (0)	95.6 (2)
N1[b]−Ru−N2	90.6 (0)	90.7 (2)
Ru−N1	2.069 (4)	2.046 (4)
Ru−N2 (C31)	2.044 (1)	2.054 (4)

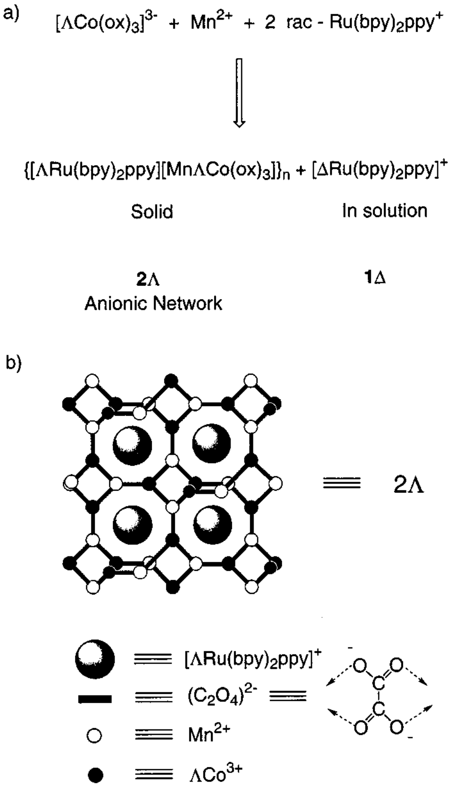
[a] $-1/2 + y, 3/2 - z, 1 - x$. − [b] $1 - z, 1/2 + x, 3/2 - y$.

dichroism and ^1H NMR spectroscopy showed that this material is composed only of nonenriched $[Ru(bpy)_2(ppy)][\Delta$-trisphat] (**3**) (equal amounts of the two diastereomers, *de* = 0%). Hence using the [Δ-trisphat] anion, we were unable to resolve the *rac*-$[Ru(bpy)_2(ppy)]^+$ complex by selective crystallization of one diastereomer.

To resolve the *rac*-$[Ru(bpy)_2(ppy)]PF_6$ complex we finally applied the "polymer formation" strategy. To ensure good enantiomeric excess for the unreacted optically active $[Ru(bpy)_2(ppy)]^+$, three conditions were required: i) A full diastereoselectivity in the formation of the polymers. ii) A rapid precipitation relative to the racemization rate of the starting anionic brick $[M^{III}(ox)_3]^{3-}$ to keep a good chiral induction over the synthesized polymer and also on the excess cation left in solution. iii) A good yield for the reaction (almost quantitative). *These conditions are fulfilled in our system*. It should be noted that tris-oxalate cobalt $[Co(ox)_3]^{3-}$ was used instead of $[Cr(ox)_3]^{3-}$ (as previously) because its racemization rate is slower,[29] affording an enhanced enantiomeric excess for the resolved cation (*ee* = 34% versus 44% or 50% according to NMR studies). Thus, the use of resolved $K_3[Co(ox)_3]$ $\{[\alpha]_D = +1667$ (Δ form) or -1892 (Λ form)$\}$ (maximum rotation reported in the literature:[30] $[\alpha]_D = +1928$ or -1940), $MnCl_2$ and racemic $[Ru(bpy)_2(ppy)]PF_6$ (**1**) (twofold excess) in a $DMSO/H_2O$ solution results, after five minutes, in the precipitation of the respective polymers either $\{[\Delta\text{-}Ru(bpy)_2(ppy)][Mn\text{-}\Delta\text{-}Co(ox)_3]\}_n$ (**2Δ**) or $\{[\Lambda\text{-}Ru(bpy)_2(ppy)][Mn\text{-}\Lambda\text{-}Co(ox)_3]\}_n$ (**2Λ**) (yield = 90%), depending on the configuration of the $[Co(ox)_3]^{3-}$ building block. As a consequence, the mother liquor phase is now enriched in the opposite enantiomer of $[Ru(bpy)_2(ppy)]PF_6$ (either **1Λ** or **1Δ**) and is thus recovered from the filtrate as a precipitate by addition of diethyl ether (Scheme 1a). Scheme 1b shows a schematic representation[22] of the anionic optically active polymer **2Λ** hosting the $[\Lambda\text{-}Ru(bpy)_2(ppy)]^+$ monocation counter part.

Assignment of the Metallic Configurations in the Polymers 2Δ and 2Λ and in the Resolved Cations 1Δ and 1Λ by Circular Dichroism

The absolute configuration of the Co and Ru centers in the polymers **2Δ** and **2Λ** and in the enriched cations **1Δ** and **1Λ** was determined by circular dichroism by comparison of their spectra with those of Δ and Λ enantiomers of $[Co(ox)_3]^{3-}$ and $[Ru(bpy)_2L]$. This is based on the principle that two related optically active molecules have the same absolute configuration if they give a Cotton effect of the same sign in the absorption wavelength region of an electronic transition common to both molecules.[31] Due to the extreme insolubility of the polymers, solid state circular dichroism was employed for all compounds. The circular dichroism curves of the polymers **2Δ** and **2Λ** are depicted in Figure 2. They show optical activity and opposite signals typical for two enantiomers. All bands (λ_{max} = 548, 493, 432, 376, 322, 311, 279 nm) are essentially due to intra-ligand or MLCT transitions of $[Ru(bpy)_2ppy]^+$. Indeed, these bands are very strong in comparison with the weak d → d bands of $[Co(ox)_3]^{3-}$(in the monomer at λ_{max} = 618, 518, 415, 291 nm) which are totally masked. Therefore the absolute configuration of the Co centers cannot be assigned directly. However, it can be easily predicted from the configuration of the starting optically active $[Co(ox)_3]^{3-}$ salt. The Ru absolute configurations in **2Δ** and **2Λ** are assigned owing to the sign of the band due to the bipyridine ligand at λ_{max} = 322 nm (a positive Cotton effect in the 300−330 nm region is characteristic of the Λ configuration for the metal center[8,9,11,13−17,22]). The Co and Ru centers adopt the same configuration in these polymers, as is the case in the bimetallic polymers templated by $[Ru(bpy)_3]^{2+}$ obtained previously.[22]



Scheme 1. (a) Preparation of the bimetallic optically active polymer $\{[\Lambda\text{-}Ru(bpy)_2ppy][Mn\text{-}\Lambda\text{-}Co(ox)_3]\}_n$ (**2Λ**) along with the enriched monocation $[\Delta\text{-}Ru(bpy)_2(ppy)]^+$ (**1Δ**); (b) schematic representation[22] of the polymer **2Λ** hosting the $[\Lambda\text{-}Ru(bpy)_2(ppy)]^+$ cation counter part

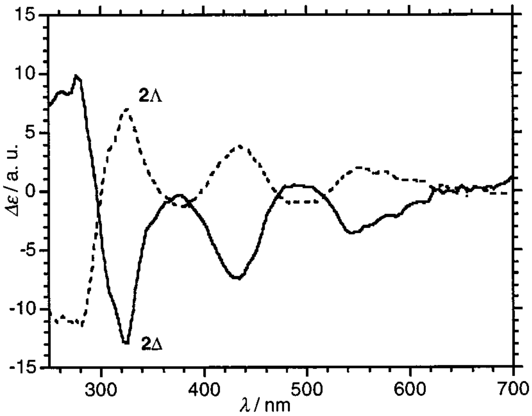


Figure 2. Circular dichroism spectra of **2Δ** and **2Λ** polymers in KBr dispersions

As expected, the circular dichroism curves of the enriched $[Ru(bpy)_2ppy]^+$ (**1Δ** or **1Λ**) (Figure 3) display signals due to the bipyridine ligands (λ_{max} = 598, 494, 390, 307, 259 nm) opposite to that of the respective precipitated polymers **2Λ** or **2Δ**, confirming the partial resolution of the monocation. The typical bipyridine band mentioned above again allows the determination of the Ru absolute configurations. It is worth noting that the dichroism spectra of the compounds **1Δ** and **1Λ** (in CH_2Cl_2 or acetone solutions) remain unchanged after five hours, showing that the racemization of $[Ru(bpy)_2(ppy)]^+$ is very slow in solution.

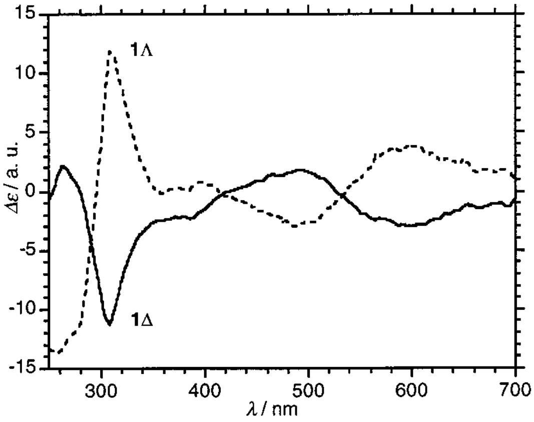


Figure 3. Circular dichroism spectra of **1Δ** and **1Λ** in KBr dispersions

Synthesis and Circular Dichroism of 3Δ and 3Λ

Even if circular dichroism in the solid state allows us to assign the absolute configurations of metal complexes in the optically active compounds, it cannot be used as a device to measure the enantiomeric or diastereomeric excesses.[22] The circular dichroism spectrum of pure $[Ru(bpy)_2(ppy)]^+$ (*ee* = 100%) is still unknown, precluding a useful comparison of the relative intensities. The very deep purple color of the $[Ru(bpy)_2(ppy)]^+$ complex (due to the intraligand bipyridine transitions) also wrecked all attempts to measure the optical rotation. For this purpose the optically active enriched **1Δ** and **1Λ** $[Ru(bpy)_2ppy]^+$ salts were converted into their enriched diastereomeric salts [Δ-$Ru(bpy)_2$(ppy)][Δ-trisphat] (**3Δ**) and [Λ-$Ru(bpy)_2$(ppy)][Δ-trisphat] (**3Λ**) with [Δ-trisphat] as the counter-anion. The diastereomeric excesses in these two species were determined by ^1H NMR spectroscopy.

Treatment of a solution of **1Δ** (or **1Λ**) with one equivalent of [l-cinchonidinium][Δ-trisphat] for 30 minutes in acetone at room temperature afforded either **3Δ** (or **3Λ**). Subsequent separation of the mixture by column chromatography on an aluminum oxide column (10 cm, CH_2Cl_2) provided **3Δ** (or **3Λ**) as the less-polar purple band while the starting $[Ru(bpy)_2(ppy)]PF_6$ **1Δ** (or **1Λ**) was then eluted as the more polar fraction. We assume in this reaction that the diastereomeric excess in **3Δ** and **3Λ** reflects exactly the enantiomeric excess in **1Δ** and **1Λ** for the following reasons:

– the [l-cinchonidinium][Δ-trisphat] salt is optically pure (*de* = 98%).

– the [l-cinchonidinium][Δ-trisphat] reacts equally (see above and ref.[32]) with both enantiomers of $[Ru(bpy)_2ppy]^+$ even if the transformation of $[Ru(bpy)_2ppy]^+$ into the related diastereomeric salt $[Ru(bpy)_2(ppy)]$[Δ-trisphat] is not quantitative (yield: 60%).

Circular dichroism measurements of **3Δ** and **3Λ** were performed in CH_2Cl_2 (Figure 4). The curves of the two diastereomers exhibited two well-separated regions where the borderline is centered at 270 nm. For the region $\lambda > 270$ nm, the spectra present opposite signals due exclusively to the optically active $[Ru(bpy)_2(ppy)]^+$. Below 270 nm, [Δ-trisphat] bands are predominant exhibiting similar and negative Cotton effects.

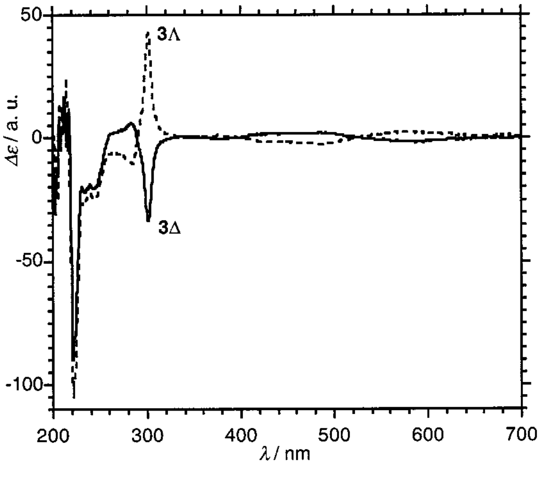


Figure 4. Circular dichroism spectra of **3Δ** and **3Λ** in CH_2Cl_2 solutions ($c = 7.5-9.10^{-5}$ mol·L^{-1})

Determination of the Diastereomeric Excess of [Δ-Ru(bpy)₂(ppy)][Δ-trisphat] (3Δ) and [Λ-Ru(bpy)₂(ppy)][Δ-trisphat] (3Λ) by ¹H NMR Spectroscopy

The ^1H NMR spectra of *rac*-$[Ru(bpy)_2ppy]PF_6$ (**1**), $[Ru(bpy)_2(ppy)]$[Δ-trisphat] (**3**) (*de* = 0%) and enriched [Δ-$Ru(bpy)_2$(ppy)][Δ-trisphat] (**3Δ**) and [Λ-$Ru(bpy)_2$(ppy)][Δ-trisphat] (**3Λ**) were recorded in acetone solution (Figure 5a−d). These ^{1}H NMR studies allowed us to determine the enantiomeric excess of the enriched complex [Δ-Ru(bpy)$_2$ppy]PF$_6$ (**1Δ**) and [Λ-Ru(bpy)$_2$ppy]PF$_6$ (**1Λ**) by measurement of the diastereomeric excess in **3Δ** and **3Λ**. As a first approach, we measured the ^{1}H NMR spectrum of *rac*-[Ru(bpy)$_2$ppy]PF$_6$. The latter was previously studied by Constable[24] in [D$_6$]DMSO solution. Based on previous studies, and on our own ^{1}H-^{1}H NMR homonuclear decoupling and 2D ^{1}H-^{1}H experiments, we assigned the multiplet centered at $\delta = 7.57$ to the proton H-10. The spectrum of [Ru(bpy)$_2$(ppy)][Δ-trisphat] in its nonenriched form **3** appears more intricate than that of the [Ru(bpy)$_2$ppy]PF$_6$ complex; some resonances split into two components because the two diastereomers exhibit different chemical shifts in their ^{1}H NMR spectra. The spectra of **3Δ** and **3Λ** clearly show an enrichment in one of the two diastereomers. For quantitative purposes we chose the well-resolved multiplet H-10, which exhibits the most pronounced splitting in the diastereomer formation. The appearance of this multiplet in **1**, **3**, **3Δ**, **3Λ** is shown in Figure 5 (a−d). We were able to assign each peak to each of the two diastereomers by examining and comparing the spectra of **3Δ** and **3Λ**. Thus, the most and the least deshielded doublets of the multiplet are assigned respectively to the [Λ-Ru(bpy)$_2$(ppy)][Δ-trisphat] and [Δ-Ru(bpy)$_2$(ppy)][Δ-trisphat] diastereomers. These signals are sufficiently well separated to afford a precise measurement of the respective ratio of the two diastereomers, and so of the diastereomeric excesses, by integration. As can easily be seen, in the nonenriched product **3** they appear of equal intensity whereas for the enriched compounds **3Δ** and **3Λ** the ratio between the two diastereomers (ΔΔ/ΛΔ) is 72:28 and 25:75, respectively, providing an estimate of the diastereomeric excess in **3Δ** and **3Λ**, and so the enantiomeric excess in **1Δ** and **1Λ**, to be 44% and 50%, respectively.

Conclusion

In this paper we described the preparation of optically active bimetallic networks of the type {[Λ-Ru(bpy)$_2$(ppy)][Mn-Λ-Co(ox)$_3$]}$_n$ (**2Λ**) and {[Δ-Ru(bpy)$_2$(ppy)][Mn-Δ-Co(ox)$_3$]}$_n$ (**2Δ**) and showed for the first time that the synthesis of these chiral polymers is a good strategy for resolving the [Ru(bpy)$_2$(ppy)]$^+$ complex. Furthermore, **2Λ** and **2Δ** can be obtained via either the resolved tris-oxalato [M^{III}(ox)$_3$]$^{3-}$ anion or [Ru(bpy)$_2$(ppy)]$^+$ cation building block, whereby each species can play the role of the chiral template-inducer. This implies that an optically active form of either tris-chelated brick (anion or cation) affords the partial resolution of the other one owing to the matrix effect induced by the formation of the optically active polymer. This feature opens new horizons in the resolution of the hexacoordinated quasi-D_3 monocations [Ru(bpy)$_2$L]$^+$ (L is a bidentate monocharged ligand such as the 8-quinolate). Therefore, separation of enantiomers induced by specific interactions between chiral molecules and optically active molecular frameworks appears to be one of the most promising alternatives to the conventional procedures.

The use of the optically active and configurationally stable [Ru(bpy)$_2$(ppy)]$^+$ complex will provide an important control over chirality in the building of optically active polymers with various tandems M^{II}-M^{III} displaying interesting magnetic behavior.

Experimental Section

Materials: The following compounds were prepared according to literature methods: K$_3$[Co(ox)$_3$]·3H$_2$O,[33] *rac*-[Ru(bpy)$_2$ppy]PF$_6$,[24,34] [l-cinchonidinium][Δ-trisphat].[28] The resolution procedure described previously was followed to obtain the Δ and Λ K$_3$[Co(ox)$_3$]·3H$_2$O enantiomers.[30] The other reagents are commercially available and were used as purchased.

General Procedures: The IR spectra were recorded on a Bio-Rad IRFT spectrophotometer as KBr pellets in the 4000−250 cm^{-1} region. Elemental analyses were performed at the SIARE-UPMC, Paris. Metal analyses were completed at the Service Central d'Analyse-CNRS, Vernaison. The specific rotations of the starting materials were measured at 20 °C, in a 1 dm-tube containing the solutions, using the D-line in an Ameria AA5 polarimeter. The enantiomeric or diastereomeric excess was calculated by comparison with the maximum specific rotation values found in the literature.[28,30] Circular dichroism spectra were measured with a Jasco model J-710 spectropolarimeter. Solid state measurements were made on compounds **1Δ**, **1Λ**, **2Δ** and **2Λ** as dispersions of 0.1−0.5 mg in 100−110 mg of oven-dried KBr. 13 mm-diameter disks were made in a standard disk press. For **3Δ** and **3Λ**, measurements were carried out in CH$_2$Cl$_2$ solutions ($c = 7.5-9.10^{-5}$ mol·L^{-1}) in a 1 mm cuvette. The baseline correction was performed with the spectrum of a pure KBr disk or of CH$_2$Cl$_2$ prepared under the same conditions. The displayed absorption spectra result from subtraction of the spectrum of the standard KBr disk or of CH$_2$Cl$_2$. Spectra were recorded in the wavelength range 700−200 nm for all compounds. The ^{1}H NMR spectra (300 MHz) were obtained at room temperature in 5 mm o.d. tubes on a Bruker AC 300 spectrometer equipped with a QNP probehead (solutions of [D$_6$]acetone, $c = 0.014$ mol·L^{-1}). Chemical shifts are given according to the IUPAC convention with respect to SiMe$_4$. The ^{31}P NMR (121.5 MHz) spectra were measured as for ^{1}H spectra on the same tubes. The chromatography separations were carried out on a 3 cm-diameter column of alumina (10 cm; 0.05−0.15 mm neutral aluminium oxide; eluent: CH$_2$Cl$_2$).

X-ray Crystallographic Analysis: Accurate cell dimensions and orientation matrix were obtained by least-squares refinement of 25 accurately centered reflections. The data were corrected for Lorentz and polarization effects. Computations were performed by using Crystals 2000 version. Scattering factors and corrections for anomalous dispersion were taken from reference.[35] The structures were solved by direct methods (SHELXS). All final refinements were carried out by full-matrix least-squares using anisotropic displacement parameters for all phosphorus, fluorine and non-hydrogen atoms. Hydrogen atoms were introduced in calculated positions and only one overall isotropic displacement parameter was refined. All crystallographic data and diffraction parameters are listed in Table 1.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge

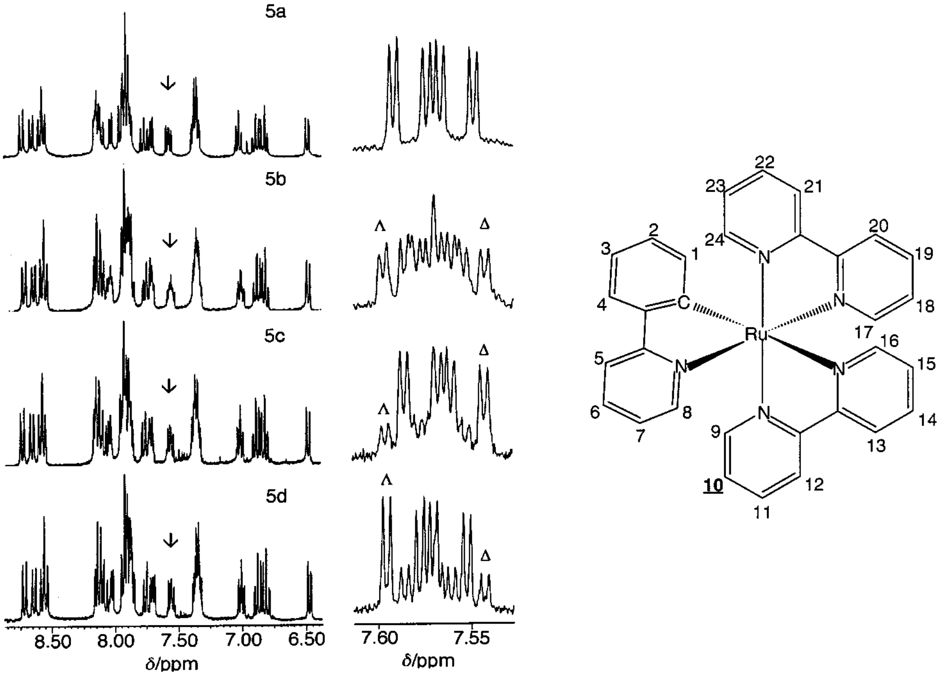


Figure 5. ^{1}H NMR spectra of **1** (5a), **3** (5b), **3Δ** (5c) and **3Λ** (5d) in acetone d^6 solutions (c = 0.014 mol·L^{-1}). Full spectra are shown on the left side and enlargement of the signal H-**10** on the right

Crystallographic Data centre as supplementary publication no. CCDC-151418. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Preparation of 1Δ, 1Λ, 2Δ and 2Λ: In a hemolysis tube, an aqueous solution (0.2 mL) of optically active $K_3[\Lambda Co(ox)_3]·3H_2O$ {39.4 mg, 0.08 mmol; [α]$_D$ = −1892 (c = 0.02 in H_2O); maximum rotation reported in the literature:[30] [α]$_D$ = −1940} and $MnCl_2·4H_2O$ (15.7 mg, 0.08 mmol) was added quickly to a DMSO solution (0.4 mL) of racemic [Ru(bpy)$_2$ppy]PF$_6$ (**1**) (100.2 mg, 0.14 mmol; not completely dissolved. To ensure the complete precipitation of the [Λ-Ru(bpy)$_2$ppy]$^+$ as a polymer we used less than two equivalents of the [Ru(bpy)$_2$ppy]PF$_6$ complex). During 5 minutes, acetone and H_2O were successively added scratching continuously the walls of the tube with a Pasteur pipette (the additions were made in this order: acetone-H_2O-acetone-H_2O-acetone, 1.2 mL each time). The purple precipitate was filtered off, washed with H_2O (5 mL) and acetone (until the filtrate became colorless) and air-dried leading to the green {[Λ-Ru(bpy)$_2$(ppy)][Mn-Λ-Co(ox)$_3$]}$_n$ (**2Λ**) (68.6 mg, 0.0724 mmol; yield: 91%). The purple filtrate was concentrated by rotary evaporator to remove acetone and, after precipitation by addition of diethyl ether (200 mL), the purple enriched [Δ-Ru(bpy)$_2$ppy]PF$_6$ (**1Δ**) (43.7 mg, 0.0612 mmol) was filtered off and air-dried. The same procedure was employed for the other enantiomers **1Λ** and **2Δ** using $K_3[\Delta Co(ox)_3]·3H_2O$ {[α]$_D$ = +1667 (c = 0.02 in H_2O); maximum rotation reported in the literature:[30] [α]$_D$ = +1928}.

2Λ: $C_{37}H_{24}CoMnN_5O_{12}Ru$ (945.56): calcd. C 47.0, H 2.56, N 7.41, Ru 10.69, Mn 5.81, Co 6.23; found C 41.93; H 2.72, N 6.11, Ru 8.15, Mn 5.66, Co 5.87. − IR (KBr): ṽ = 1652s, 1629vs, 1600vs (C=O), 1310m, 798m, 780m cm^{-1}.

1Δ: ^{1}H NMR (300.13 MHz, C_3D_6O, 300 K, TMS): δ = 6.48 (d, 1 H), 6.85 (m, 2 H), 7.02 (t, 1 H), 7.36 (m, 3 H), 7.57 (t, 1 H), 7.70 (d, 1 H), 7.76 (t, 1 H), 7.91 (m, 6 H), 8.03 (d, 1 H), 8.12 (m, 3 H), 8.57 (pseudo-t, 2 H), 8.65 (d, 1 H), 8.73 (d,1 H). − ^{31}P NMR (121.5 MHz, C_3D_6O, 300 K, 85% H_3PO_4): δ= −142.72 (sept).

Preparation of 3Δ and 3Λ: [Δ-Ru(bpy)$_2$(ppy)]PF$_6$ (**1Δ**) (128.3 mg, 0.18 mmol) and [l-cinchonidinium][Δ-trisphat] ([α]$_D$=-369 (c = 0.1 in EtOH), de = 98%)(1-fold) (191.3 mg, 0.18 mmol) were dissolved in a minimum amount of acetone and stirred for about 30 minutes. The product was first adsorbed on aluminium oxide and then chromatographed on a column of alumina (10 cm, CH_2Cl_2). The less-polar fraction contained exclusively the deep purple diastereomer **3Δ** (or **3Λ**). Enriched [Δ-Ru(bpy)$_2$(ppy)]PF$_6$ **1Δ** (or **1Λ**) appeared afterwards as a second fraction of the same color. [Δ-Ru(bpy)$_2$(ppy)][Δ-trisphat] (**3Δ**) (150.8 mg, 0.11 mmol; yield: 61%) and [Δ-Ru(bpy)$_2$(ppy)]PF$_6$ (**1Δ**) (46.4 mg, 0.065 mmol) were recuperated after evaporation of the solvent on a rotary evaporator. $C_{49}H_{24}N_5Cl_{12}O_6PRu$ (%): calcd. C 44.01, H 1.81, N 5.24; found C 44.26; H 2.03, N 5.61;IR (KBr): ṽ = 1451vs, 1421s, 1389s, 992vs, 825vs, 757s, 730s, 719m, 672vs, 650s, 620s cm^{-1}. − ^{1}H NMR (300.13 MHz, C_3D_6O, 300 K, TMS): δ = 6.48 (d, 1 H), 6.84 (m, 2 H), 7.00 (m, 1 H), 7.34 (m, 3 H), 7.55 (m, 1 H), 7.73 (m.2 H), 7.90 (m, 6 H), 8.03 (m, 1 H), 8.13 (m, 3 H), 8.55 (pseudo-t, 2 H), 8.63 (d, 1 H), 8.71 (d, 1 H). − ^{31}P NMR (121.5 MHz, C_3D_6O, 300 K, 85 % H_3PO_4): δ = −79.14 (s).

Acknowledgments

We gratefully acknowledge Dr. H. Amouri and Dr. R. Andrès for helpful discussions and Dr. M. Takahashi (Institut Curie, CNRS) for assistance in performing the circular dichroism measurements. We thank CNRS and Université Pierre et Marie Curie for financial support.

---

[1] J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982−986.
[2] S. A. Tysoe, R. Kopelman, D. Schelzig, *Inorg. Chem.* **1999**, *38*, 5196−5197.

[3] J. G. Collins, A. D. Sleeman, J. R. Aldrich-Wright, I. Greguric, T. W. Hambley, *Inorg. Chem.* **1998**, *37*, 3133−3141.

[4] P. R. Ashton, R. Ballardini, V. Balzani, E. C. Constable, A. Credi, O. Kocian, S. J. Langford, J. A. Preece, L. Prodi, E. R. Schofield, N. Spencer, J. F. Stoddart, S. Wenger, *Chem. Eur. J.* **1998**, *4*, 2413−2422.

[5] V. Balzani, A. Juris, M. Venturi, S. Campagna, S. Serroni, *Chem. Rev.* **1996**, *96*, 759−833.

[6] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, *Coord. Chem. Rev.* **1988**, *84*, 85−277.

[7] K. Kalyanasundaram, *Coord. Chem. Rev.* **1982**, *46*, 159−244.

[8] T. J. Rutherford, P. A. Pellegrini, J. R. Aldrich-Wright, P. C. Junk, F. R. Keene, *Eur. J. Inorg. Chem.* **1998**, 1677−1688.

[9] J. A. Arce Sagüés, R. D. Gillard, D. H. Smalley, P. A. Williams, *Inorg. Chim. Acta* **1980**, *43*, 211−216.

[10] N. C. Fletcher, P. C. Junk, D. A. Reitsma, F. R. Keene, *J. Chem. Soc., Dalton Trans.* **1998**, 133−138. − N. C. Fletcher, F. R. Keene, *J. Chem. Soc., Dalton Trans.* **1999**, 683−690.

[11] X. Hua, A. von Zelewsky, *Inorg. Chem.* **1995**, *34*, 5791−5797.

[12] X. Hua, A. von Zelewsky, *Inorg. Chem.* **1991**, *30*, 3796−3798.

[13] T. J. Rutherford, M. G. Quagliotto, F. R. Keene, *Inorg. Chem.* **1995**, *34*, 3857−3858.

[14] D. Hesek, Y. Inoue, S. R. L. Everitt, H. Ishida, M. Kunieda, M. G. B. Drew, *J. Chem. Soc., Dalton Trans* **1999**, 3701−3709.

[15] D. Hesek, Y. Inoue, S. R. L. Everitt, H. Ishida, M. Kunieda, M. G. B. Drew, *Chem. Commun.* **1999**, 403−404.

[16] D. Hesek, Y. Inoue, S. R. L. Everitt, M. Kunieda, H. Ishida, M. G. B. Drew, *Tetrahedron: Asymmetry* **1998**, *9*, 4089−4097.

[17] D. Hesek, Y. Inoue, S. R. L. Everitt, H. Ishida, M. Kunieda, M. G. B. Drew, *Inorg. Chem.* **2000**, *39*, 317−324. − F. Pezet, J. C. Daran, I. Sasaki, H. Aït-Haddou, G. Balavoine, *Organometallics* **2000**, *19*, 4008−4015.

[18] S. Decurtins, H. W. Schmalle, R. Pellaux, P. Schneuwly, A. Hauser, *Inorg. Chem.* **1996**, *35*, 1451−1460.

[19] S. Decurtins, H. W. Schmalle, R. Pellaux, R. Huber, P. Fisher, B. Ouladdiaf, *Adv. Mater.* **1996**, *8*, 647−651.

[20] S. Decurtins, H. W. Schmalle, P. Schneuwly, J. Ensling, P. Gütlich, *J. Am. Chem. Soc.* **1994**, *116*, 9521−9528.

[21] S. Decurtins, H. W. Schmalle, P. Schneuwly, H. R. Oswald, *Inorg. Chem.* **1993**, *32*, 1888−1892.

[22] R. Andrés, M. Gruselle, B. Malézieux, M. Verdaguer, J. Vaissermann, *Inorg. Chem.* **1999**, *38*, 4637−4646.

[23] M. Gruselle, R. Andrés, B. Malézieux, M. Brissard, C. Train, M. Verdaguer *The 14th International Symposium on Chirality ISCD 12 Chirality* **2000**, Chamonix (France).

[24] E. C. Constable, J. M. Holmes, *J. Organomet. Chem.* **1986**, *301*, 203−208.

[25] M. Biner, H. B. Burgi, A. Ludi, C. Rohr, *J. Am. Chem. Soc.* **1992**, *114*, 5197−5203.

[26] J. Lacour, S. Torche-Haldimann, J. J. Jodry, C. Ginglinger, F. Favarger, *Chem. Commun.* **1998**, 1733−1734.

[27] J. Lacour, C. Ginglinger, F. Favarger, S. Torche-Haldimann, *Chem. Commun.* **1997**, 2285−2286.

[28] J. Lacour, C. Ginglinger, C. Grivet, G. Bernardinelli, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 608−610; *Angew. Chem.* **1997**, *109*, 660−662.

[29] C. H. Johnson, *Trans. Faraday Soc.* **1935**, *31*, 1612−1621.

[30] G. B. Kauffman, L. T. Takahashi, N. Sugisaka, *Inorg. Synth.* **1966**, *8*, 227−232.

[31] A. J. McCaffery, S. F. Mason, R. E. Ballard, *J. Chem. Soc.* **1965**, 2883−2892.

[32] Similar experiments were carried out using the same method of synthesis of the polymers **2Δ** and **2Λ** for the partial resolution of the monocation but starting from the nonenriched $[Ru(bpy)_2(ppy)]$[Δ-trisphat] (**3**) instead of *rac*-$[Ru(bpy)_2(ppy)]PF_6$ (**1**). Thus, enriched $[Ru(bpy)_2(ppy)]$[Δ-trisphat] **3Δ** and **3Λ** can be directly obtained after filtration of the polymer and precipitated by addition of water. Diastereomeric excesses calculated by ^{1}H NMR on these compounds leads to the same results that for the experiments with *rac*-$[Ru(bpy)_2(ppy)]PF_6$ (**1**). This fact confirms that the reaction of transformation of $[Ru(bpy)_2ppy]^+$ into diastereomer is no diastereoselective and that the partial resolution of the monocation is exclusively due to the diastereoselective formation of the polymer **2Δ** and **2Λ**.

[33] J. C. Bailar, E. M. Jones, *Inorg. Synth.* **1939**, *1*, 35−38.

[34] B. P. Sullivan, D. J. Salmon, T. J. Mayer, *Inorg. Chem.* **1978**, *17*, 3334−3341.

[35] D. T. Cromer, *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, UK, **1974**; Vol IV.

Received February 7, 2001
[I01043]